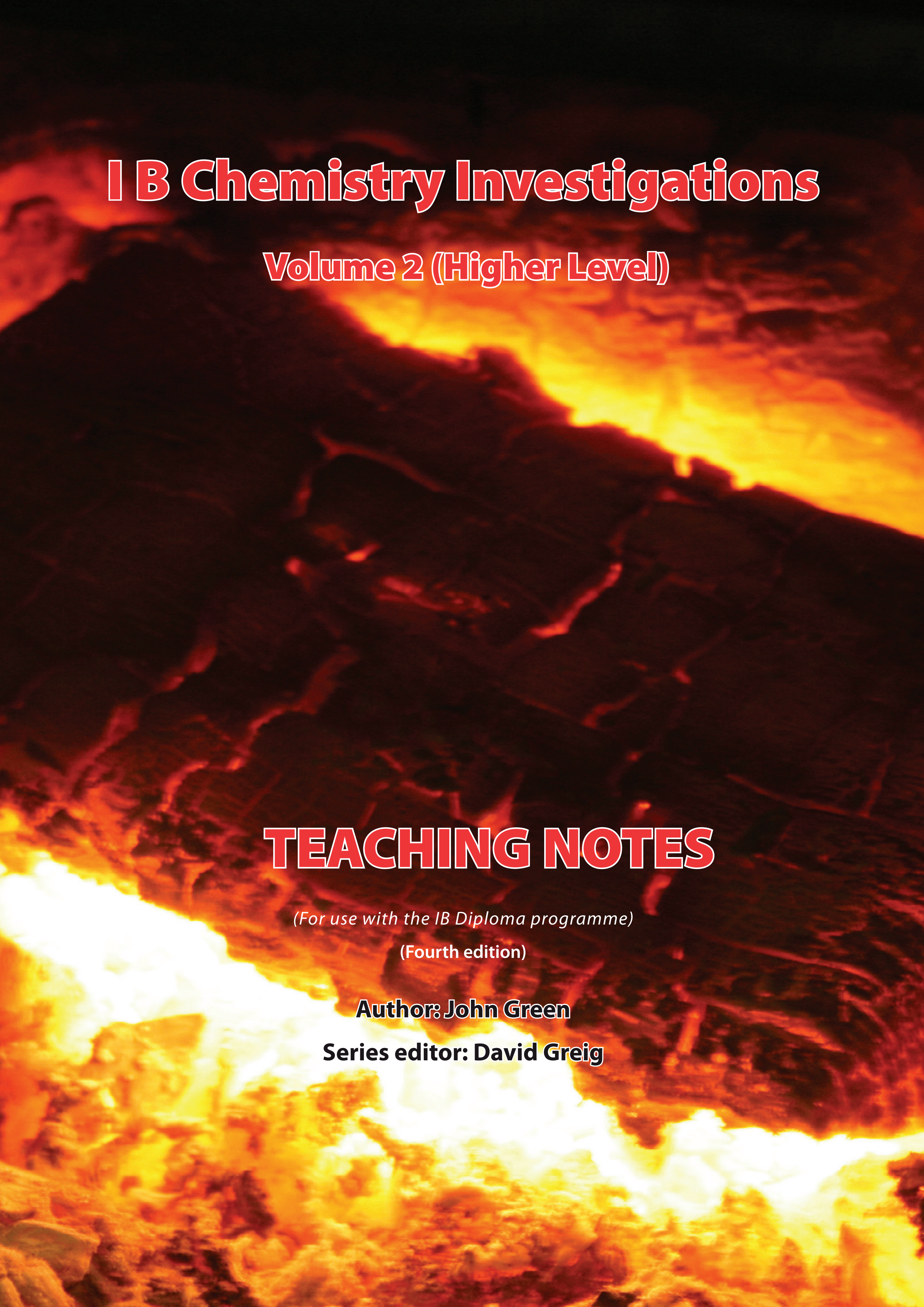

I B Chemistry Investigations

Volume 2 (Higher 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>

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

Syllabus Correlation Table

Standard Level

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 (Group 7)	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: H_2SO_4 (aq), HCl (aq), HNO_3 (aq), NaOH (aq), 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}H NMR or IR.
OPTION TOPICS			
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.

Higher Level

No.	Title	Topic	Syllabus reference
13A	Some Chemical Reactions of Transition Metals	13.1 & 13.2	The oxidation states of vanadium and manganese, for example, could be investigated experimentally.
15A	Enthalpy of Solution	15.1	Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.
15B	Determining the enthalpy change of a reaction	15.1 / 19.1	Perform lab experiments which could include single replacement reactions in aqueous solutions.
15C	Determining Entropy Changes	15.2	Application of $\Delta G° = \Delta H° - T\Delta S°$.
16A	Determining the Rate Expression for a Reaction	16.1	Deduction of the rate expression for an equation from experimental data and solving problems involving the rate expression.
16B	Measuring the Activation Energy for a Reaction	16.2	Determining and evaluating values of activation energy and frequency factors from data.
17A	Measuring an Equilibrium Constant by Light Absorption	17.1	The equilibrium constant for an esterification reaction and other reactions could be experimentally investigated.
17B	Investigating an Ester Formation Equilibrium	17.1	The equilibrium constant for an esterification reaction and other reactions could be experimentally investigated.
18A	Some Measurements on Weak Acids and Bases	18.2	The properties of strong and weak acids could be investigated experimentally. Experiments could include determination of the pK_a of a weak acid.
18B	pH Changes during Acid-Base Titrations	18.3	Experiments could include investigation of pH curves.
18C	The Acid Dissociation Constant of an Indicator	18.3	Experiments could include investigation of the pK_a of an indicator.
19A	Understanding Electrode Potentials	19.1	Calculation of cell potentials using standard electrode potentials.
19B	The electrolysis of aqueous sodium chloride	19.1	Explanation of the products formed during the electrolysis of aqueous solutions.
19C	A Quantitative Investigation into Electrolysis	19.1	Determination of the relative amounts of products formed during electrolytic processes.
20A	Some Factors Affecting Halogenoalkane Reactions	20.1	A range of experiments exploring various types of reactions and functional group interconversions could be done.
OPTION TOPICS			
20B	The nitration of methyl benzoate	20.1	A range of experiments of organic synthetic reactions could be done. Core techniques of organic chemistry could include reflux, distillation, filtration, purification (including chromatographic techniques), separations and extractions.
22B	Solubility product of a sparingly soluble compound	A.10	Experiments could include investigations of Ksp.
23B	Enzyme activity and the Michaelis constant	B.7	Experiments could include measuring enzyme activity with changing conditions of temperature, pH and heavy metal ion concentration.
24B	Factors affecting cell potential	C.6	The factors that affect the voltage of a cell and the lead–acid battery could be investigated experimentally.
25B	Investigating optical activity	20.3 / D.7	Distinction between optical isomers using a polarimeter. Explanation of the use of a polarimeter to identify enantiomers.

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.

ELECTRICITY

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.

POISON

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.

LASER

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

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.

DANGER

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.

ETHICS

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.

ENVIRONMENT

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 NOTE

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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TEACHING NOTES for Investigation 1A
DETERMINING THE AMOUNT OF WATER OF CRYSTALLIZATION

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!

POISON

Class data

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

m_1 /g	m_2 /g	m_3 /g	$CuSO_4$ /g	H_2O /g	$CuSO_4$ /mol	H_2O /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 gray 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 power 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 power.
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
						Mean	**5.52**	

TEACHING NOTES for Investigation 1A
DETERMINING THE AMOUNT OF WATER OF CRYSTALLIZATION

Sample results

Mass of empty crucible and lid = 35.096 ± 0.005 g
Mass of crucible, lid and hydrated salt = 37.986 ± 0.005 g
Mass of crucible and salt after heating = 36.866 ± 0.005 g

Data Analysis

a) Mass of salt remaining = (36.866 ±0.0005) – (35.096 ±0.0005)

= 1.790 ±0.001 g (= ±0.0559%)

Molar mass $CuSO_4$ = 63.55 + 32.07 + (4 × 16.00) [each ±0.005]

= 159.62 ±0.03 g mol^{-1} (= ±0.0188%)

Amount of salt remaining = 1.790/159.62 (= ±0.0747%) = 0.011214 ±0.000008 mol

b) Mass of water lost = (37.986 ±0.005) - (36.866 ±0.0005))

= 1.120 ±0.001 g (= ±0.0893%)

Molar mass water = 16.00 + (2 × 1.01) [each ±0.005]

= 18.02 ±0.015 g mol^{-1} (= ±0.0849%)

Amount of water lost = 1.120/18.02 (= ±0.174%)

= 0.06215 ±0.00011 mol

c) Ratio of mol(H_2O) : mol($CuSO_4$) = 0.06215/0.011214 (±0.249%) : 1

= 5.5421 ±0.00138 : 1, or 5.542 ±0.001 : 1

d) If the number is an integer it would be $CuSO_4 \bullet 6\,H_2O$

e) The precision of the weighings was ±0.0005 g. When propagated (see calculations above)., this results in an uncertainty in the final value of ±0.001 or about ±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 (±0.001 or ±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°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.

TEACHING NOTES for Investigation 1B
DETERMINING THE COMPOSITION OF 'COPPER(II) CARBONATE'

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

a) M_r $CuCO_3$ $= 63.55 + 12.01 + (3 \times 16.00) = 123.56$

M_r CuO $= 63.55 + 16.00 = 79.55$

Mass of $CuCO_3$ $= 32.404 - 28.993 = 3.411$ g

Mass of CuO $= 3.411 x \dfrac{79.55}{123.56} = 2.196 g$

b) M_r $Cu(OH)_2$ $= 63.55 + (2 x 16.00) + (2 x 1.01) = 97.57$

Mass of CuO $= 3.411 x \dfrac{79.55}{97.57} = 2.781 g$

c) $31.442 - 28.993$ $= 2.449$ g

d) $2.196\,y + 2.781\,(100 - y) = 2.449 \times 100$

$2.781\,y - 2.196\,y = 0.585\,y = 278.1 - 244.9 = 33.2$

$$y = \frac{33.2}{0.585} = 56.75\ \%$$

e) Deduce the uncertainty of the value you have obtained by propagating the uncertainties in the weighings.

Uncertainty in mass of substances = 0.0005 + 0.0005 = ±0.001 g

Percent uncertainty in original mass of solid = $\dfrac{0.001}{3.411} x 100 = 0.029\%$

Percent uncertainty in final mass of product = $\dfrac{0.001}{2.449} x 100 = 0.041\%$

Uncertainty in molar masses = ±0.005

Percent uncertainty in molar mass of $CuCO_3$ = $\dfrac{5 x 0.005}{123.56} x 100 = 0.020\%$

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

Percent uncertainty in molar mass of CuO = $\dfrac{2 x 0.005}{79.55} x 100 = 0.013\%$

Percent uncertainty in 2.196 = 0.029 + 0.020 + 0.013 = 0.062%

Absolute uncertainty in 2.196 = $2.196 x \dfrac{0.062}{100} = 0.0014$

Percent uncertainty in 2.781 = 0.029 + 0.026 + 0.013 = 0.068%

Absolute uncertainty in 2.781 = $2.781 x \dfrac{0.0678}{100} = 0.0019$

Absolute uncertainty in 0.585 = 0.0014 + 0.0019 = 0.0033

Percent uncertainty in 0.585 = $\dfrac{0.0033}{0.585} x 100 = 0.56\ \%$

Absolute uncertainty in 33.2 = 100 × (0.0019 + 0.001) = 0.29

Percent uncertainty in 33.2 = $\dfrac{0.29}{33.2} x 100 = 0.87\ \%$

Percent uncertainty in y = 0.56 + 0.87 = 1.43%

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

Final percentage of $CuCO_3$ = 56.8 ±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 $CaCl_2$?) would help.

(c) The best way to do this would be to find the percentage of $CuCO_3$ 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 $[Cu^{2+}]$ by adding excess potassium iodide and titrating the liberated iodine with aqueous sodium thiosulfate:

$$2\,Cu^{2+} + 4\,I^- \rightarrow 2\,CuI + I_2$$

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$$

Alternatively the $[Cu^{2+}]$ 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.

TEACHING NOTES for Investigation 1C
HOW CONCENTRATED IS 'CONCENTRATED' NITRIC ACID?

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^3 pipette
- 10 cm^3 pipette
- Pipette filler
- 100 cm^3 volumetric flask
- 250 cm^3 volumetric flask
- Weighing bottle
- 2 × 100/150 cm^3 conical flask

General

- Balance capable of weighing to at least 0.01 g

Chemicals required

Concentrated nitric acid (~10 cm^3 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^3
Volume of concentrated nitric acid used	= 1.000 ± 0.012 cm^3

which was diluted to 100.00 ±0.16 cm^3

Titration No.	1	2	3	4
Final reading (cm^3)	41.2	18.1	35.6	39.5
Initial reading (cm^3)	23.4	0.7	18.1	22.1
Titre of Na_2CO_3 (cm^3)	17.8	17.4	17.5	17.4

Precision of burette readings = ± 0.05 cm^3

Volume of pipette = 20.00 ±0.06 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 ±0.001 g

Amount of sodium carbonate used $= \frac{1.091}{105.99}$ = 0.01029 mol)

Concentration of solution $= \frac{0.01029}{0.100}$ = 0.1029 mol dm^{-3}

b) Equation for the reaction $Na_2CO_3 + 2\ HNO_3 \rightarrow 2\ NaNO_3 + CO_2 + H_2O$

Mean titre of aqueous sodium carbonate = ⅓ (17.4 + 17.5 + 17.4) = 17.43 cm^3

Amount of sodium carbonate from burette = 0.01743 × 0.1029 = 0.001790 mol

Amount of nitric acid this reacted with = 2 × 0.001790 mol = 0.003580 mol

Concentration of diluted nitric acid $= \frac{0.003580}{0.02000}$ = 0.1790 mol dm^{-3}

Concentration of original nitric acid = 100 × 0.1790 = 17.90 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 ±Range/2√n:

Quantity	Value	Absolute uncertainty	Percentage uncertainty
Mass of Na_2CO_3	1.091	0.001	0.0917
Volume of volumetric flask	100.00	0.16	0.160
Concentration of Na_2CO_3			0.252
Mean titre	17.43	0.029	0.166
Amount of Na_2CO_3			0.417
Amount of HNO_3			0.417
Volume of titration pipette	20.00	0.06	0.300
Concentration of dil 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 HNO_3	17.90	0.25	2.08

Concentration of concentrated nitric acid = 17.9 ±0.3 mol dm^{-3}

Evaluation

a) Nitric acid is usually sold as a 70% solution, with a nominal concentration of 15.8 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 that the true value. The "extra drop" will be a systematic error making the titre too high and hence the concentration of the acid lower that 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 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.

Teaching Notes for Investigation 1D
DETERMINING THE MOLAR MASS OF A SOLUBLE ACID

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^{-3} (~300 cm^3 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^3

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

Precision of burette readings = ± 0.05 cm^3

Volume of potassium hydrogenphthalate solution taken = 20.00 ±0.06 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 ±0.0005 g

Mass of weighing bottle after emptying = 1.188 ±0.0005 g

Volume of solution prepared = 100.00 ±0.16 cm^3

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

Precision of burette readings = ± 0.05 cm^3

Volume of Acid X solution taken = 20.00 ±0.06 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 ±0.001 g

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

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

Equation for the reaction $KHC_8H_4O_4 + NaOH \rightarrow NaKC_8H_4O_4 + H_2O$

Amount of potassium hydrogenphthalate from pipette = 0.0200 × 0.0973 = 0.00195 mol

Which reacts with 0.00195 mol of sodium hydroxide.

Mean titre of aqueous sodium hydroxide = 20.1 ±0.1 cm^3

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

Quantity	Value	Absolute uncertainty	Percentage uncertainty
Mass of $KHC_8H_4O_4$	1.987	0.001	0.0503
Volume of volumetric flask	100.00	0.16	0.160
Concentration of $KHC_8H_4O_4$		0.0002	0.210
Volume of titration pipette	20.00	0.06	0.300
Amount of $KHC_8H_4O_4$/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 ±0.001 mol dm^{-3}

Molar mass determination

Mean titre of aqueous sodium hydroxide = 30.3±0.1 cm^3

Equation for the reaction $HX + NaOH \rightarrow NaX + H_2O$

Amount of sodium hydroxide used = 0.0968 x 0.0303 = 0.00293 mol

Which reacts with 0.00293 mol of HX in the 20 cm^3 titre.

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

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

Mass of HX used = 1.015 ±0.001 g

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

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 ±1 mol dm^{-3}

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

Evaluation

a) The value of 0.097 ±0.001 mol dm^{-3} is very credible for a solution that is nominally 0.1 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 ±1 mol dm^{-3}) is significantly different to the literature value of 64.0 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 that 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 that 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.

TEACHING NOTES for Investigation 1E
IDENTIFYING FUELS FROM THEIR MOLAR MASSES

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^3 PET carbonated drink bottles are fine)
- Measuring cylinder of volume slightly greater than drink bottle
- Stoppered 100 cm^3 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^3 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 = ±0.0005 g

Volume of bottle = 1585 ±5 cm^3

Room temperature = 23.7 ±0.1 °C

Room pressure = 103.2 ±0.2 kPa

Liquid fuel

Mass of empty flask = 138.624 ±0.0005 g

Mass of flask + liquid = 138.792 ±0.0005 g

Mass of flask + water = 256.813 ±0.0005 g

Temperature of water bath = 98.8 ±0.1 °C

Room pressure = 103.2 ±0.2 kPa

Data Analysis

Gaseous fuel

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

$$Mass\ of\ air = 1.585\,x\,1.211 = 1.919\,g$$

$$Mass\ of\ empty\ bottle = 47.832 - 1.919 = 45.913\,g$$

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

$$=1.919\,x\,\frac{0.542}{100} = \pm 0.0104\,g$$

$$Uncertainty\ of\ mass\ of\ bottle = 0.0005 + 0.0104 = \pm 0.0109\,g$$

b) $Mass\ of\ gaseous\ fuel = 47.044 - 45.913 = 1.131\,g$

Uncertainty = $0.0005 + 0.0109 = \pm 0.0114\,g$

c)

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

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

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

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

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

Molar mass of gaseous fuel = 17.1 0.3 g mol^{-1}

Liquid fuel

d) Volume of flask = 256.813 – 138.624 = 118.189 ±0.001 cm^3

Mass of vapour = 138.792 – 138.624 = 0.168 ±0.001 g

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

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

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

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

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

Molar mass of liquid fuel = 42.6 ±0.3 g mol^{-1}

Evaluation

Gaseous fuel

a) Methane.

b) The accuracy of the value is quite poor with an error of +2 g mol^{-1} (+12.5%), ten times greater than the precision of ±0. 2 g mol^{-1}.

c) The measurements of P, V and T all have uncertainties of a similar order of magnitude (~0.03–0.3 %). The precision of the weighings seems much greater (~0.001%) but because of the small difference between the weighings this small uncertainty becomes the greatest single factor in calculating the final uncertainty (~0.5%), approximately equal in magnitude to the combination of all the other uncertainties.

d) 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 ~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.

e) 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.

f) The systematic error is probably quite small provided the bottle is weighed and refilled sufficient times and probably less than the ~1% uncertainty in the values calculated, hence random errors are probably dominant.

g) 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 (~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 kg dm^{-3}. A more precise determination of the pressure (~0.2%) would also be an improvement. The uncertainty in the temperature determination, though it seems quite large (0.1 °C in 23.7 °C) is greatly reduced by the conversion of the temperature to Kelvin.

h) 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.

i) 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

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

$$46y+32(100-y)=42.6x100$$

which on solving gives a value of y = 75.7%. Hence methylated spirits would appear to be ~75% ethanol.

k) 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.

l) 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 ~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 dm3) 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^{-1})	891	1367
Mass (kJ g^{-1})	55.7	29.7
Volume (kJ dm^{-3})	36	23,450
Cost (kJ $^{-1})	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^{-1}) 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^{-1}). 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^3 at room temperature and pressure, whereas a mole of ethanol occupies a volume of ~60 cm^3; 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^{-3} and methylated spirit $5 dm^{-3}. 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.

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TEACHING NOTES for Investigation 2A
OBSERVING EMISSION SPECTRA

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^3 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

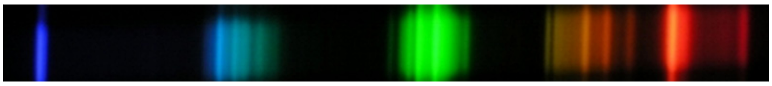
This is the familiar "rainbow" spectrum:

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>.

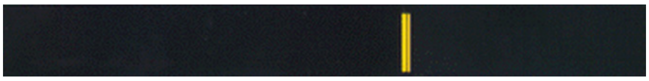
3) Discharge tubes

These should give reasonable line spectra:

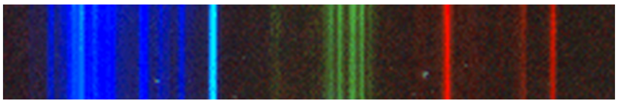
Hydrogen

Helium

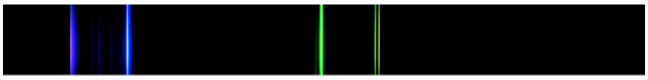
Neon



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>

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 (ν), and the shorter the wavelength (λ), the light the greater the energy (E) carried by each photon. These are related by the expression:

$$E = h \, . \, \nu = h \, . \, \frac{c}{\lambda}$$

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.

TEACHING NOTES for Investigation 3A
SOME REACTIONS OF THE HALOGENS (GROUP 17)

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^3 per student of:

Aqueous sodium hydroxide (~1 mol dm^{-3})

- Dilute sulfuric acid (~1 mol dm^{-3})
- Chlorine water
- Bromine water
- Aqueous lead nitrate (~0.1 mol dm^{-3})
- Aqueous silver nitrate (~0.01 mol dm^{-3})
- Iodine in aqueous potassium iodide (~0.1 mol dm^{-3}) labelled “Iodine solution”
- Ethanol
- Hexane

About 50 cm^3 per student of:

- Aqueous sodium chloride (~0.1 mol dm^{-3})
- Aqueous sodium bromide (~0.1 mol dm^{-3})
- Aqueous sodium (or potassium) iodide (~0.1 mol dm^{-3})

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:

   $I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$

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.

   $X_2(aq) + H_2O(l) \rightarrow XOH\ (aq) + H^+(aq) + X^-(aq)$

   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.

   $Br_2(aq) + H_2O(l) \rightarrow H^+(aq) + BrOH\ (aq) + Br^-(aq) \rightarrow 2\ H^+(aq) + BrO^-(aq) + Br^-(aq)$

   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**
Chlorine water	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
Bromine water	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
Iodine solution	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.

$Cl_2(aq) + 2\ Br^-(aq) \rightarrow 2\ Cl^-(aq) + Br_2(aq)$

$Cl_2(aq) + 2\ I^-(aq) \rightarrow 2\ Cl^-(aq) + I_2(aq)$

$Br_2(aq) + 2\ I^-(aq) \rightarrow 2\ Br^-(aq) + I_2(aq)$

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
With aqueous silver nitrate	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
Effect of sunlight	Darkens through purple and grey to black	Very slowly darkens	Little if any effect

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

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

$Pb^{2+}(aq) + 2\ Cl^{-}(aq) \rightarrow PbCl_2(s)$

$Pb^{2+}(aq) + 2\ Br^{-}(aq) \rightarrow PbBr_2(s)$

$Pb^{2+}(aq) + 2\ I^{-}(aq) \rightarrow PbI_2(s)$

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^3 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^3 per group of:

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

Hexene

~50 cm^3 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)

Solvent Solute	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 ~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^3	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.

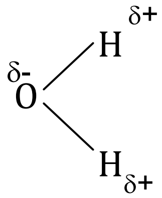
Hexane and hexene both have dispersion forces between their molecules so that bonding between the two compounds is similar to that in the pure substances, so they are readily miscible. The bonds involved are weak so any differences are very small and do not result in observable changes in volume or temperature.

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

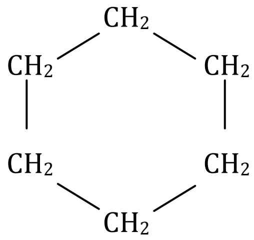
Stream of liquid does not deviate–cyclohexane, tetrachloromethane

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.

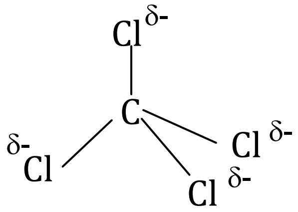
In the case of water, oxygen is much more electronegative than hydrogen, giving rise to polar bonds and, as the molecule is non-linear, this results in it having a permanent dipole.



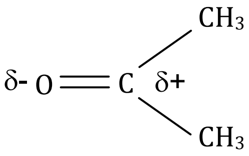
In the case of cyclohexane, not only are carbon and hydrogen very similar in electronegativity, giving rise to bonds of low polarity, the molecule is very symmetrical ensuring that it is non-polar.



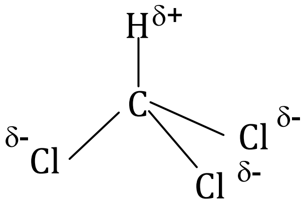
In the case of tetrachloromethane, the carbon-chlorine bonds are quite polar owing to their significant difference in electronegativity, but the molecule is very symmetrical so that these polar bonds cancel, resulting in a non-polar molecule.



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.



Teaching Notes for Investigation 5A
MEASURING ENTHALPY CHANGES

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^3 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^{-3} hydrogen peroxide (~50 cm^3 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 ± 0.0005 g

Mass of filter paper and water = 8.135 ± 0.0005 g

Initial temperature of water = 66.8 ± 0.1 °C

Final temperature of water = 37.4 ± 0.1 °C

Volume of water = 100 ± 0.5 cm^3

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) $Q = m \,.\, c \,.\, \Delta T = 100 \times 4.18 \times (66.8 - 37.4) = 12289.2\ \text{J} = 12.29\ \text{kJ}$

b) $Q = m \,.\, c \,.\, \Delta T = (31.104 - 8.135) \times 4.18 \times (37.4 - 0) = 3590.8\ \text{J} = 3.59\ \text{kJ}$

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) g of ice required 8.70 kJ to melt so 1 mole (18.02 g) would require:

$$8.70 \times \frac{18.02}{22.969} = 6.83\ \text{kJ mol}$$

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 ±0.1 kJ mol^{-1}

Part B

Time /s	Temperature /°C	Time /s	Temperature /°C	Time /s	Temperature /°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 = ± 1 s

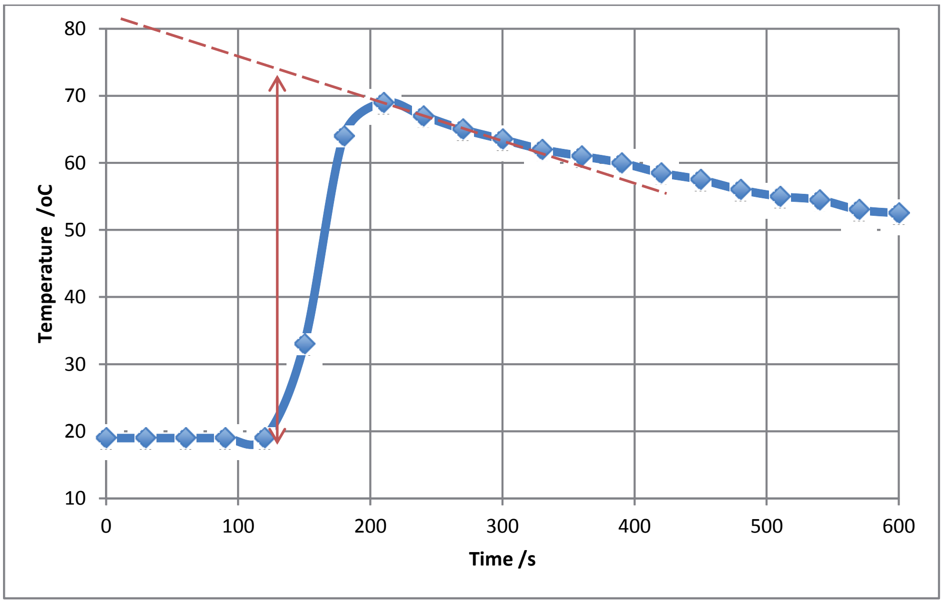
Precision of temperature measurements = ± 0.25 °C

Volume of aqueous hydrogen peroxide = 50 ± 0.5 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:

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

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

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

Uncertainty in mass = uncertainty in volume = ±1%

Uncertainty in temperature change = 1.8%

Total uncertainty in Q = ±2.8%

c) Amount of H_2O_2 = n = c.V = 1.0 × 0.050 = 0.050

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

Uncertainty in n = uncertainty in V = ±1%

Total uncertainty in ΔH = 3.8% = ±8.7 kJ

Enthalpy change of reaction:

$2\ H_2O_{2\ (aq)} \rightarrow 2\ H_2O_{(l)} + O_{2\ (g)}$ = -115 ±9 kJ (negative as reaction is exothermic)

Conclusion & Evaluation

a) The accepted value for the enthalpy of fusion of ice is 6.01 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) $\Delta H = \Sigma\Delta H_f\,(\text{products}) - \Sigma\Delta H_f\,(\text{reactants}) = (2 \times 285.5) - (2 \times 187.8) = -195.4$ kJ mol $^{-1}$

(Remember ΔH_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

$\Delta H = (2 \text{ x } +144) - (498) = -210$ 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 kJ mol^{-1} compared to 195 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 J g^{-1} 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°C) would be below the true value so the heat lost by the water (12.29 kJ) would be greater than the true value and the heat gained by the molten ice (3.59 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 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.

TEACHING NOTES for Investigation 5B
INDIRECTLY DETERMINING AN ENTHALPY CHANGE

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^3 measuring cylinder
- Weighing bottle
- Polystyrene cup (at least 250 cm^3 capacity)

General

Balance reading to 0.01 g

Chemicals required

- 2 mol dm^{-3} hydrochloric acid (~250 cm^3 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 = ± 1 s Temp = ± 0.2 oC

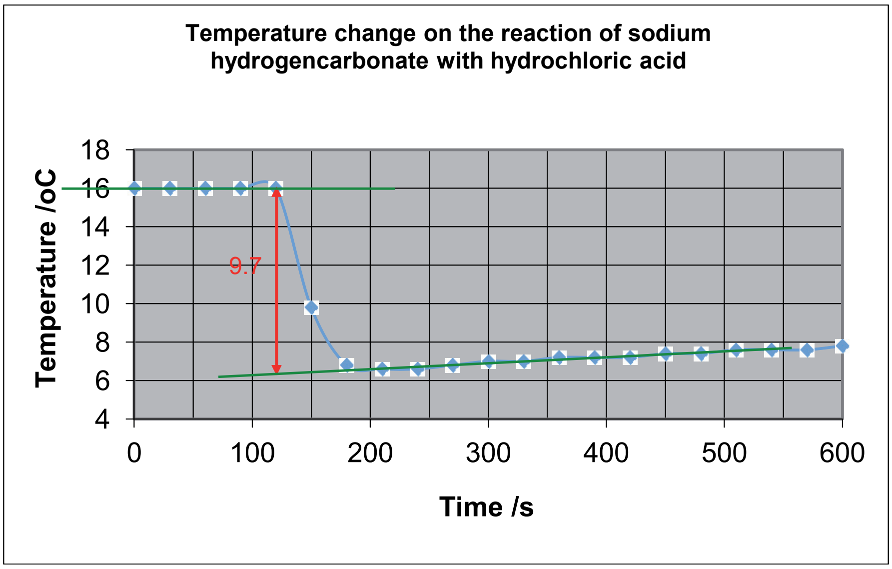
Volume of 2 mol dm^{-3} HCl for both = 100 ± 0.5 cm^3

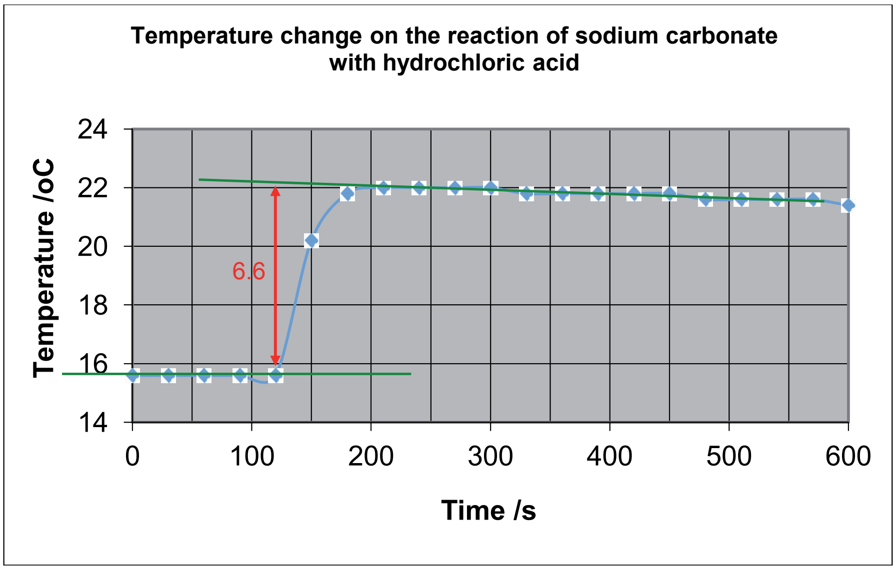
Relevant qualitative observations

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 ± 0.1 °C

b) $Q = m \, . \, c \, . \, \Delta T = 0.100 \times 4.18 \times 9.7 = 4.055 \text{ kJ}$

(assuming density and specific heat capacity of 2 mol dm^{-3} HCl is the same as that of water)

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

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

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

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

$\Delta H = +25.8 \pm 0.4$ kJ

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

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

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

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

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

$\Delta H = -35.6 \pm 0.7$ kJ

d) $NaHCO_3\,(s) + H^+\,(aq) \Rightarrow Na^+\,(aq) + H_2O\,(l) + CO_2\,(g) \qquad \Delta H = +25.77 \text{ kJ}$

$Na_2CO_3\,(s) + 2\,H^+\,(aq) \Rightarrow 2\,Na^+\,(aq) + H_2O\,(l) + CO_2\,(g) \qquad \Delta H = -35.55 \text{ kJ}$

e)

$$\begin{tikzcd}
2\,NaHCO_3\,(s) \arrow[rr, Rightarrow, "\Delta H"] \arrow[dr, "\Delta H = 2 \text{ x } +25.77 \text{ kJ mol}^{-1}"'] & & Na_2CO_3\,(s) + H_2O\,(l) + CO_2\,(g) \arrow[dl, "\Delta H = -35.55 \text{ kJ mol}^{-1}"] \\
& 2\,Na^+\,(aq) + H_2O\,(l) + CO_2 &
\end{tikzcd}$$

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

Uncertainty $= (2\,x\,0.395) + 0.718 = 1.508$

$\Delta H = +87.1 \pm 1.5$ 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 ~2½ % of the accepted value. The estimated uncertainty of ~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 ½ % 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 ΔH), 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^{-3} and 4.04 J g^{-1} K^{-1} 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 (± 0.2 °C, hence ± 0.4 °C for ΔT, 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 ΔT 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.

TEACHING NOTES for Investigation 6A
TECHNIQUES FOR MEASURING REACTION RATES

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

Chemicals required

- 1.0 mol dm^{-3} hydrochloric acid (~50 cm^3 per group)
- Magnesium ribbon (~4 cm per group)

Technique B

Apparatus required

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

Chemicals required

- 0.5 mol dm^{-3} hydrogen peroxide (~50 cm^3 per group)
- Manganese(IV) oxide (manganese dioxide, ~1 g per group)

Technique C

Apparatus required

- Burette
- 10 cm^3 pipette and pipette filler
- 250 cm^3 conical flask
- 100 cm^3 conical flask
- 50 cm^3 measuring cylinder
- 25 cm^3 measuring cylinder
- Stop watch

Chemicals required

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

Technique D

Apparatus required

- Spectrophotometer or colorimeter
- 100 cm^3 conical flask
- 25 cm^3 measuring cylinder
- 10 cm^3 measuring cylinder
- Stop watch

Chemicals required

- 0.02 mol dm^{-3} aqueous sodium thiosulfate (~20 cm^3 per group)
- 2 mol dm^{-3} hydrochloric acid (~5 cm^3 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

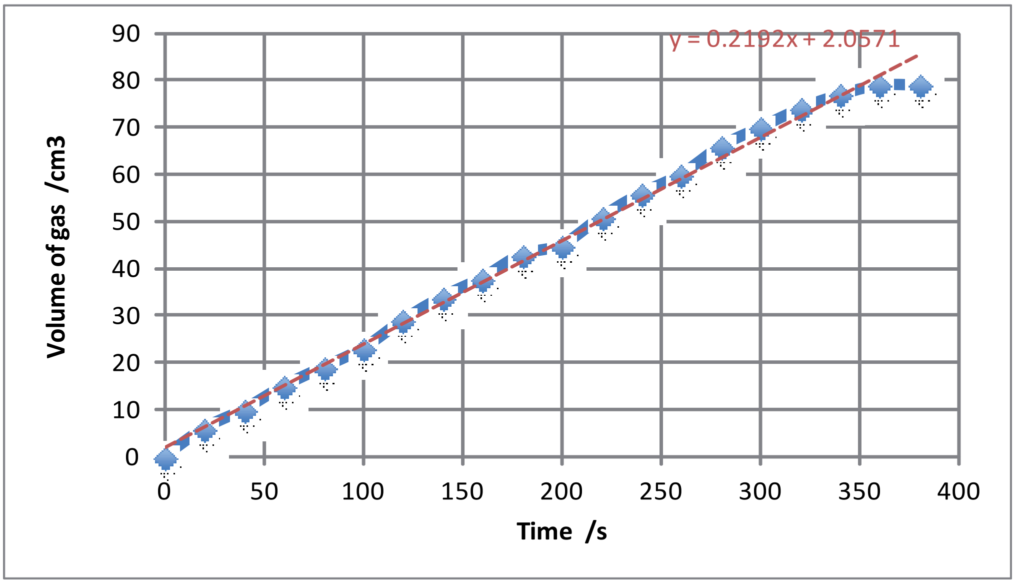
Time /s	Gas volume /cm^3	Time /s	Gas volume /cm^3
0	0	200	45
20	6	220	51
40	10	240	56
60	15	260	60
80	19	280	66
100	13	300	70
120	29	320	74
140	34	340	77
160	38	360	79
180	43	380	79

Precision of time measurements = ± 1 s   Precision of volume measurements = ± 1 cm^3

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 $cm^3\ s^{-1}$

Conclusion & Evaluation

a) 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.

b) Very simple apparatus and easy to employ.

c) 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.

d) 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

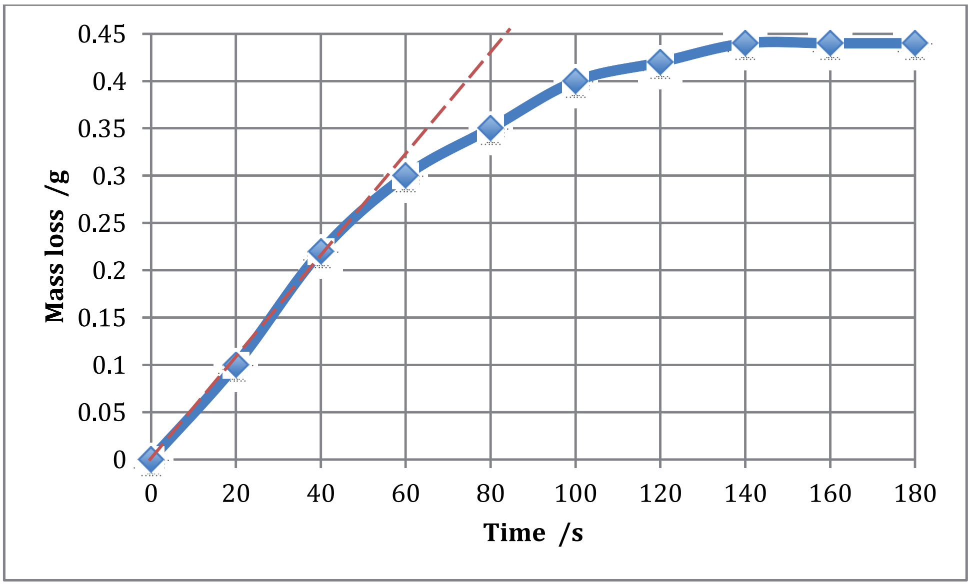
Time /s	System mass /g
0	157.98
20	157.88
40	157.76
60	157.68
80	157.63
100	157.58
120	157.56
140	157.54
160	157.54
180	157.54

Precision of time measurements = ± 1 s Precision of mass measurements = ± 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 g s^{-1}

Conclusion & Evaluation

a) 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).

b) Probably the simplest possible apparatus and can be easily connected to data-logging programmes for direct recording of the results.

c) 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.

d) 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 $Na_2S_2O_3$ /cm³
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

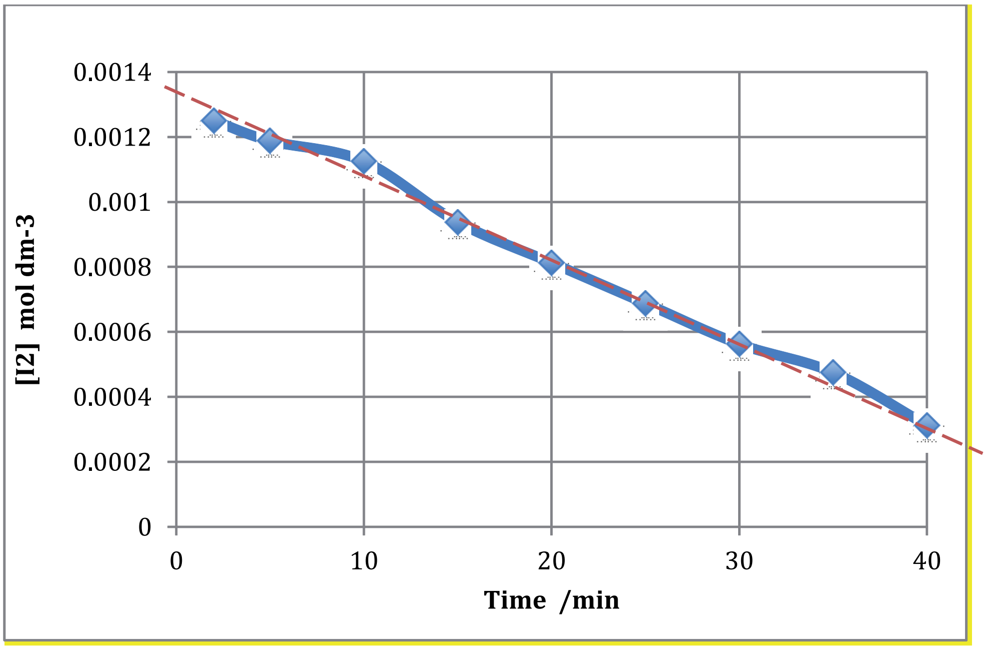
Precision of time measurements ± 0.02 min

Precision of burette readings ± 0.1 cm³

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 = 4.3×10^{-7} mol dm^{-3} s^{-1}

Conclusion & Evaluation

a) Can only be used for quite slow reactions, even if the samples are quenched when removed. Slow and quite time consuming.

b) Very simple apparatus and can be applied to almost all reactions by choosing a suitable titration reaction.

c) 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.

d) 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

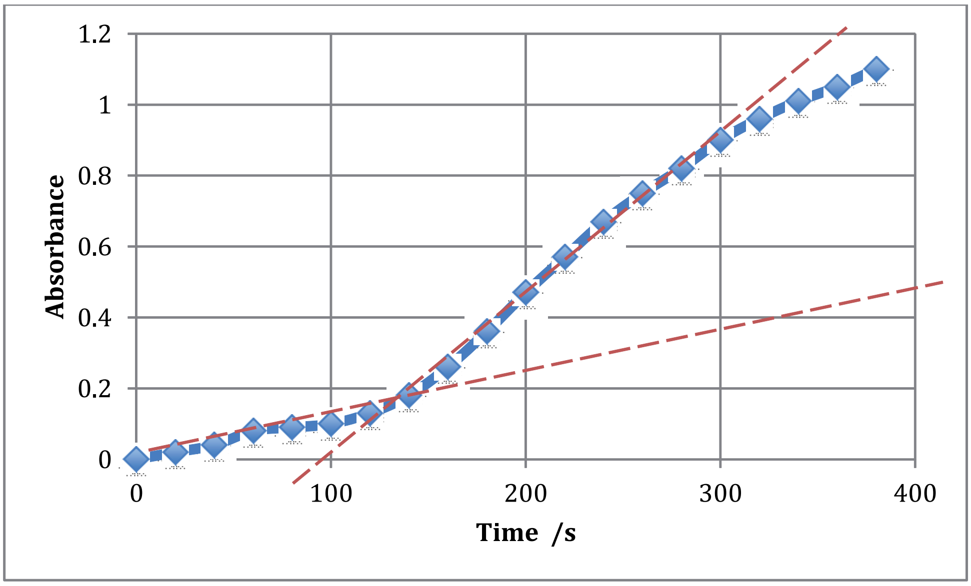
Time /s	Absorbance	Time /s	Absorbance
0	0.00	200	0.47
20	0.02	220	0.57
40	0.04	240	0.67
60	0.08	260	0.75
80	0.09	280	0.82
100	0.10	300	0.90
120	0.13	320	0.96
140	0.18	340	1.01
160	0.26	360	1.05
180	0.36	380	1.10

Precision of time measurements = ± 1 s Precision of absorbance measurements ± 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 s^{-1}, but soon increases to ~0.0045 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.

Teaching Notes for Investigation 6B
FACTORS AFFECTING RATES OF CHEMICAL REACTIONS

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^3 conical flask
- 50 cm^3 measuring cylinder
- 0–110ºC thermometer
- Stop watch
- Balance reading to at least 0.1 g

Chemicals required

- 5 mol dm^{-3} hydrochloric acid (~400 cm^3 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^3 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^3 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_30_4), like all lead compounds, is quite toxic.

GLOVES GOGGLES CORROSIVE

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^3 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

	Total mass /g					
Time /s	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 $CaCO_3$ /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

a) $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2$

b) Amount of $CaCO_3 = \dfrac{m}{M_r} = \dfrac{5}{100} = 0.05\,mol$

Amount of HCl = c × V = 5 × 0.050 = 0.25 mol

As 0.1 mol HCl would be required to react with the 0.05 mol of $CaCO_3$, HCl is in excess and the limiting reagent is therefore $CaCO_3$. In Part C the amount of acid is halved (0.125 mol), but even so the acid will still remain in excess.

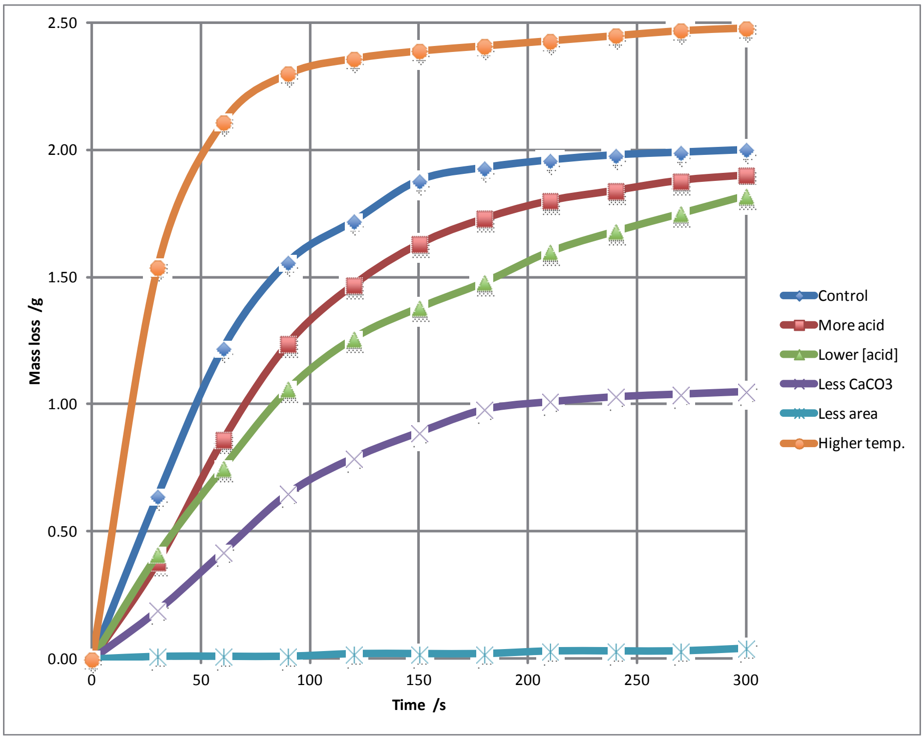
d) 0.25 – 0.10 = 0.15 mol (or 60%) of the HCl will remain in excess.

e) Amount of $CaCO_3 = \dfrac{m}{M_r} = \dfrac{5.01}{100.09} = 0.0501\,mol$

Mass of CO_2 = n × M_r = 0.0501 × 44.01 = 2.20 g

e) continued

	Mass loss /g					
Time /s	Control	More acid	Lower [acid]	Less $CaCO_3$	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^{-1}
A	0.0217
B	0.0152
C	0.0125
D	0.00877
E	0.000013
F	0.0581

g) $0.0217\ g\ s^{-1} = \dfrac{0.0217}{44.01} = 0.000493\,mol\,s^{-1}$

h) Each CO_2 formed requires two HCl, so rate of change of amount of HCl = $0.000986\,mol\,s^{-1}$

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

Conclusion & Evaluation

a) The mass of 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 $CaCO_3$ 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 $CaCO_3$ 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 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

Teaching Notes for Investigation 6C
A QUANTITATIVE INVESTIGATION OF REACTION RATES

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 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 cm^3 measuring cylinder add 20 cm^3 of water to a 100 cm^3 conical flask.
3. Using a 10 cm^3 measuring cylinder measure out 5 cm^3 of 5 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 cm^3 of water add 5 cm^3 of propan-1.2.3-triol and 15 cm^3 of water, then 10 : 10 and finally 15 : 5.

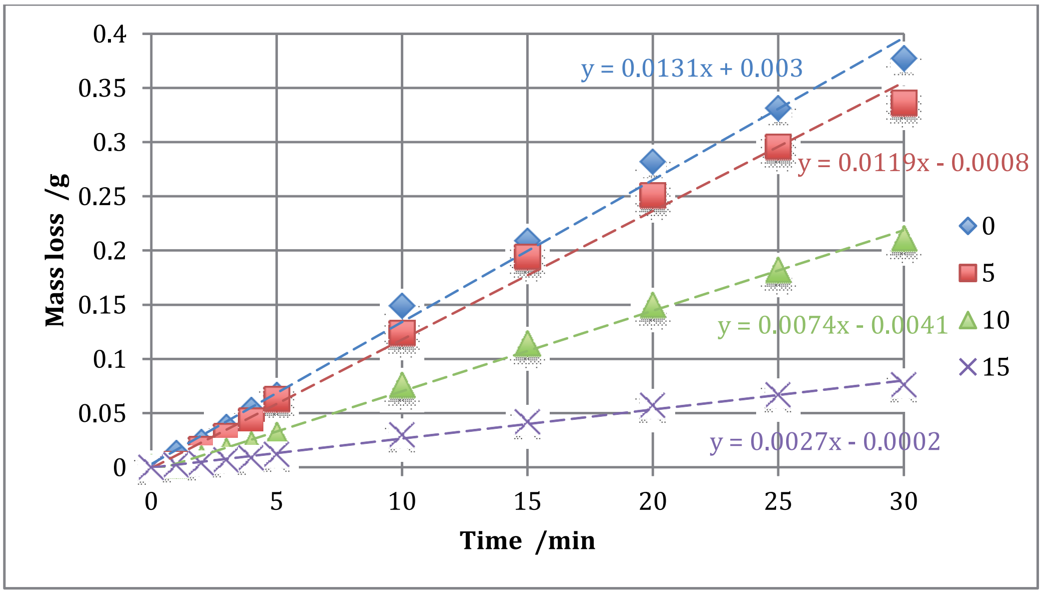
(Sample) Data Collection

Volume propan-1.2.3-triol /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

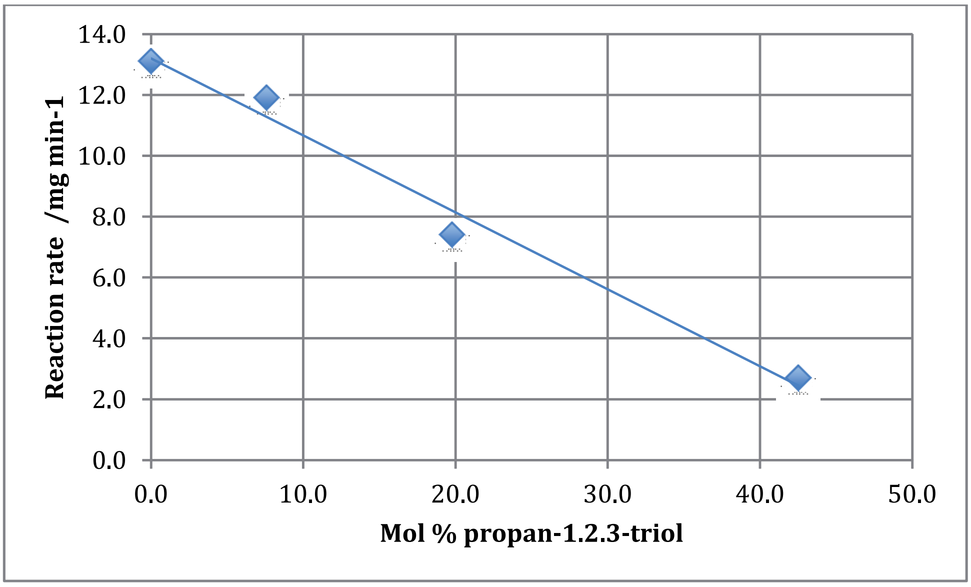
Calculating the loss in mass and plotting a graph:

Time /min	Vol triol /cm^3			
	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^{-3}

Volume propan-1.2.3-triol /cm^3	Mass propan-1.2.3-triol /g	Amount propan-1.2.3-triol /mol	Volume water / cm^3	Mass water /g	Amount water / mol	Mol % propan-1.2.3-triol	Rate / mg min^{-1}
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

a) 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.

b) 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.

c) 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 have 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.

d) The investigation should be repeated but with a greater range of compositions. Changing the volume of propan-1.2.3-triol by 2cm^3 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^3. 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.

TEACHING NOTES for Investigation 7A
AN INTRODUCTION TO EQUILIBRIUM

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^3 measuring cylinder
- 10 cm^3 measuring cylinder
- 4 × 100 cm^3 beaker

Chemicals required

- 0.02 mol dm^{-3} aqueous potassium thiocyanate (~100 cm^3 per group)
- 1.0 mol dm^{-3} aqueous potassium thiocyanate (~2 cm^3 per group)
- 0.01 mol dm^{-3} aqueous iron(III) nitrate (~20 cm^3 per group)
- ~1 mol dm^{-3} aqueous sodium fluoride (~20 cm^3 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

a) The colour of the solution became a much more intense blood-red colour.

b) 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.

c) 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

a) The colour of the solution again became more intense, but less so than in Part B.

b) Adding the thiocyanate, like adding iron(III) ions, has increased the amount of the complex ion.

c) 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

a) 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.

b) The concentration of the complex ion has been reduced to almost zero.

c) 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.

TEACHING NOTES for Investigation 7B
FACTORS AFFECTING VAPOUR PRESSURE

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 × 5 cm^3 syringe with long tube attached
- Water bath at ~40°C

Chemicals required

- Propanone (~10 cm^3 per group)
- Propan-2-ol (~2 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

a) Molecules of propanone in the liquid phase escape from the surface into the vapour phase, increasing the total pressure.

b) 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

a) The pressure–time graph for propan-2-ol has a smaller gradient and reaches a lower final level than that for propanone.

b) 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

a) Doubling the volume of the liquid has no effect on the pressure–time graph.

b) 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

a) At a lower temperature, the gradient of the pressure–time graph is smaller and it reaches a lower final pressure.

b) 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

a) With a reduced surface area the gradient of the pressure–time graph is smaller but it still reaches the same final value.

b) 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

a) With a larger container the gradient of the pressure–time graph is smaller but it still reaches the same final level.

b) 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.

TEACHING NOTES for Investigation 7C
SHIFTING THE POSITION OF AN EQUILIBRIUM

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^{-3} aqueous potassium dichromate(VI) (~10 cm^3 per group)
- 1 mol dm^{-3} aqueous sodium hydroxide (~10 cm^3 per group)
- 1 mol dm^{-3} sulfuric acid (~10 cm^3 per group)
- 0.1 mol dm^{-3} aqueous cobalt(II) chloride (~10 cm^3 per group)
- Concentrated hydrochloric acid (~10 cm^3 per group)
- 1 mol dm^{-3} aqueous magnesium sulfate (~10 cm^3 per group)
- 5 mol dm^{-3} aqueous ammonia (~10 cm^3 per group)
- Solid ammonium chloride (~2 g per group)
- Fresh lime water (~10 cm^3 per group)
- Carbon dioxide cylinder or generator
- 2 gas syringes ¾ 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.

Equation: $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ CrO_4^{2-} + 2\ H^+$

Prediction from Le Châtelier's Principle: Increasing the pH by adding sodium hydroxide, would decrease $[H^+]$, so the position of equilibrium would shift to the right to produce more H^+, so converting orange $Cr_2O_7^{2-}$ to yellow CrO_4^{2-}. Decreasing the pH, by adding sulfuric acid, would increase $[H^+]$, so the equilibrium would try to decrease it again by shifting to the left.

Reaction rate explanation: Increasing the pH would reduce $[H^+]$ 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 $[H^+]$ & $[CrO_4^{2-}]$ and the decrease in $[Cr_2O_7^{2-}]$ cause the rates of forward and reverse reactions to once again become equal. Similarly, if the $[H^+]$ 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.

Equation: $Co(H_2O)_6^{2+}{}_{(aq)} + 4\ Cl^-{}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6\ H_2O_{(l)}$

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 $[CoCl_4^{2-}]$ and decreased concentration of $[Co(H_2O)_6^{2+}]$ & $[Cl^-]$ 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.

Equation: $2\ NO_{2\ (g)} \rightleftharpoons N_2O_{4\ (g)}$

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 $p(NO_2)^2$} more than the reverse reaction {proportional to $p(N_2O_4)$} so the equilibrium will shift to the right until the greater $[N_2O_4]$ and lower $[NO_2]$ 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.

Equations: $NH_{3\ (aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$Mg^{2+}{}_{(aq)} + 2\ OH^-{}_{(aq)} \rightleftharpoons Mg(OH)_{2\ (s)}$

Explanation: When aqueous ammonia is added to aqueous $MgSO_4$ the hydroxide ions, in equilibrium with the ammonia in the first equilibrium, displace the second equilibrium to the right and solid $Mg(OH)_2$ is precipitated. If NH_4Cl is dissolved in the solution however the 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 $Mg(OH)_2$ 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.

Equations: $Ca(OH)_{2\ (aq)} + CO_{2\ (aq)} \rightleftharpoons CaCO_{3\ (s)} + H_2O_{(l)}$

$CaCO_{3\ (s)} + H_2O_{(l)} + CO_{2\ (aq)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2\ HCO_3^-{}_{(aq)}$

Explanation: When carbon dioxide is initially passed through aqueous $Ca(OH)_2$ the first equilibrium is displaced to the right, causing a precipitate of $CaCO_3$. 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 CO_2 decreases and its concentration falls so the position of the second equilibrium shifts to the left reforming solid $CaCO_3$. The concentration of CO_2 however remains high enough for the position of the first equilibrium to remain to the right.

TEACHING NOTES for Investigation 8A
DETERMINING THE SOLUBILITY OF ETHANEDIOIC (OXALIC) ACID

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^3 beaker
- 100 cm^3 conical flask
- Burette and burette funnel
- 20 cm^3 pipette and pipette fillers

Chemicals required

- Ethanedioic acid dihydrate (~20 g per group)
- 1 mol dm^{-3} aqueous sodium hydroxide (~200 cm^3 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.

TEACHING NOTES for Investigation 8A
DETERMINING THE SOLUBILITY OF ETHANEDIOIC (OXALIC) ACID

Data Collection

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

Precision of burette readings = ± 0.05 cm^3

Volume of acid solution taken = 20.00 ± 0.06 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 = $^1/_3$ (30.00 + 29.80 + 30.10) = 29.97 cm^3

Amount of alkali consumed = c.V = 1.00 × 0.02997 = 0.02997 mol

Amount of acid this reacts with = ½ × 0.02997 = 0.01498 mol (as acid dibasic)

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

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

So uncertainty in amount of alkali = ±0.29% (ignoring uncertainty in concentration)

Uncertainty in volume of acid = ±0.30%

Uncertainty in concentration of acid = ±0.59% = ±0.004

Concentration of acid = 0.749 ± 0.004 mol dm^{-3}

b) Molar mass = 126.08 g mol^{-1} (as the acid is a dihydrate, $C_2O_4H_2 \bullet 2\,H_2O$)

In 100 cm^3 there will be 0.0749 mol = 0.0749 × 126.4 = 9.44 g

Alternative method

1. Measure out 100 cm3 of water using a 100 cm3 measuring cylinder and add it to a 250 cm3 beaker.
2. Weigh out accurately about 20 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^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. 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^3 solution = 20.06 – 10.67 = 9.39 ±0.015 g

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

Conclusion & Evaluation

a) The two values obtained for the solubility 0.749 ± 0.004 mol dm^{-3} and 0.743± 0.001 mol dm^{-3}, or 9.47 and 9.39 g/100 cm^3, 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^3 at 20°C, and 14.3 g/100 cm^3at 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^3 pipette
- 10 cm^3 pipette
- Pipette filler
- Weighing bottle
- 250 cm^3 conical flask
- 100 cm^3 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^{-3} hydrochloric acid (~300 cm^3 per group, give concentration and uncertainty on the container)
- *Approximately* 2 mol dm^{-3} aqueous sodium hydroxide (~200 cm^3 per group)
- Solid ammonium sulfate, labelled "Fertiliser" (~10 g per group)
- Bromothymol blue indicator (2-3 cm^3 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^3)	22.0	41.4	45.3
Initial reading (cm^3)	4.5	22.0	27.5
Titre (cm^3)	17.5	19.4	17.8

Precision of balance = ± 0.0005 g

Volume of aqueous sodium hydroxide taken = 25 ± 0.06 cm^3

Precision of burette = ± 0.05 cm^3

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^3)	43.7	25.5	45.1	23.4
Initial reading (cm^3)	22.9	5.8	25.5	3.7
Titre of HCl (cm^3)	20.8	19.7	19.6	19.7

Concentration of hydrochloric acid = 1.00 ± 0.005 mol dm^{-3}

Volume of aqueous sodium hydroxide taken = 10.00 ± 0.04 cm^3

Precision of burette = ± 0.05 cm^3

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 cm^3 (Rough titre omitted)

As it is a 1:1 reaction: $c_1.V_1 = c_2.V_2$

Substituting: $1.00 \times 19.67 = c_2 \times 10.0$

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

Uncertainty of concentration of HCl = ±0.5%

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

Uncertainty of volume of NaOH = ±0.4%

Uncertainty of concentration of NaOH = 0.5 + 0.15 + 0.4 = ±1.05%

b) Amount of NaOH added = 1.967 × 0.025 = 0.0492 mol

Uncertainty of volume of NaOH added = ±0.6%

Uncertainty of amount of NaOH added = 1.05 + 0.6 = ±1.65% = 0.00081

c) Amount of HCl added = 1.00 x 0.0175 = 0.0175 mol

Amount of NaOH neutralised by fertiliser = 0.0492–0.0175 = 0.0317 mol

Uncertainty of concentration of HCl = ±0.5%

Uncertainty of volume of HCl 0.1 cm^3 = ±0.571%

Uncertainty of amount of HCl = 0.5 + 0.571 = ±1.07% = 0.00019

Uncertainty of amount of NaOH neutralised by fertiliser = 0.00081 + 0.00019 = 0.001 = 3.15%

d) Equation: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

Amount of N = 0.0317 mol

Mass of N = 14.01 × 0.0317 = 0.444 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 = ±3.2% = ±0.69

Sample B

Amount of NaOH neutralised by fertiliser = 0.0492–0.0194 = 0.0298 mol

Mass of N = 14.01 x 0.0298 = 0.417 g

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

Sample C

Amount of NaOH neutralised by fertiliser = 0.0492 – 0.0178 = 0.0314 mol

Mass of N = 14.01 × 0.0314 = 0.440 g

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

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

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

Percentage of N = 21.6 ± 0.1

Conclusion & Evaluation

a) The result obtained of 21.6 is ~2% greater than the accepted value of 21.2. The discrepancy is greater than the uncertainty of ±0.1 calculated from replicate determinations. It is however well within the instrumental uncertainty of each value ±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.

b) 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.

c) 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.

TEACHING NOTES for Investigation 8C
STRONG AND WEAK ACIDS AND BASES

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: H_2SO_4 (aq), HCl (aq), HNO_3 (aq), NaOH (aq), NH_3 (aq).

Apparatus (per group)

- 6 × Test tubes
- 4 × Boiling tubes
- 10 cm^3 measuring cylinder
- 100 cm^3 conical flask
- Burette and funnel

also generally available

- Conductivity apparatus

Chemicals required

- 1 mol dm^{-3} hydrochloric acid (~100 cm^3 per group)
- 1 mol dm^{-3} sulfuric acid (~100 cm^3 per group)
- 1 mol dm^{-3} nitric acid (~100 cm^3 per group)
- 1 mol dm^{-3} ethanoic acid (~100 cm^3 per group)
- 0.1 mol dm^{-3} hydrochloric acid (~100 cm^3 per group)
- 0.01 mol dm^{-3} hydrochloric acid (~100 cm^3 per group)
- 1 mol dm^{-3} aqueous sodium hydroxide (~100 cm^3 per group)
- 0.1 mol dm^{-3} aqueous sodium hydroxide (~20 cm^3 per group)
- 0.01 mol dm^{-3} aqueous sodium hydroxide (~20 cm^3 per group)
- 1 mol dm^{-3} aqueous ammonia (~20 cm^3 per group)
- 1 mol dm^{-3} aqueous ammonium chloride (~20 cm^3 per group)
- 1 mol dm^{-3} aqueous potassium hydroxide (~2 cm^3 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

TEACHING NOTES for Investigation 8C STRONG AND WEAK ACIDS AND BASES

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^{-1}
Distilled water	6.5	0.05
0.01 mol dm^{-3} hydrochloric acid	2.0	0.49
0.1 mol dm^{-3} hydrochloric acid	1.0	4.0
1 mol dm^{-3} hydrochloric acid	0.5	36
1 mol dm^{-3} ethanoic acid	2.5	0.89
0.01 mol dm^{-3} aqueous sodium hydroxide	12.0	0.22
0.1 mol dm^{-3} aqueous sodium hydroxide	13.0	2.0
1 mol dm^{-3} aqueous sodium hydroxide	13.5	20
1 mol dm^{-3} aqueous ammonia	12.0	0.10

a) The pH increased with decreasing concentration as it is a measure of the concentration of H^+ 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 $[H^+]$. This is reflected between 0.1 and 0.01 mol dm^{-3} HCl, but the value for the 1 mol dm^{-3} solution is higher than expected.

b) The pH of CH_3COOH 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^{-3} HCl so, if HCl is fully dissociated, less than 1% of the CH_3COOH is dissociated.

c) The conductivity of the acid depends on the movement of H^+ 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.

d) The conductivity of CH_3COOH 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^{-3} HCl indicating about 1% dissociation.

e) NaOH is a strong base and hence fully dissociated into ions. The greater the concentration of OH^- the greater the pH (increased $[OH^-]$ means decreased $[H^+]$) and the greater the conductivity of the solution, but once again the pH of the 1 mol dm^{-3} 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^{-3} hydrochloric acid	Rapid effervescence of a colourless gas. The size of the marble chip gradually decreases.
1 mol dm^{-3} 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^{-3} nitric acid	Rapid effervescence of a colourless gas. The size of the marble chip gradually decreases.
1 mol dm^{-3} ethanoic acid	Slow effervescence of a colourless gas. The decrease in size of the marble chip is hardly perceptible.
0.1 mol dm^{-3} hydrochloric acid	Steady effervescence of a colourless gas. The decrease in size of the marble chip is just visible.
0.01 mol dm^{-3} 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_3 and H_2SO_4 are very similar, though the latter rapidly ceases to react. The rate of reaction of HCl decreases with concentration as less H^+ ions are present in the solution. The ethanoic acid reacts much more slowly than the other 1 mol dm^{-3} acids showing that the concentration of hydrogen ions is much less.

g) $CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + H_2O + CO_2$

h) The reaction quickly slowed and ceased. This is because the product, $CaSO_4$, 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^{-3} hydrochloric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm^{-3} sulfuric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm^{-3} nitric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm^{-3} 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) $Mg + 2\,H^+ \rightarrow Mg^{2+} + H_2$

k) The CH_3COOH reacted much more slowly than the other acids because it is only partially dissociated and hence the $[H^+]$ is much less than in the strong acids.

5)

Acid	Observations
1 mol dm^{-3} hydrochloric acid	The black powder slowly dissolves to give a clear blue-green solution. No gas is evolved.
1 mol dm^{-3} sulfuric acid	The black powder slowly dissolves to give a clear blue solution. No gas is evolved.
1 mol dm^{-3} nitric acid	The black powder slowly dissolves to give a clear blue solution. No gas is evolved.
1 mol dm^{-3} 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_3COOH.

m) $CuO + 2\ HCl \rightarrow CuCl_2 + H_2O$ Copper(II) chloride

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$ Copper(II) sulfate

$CuO + 2\ HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$ Copper(II) nitrate

$CuO + 2\ CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2O$ Copper(II) ethanoate

n) $CuO + 2\ H^+ \rightarrow Cu^{2+} + H_2O$

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 whit solid does not dissolve.

o) Ammonia.

p) $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

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 /cm³	Final burette reading /cm³	Volume of acid added /cm³
1 mol dm^{-3} hydrochloric acid	0.0	10.8	10.8
1 mol dm^{-3} sulfuric acid	11.0	31.4	20.4
1 mol dm^{-3} nitric acid	31.5	42.9	11.4
1 mol dm^{-3} ethanoic acid	20.0	29.8	9.8
0.1 mol dm^{-3} hydrochloric acid	30.0	31.2	1.2
0.01 mol dm^{-3} hydrochloric acid	32.0	32.1	0.1

r) Hydrochloric, nitric and ethanoic acid all require about 10 cm³ 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 $^{1}/_{10}$ and $^{1}/_{100}$ values that would be predicted.

u) As it depends only on the amount of H^+ that can be produced, there is no difference between CH_3COOH and the other 1 mol dm^{-3} acids. The reaction of the OH^- with the H^+ causes the equilibrium in aqueous CH_3COOH to be displaced to the right and this continues until all the CH_3COOH has been converted to H^+ and CH_3COO^-.

v) $H^+ + OH^- \rightarrow H_2O$

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: $CH_3COOH \rightarrow CH_3COO^- + H^+$

The lower $[H^+]$ 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_3^{2-}, the O^{2-} in CuO and OH^- 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^{2+} ion

TEACHING NOTES for Investigation 9A
COMMON OXIDISING AND REDUCING AGENTS

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^3 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_2O_3, ignited by a fuse of Mg ribbon), or the formation of aluminium iodide (powdered Al & I_2, 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 $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Reduction half equation $H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$

Overall ionic equation $2\ Fe^{2+} + H_2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O$

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 $Zn \rightarrow Zn^{2+} + 2\ e^-$

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

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

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 $2\ I^- \rightarrow I_2 + 2\ e^-$

Reduction half equation $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$

Overall ionic equation $2\ I^- + Cl_2 \rightarrow I_2 + 2\ Cl^-$

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
Oxidation half equation: $2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ e^-$
Reduction half equation: $I_2 + 2\ e^- \rightarrow 2\ I^-$
Overall ionic equation: $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + 2\ S_4O_6^{2-}$

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
Oxidation half equation: $S_2O_3^{2-} + H_2O \rightarrow 2\ SO_2 + 2\ H^+ + 4\ e^-$
Reduction half equation: $S_2O_3^{2-} + 6\ H^+ + 4\ e^- \rightarrow 2\ S + 3\ H_2O$
Overall ionic equation: $S_2O_3^{2-} + 2\ H^+ \rightarrow SO_2 + S + H_2O$

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
Oxidation half equation: $SO_2 + 2\ H_2O \rightarrow SO_4^{2-} + 4\ H^+ + 2\ e^-$
Reduction half equation: $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$
Overall ionic equation: $3\ SO_2 + Cr_2O_7^{2-} + 2\ H^+ \rightarrow 3\ SO_4^{2-} + 2\ Cr^{3+} + H_2O$

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
Oxidation half equation: $Mg \rightarrow Mg^{2+} + 2\ e^-$
Reduction half equation: $2\ H^+ + 2\ e^- \rightarrow H_2$
Overall ionic equation: $Mg + 2\ H^+ \rightarrow Mg^{2+} + H_2$

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: $(COOH)_2 \rightarrow 2\ CO_2 + 2\ H^+ + 2\ e^-$

Reduction half equation: $MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

Overall ionic equation: $5\ (COOH)_2 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{2+} + 8\ H_2O$

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: $H_2O_2 \rightarrow O_2 + 2\ H^+ + 2\ e^-$

Reduction half equation: $MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

Overall ionic equation: $5\ H_2O_2 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ O_2 + 2\ Mn^{2+} + 8\ H_2O$

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, produce by the reduction of water, to form calcium hydroxide.

Oxidised species–calcium Reduced species–water

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

Reduction half equation: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

Overall ionic equation: $Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$

TEACHING NOTES for Investigation 9B
BIOCHEMICAL OXYGEN DEMAND (BOD) BY REDOX TITRATION

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^3 pipette
- 50 cm^3 pipette
- 10 cm^3 pipette
- Pipette filler
- 50 cm^3 measuring
- 100 cm^3 conical flask
- 250 cm^3 conical flask
- cylinder
- 2 × BOD bottle (~250 cm^3 with tight fitting ground glass stoppers)

Chemicals required

- 0.0025 mol dm^{-3} aqueous sodium thiosulfate (~250 cm^3 per group)
- 0.001 mol dm^{-3} aqueous potassium manganate(VII) (permanganate, ~100 cm^3 per group)
- 1 mol dm^{-3} sulfuric acid (~100 cm^3 per group)
- 2.5 mol dm^{-3} aqueous manganese sulfate (~10 cm^3 per group)
- Alkaline iodide solution (50g NaOH & 13.5 g NaI in 100 cm^3, ~10 cm^3 per group)
- Concentrated sulfuric acid (~10 cm^3 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^3	18.60	37.10	41.60
Initial reading /cm^3	0.00	18.60	23.20
Titre of $Na_2S_2O_3$ /cm^3	18.60	18.50	18.40

Mean titre = 18.50 cm^3

Concentration of aqueous potassium manganate(VII) = 0.00100 ± 0.00001 mol dm^{-3}

Volume of aqueous potassium manganate(VII) taken = 10.00 ± 0.06 cm^3

Precision of burette = ± 0.05 cm^3

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^3	15.10	31.30	46.60
Initial reading /cm^3	0.00	16.00	31.50
Titre of $Na_2S_2O_3$ /cm^3	15.10	15.30	15.30

Mean titre = 15.23 cm^3

Volume of water sample taken = 50 ± 0.12 cm^3

Precision of burette = ± 0.05 cm^3

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^3	10.80	21.50	32.20
Initial reading /cm^3	0.00	10.80	21.50
Titre of $Na_2S_2O_3$ /cm^3	10.80	10.70	10.70

Mean titre = 10.73 cm^3

Volume of water sample taken = 50 ± 0.12 cm^3

Precision of burette = ± 0.05 cm^3

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

a) $10\ I^- + 2\ MnO_4^- + 16\ H^+ \rightarrow 5\ I_2 + 2\ Mn^{2+} + 8\ H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

b) Amount of MnO_4^- used = c.V = $0.001 \times 0.010 = 1.00 \times 10^{-5}$ mol

Amount of $S_2O_3^{2-}$ = 5 × amount MnO_4^- = 5.00×10^{-5} mol

$[S_2O_3^{2-}] = \frac{n}{V} = \frac{5\times10^{-5}}{0.0185} = 0.00270\ mol\ dm^{-3}$

c) $Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_2$

$4\ Mn(OH)_2 + O_2 + 2\ H_2O \rightarrow 4\ Mn(OH)_3$

$Mn(OH)_3 + 3\ H^+ \rightarrow Mn^{3+} + 3\ H_2O$

$2\ Mn^{3+} + 2\ I^- \rightarrow 2\ Mn^{2+} + I_2$

$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$

d) Amount of O_2 = ¼ × amount of $S_2O_3^{2-}$ = ¼ . c . V

= ¼ × 0.0027 × 0.01523 = 0.0000103 mol

$[O_2] = \frac{n}{V} = \frac{0/0000103}{0.050} = 0.000206\ mol\ dm^{-3}$

Mass of O_2 = n × M_r = 0.000206 × 32.00 = 0.00658 g

Concentration in ppm = mg in 1 dm^3 = 6.58 ppm

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

e) Amount of O_2 = ¼ × amount of $S_2O_3^{2-}$ = ¼ . c . V

= ¼ x 0.0027 × 0.01073 = 0.00000724 mol

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

Mass of O_2 = n × M_r = 0.000145 x 32.00 = 0.00464 g

Concentration in ppm = mg in 1 dm^3 = 4.64 ppm

BOD of sample = 6.58 – 4.64 = 1.94 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

Uncertainty in $[KMnO_4]$ = 1%

Uncertainty in volume of $KMnO_4$ = 0.6%

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

Total uncertainty in $[Na_2S_2O_3]$ = 1 + 0.6 + 0.3 = 1.9%

Initial dissolved oxygen determination

Uncertainty in $[Na_2S_2O_3]$ = 1.9%

Uncertainty in volume of water = 0.24%

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

Uncertainty in $[O_2]$ = 1.9 + 0.24 + 0.3 = 2.44% = 0.161 ppm

Final dissolved oxygen determination

Uncertainty in $[Na_2S_2O_3]$ = 1.9%

Uncertainty in volume of water = 0.24%

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

Uncertainty in $[O_2]$ = 1.9 + 0.24 + 0.3 = 2.44% = 0.113 ppm

BOD value

Uncertainty in BOD = 0.161 + 0.113 = 0.274 = 14.1%

Final BOD value = 1.9 ± 0.3 ppm

Teaching Notes for Investigation 9C
AN INTRODUCTION TO ELECTROCHEMISTRY

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^3 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^3 of each of the following ~0.1 mol dm^{-3} 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^3 of each of the following ~0.1 mol dm^{-3} 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 Metal	Iron(II) sulfate		Lead(II) nitrate		Magnesium sulfate		Silver nitrate	
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.

f) $Fe_{(s)} + Pb(NO_3)_{2\,(aq)} \rightarrow Fe(NO_3)_{2\,(aq)} + Pb_{(s)}$ or better

$Fe_{(s)} + Pb^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Pb_{(s)}$

$Fe_{(s)} + 2\,AgNO_{3\,(aq)} \rightarrow Fe(NO_3)_{2\,(aq)} + 2\,Ag_{(s)}$ or better

$Fe_{(s)} + 2\,Ag^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2\,Ag_{(s)}$

$Pb_{(s)} + 2\,AgNO_{3\,(aq)} \rightarrow Pb(NO_3)_{2\,(aq)} + 2\,Ag_{(s)}$ or better

$Pb_{(s)} + 2\,Ag^{+}_{(aq)} \rightarrow Pb^{2+}_{(aq)} + 2\,Ag_{(s)}$

$Mg_{(s)} + FeSO_{4\,(aq)} \rightarrow MgSO_{4\,(aq)} + Fe_{(s)}$ or better

$Mg_{(s)} + Fe^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Fe_{(s)}$

$Mg_{(s)} + Pb(NO_3)_{2\,(aq)} \rightarrow Mg(NO_3)_{2\,(aq)} + Pb_{(s)}$ or better

$Mg_{(s)} + Pb^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Pb_{(s)}$

$Mg_{(s)} + 2\,AgNO_{3\,(aq)} \rightarrow Mg(NO_3)_{2\,(aq)} + 2\,Ag_{(s)}$ or better

$Mg_{(s)} + 2\,Ag^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2\,Ag_{(s)}$

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 $Zn \rightarrow Zn^{2+} + 2\,e^{-}$

Oxidation/Reduction? Oxidation Anode/Cathode? Anode

i) Half equation $Cu^{2+} + 2\,e^{-} \rightarrow Cu$

Oxidation/Reduction? Reduction Anode/Cathode? Cathode

j) $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

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 $2\,Br^{-} \rightarrow Br_2 + 2\,e^{-}$

o) Oxidation/Reduction? Reduction Anode/Cathode? Cathode

Half equation $Cu^{2+} + 2\,e^{-} \rightarrow Cu$

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.

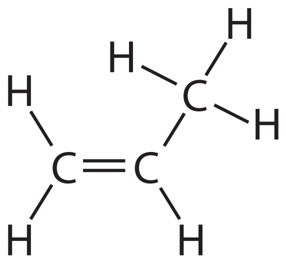
Sample answers

1) 2- or 3-dimensions?

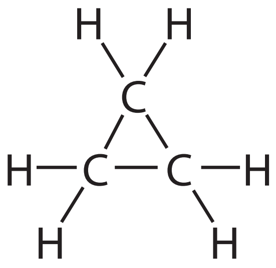
a) When carbon has four single bonds these point to the corners of a tetrahedron and hence extend in three dimensions. This means that all of the positions are equivalent and hence structures that only differ in whether groups are at 90° or 180° to each other in a two-dimensional structure are in fact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

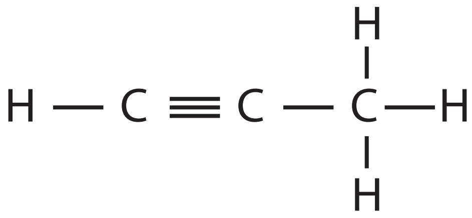


Propene

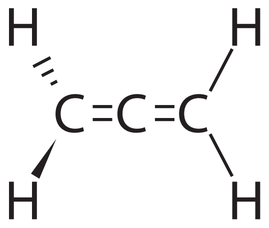


Cyclopropane

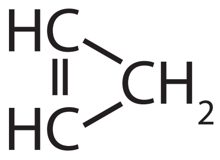
c) There are three possibilities for losing two more hydrogens. Firstly the two carbons either side of the double bond in propene could lose hydrogens to form a triple bond (to give propyne), and secondly the two carbons either side of the single bond in propene could lose hydrogens to form a second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

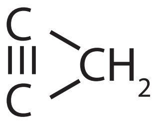


Propadiene

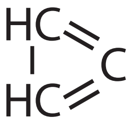


Cyclopropene

d)



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

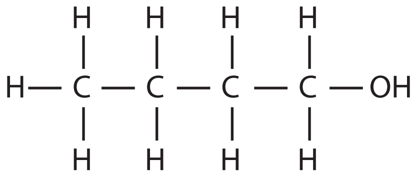
iii.) Hydroxyl group

iv.) The names all end in –anol, following a prefix indicating the hydrocarbon chain length.

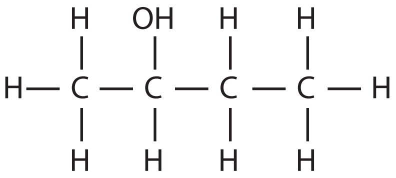
k) The hydrocarbon part of a molecule is chemically rather inert, hence chemical reactivity is mainly a result of the functional groups present. In this case the molecules all have a primary hydroxyl group ($-CH_2-OH$), hence they will have similar chemical reactions.

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 ($-CO-NH_2$)	$C_nH_{(2n+1)}-CO-NH_2$

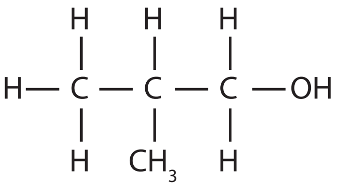
4) Structural isomers



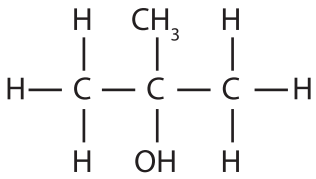
Butan-1-ol



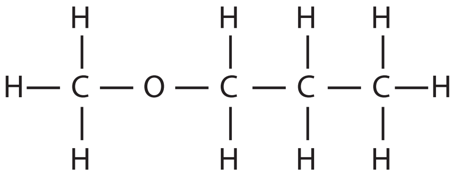
Butan-2-ol (actually two enantiomers of this)



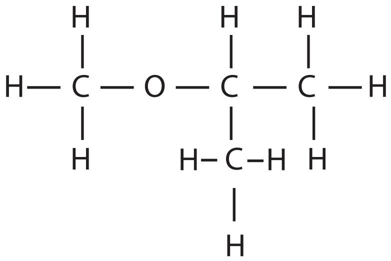
methylpropan-1-ol



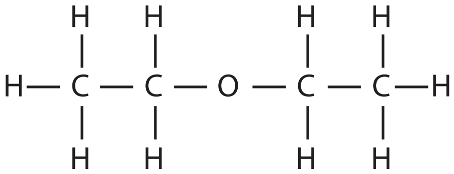
methylpropan-2-ol



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_3-O-) or ethoxy (C_2H_5-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

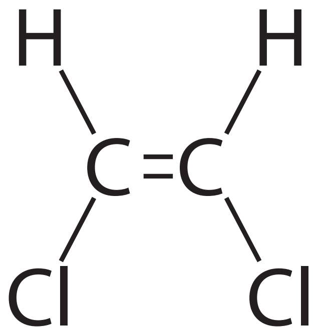
HL Extension

5) Cis/trans and E/Z isomers

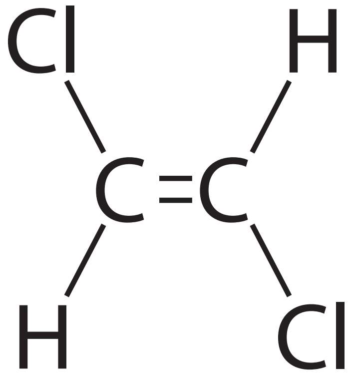
p) There are many possible configurations as the two ends of the molecule are free to rotate relative to each other around the carbon-carbon bond.

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)

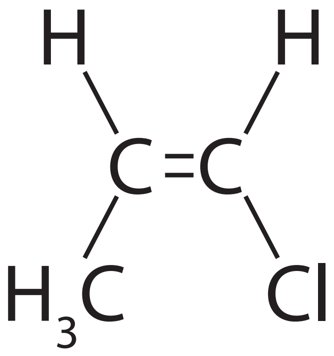


Cis-1,2-dichloroethene

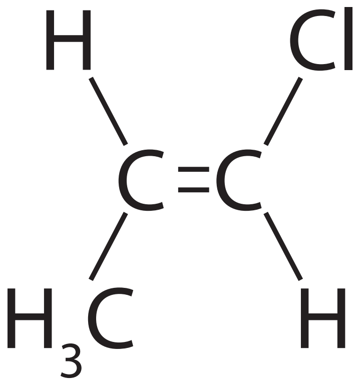


Trans-1,2-dichloroethene

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*).

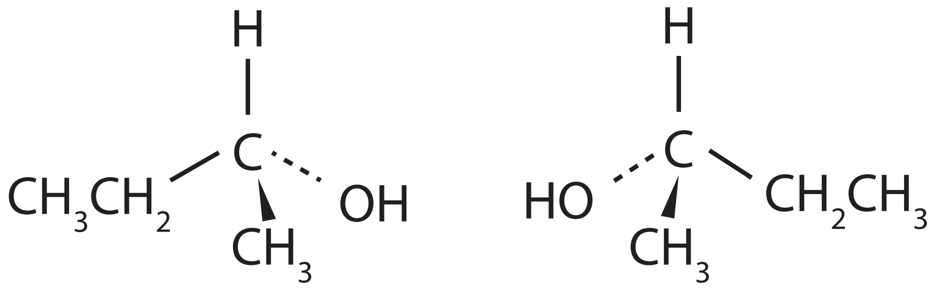
t) There are eight possible geometric isomers of 1,2,3,4,5,6-hexachlorocyclohexane. Considering U to have the chlorine above the ring (considered planar, which it isn't, but the method is still valid!) and D below the ring, the following combinations are possible:

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.

TEACHING NOTES for Investigation 10B
SOME REACTIONS OF HYDROCARBONS

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^3)
- Cyclohexene (~10 cm^3)
- Methylbenzene (toluene, ~10 cm^3 in total)
- Bromine water (Freshly prepared, ~5 cm^3)
- Aqueous ammonia (~10 cm^3 in total)
- Aqueous acidified potassium manganate(VII) (~5 cm^3) (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.

TEACHING NOTES for Investigation 10B
SOME REACTIONS OF HYDROCARBONS

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_6H_{14}) has a C:H ratio of 1:2.33

Cyclohexene (C_6H_{10}) has a C:H ratio of 1:1.67

Methylbenzene (C_7H_8) 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) $C_6H_5\text{-}CH_3 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O$

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:

$C_6H_5\text{-}CH_3 + 6\ O_2 \rightarrow 3\ CO_2 + 2\ CO + 2\ C + 4\ H_2O$

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.

$Br_2 \rightarrow 2\ Br\bullet$

$Br\bullet + C_6H_{14} \rightarrow C_6H_{13}\bullet + HBr$

$C_6H_{13}\bullet + Br_2 \rightarrow C_6H_{13}Br + Br\bullet$

$Br\bullet + Br \rightarrow Br_2$

$C_6H_{13}\bullet + Br\bullet \rightarrow C_6H_{13}Br$

$C_6H_{13}\bullet + C_6H_{13}\bullet \rightarrow C_{12}H_{26}$

j) Ammonia reacts with hydrogen bromide to form solid ammonium bromide, which may be detected as a white smoke.

k) $C_6H_{14} + Br_2 \rightarrow C_6H_{13}Br + HBr$ It is an substitution reaction

l) Further substitution of hydrogen atoms in the product can occur, so that substances such as $C_6H_{12}Br_2$ might be produced. With a large excess of bromine eventually all the hydrogen atoms could be substituted by bromine to give C_6Br_{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 (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.

TEACHING NOTES for Investigation 10C
REACTIONS OF ALCOHOLS AND HALOGENOALKANES

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^3 of dil H_2SO_4, then 20 cm^3 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) $C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

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.

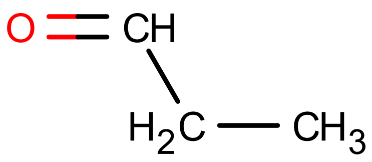
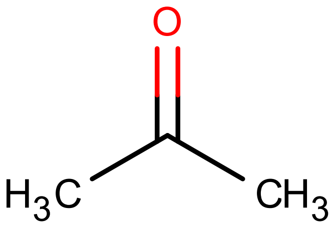
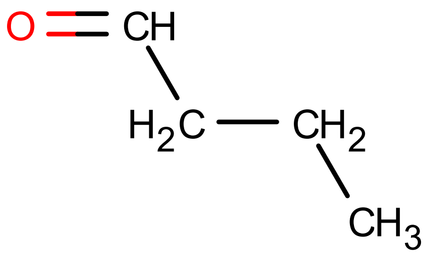
f) Reduction of the dichromate(VI) ion: $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$

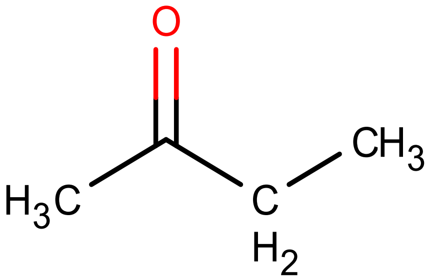
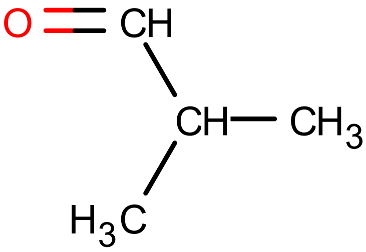
Oxidation of the ethanol: $C_2H_5OH \rightarrow CH_3CHO + 2\ H^+ + 2\ e^-$

Overall ionic equation: $Cr_2O_7^{2-} + 8\ H^+ + 3\ C_2H_5OH \rightarrow 2\ Cr^{3+} + 3\ CH_3CHO + 7\ H_2O$

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) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl\ (s)$

q) Because the chlorine is joined to the molecule by a covalent bond, so chloride ions are not present.

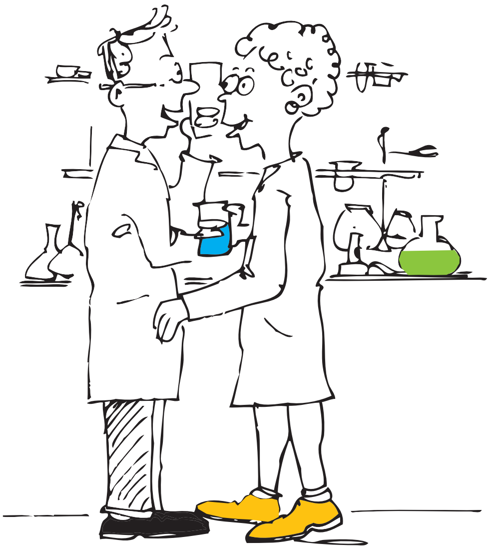
r) $C_4H_9Cl + OH^- \rightarrow C_4H_9OH + Cl^-$

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.



TEACHING NOTES for Investigation 11A
ANALYSIS OF ORGANIC SPECTRA

SYLLABUS REFERENCE: TOPIC 11.3

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

Apparatus & 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.

a) Amount of CO_2 = amount of C = $\frac{3.107}{44.01} = 0.07060$ mol

Amount of H_2O = ½ amount of H = $\frac{1.272}{18.02} = 0.07059$ mol

Mass of C = 12.01 × 0.7060 = 0.8479 g

Mass of H = 2 × 1.01 × 0.7059 = 0.1426 g

Mass of O = 1.273 – 0.8479 – 0.1426 = 0.2825 g

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

Ratio of C:H:O = 0.07060:0.1412:0.01766 = 3.998: 7.995:1

Empirical formula of A is C_4H_8O

b) The highest significant peak is at m/z = 72, hence the molar mass of the compound is probably 72 g mol^{-1}. The molecular formula is therefore the same as the empirical formula; C_4H_8O.

c) As they are all isomers they have the same molecular formula and hence all have a molar mass of 72 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}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 (CH_3-).

ii) m/z = 43: This could correspond to the loss of an ethyl group (C_2H_5-) or an aldehyde group (-CHO).

g) Yes, all of the mass spectra have peaks at m/z=15 (CH_3^+) and m/z=29 ($C_2H_5^+$ or CHO^+).

h) $C_3H_8^{+}$.

i) A saturated C_4 compound would have 10 (2 × 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 cm^{-1} >C=O: 1700-1750 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 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 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 Group	A	B	C	D	E	F	G
-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 {$(CH_3)_2$CH-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 CH_2=CH-CH(OH)-CH_3 (but-1-en-3-ol) HL students will also notice that the methyl group is a doublet, split by the –CH(OH)- hydrogen.

Pair 3: There are three possible cycloalkane alcohols, cyclobutanol (C_4H_7-OH), methylcyclopropanol (CH_3-C_3H_4-OH) and cyclopropylmethanol (C_3H_5-CH_2-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 –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 –CH_2-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 –CH_2-OH, or on the opposite side.

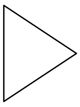
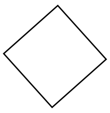
r) There are strong absorptions in the 600-800 cm^{-1} region in the spectra of compounds H to L.

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}Cl and ^{37}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 $C_3H_7{}^{35}Cl$) 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 ~110-120 ($C_3H_6{}^{35}Cl_2$ 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 ~146 so it probably contains three chlorines ($C_3H_5{}^{35}Cl_3$ has M_r = 146).

There are two isomers of C_3H_7Cl and, as the NMR spectrum of L is very simple (2 peaks with a 1:6 ratio) it would appear to be 2-chloropropane (CH_3-CHCl-CH_3). The spectrum of I shows three peaks in a 2:2:3 ratio and so this would correspond to 1-chloropropane (CH_3-CH_2-CH_2Cl). 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 (CH_3-CCl_2-CH_3). 1,3-dichloropropane (Cl-CH_2-CH_2-CH_2-Cl) has two hydrogen environments (1:2 ratio), whereas 1,1-dichloropropane ($CHCl_2$-CH_2-CH_3) and 1,2-dichloropropane (Cl-CH_2-CHCl-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 ~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 (Cl-CH_2-CHCl-CH_2-Cl).

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

Letter	Name	Formula
A	Butanal	CH_3-CH_2-CH_2-CO-H
B	Methylpropanal	CH_3-CH(CH3)-CO-H
C	Butanone	CH_3-CH_2- CO-CH_3
D	But-1-en-3-ol	CH_2=CH-CH(OH)-CH_3
E	Cyclopropylmethanol	 -CH_2-OH
F	Cyclobutanol	 -OH
G	But-1-en-4-ol	CH_2=CH-CH_2-CH_2OH
H	2,2-dichloropropane	CH_3-CCl_2-CH_3
I	1-chloropropane	CH_3-CH_2-CH_2-Cl
J	1,2,3-trichloropropane	Cl-CH_2-CHCl-CH_2-Cl
K	1,2-dichloropropane	Cl-CH_2-CHCl-CH_3
L	2-chloropropane	CH_3-CHCl-CH_3

TEACHING NOTES for Investigation 22A
INVESTIGATING CATALYSTS

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^3 measuring cylinder
- 4 × 100 cm^3 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^{-3} hydrogen peroxide (100 cm^3 per group)
- Solid manganese(IV) oxide (manganese dioxide, ~5 g per group)
- Dilute hydrochloric acid (~50 cm^3 per group)
- 0.1 mol dm^{-3} iron(II) sulfate (~10 cm^3 per group)
- 0.1 mol dm^{-3} iron(III) sulfate (~10 cm^3 per group)
- 0.1 mol dm^{-3} potassium iodide(~10 cm^3 per group)
- Hexane (~5 cm^3 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^3 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^3 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_3O_4), like all lead compounds, is quite toxic.*

CORROSIVE

GOGGLES

GLOVES

Sample results

Heterogeneous catalysis

Quantity	Room temperature Initial	Final	Heated water bath 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) & 5)

	Room temp.	Reduced temp.
Temp. /°C	**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_2	5.77 g
Mass of weighing bottle after emptying	5.28 g
Mass of MnO_2 added	0.49 g
Mass of filter paper	1.07 g
Mass of filter paper & MnO_2 after drying	1.49 g
Mass of MnO_2 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.

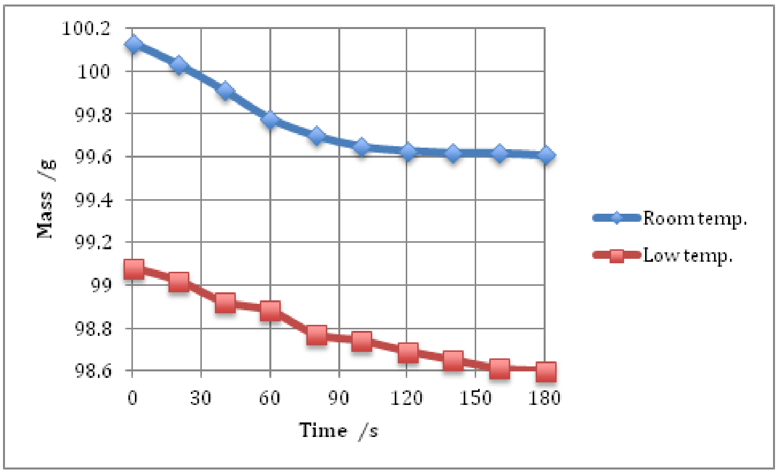
9) The same colour change as in 8) occurs but much more rapidly and then a black precipitate forms.

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 ~50°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^{-1}
H_2O_2 at room temperature	22	8.05×10^{-6}
H_2O_2 in water bath	72	9.49×10^{-5}
H_2O_2 + MnO_2 at room temperature	22	6.37×10^{-3}
H_2O_2 + MnO_2 cooled	12.5	4.00×10^{-3}

b) The manganese(IV) oxide increased the rate of reaction tremendously.

c) For the uncatalysed reaction a 50°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°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 kJ mol^{-1} for the uncatalysed reaction and 34 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):

$2\ Fe^{2+} + H_2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O$

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

$2\ I^- + 2\ Fe^{3+} \rightarrow I_2 + 2\ Fe^{2+}$

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

$2\ I^- + H_2O_2 + 2\ H^+ \rightarrow I_2 + 2\ H_2O$

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 ($I_2 + I^- \rightleftharpoons I_3^-$).

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.

TEACHING NOTES for Investigation 23A
THE CHROMATOGRAPHIC SEPARATION OF AMINO ACIDS

SYLLABUS RELEVANCE: TOPIC B2

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

Apparatus (per group)

- 3 × 250 cm^3 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^3 of each)
  (Argenine, glycine, leucine and valine work well, but probably others do too)

A mixture of 2 or 3 of these (~10 cm^3)

- Eluent solutions (~10 cm^3 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^3 of a 0.02 mol dm^{-3} 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.*

CORROSIVE
GLOVES
GOGGLES

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

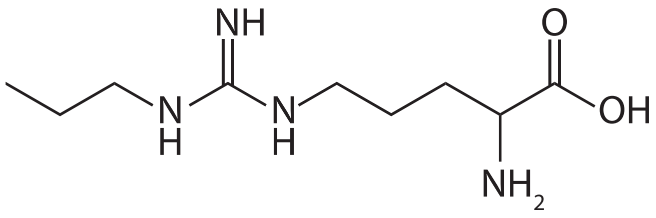
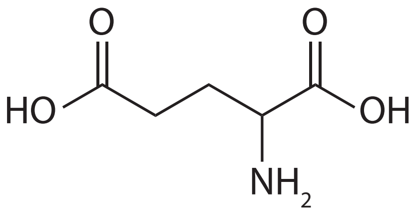
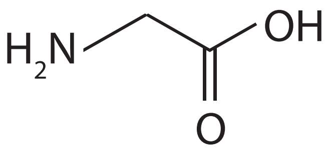
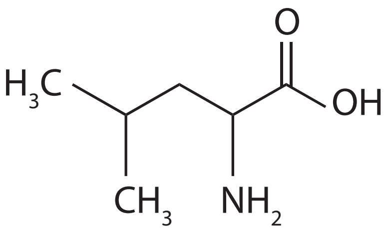
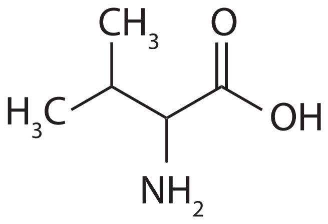
Data Analysis

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 0.12 to 0.20	-0.03 to +0.05 0.07 to 0.11 0.20 to 0.30	0 to 0.09 0.17 to 0.32 0.32 to 0.46

b)

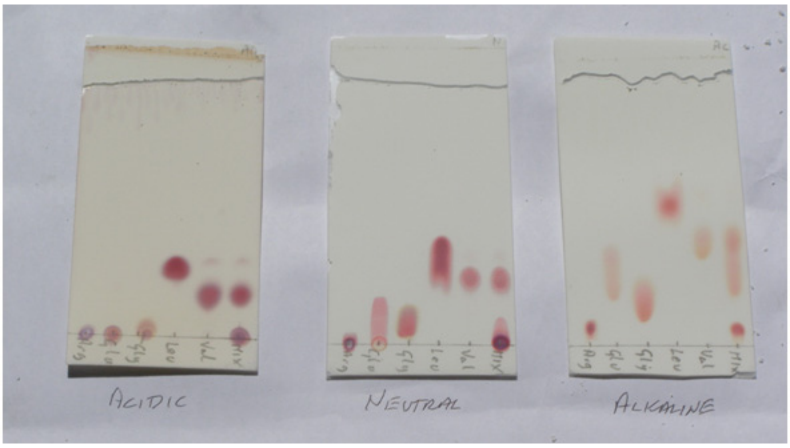
Arginine	
Glutamic acid	
Glycine	
Leucine	
Valine	

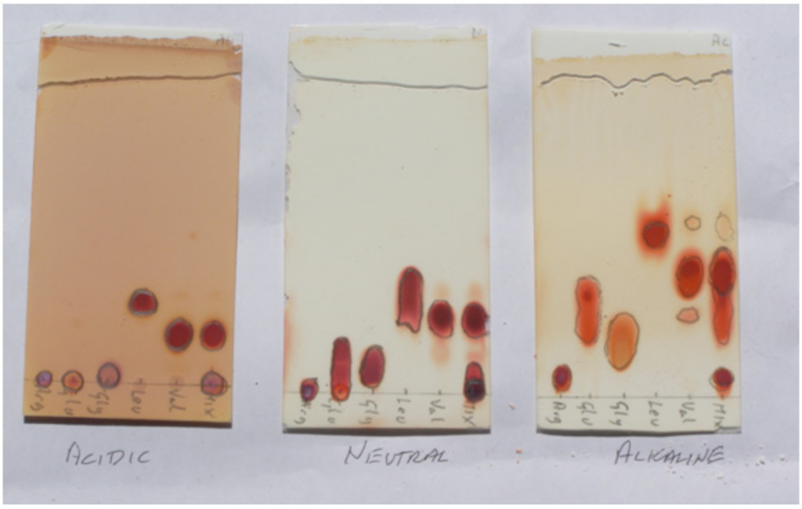
As can be seen from the structures above Arginine has lots of polar groups and hence can bond quite tightly to the polar stationary phase, so it has a very low R_f in all solvents. This is also true for glutamic acid in acidic and neutral media, but the acid groups cause it to be quite soluble in the 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 assignations.

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.





TEACHING NOTES for Investigation 24A
THE ENTHALPY OF COMBUSTION OF FUELS

SYLLABUS RELEVANCE; TOPIC C1

The energy density of different fuels could be investigated experimentally.

Apparatus (per group)

- Copper calorimeter
- 100 cm^3 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 Initial**	**Final**	**Temperature ± 0.5 °C 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^3

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) & c)

Fuel	Temperature change ± 1 °C	Heat evolved /kJ	Mass change ± 0.01 g	Specific energy kJ g^{-1}	Density g dm^{-3}	Energy density 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

Approximate uncertainty of temperature change $= \frac{1}{25} \times 100 = \pm 4\%$

Approximate uncertainty of mass change $= \frac{0.01}{0.60} \times 100 = \pm 1.5\%$

Approximate uncertainty of water volume $= \frac{0.5}{100} \times 100 = \pm 0.5\%$

Approximate overall uncertainty $= \pm 6\%$

d)

Fuel	Heat evolved /kJ	Mass change / g	Molar mass /g mol^{-1}	Amount used /mol	ΔH_{comb} /kJ mol^{-1}
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 ΔH_{comb} /kJ mol^{-1}	Literature value /kJ mol^{-1}	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 (±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 lod 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.

TEACHING NOTES for Investigation 25A
THE SYNTHESIS OF ASPIRIN

SYLLABUS RELEVANCE: TOPIC D2

Experiments could include the synthesis of aspirin.

Apparatus (per group)

- 100 cm^3 Quickfit flask
- Condenser for flask
- 10 cm^3 measuring cylinder
- 25 cm^3 measuring cylinder
- 250 cm^3 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^3 per student)
- Concentrated phosphoric acid (~1 cm^3 per student)
- 2-hydroxybenzoic (salicylic) acid (~10 g per student)
- 2 mol dm^{-3} aqueous sodium hydroxide (~5 cm^3 per student)
- 0.1 mol dm^{-3} aqueous iron(III) chloride (~1 cm^3 per student)
- 50% aqueous ethanoic (acetic) acid (~40 cm^3 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

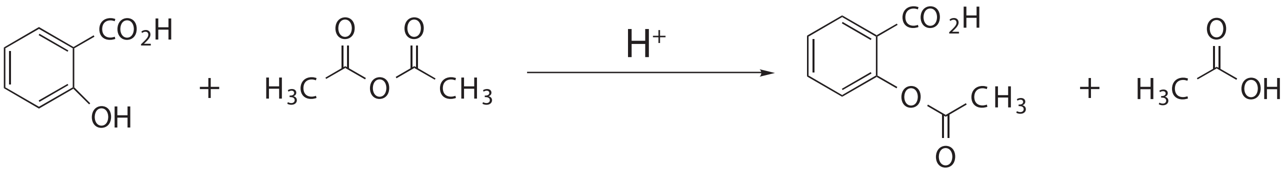
The white powder dissolved readily to produce a colourless solution.

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^{-1}

Molar mass of acetylsalicylic acid = 180.16 g mol^{-1}

Amount of 2-hydroxybenzoic acid $= \frac{10.00}{138.13} = 0.0724\,mol$

Theoretical mass of acetylsalicylic acid = 0.0724 × 180.16 = 13.0 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 cm^{-1}) and the broader and more intense -O-H absorption (3000 - 3400 cm^{-1}) in the 2-hydroxybenzoic acid.

ii. Both spectra clearly show carbonyl (>C=O) absorptions at 1700-1750 cm^{-1}, as well as C-H absorptions at 2850-3090 cm^{-1}.

iii. 2-hydroxybenzoic acid has a strong absorption at 2930 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 ~3250 cm^{-1} would also work quite well.

TEACHING NOTES for Investigation 13A
SOME CHEMICAL REACTIONS OF TRANSITION METALS

Syllabus relevance: Topic 13.1 & 13.2

The oxidation states of vanadium and manganese, for example, could be investigated experimentally.

Apparatus (per group)

- 6 × test tubes
- 2 × boiling tubes
- 100 cm^3 beaker
- Wooden splints

Chemicals required

About 10 cm^3 per student of aqueous solutions of the following: The concentration is not vital, from 1 mol dm^{-3} to 0.1 mol dm^{-3} will do unless stated otherwise.

- Acidified ammonium vanadate(V) (1.2 g of solid dissolved in 100 cm^3 dil H_2SO_4)
- Chromium(III) sulfate
- Potassium chromate (VI)
- Hydrogen peroxide
- Manganese(II) sulfate
- Potassium manganate(VII) [0.01 mol dm^{-3}]
- Iron(II) ammonium sulfate
- Iron(III) chloride
- Potassium thiocyanate
- Potassium iodide
- Cobalt(II) chloride
- Nickel(II) sulfate
- Copper(II) sulfate
- Sodium thiosulfate [0.2 mol dm^{-3}]

Supplies of the following normal laboratory reagents (~50 cm^3 per student)

- Aqueous sodium hydroxide [2 mol dm^{-3}]
- Aqueous ammonia [2 mol dm^{-3}]
- Dilute sulfuric acid [1 mol dm^{-3}]
- Concentrated hydrochloric acid

The following solids:

- Granulated zinc (~2 g per group)
- Solid manganese(IV) oxide (~2 g per group)
- Solid glucose (~2 g per group)

Notes

Probable timing–90 minutes laboratory time

TEACHING NOTES for Investigation 13A
SOME CHEMICAL REACTIONS OF TRANSITION METALS

1. Vanadium

a) **Observations** – The yellow solution starts to effervesce when the piece of zinc is added. It initially goes through green to a blue solution. The solution then gradually turns green again and eventually changes to a lilac colour.

Interpretation – The first green colour is a mixture of the original yellow, vanadium(V) and the blue of the vanadium(IV) state that is being produced. The solution then turns green owing to the formation of the vanadium(III) ion and then changes to the lilac colour of vanadium(II).

Equation(s)

$VO_3^- + 4\,H^+ + e^- \rightarrow VO^{2+} + 2\,H_2O$

Yellow → Blue

$VO^{2+} + 2\,H^+ + e^- \rightarrow V^{3+} + H_2O$

Blue → Green

$V^{3+} + e^- \rightarrow V^{2+}$

Green → Lilac

$Zn \rightarrow Zn^{2+} + 2\,e^-$

2. Chromium

a) **Observations** – The chromium(III) ions react with the hydroxide ions to form a murky green precipitate, which redissolves in excess of the alkali to form a clear bright green solution.

Interpretation – The initial precipitate is chromium(III) hydroxide which is amphoteric and redissolves to form a solution of the chromate(III) ion.

Equation(s)

$Cr^{3+}(aq) + 3\,OH^-(aq) \rightarrow Cr(OH)_3(s)$

$Cr(OH)_3(s) + OH^-(aq) \rightarrow Cr(OH)_4^-(aq)$

b) **Observations** – The bright green solution becomes gradually more yellow in colour until eventually the solution becomes a bright yellow. There is gentle bubbling of the mixture, especially when heated.

Interpretation – The hydrogen peroxide, which is being reduced to water, oxidises the chromate(III) ion to the chromate(VI) ion,

Equation(s)

$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$

$Cr(OH)_4^- + 4\,OH^- \rightarrow CrO_4^{2-} + 4\,H_2O + 3\,e^-$

c) **Observations** – The yellow solution turns an orange colour as the acid is added to it and then this colour change is reversed by addition of the alkali.

Interpretation – The yellow dichromate ion is in equilibrium with the orange dichromate ion. The hydrogen ions from the acid drive the position of equilibrium to the right, whereas the hydroxide ions from the alkali drive it to the left.

Equation(s)

$CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

Yellow→ Orange

3. Manganese

a) **Observations** – When the alkali is added to the almost colourless solution, a pale buff coloured precipitate forms. On shaking, the colour slowly darkens to a brown.

Interpretation – The hydroxide ions react with the manganese(II) ions to precipitate out manganese(II) hydroxide. This is then slowly oxidised by oxygen in the air to form the darker coloured manganese(III) hydroxide.

Equation(s)

$Mn^{2+}(aq) + 2\ OH^{-}(aq) \rightarrow Mn(OH)_2(s)$

$Mn(OH)_2(s) + H_2O \rightarrow Mn(OH)_3(s) + H^+ + e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

b) **Observations** – When the black solid is added to the colourless solution there is rapid effervescence, a colourless gas is evolved and the mixture becomes significantly warmer.

Interpretation – The manganese(IV) oxide catalyses the decomposition of hydrogen peroxide into water and oxygen.

Equation(s)

$H_2O_2 \rightarrow 2\ H_2O + O_2$

c) **Observations** – The initial colour of the manganate(VII) solution is purple in all three cases. In the acidic solution the cyclohexene forms a colourless layer and slowly the aqueous layer is decolourised to leave a clear, colourless solution. In the case of the neutral solution the reaction with the cyclohexene causes the aqueous layer to become brown and cloudy, whilst with the alkaline solution it changes from purple to a deep dark green colour.

Interpretation – In each case the manganate(VII) ion is oxidising the cyclohexene to cylohexan-1,2-diol. The reduction product varies according to the concentration of hydrogen ions. In acidic solution manganate(VII) ion is reduced to the almost colourless manganese(II) ion; in neutral solution insoluble, brown manganese(IV) oxide is produced, and in alkaline conditions the product is the dark green manganate(VI) ion.

Equation(s)

$C_6H_{10} + 2\ H_2O \rightarrow C_6H_{12}O_2 + 2\ H^+ + 2\ e^-$

$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

$MnO_4^- + 4\ H^+ + 3\ e^- \rightarrow MnO_2 + 2\ H_2O$

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$

4. Iron

a) **Observations** – The very pale green solution reacts with the alkali to form a murky green gelatinous precipitate. Whilst there is no immediate sign of further reaction over the next hour the precipitate gradually darkens and near the surface of the solution becomes reddish-brown in colour.

Interpretation–The hydroxide ions react with the iron(II) ions to precipitate out iron(II) hydroxide. This oxidation by oxygen in the air to form the reddish brown iron(III) hydroxide, is much slower than in the case of manganese.

Equation(s)

$Fe^{2+}(aq) + 2\ OH^{-}(aq) \rightarrow Fe(OH)_2(s)$

$Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s) + H^+ + e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

b) **Observations** – The yellow-brown solution reacts with the alkali to form a gelatinous red-brown precipitate, but no further change occurs on adding excess of the reagent.

Interpretation – The hydroxide ions react with the iron(III) ions to precipitate out iron(III) hydroxide. Unlike the chromium and aluminium equivalents this is not amphoteric in the normal sense and unless very high concentrations of hydroxide ions are present it will not redissolve.

Equation(s)

$Fe^{3+}(aq) + 3\ OH^{-}(aq) \rightarrow Fe(OH)_3(s)$

c) **Observations** – With the iron(II) solution there is a slight darkening of the almost colourless solutions to a pale straw colour. With the iron(III) the yellow-brown solution turns an intense blood-red colour when the colourless thiocyanate solution is added.

Interpretation – Iron(III) ions react with the thiocyanate ion to produce a very highly coloured complex ion. With iron(II) ions there is no reaction, but solutions of iron(II) salts almost always give a mild positive reaction owing to the presence of iron(III) ions in them as a result of oxidation by atmospheric oxygen.

Equation(s)

$Fe^{3+} + SCN^{-} \rightarrow Fe(SCN)^{2+}$

5. Cobalt

a) **Observations** – The pale pink solution gradually changes colour, through shades of purple, to a bright blue colour as the concentrated acid is added. This colour change is reversed on dilution, but restores as the mixture is heated.

Interpretation – The chloride ions from the acid gradually displace the water ligands from around the pink hexaaquacobalt(II) ion to form the blue tetrachlorocobalt(II) ion. On reducing the chloride ion concentration the equilibrium is displaced back to the left, but heating causes it to shift to the right once more, indicating that the forward reaction is endothermic.

Equation(s)

$Co(H_2O)_6^{2+} + 4\ Cl^{-} \rightleftharpoons CoCl_4^{2-} + 6\ H_2O$

6. Nickel

a) **Observations**–The green coloured solution gradually changes colour to a brighter yellow-green shade.

Interpretation–The chloride ions from the acid gradually displace the water ligands from around the green hexaaquanickel(II) ion to form the yellow-green tetrachloronickel(II) ion.

Equation(s)

$Ni(H_2O)_6^{2+} + 4\ Cl^{-} \rightleftharpoons NiCl_4^{2-} + 6\ H_2O$

b) **Observations**–Initially the green solution becomes cloudy owing to the formation of a pale green precipitate. As excess ammonia is added the solution clears to a clear, pale blue colour.

Interpretation – Initially the hydroxide ions present in the aqueous ammonia react with the nickel(II) ions to form a precipitate of nickel(II) hydroxide, though if the concentrations of the two solutions are low this stage may not be apparent. On adding excess ammonia the precipitate redissolves to form the pale blue coloured hexaamminenickel(II) complex ion.

Equation(s)

$Ni^{2+}(aq) + 2\ OH^{-}(aq) \rightarrow Ni(OH)_2(s)$

$Ni(OH)_2(s) + 6\ NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq) + 2\ OH^{-}(aq)$

7. Copper

a) **Observations** – The blue coloured solution reacts with the alkali to form a pale blue precipitate, but there is no further reaction with excess alkali.

Interpretation – The blue hexaaquacopper(II) ions react with the hydroxide ions in the alkali to precipitate copper(II) hydroxide, which is not amphoteric and hence does not redissolve in excess.

Equation(s)

$Cu^{2+}(aq) + 2\,OH^{-}(aq) \rightarrow Cu(OH)_2(s)$

b) **Observations**–Initially the blue solution becomes cloudy and a pale blue precipitate forms. As excess ammonia is added the precipitate redissolves to form a clear, intense royal blue coloured solution.

Interpretation–Initially the hydroxide ions present in the aqueous ammonia react with the copper(II) ions to form a precipitate of copper(II) hydroxide. On adding excess ammonia the precipitate redissolves to form the strongly coloured, royal blue tetraamminecopper(II) complex ion.

Equation(s)

$Cu^{2+}(aq) + 2\,OH^{-}(aq) \rightarrow Cu(OH)_2(s)$

$Cu(OH)_2(s) + 4\,NH_3(aq) + 2H_2O \rightleftharpoons Cu(H_2O)_2(NH_3)_4^{\,2+}(aq) + 2\,OH^{-}(aq)$

c) **Observations** – The blue colour solution gradually changes colour, through shades of green, to a yellow colour when a large excess of the concentrated acid is added.

Interpretation–The chloride ions from the acid gradually displace the water ligands from around the blue hexaaquacopper(II) ion to form the yellow tetrachlorocopper(II) ion, the intermediate colours being caused by a mixture of these colours and/or partial ligand replacement.

Equation(s)

$Cu(H_2O)_6^{\,2+} + 4\,Cl^{-} \rightleftharpoons CuCl_4^{\,2-} + 6\,H_2O$

d) **Observations** – The white glucose dissolves readily in the blue solution without any significant change in its colour, even on heating. On adding the alkali the mixture becomes cloudy and the colour changes through green and yellow to a red-brown precipitate.

Interpretation – In alkaline conditions the glucose reduces copper(II) ions to the insoluble, red-brown copper(I) oxide.

Equation(s)

$C_6H_{12}O_6 + 6\,H_2O \rightarrow 6\,CO_2 + 12\,H^{+} + 12\,e^{-}$

$2\,Cu^{2+} + H_2O + 2\,e^{-} \rightarrow Cu_2O + 2\,H^{+}$

e) **Observations** – The blue solution reacts with the colourless iodide solution to give a cloudy brown mixture. On adding the thiosulfate the brown colouration disappears to leave an off-white precipitate in a colourless solution.

Interpretation – The blue copper(II) ions are reduced to copper(I) ions which react with iodide ions to form an off-white precipitate of insoluble copper(I) iodide. The oxidation of the iodide ions produces a brown solution of iodine. When aqueous thiosulfate ions are added these react with the iodine, converting it back to colourless iodide ions so the colour of the copper(I) iodide is clearer.

Equation(s)

$Cu^{2+} + I^{-} + e^{-}\ CuI$

$2\,I^{-} \rightarrow I_2 + 2\,e^{-}$

$I_2 + 2\,S_2O_3^{\,2-} \rightarrow 2\,I^{-} + S_4O_6^{\,2-}$

TEACHING NOTES for Investigation 15A
ENTHALPIES OF SOLUTION

Syllabus relevance; Topic 15.1

Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.

Apparatus required

Per group

- Thermometer (0–110°C) or data logging sensor
- Stop watch
- 100 cm^3 measuring cylinder
- 100 cm^3 beaker
- Polystyrene cup

Generally available

- Balance capable of weighing to at least 0.01 g

Chemicals required

- Ammonium chloride (~25 g per group)
- Sodium chloride (~25 g per group)
- Sodium iodide (~25 g per group)
- Calcium chloride (anhydrous, ~25 g per group)

Notes

Probable timing–60 minutes laboratory time

A data logger can be used to record the temperature changes, though the time scale is such that it is not really necessary and as the enthalpy of solution measurements and calculations are rather repetitive you may wish to assign each group of students just one of the solids and the results can then be shared. Using a spreadsheet to carry out the repetitive calculations should be encouraged.

The results obtained should be in reasonable agreement with literature values. The temperature changes for most of the systems are relatively small, indeed so small that the uncertainty arising from the temperature change for the sodium salts is significant. The fact that entropy changes must be taken into account to explain why substances dissolve endothermically can provide a nice lead in to a more complete discussion of entropy.

Sample Data

	Solid Weighings			
	NH_4Cl	NaI	NaCl	$CaCl_2$
Beaker + solid /g	34.70	34.62	34.66	34.79
Empty beaker /g	14.65	14.68	14.64	14.64

Time /s	Temperature /°C			
0	21.0	21.0	20.8	20.8
30	21.0	21.0	20.8	20.8
60	21.0	21.0	20.8	20.8
90	21.0	21.0	20.8	20.8
120	21.0	21.0	20.8	20.8
150	8.0	19.0	19.0	28.0
180	7.2	19.0	19.0	31.0
210	7.4	19.0	19.0	31.4
240	7.6	19.2	19.0	31.4
270	7.8	19.2	19.0	31.2
300	8.0	19.4	19.2	31.2
330	8.0	19.4	19.2	31.2
360	8.2	19.4	19.2	31.0
390	8.2	19.4	19.2	31.0
420	8.2	19.6	19.2	31.0
450	8.2	19.6	19.2	30.8
480	8.4	19.6	19.2	30.8
510	8.4	19.6	19.2	30.6
540	8.4	19.6	19.2	30.4
570	8.6	19.6	19.2	30.4
600	8.6	19.6	19.2	30.2

Volume of water = 100 ± 0.5 cm^3

Precision of time measurements ± 1 s

Precision of temperature measurements ± 0.1 °C

Relevant qualitative data

The solutes were all white solids that dissolved easily to form clear colourless solutions, some endothermically and others exothermically.

Data Analysis

Solid Quantity	NH_4Cl	NaI	NaCl	$CaCl_2$
Temperature change /°C	-13.8	-2.0	-1.8	+10.6
Heat change /J	-5768	-836	-752	+4431
Mass of solid /g	20.05	19.94	20.02	20.15
Molar mass /g mol^{-1}	53.50	149.89	58.44	110.98
Amount of solid /mol	0.3832	0.133	0.343	0.182
Enthalpy of solution /kJ mol^{-1}	+15.05	+6.28	+2.20	-24.40

Conclusion & Evaluation

a) Ammonium chloride has quite an endothermic enthalpy of solution. Spontaneous endothermic changes must have a significant increase in entropy. In this case the entropy of ions is, in most cases, significantly greater than the solid salt they are produced from.

b) ΔH(solution) = Lattice enthalpy + $\Sigma\ \Delta H$(hydration of ions) = L.E. + $\Delta H(NH_4^+)$ + $\Delta H(Cl^-)$

+14.78 = L.E. + (-307) + (-359)

L.E. = 666 + 14.78 = +681 kJ mol^{-1}

This is a reasonable value, midway between those of rubidium and caesium.

c) Though this experiment gave a positive value for both, the values in the data booklet give the enthalpy of solution of sodium chloride as slightly endothermic and that of sodium iodide slightly exothermic. The difference between the values may have resulted from the sodium iodide being slightly damp (the crystals appeared to clump together). The difference between the two is the size of the anion and considering the data book values, this would appear to reduce the lattice enthalpy more than it reduces the hydration enthalpy.

d) The sodium and calcium ions are almost exactly the same size, so the major difference is the charge that they carry. The enthalpy of solution of sodium chloride is slightly endothermic whereas calcium chloride is quite exothermic. Remembering that as a consequence of the greater charge there are now two anions rather than one, this increases the hydration enthalpy more than it increases the lattice enthalpy, which is slightly lower than might have been anticipated owing to the 2:1 anion:cation ratio.

e) Calcium fluoride is insoluble. Calculating the enthalpy of solution using data from the data booklet gives a value of +27 kJ mol^{-1} (+2651–1616 – 2x-504) and presumably the increase in entropy at room temperature is not sufficient to overcome this.

f) The values found compared to the literature values are:

Solid Quantity	NH_4Cl	NaI	NaCl	$CaCl_2$
Experimental value /kJ mol^{-1}	+15.05	+6.28	+2.20	-24.40
Literature value /kJ mol^{-1}	+14.78	-7.53	+3.88	-63

(The value for $CaCl_2$ was found by summing lattice enthalpy and hydration enthalpy data.)

There is very good agreement for the enthalpy of solution of ammonium chloride and quite good agreement for sodium chloride. The agreement is less good for sodium iodide, however the solid gave the appearance of being damp, which could have made its dissolution less exothermic. The value for calcium chloride is very different and it is very likely that the solid used was already partly hydrated, calcium chloride is a well known desiccant. It would have been better if the solid had been heated in an oven overnight, to drive off any absorbed water, before carrying out the determination.

g) As is usually the case with thermochemistry experiments, the major source of error is heat exchange with the surroundings. A simple way to improve on this is to have a lid on the cup and to employ a magnetic stirrer, in addition having a double thickness cup would reduce heat exchanges. Another technique would be to heat or cool the water so that the final temperature was an equal amount the other side of room temperature, hence heat gains and heat losses will compensate to some extent. A second major problem is the well documented ability of many solids to absorb water vapour from the atmosphere. This partly hydrates the solids and also affects the effective molar mass of the compound. Another relatively small source of discrepancy is that literature values almost always refer to "infinite dilution" whereas the solutions produced in this investigation are quite concentrated.

h) The temperature measurements are almost certainly the major source of uncertainty, especially for the determinations with a small change in temperature. This is probably a significant factor unless a quite accurate data logging sensor has been used. Whilst large temperature changes reduce the uncertainty of ΔT, they do result in greater heat exchange with the environment, which is also a source of error.

TEACHING NOTES for Investigation 15B
THE ENTHALPY CHANGE OF A DISPLACEMENT REACTION

Syllabus relevance: Topic 15.1 / 19.1

Perform lab experiments which could include single replacement reactions in aqueous solutions.

Apparatus required

Per group

- Thermometer (0–110°C) or data logging sensor
- Stop watch
- 50 cm^3 measuring cylinder
- Polystyrene cup

Generally available

- Balance capable of weighing to at least 0.01 g
- Chemicals required
- 1 mol dm^{-3} aqueous copper(II) sulfate (~50 cm^3 per group)
- Zinc powder (~5 g per group)

Notes

Probable timing–60 minutes laboratory time

A data logger can be used to record the temperature changes, though the time scale is such that it is not really necessary.

Discussion of the results, especially in relation to the assumptions made, both with regard to allowing for heat losses during the reaction and to do with what absorbs heat as the temperature is raised can be quite revealing. The significant role of the differences in the enthalpy of atomisation, that comes out of the conclusion, is also rather unexpected.

Sample data

Time /s	Temp. /°C	Time /s	Temp. /°C	Time /s	Temp. /°C	Time /s	Temp. /°C
0	16.0	210	38.0	420	51.2	630	50.6
30	16.0	240	41.4	450	51.0	660	50.2
60	16.0	270	42.8	480	51.0	690	49.8
90	16.0	300	43.6	510	51.0	720	49.6
120	19.2	330	46.2	540	51.0	750	49.2
150	30.5	360	48.8	570	51.0	780	49.0
180	36.8	390	49.6	600	51.0	810	48.8

Precision of temperature measurements ± 0.1 °C Precision of time measurements ± 1 s

Mass of weighing bottle and zinc = 6.087 ± 0.0005 g

Mass of weighing bottle after emptying = 1.064 ± 0.0005 g

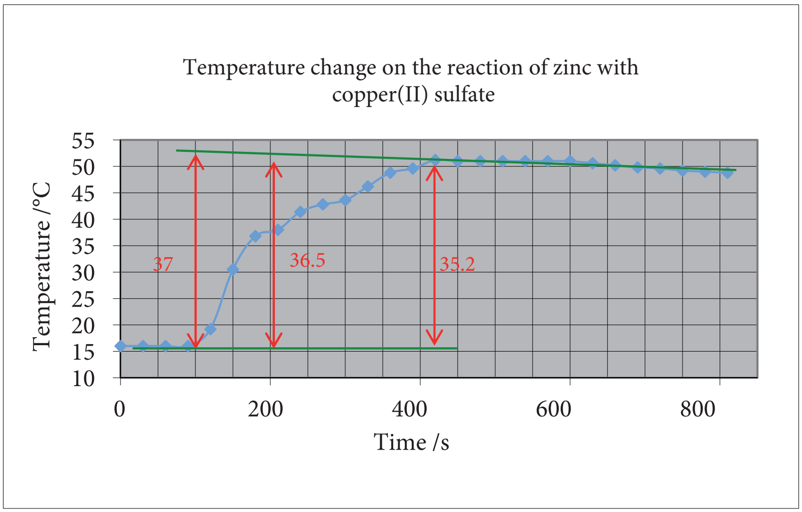
Volume of aqueous copper(II) sulfate = 50 ± 0.5 cm^3

Relevant qualitative data

Grey coloured zinc powder is added to bright blue aqueous copper(II) sulfate. The colour of the powder rapidly darkens and then, in a few places takes on a red-brown colour. At the same time the blue colour of the solution gradually fades. A few bubbles were also noted rising from the powder.

Data Analysis

a)



The maximum recorded temperature gives ΔT = 35.2°C; extrapolation to when the zinc was added gives T ≈ 37°C, but as heat would not have been lost so rapidly at the start of the reaction, then this is an overestimate and so a value of T = 36.5 ±0.5 °C will be used

b) In these calculations it is assumed that the dilute aqueous solutions involved have a density of 1 g cm^{-3} and a specific heat capacity of 4.18 kJ dm $^{-3}$ K^{-1}. In addition the heat capacity of the polystyrene cup and the solid metals present are assumed to be negligible.

Heat evolved = Q = m × c × ΔT = 0.050 × 4.18 × 36.5 = 7.6285 kJ

Uncertainty of m = uncertainty of volume = $\frac{0.5}{50} \times 100 = 1\%$

Uncertainty of ΔT = $\frac{0.5}{36.5} \times 100 = 1.37\%$

Uncertainty in Q = 1 + 1.37 = 2.37%

c) Amount of Cu^{2+} = c × V = 1 x 0.050 = 0.050 mol

Amount of Zn = $\frac{m}{M_r} = \frac{(6.087 - 1.064)}{65.38} = 0.0768$ mol

Hence, as it is a 1:1 reaction the copper(II) ions are the limiting reagent.

d) ΔH = $-\frac{Q}{n} = \frac{7.63}{0.050} = -152.6$ kJ

Uncertainty of n = uncertainty of volume = $\frac{0.5}{50} \times 100 = 1\%$

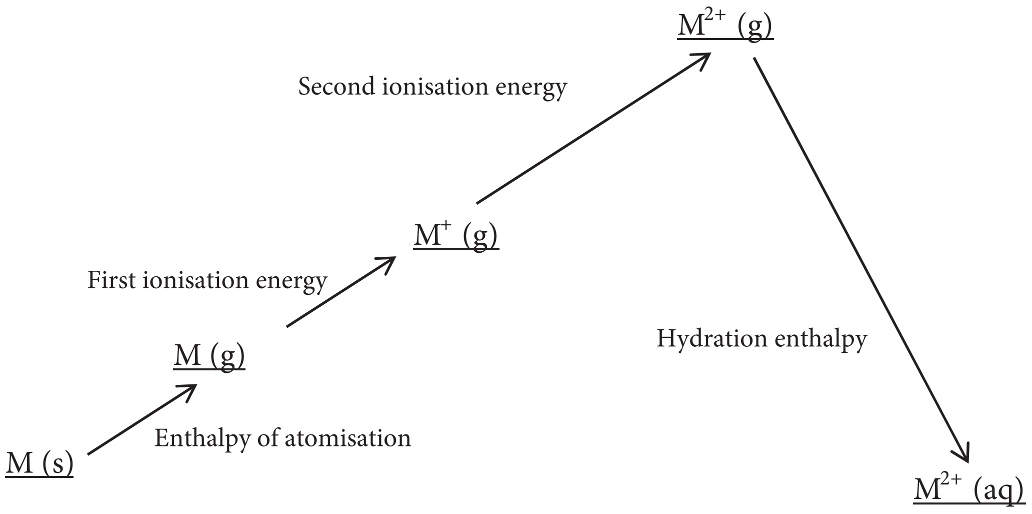
Uncertainty in ΔH = 1 + 2.37 = 3.37%

Absolute uncertainty = $152.6 \times \frac{3.37}{100} = 5.14$

ΔH = -153 ±5 kJ

Conclusion & Evaluation

a)



b)

Quantity	Copper	Zinc
Enthalpy of atomisation /kJ mol^{-1}	+338	+131
First ionisation energy /kJ mol^{-1}	+745	+906
Second ionisation energy /kJ mol^{-1}	+1958	+1733
Hydration enthalpy /kJ mol^{-1}	-2099	-2047
Sum /kJ mol^{-1}	+942	+723

Enthalpy of reaction = +723 – 942 = -219 kJ mol^{-1}

c) $\Delta G = \Delta H - T.\Delta S = -z.F.E \qquad \Delta H = T.\Delta S - z.F.E$

$$E = \frac{\Delta S}{zF}.T - \frac{\Delta H}{z.F}$$

Hence a graph of electrode potential against temperature will have a gradient of $\frac{\Delta S}{zF}$ and an intercept of $-\frac{\Delta H}{z.F}$.

d) If $\Delta S = 0$ then

$$E = -\frac{\Delta H}{z.F} = \frac{-219000}{2 \times 96500} = -1.13\ V$$

e) The value obtained (-153 kJ) is about 30% less exothermic than the theoretical value (-219 kJ); which is well outside the uncertainty (±5 kJ). This leads to the conclusion that there are probably significant systematic errors present.

f) The density of the solution is almost certainly greater than that of water and this would mean that the heat change would be greater than that calculated. The neglect of the heat capacities of the cup and the solids present would also have the same effect. These would lead to a lower value for the enthalpy of reaction as has been observed. There has been an attempt to allow for the loss of heat to the surroundings. If this underestimated the loss then that too would affect the result in the same direction.

g) 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. Inaccuracies associated with the assumptions about the density and specific heat capacity of the aqueous solution could be removed by actually determining these values experimentally. Finally the masses of the solids and their specific heat capacities are known so these could be included in the calculations.

TEACHING NOTES for Investigation 15C
DETERMINING ENTROPY CHANGES

Syllabus relevance: Topic 15.2

Application of $\Delta G = \Delta H - T.\Delta S$

Apparatus required

Per group

- Thermometer (as accurate as possible, max temp. <50°C)
- 100 cm^3 measuring cylinder
- 100 cm^3 conical flask
- 20 cm^3 pipette and filler
- 50 cm^3 burette with filling funnel and white tile
- Polystyrene cup (~250 cm^3 capacity)
- Steam generator (flask with a delivery tube and preferably a safety tube to guard against pressure build up)

Generally available

- Balance capable of weighing to at least 0.01 g

Chemicals required

- Solid sodium hydrogencarbonate (~25 g per group)
- Aqueous 2 mol dm^{-3} hydrochloric acid (~150 cm^3 per group)
- Methyl orange indicator

Notes

Probable timing–90 minutes laboratory time

The determination of the entropy change of vaporisation based on the latent heat of steam, gives surprisingly good results, which are slightly dependent on how long and how well lagged the tube of the steam generator is.

In Part B, students should notice how slowly the suspension settles and comment on it as a source of error – often the titre decreases noticeably for successive titrations! Strictly speaking the ΔH employed should not be the overall value but the value when an infinitesimally small quantity dissolves at equilibrium, but hopefully not too many students will notice. The same probably applies to the relationship used to obtain a value for K_c, which really only applies to K_p! The intent is more to get students using the various relationships rather than producing accurate (or even valid!) data.

Sample data

Part A

Initial temperature of water	= 24.0 ± 0.25 °C
Final temperature of water	= 50.0 ± 0.25 °C
Mass of polystyrene cup	= 2.873 ± 0.0005 g
Initial mass of water in polystyrene cup	= 153.130 ± 0.0005 g
Final mass of water in polystyrene cup	= 159.983 ± 0.0005 g

Mass of cup was visibly decreasing, so final mass is not as accurate as uncertainty quoted

Part B

Initial temperature of water = 24.0 ±0.25 °C

Final temperature of water = 21.0 ±0.25 °C

Volume of water in polystyrene cup = 100 ±0.5 cm^3

Volume of solution titrated = 20 ±0.06 cm^3

Titration No.	1	2	3
Final reading (cm^3)	7.9	15.8	24.1
Initial reading (cm^3)	0.0	7.9	15.8
Titre (cm^3)	7.9	7.9	8.3

Precision of burette readings = ± 0.05 cm^3

Part C

Mass of $NaHCO_3$ = 14.001 ± 0.0005 g

Volume of HCl in polystyrene cup = 100 ± 0.5 cm^3

Initial temperature of HCl = 23.0 ± 0.25 °C

Final temperature of HCl = 13.5 ± 0.25 °C

Data Analysis

Part A

a) Heat absorbed = $Q_{abs} = m \times c \times \Delta T = (.153130 - 0.002873) \times 4.18 \times (50.0 - 24.0)$

$= 0.150257 \times 4.18 \times 26.0 = 16.33$ kJ

Uncertainty of m = uncertainty of mass = $\frac{0.001}{150.257} \times 100 = 0.0007\%$

Uncertainty of $\Delta T = \frac{0.5}{26} \times 100 = 1.92\%$

Uncertainty in $Q_{abs} = 1.92 + 0.0007 = 1.921$ %

$= 16.33 \times \frac{1.921}{100} = = 0.314$ kJ

b) Heat evolved = $Q_{evl} = m \times c \times \Delta T = (0.159983 - 0.153130) \times 4.18 \times (100.0 - 50.0)$

$= 0.006853 \times 4.18 \times 50.0 = 1.43$ kJ

Uncertainty of m = uncertainty of mass = $\frac{0.001}{6.853} \times 100 = 0.015\%$

Uncertainty of $\Delta T = \frac{0.5}{50} \times 100 = 2.000\% =$

Uncertainty in $Q_{evl} = 2.000 + 0.015 = 2.015\%$

$= 1.43 \times \frac{2.015}{100} = = 0.029$ kJ

c) Heat gained by water (Q_{abs}) = Heat lost by hot water (Q_{evl}) + Heat from condensing steam (Q_{LH})

$Q_{LH} = Q_{abs} - Q_{evl} = 16.33 - 1.43 = 15.10$ kJ

Amount of water condensed = n = $\frac{m}{M_r} = \frac{6.853}{18.02} = 0.380\ mol$

Latent heat = $\frac{Q_{LH}}{n} = \frac{15.10}{0.380} = 39.71\ kJ\ mol^{-1}$

Uncertainty in QLH = 0.314 + 0.029 = 0.343 kJ = $\frac{0.343}{15.10} \times 100 = 2.27\%$

Uncertainty in n = $\frac{0.001}{6.853} \times 100 = 0.015\%$

Uncertainty in latent heat = 2.27 + 0.015 = 2.285%

$= 39.71 \times \frac{2.285}{100} =$ 0.907 kJ

Latent heat = 39.7 ±0.9 kJ mol^{-1}

d) ΔG = ΔH – T.ΔS = 0, so ΔH = T.ΔS

$\Delta S = \frac{\Delta H}{T} = \frac{39700}{323} = 122.9$ J mol^{-1} K^{-1} (*Note temperature is final mixture temperature*)

Uncertainty in entropy change = uncertainty in latent heat = ±2.285% = ± 2.4 J mol^{-1} K^{-1}

Entropy change of vaporisation = 123 ± 2 J mol^{-1} K^{-1}

This is for the liquid turning to the gas (an endothermic change). The entropy change is, as would be expected large and positive as gases have much higher entropies than liquids.

Part B

e) Heat absorbed = Q = m × c × ΔT = 0.100 × 4.18 × (21.0 – 24.0) = 1.254 kJ

Uncertainty of m = $\frac{0.5}{100} \times 100 = 0.5\%$

Uncertainty of ΔT = $\frac{0.5}{3} \times 100 = 16.7\%$

Uncertainty in Q = 16.7 + 0.5 = 17.2 %

f) Mean titre = 8.03 cm^3

Amount of HCO_3^- = Amount of HCl = n = c.V = 2.0 × 0.00803 = 0.01607 mol

Concentration of $NaHCO_3$ = $\frac{n}{V} = \frac{0.01607}{0.020} = 0.8035$ mol dm^{-3}

Uncertainty of titre = $\frac{0.1}{8.03} \times 100 = 1.25\%$

Uncertainty of pipette = $\frac{0.06}{20} \times 100 = 0.3\%$

Uncertainty of concentration = 1.25 + 0.3 = 1.55%

g) Amount of $NaHCO_3$ dissolving in 100 cm^3 = c.V = n = 0.8035 × 0.1 = 0.08035 mol

Enthalpy of solution = $\frac{Q}{n} = \frac{1.254}{0.08035} = +15.61\ kJ\ mol^{-1}$ (positive as it is endothermic)

Uncertainty of water volume = $\frac{0.5}{100} \times 100 = 0.5\%$

Uncertainty of amount of $NaHCO_3$ dissolving = 1.55 + 0.5 = 2.05%

Uncertainty of enthalpy of solution = 17.2 + 2.05 = 19.25%

Absolute uncertainty in enthalpy of solution = $\pm 15.61 \times \frac{19.25}{100} = \pm 3.00$ kJ = ± 3000 J

h) $NaHCO_3$ (s) $\rightleftharpoons$ Na^+(aq) + HCO_3^-(aq)

K = [Na^+(aq)].[HCO_3^-(aq)] (Note: [$NaHCO_3$ (s)] is not included as its value is constant)

i) As [Na^+(aq)] = [HCO_3^-(aq)] = 0.8035

K = [Na^+(aq)].[HCO_3^-(aq)] = 0.80352 = 0.6456

As concentration is squared, uncertainty is 2 × 1.55 = 3.1%

j) $\Delta G = -R.T.\ln K = -8.31 \times (273 + 21) \times \ln(0.6456) = -1069$ J

If K 3.1% less then $\Delta G = 994$ and if K 3.1% less then $G = 1146$, so $\Delta G = 1069 \pm 76$ J

k) $\Delta G = \Delta H - T.\Delta S = 15610 - 294.\Delta S = -1069$

$\Delta S = \frac{15610+1069}{294} = +56.73$ J mol^{-1} K^{-1}

Uncertainty in $\Delta H = \pm 3000$ J

Uncertainty in $\Delta G = \pm 76$ J

Uncertainty in $\Delta S = \pm\frac{3076}{294} = \pm 10.46$ J mol^{-1} K^{-1}

$\Delta S = +57 \pm 10$ J mol^{-1} K^{-1}

l) As would be expected for the decrease in order that occurs when a solid dissolves, the sign of the entropy change is quite large and positive.

Part C

m) Heat absorbed = $Q = m \times c \times \Delta T = 0.100 \times 4.18 \times (23.0 - 13.5) = 3.971$ kJ

Uncertainty of m = $\frac{0.5}{100} \times 100 = 0.5\%$

Uncertainty of $\Delta T = \frac{0.5}{9.5} \times 100 = 5.3\%$

Uncertainty in Q = 5.3 + 0.5 = 5.8 %

Amount of $NaHCO_3$ = $n = \frac{m}{M_r} = \frac{14.001}{84.01} = 0.1667$ mol (Uncertainty negligible)

$\Delta H = \frac{Q}{n} = \frac{3.971}{0.1667} = +23.83$ kJ mol^{-1} (positive sign as endothermic)

Uncertainty in ΔH = uncertainty in Q = 5.8 % = 1.38 kJ mol^{-}

$\Delta H = +23.8 \pm 1.4$ kJ mol^{-1}

n) For a reaction to be spontaneous ΔG has to be negative so for an endothermic reaction; as $\Delta G = \Delta H - T.\Delta S$, so $T.\Delta S > \Delta H$.

o) $\Delta S = \frac{\Delta H}{T} = \frac{23800}{(273+13.5)} = +83.07$ J mol^{-1} K^{-1}

Hence the entropy change for the reaction of sodium hydrogencarbonate with dilute acid must be +83 J mol^{-1} K^{-1} or greater.

Conclusion & Evaluation

P) The literature value for the latent heat of vaporisation is 44 kJ mol^{-1} and that of the entropy of vaporisation is 118.8 J mol^{-1} K^{-1}, compared to the 39.7 ±0.9 kJ mol^{-1} and 123 ±2 J mol^{-1} K^{-1} respectively, which are lower than the literature values by 9.8% and 3.4% respectively. The literature values are outside of the uncertainties, but for thermochemical determinations the correspondence is quite reasonable, especially for the entropy change, so the accuracy of the determinations is quite high.

q) As usual with calorimetric experiments, heat exchange with the surroundings is probably the major source of systematic error, especially with no lid on a container with quite hot liquid. This would be expected to lead to a decrease in the temperature change and hence a lower value for the enthalpy change, as was in fact found. Instrumental random errors are quite minimal compared to this. With regard to the entropy change the accuracy is quite a lot better, so there would appear to be some cancelling of errors. One factor might be the equilibrium temperature which may in fact have been slightly higher than the final temperature of the bulk of the solution leading to the value calculated probably being higher than the true value. Water vapour coming off from the surface of the liquid should not affect the situation as when it evaporates it would have to absorb the latent heat of vaporisation.

r) Probably the best thing to do would be to increase the thermal insulation of the system by putting a second polystyrene cup outside the first one and, probably more importantly, putting a loose fitting lid on the cup. Better stirring would also be useful to ensure that the temperature of the equilibrium would be closer to the final temperature of the mixture.

s) The precision of the temperature measurement is the limiting factor. As it is a saturated solution it is not possible to increase the concentration and hence the temperature change. Thus improving this aspect would depend on more precise measurement of the temperature.

TEACHING NOTES for Investigation 16A
DETERMINING THE RATE EXPRESSION FOR A REACTION

Syllabus relevance; Topic 16.1

Deduction of the rate expression for an equation from experimental data and solving problems involving the rate expression.

Apparatus required

Per group

- 2 × 100/150 cm^3 conical flask
- 2 × boiling tube
- Stopwatch
- Thermometer

Generally available

- 6 × burettes for reagents

Chemicals required

About 50 cm^3 per group of:

- 1 mol dm^{-3} hydrogen peroxide
- 0.1 mol dm^{-3} sulfuric acid
- 0.01 mol dm^{-3} aqueous potassium iodide
- 0.01 mol dm^{-3} aqueous sodium thiosulfate
- Fresh starch solution (~2%)

Notes

Probable timing – 60 minutes laboratory time

This is a fairly standard clock reaction adapted to allow students to elucidate a rate expression. The reaction gives fairly good first order kinetics in iodide and peroxide. In the case of hydrogen ion it is slightly more complex. There appears to be a dependence on $[H^+]$, but not a simple first order dependency. Probably there are two pathways, one acid catalysed and the other not. At least it provides something more interesting for the students to discuss!

Sample data

Mixture	Volume of each reagent taken /cm³							Time	Relative rate
	Solution A			Solution B					
No.	H_2O_2	H_2SO_4	Water	KI	$Na_2S_2O_3$	Starch	Water	/s	$/s^{-1}$
1	5	5	15	5	5	5	10	278	0.003597
1a	5	5	15	5	5	5	10	279	0.003584
2	10	5	10	5	5	5	10	154	0.006494
2a	10	5	10	5	5	5	10	177	0.005650
3	15	5	5	5	5	5	10	124	0.008065
4	20	5	0	5	5	5	10	90	0.011111
5	5	10	10	5	5	5	10	244	0.004098
6	5	15	5	5	5	5	10	222	0.004505
7	5	20	0	5	5	5	10	160	0.006250
7a	5	20	0	5	5	5	10	168	0.005952
8	5	5	15	10	5	5	5	152	0.006579
8a	5	5	15	10	5	5	5	161	0.006211
9	5	5	15	15	5	5	0	108	0.009259

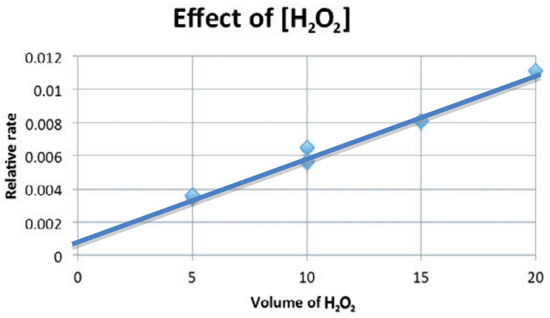
Note this contains some replicate data, indicated by 'a'.

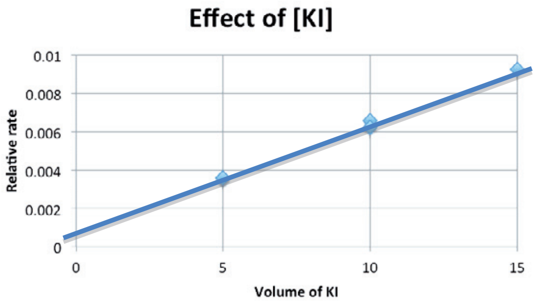
Relevant qualitative data

Solution A and Solution B are both clear, colourless solutions. When they are mixed, the mixture remains clear and colourless until it suddenly (<1 second) turns dark blue.

Data Analysis

a)





b) Rate = k.[H_2O_2].[KI]

c) $H_2O2_{(aq)} + 2\ I^-_{(aq)} + 2\ H^+_{(aq)} \rightarrow I_{2\,(aq)} + 2\ H_2O_{(l)}$

$I_{2\,(aq)} + 2\ S_2O_3^{2-}{}_{(aq)} \rightarrow 2\ I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

Amount of $S_2O_3^{2-}$ consumed = c.V = 0.01 × 0.005 = 5×10^{-5} mol

Amount of H^+ consumed = Amount of $S_2O_3^{2-}$ consumed = 5×10^{-5} mol

Amount of H_2O_2 consumed = ½ Amount of $S_2O_3^{2-}$ consumed = 2.5×10^{-5} mol

Original amount of H^+ = c.V = 0.1 × 0.005 = 5×10^{-4} mol

Original amount of H_2O_2 = c.V = 1 × 0.005 = 5×10^{-3} mol

10% of the H^+ and 0.5% of the H_2O_2 are consumed, so it is quite initial.

d) Concentration change of H_2O_2 to turn solution blue = $\frac{n}{V} = \frac{2.5\times10^{-5}}{.05} = 0.0005$ mol dm^{-3}

Rate for Mixtures 1, 2, 3 & 4 are given in table below.

e)

Mixture	Time /s	Rate /mol dm^{-3} s^{-1}	[H_2O_2] /mol dm^{-3}	[KI] /mol dm^{-3}	Rate constant /mol-1 dm^3 s^{-1}
1	278	0.899×10^{-6}	0.1	0.001	0.00899
2	154	3.35×10^{-6}	0.2	0.001	0.0168
3	124	4.03×10^{-6}	0.3	0.001	0.0134
4	90	5.56×10^{-6}	0.4	0.001	0.0139

It can be seen that these results are not in very good agreement. The mean value is 0.0133 mol^{-1} dm^3 s^{-1}, so that it is really the first two results that appear to differ tremendously.

f) The potassium iodide concentration, though low, will remain constant because the iodide ion is reformed by the rapid reaction of the iodine produced with the thiosulfate ion.

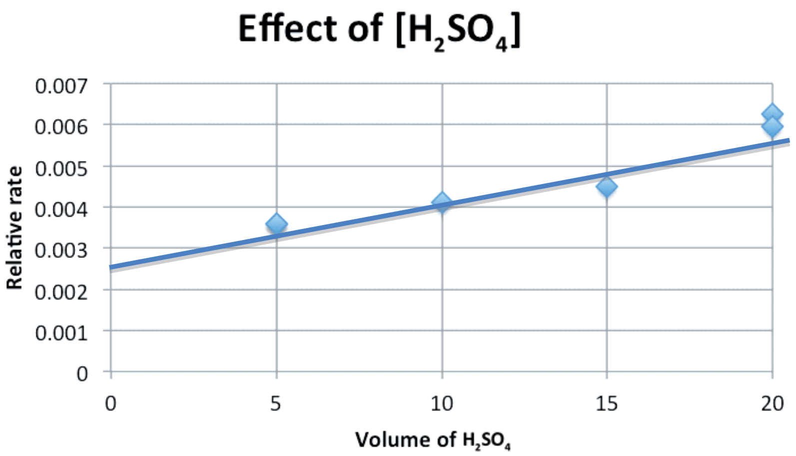
g) **In agreement:**

$H_2O_2 + I^- \rightarrow IO^- + H_2O$	Slow RDS
$IO^- + H^+ \rightarrow HOI$	Fast
$HOI + I^- \rightarrow I_2 + OH^-$	Fast
$H^+ + OH^- \rightarrow H_2O$	Fast

Not in agreement:

$H_2O_2 + H^+ \rightarrow H_3O_2^+$	Slow RDS
$H_3O_2^+ + I^- \rightarrow HOI + H_2O$	Fast
$HOI + I^- \rightarrow I_2 + OH^-$	Fast
$H^+ + OH^- \rightarrow H_2O$	Fast

h) The results show that whilst the rate does increase with hydrogen ion concentration, there is also an intercept on the rate access:



This is probably because there are two mechanisms, one independent of hydrogen ion concentration the other first order in hydrogen ion concentrations.

Conclusion & Evaluation

I) Rate = $(k_1 + k_2.[H_2SO_4])[H_2O_2].[KI]$

j) The activation energy could be found by repeating the experiment with solutions of the same concentrations, but at different temperatures. The activation energy can then be found by plotting $\ln(^1/_t)$ against $^1/_T$, where t is the time for the solution to turn blue and T is the temperature in Kelvin.

The gradient of the best fit line will be $-\frac{E_a}{R}$.

k) The method was easy to carry out and variations in concentrations easy to implement, so from that point of view it was satisfactory. Four sets of replicate data were taken (Mixtures 1, 2, 7 & 8) and generally these showed only minor discrepancies (278 & 279; 154 & 177, 160 & 168, 152 & 161), ~5% except for Mixture 2, so again this seems reasonably satisfactory, though it is difficult to explain why Mixture 2 should vary 14% as it is unlikely that the amounts of reagents would vary by this amount.

l) Measuring out the volumes of reagents using pipettes rather than burettes would have been more precise but rather more time consuming. The uncertainty with the timing is probably associated with reaction times and this could be eliminated if a colorimeter and data logger were used for the timing. One major variable that was not specifically controlled was temperature, which does have a significant effect on reaction rates. It was assumed that an air conditioned laboratory provided a constant temperature environment, but placing the reagents in a thermostatically controlled water bath before mixing would have provided better control.

TEACHING NOTES for Investigation 16B
DETERMINING THE ACTIVATION ENERGY FOR A REACTION

Syllabus relevance; Topic 16.2

Determining and evaluating values of activation energy and frequency factors from data.

Apparatus required

As with any student designed practical, it is difficult to produce a precise list of requirements, but below is a list of materials that students are likely to request.

- Thermometers
- Beakers (various sizes)
- Conical flasks (various sizes)
- Measuring cylinders (various sizes)
- Volumetric flasks (various sizes)
- Pipettes (various sizes)
- Test tubes
- Boiling tubes
- Water baths at various temperatures (you may wish to fix these for all the groups)
- Refrigerator
- Stop watches

Chemicals required

The students decide on suitable concentrations for the reagents, so quite large stocks of rather concentrated solutions is all that is required:

- Dilute hydrochloric acid (2 mol dm^{-3})
- Aqueous sodium thiosulfate (~1 mol dm^{-3})

I find it is best to allow students a short laboratory session to decide on suitable concentrations and then to hold the main laboratory session after giving them time to convert these preliminary findings into a viable method.

Notes

Probable timing–60 minutes laboratory time

This Investigation gives quite good results and, as it is probably coming early in the second year of the course, it is probably a good time to give students some extra planning practice. If you prefer to give the students a method, this one works fine:

1. Pipette out 2 cm^3 of 1.00 mol dm^{-3} hydrochloric acid into a test tube.
2. Do the same for 0.02 mol dm^{-3} aqueous sodium thiosulfate solution.
3. Place them both in the water bath at 10°C.
4. When they have been in the water bath for 2 minutes, rapidly mix them, start the stopwatch then transfer the liquid to a cuvette and place it into a colorimeter with a yellow filter.
5. When the absorbance increases to 0.5 stop the stopwatch and record the time elapsed.
6. Raise the temperature of the water bath by 10°C and repeat, up to a temperature of 80°C.

I also have not broken down the process of converting the data into a graph of lnk -v- $^1/_T$ into simple steps to allow students who are capable of working this out for themselves to do so. You will know which students might need a little extra support and how much would be appropriate in each case.

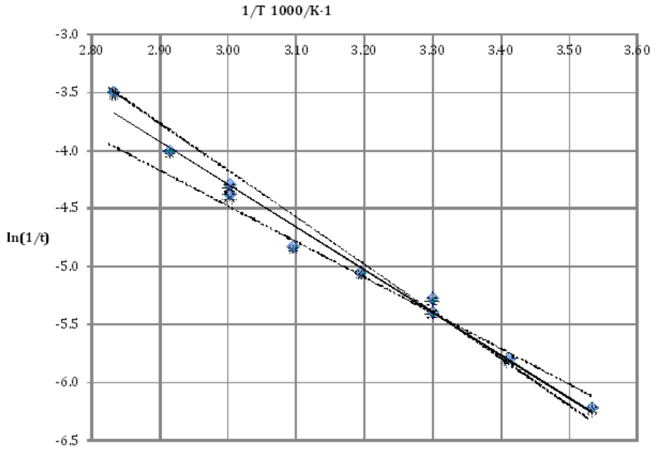
Sample data

Using the method above:

Temperature (T) / K	**Time (t) /s**	**Relative rate (1/t) /s^{-1}**	**Ln (1/t)**	**10^3/T $10^{-3} \times K^{-1}$**
283	502	0.00199	-6.219	3.53
293	329	0.00304	-5.796	3.41
303	196	0.00510	-5.278	3.30
303	220	0.00455	-5.394	3.30
313	156	0.00641	-5.050	3.19
323	126	0.00794	-4.836	3.10
333	80	0.01250	-4.382	3.00
333	74	0.01351	-4.304	3.00
343	55	0.01818	-4.007	2.92
353	33	0.03030	-3.497	2.83

Uncertainty in T = ±1K   Uncertainty in t = ±1 s

a)



Best fit line: y = -3.6675x + 6.7102

$E_a = 3.6675 \times 10^3 \times 8.31 = 3.0477 \times 10^4$ J mol^{-1} = 30.5 kJ mol^{-1}

Maximum gradient = $\frac{E_a}{R} = -\frac{(6.3-3.5)}{(3.53-2.83)x10^{-3}} = 4.000x10^3$

Maximum E_a value: 33.24 kJ mol^{-1}

Minimum gradient = $\frac{E_a}{R} = -\frac{(6.1-3.9)}{(3.53-2.83)x\ 10^{-3}} = 3.143x10^3$

Minimum E_a value: 26.12 kJ mol^{-1}

$E_a = 30 \pm 4$ kJ mol^{-1}

Conclusion & Evaluation

b) The value obtained for the activation energy is perfectly reasonable, being the correct order of magnitude. The only literature value that could be found was a figure of 47 kJ mol-1, significantly higher than the value found in this investigation. Its provenance is uncertain and it was from a single series of rate measurements over a smaller temperature range using more concentrated thiosulfate and a slightly lower concentration of acid leading to faster reaction times. Because it is a logarithmic function the uncertainty in the value of A is much greater and no literature value for it could be found.

c) The precision of the method was not brilliant with an uncertainty >10%, but this is often typical for kinetics experiments. If the value at 80°C was discounted then there would be a significantly lower uncertainty. The replicate values at 30°C and 60°C also differed by ~10%. The uncertainty precisions on the recorded data (~±1% for both temperature difference and time) are much lower than the uncertainty of the final result and so improving the precision of these will probably not improve the situation.

d) The problems are not obvious, but the individual data points do not tightly define a single straight line. In addition there were significant variations between replicates, which naturally casts doubt on the reliability of single values at a temperature. The method of using a water bath for temperature and a colorimeter to determine a particular point in the reaction should work better. The mixing time could be an issue, as could any effect temperature has on the state of division of the solid sulfur, and hence the concentration of particles required to obscure the light beam.

e) The only obvious way to improve the situation would be to repeat the values at each temperature until a reliable mean value can be obtained. Once this has been achieved then it may be worth considering how to improve the precision of the time and temperature measurements.

TEACHING NOTES for Investigation 17A MEASURING AN EQUILIBRIUM CONSTANT

Syllabus relevance: Topic 17.1

The equilibrium constant for an esterification reaction and other reactions could be experimentally investigated.

Apparatus required

Per group

- 5 test tubes
- Colorimeter/spectrophotometer
- Supply of cuvettes

Generally available

- 3 × burette (for the solutions below)

Chemicals required

- 0.001 M iron(III) nitrate (~50 cm^3 per group)
- 0.1 M potassium thiocyanate (~50 cm^3 per group)
- 0.01 M potassium thiocyanate (~30 cm^3 per group)

(N.B. these last two need to be very clearly labelled!)

Notes

Probable timing–60 minutes laboratory time

This introduces students to the spectrophotometer/colorimeter as well as to the idea of a calibration graph. Unfortunately the investigation does not yield good results, even with good students! This is because other complex ions, such as $[Fe(SCN)_2(H_2O)_4]^+$, are formed – see how many students come up with this explanation!

Sample data

Part A The preparation of standard solutions

Mix together in a labelled test tube the appropriate volumes of 0.001 mol dm^{-3} aqueous iron(III) nitrate and 0.1 mol dm^{-3} aqueous potassium thiocyanate from burettes to prepare the mixtures below (make sure you get the correct concentration!) . Measure the absorbance of each of the standard solutions and record these in the table below.

Solution	Volume of 0.001 mol dm^{-3} $Fe(NO_3)_3$ /cm^3	Volume of 0.1 mol dm^{-3} KSCN /cm^3	Absorbance
A	1.0	9.0	0.26
B	2.0	8.0	0.63
C	3.0	7.0	0.84
D	4.0	6.0	0.93
E	5.0	5.0	0.97

Relevant qualitative data

In Part A there was a gradual increase in the intensity of the colour,

Part B Measuring the equilibrium constant for the formation of the complex ion

Make up the following mixtures of 0.001 mol dm^{-3} aqueous iron(III) nitrate and 0.01 mol dm^{-3} aqueous potassium thiocyanate (again check the concentration) in a test tube, measuring the volumes using a burette. Transfer the solution to a cuvette, measure its absorbance and record this in the table below.

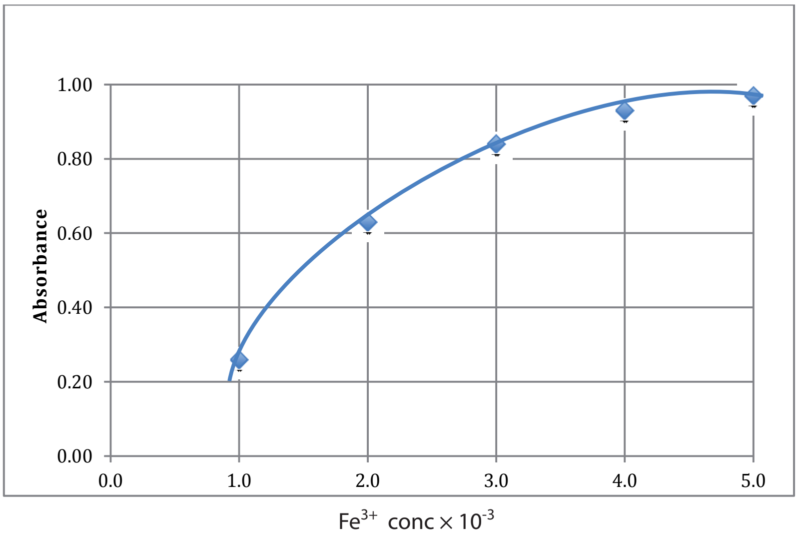
Solution	Volume of 0.001 mol dm^{-3} $Fe(NO_3)_3$ /cm^3	Volume of 0.01 mol dm^{-3} KSCN /cm^3	Absorbance
I	5.0	1.0	0.43
II	4.0	2.0	0.50
III	3.0	3.0	0.48
IV	2.0	4.0	0.33
V	1.0	5.0	0.15

Relevant qualitative data

In Part B the variation in colour was less, with lower intensity at both ends.

Data Analysis

a)



b)

Solution	Initial concentration /mol dm^{-3}		Equilibrium concentration /mol dm^{-3}			K_c
	Fe^{3+}	SCN^-	Fe^{3+}	SCN^-	$FeSCN^{2+}$	
I	8.33×10^{-4}	1.67×10^{-3}	7.03×10^{-4}	1.54×10^{-3}	1.3×10^{-4}	120
II	6.67×10^{-4}	3.33×10^{-3}	5.17×10^{-4}	3.18×10^{-3}	1.5×10^{-4}	91
III	5.00×10^{-4}	5.00×10^{-3}	3.60×10^{-4}	4.86×10^{-3}	1.4×10^{-4}	80
IV	3.33×10^{-4}	6.67×10^{-3}	2.23×10^{-4}	6.56×10^{-3}	1.1×10^{-4}	75
V	1.67×10^{-4}	8.33×10^{-3}	0.87×10^{-4}	8.25×10^{-3}	0.8×10^{-4}	111

Mean value of K_c = 95

Conclusion & Evaluation

C) The Beer-Lambert law would lead us to expect a linear dependence of absorbance on concentration and this is obviously not the case here. This may well be because there are a variety of different complex ions present and their relative concentrations vary with [Fe3+]. It also seems as if the calibration curve will intercept the [Fe3+], rather than passing through the origin. Having a non-linear calibration curve makes the determination of [Fe3+] in the equilibrium mixture more difficult and hence, as it will affect all three concentrations, significantly increases the uncertainty of the equilibrium constant.

The value of the equilibrium constant varies quite significantly (>20%) between the different mixtures. There seems to be a pattern with the value of the equilibrium constant decreasing as the ratio $[Fe^{3+}]:[SCN^-]$ decreases, until it comes to the final value which again is much higher.

d) The major issue would seem to be the assumption that the only complex ion is $[FeSCN]^{2+}$. Actually the SCN^- ligand can gradually replace more water ligands in $[Fe(H_2O)]^{3+}$, so a range of complexes with different absorption coefficients can be produced. With a non-linear calibration curve the precision of the determination of the equilibrium concentration of the complex is ±0.05, ~±5%, which then impinges significantly on the other equilibrium concentrations. For the first value of K_c, if the lower value of $1.25x10^{-4}$ is used for $[FeSCN]^{2+}$ then, ignoring other uncertainties, the value of K_c is 113, so an order of magnitude uncertainty is ±7%, which is not enough to explain the variation observed.

e) The most significant improvement would be to choose a system in which there is only one complex ion formed! If one looks at improving an investigation of this system then the greatest improvement might be to have a large number of calibration standards covering the region actually used for the equilibrium samples; approximately $0 – 2 \times 10^{-4}$ mol dm^{-3}. That way more precise values of the equilibrium concentrations could be obtained.

TEACHING NOTES for Investigation 17B
INVESTIGATION OF THE ESTER FORMATION EQUILIBRIUM

Syllabus relevance: Topic 17.1

The equilibrium constant for an esterification reaction and other reactions could be experimentally investigated.

Apparatus required

As with any student planned practical, it is difficult to be precise about the requirements. It is likely that they will need quite large volumes of propanone as a solvent and aqueous alkali (~1 mol dm^{-3} is probably appropriate).

As it needs to be a closed system, stoppered volumetric flasks are often the best containers in which to leave the mixtures to reach equilibrium. In the second lesson titration apparatus will be required

Notes

Probable timing – planning time, plus 2 × 60 minutes laboratory time about a week apart

This is another opportunity for students to plan an open ended practical investigation, providing excellent preparation for the challenge they will have in producing their Internal Assessment exercise. The sample data given below relates to an investigation regarding the effect that solvent composition (using a mixture of water and propanone) has on the equilibrium constant. Other possibilities students might investigate include the effect of chain length of the alcohol/acid (or maybe the total number of carbons in the ester), chain branching, temperature (unfortunately not much of an effect as ΔH is small) and the type of catalyst (HCl, H_2SO_4, H_3PO_4) etc.

As well as reinforcing the ideas relating to equilibrium and Le Chatelier, this also gives students some practice in a few tricky calculations!

If you find that this is not an appropriate time to give your students an open ended investigation, maybe because they have already completed their IA task, you can use the same method to evaluate the equilibrium constant for the ethyl ethanoate equilibrium and demonstrate Le Chatelier's principle by varying the initial composition of the system. A suitable series of solutions may be produced by adding, from a burette, the volume of reagent in the table below to a 50 cm^3 volumetric flask and fill it up to the mark with propanone. Stopper the flask, shake and label it and leave it to stand at least overnight, but preferably for about a week.

Mixture	Ethanoic acid /cm^3	Ethanol /cm^3	Ethyl ethanoate /cm^3	Water /cm^3	Hydrochloric acid /cm^3
A	-	-	-	-	2
B	5	5	5	1	2
C	5	5	-	-	2
D	10	5	-	-	2
E	5	10	-	-	1
F	-	-	5	1	1
G	-	-	10	1	1
H	-	-	5	2	1

At the end of this time, titrate 10 cm^3 aliquots of the mixture with 1 mol dm^{-3} aqueous sodium hydroxide, using phenolphthalein as the indicator. If an initial rough titration gives a small value then dilute the sodium hydroxide solution by an appropriate factor.

You may prefer to use the methanol, methanoic acid, methyl methanoate system as there is no need for a solvent because the ester is water soluble.

Sample Investigation

Design

Research problem

Does the amount of propanone present in the aqueous solvent mixture affect the equilibrium constant for the formation of ethyl ethanoate from ethanol and ethanoic acid?

Independent variable Proportions of propanone and water in the solvent mixture

Dependent variable The value of the equilibrium constant for the formation of ethyl ethanoate

Controlled variables

- Amounts of other components in the mixture (ethanol, ethanoic acid, hydrochloric acid)
- Total volume of reaction mixture
- Temperature
- Degree to which equilibrium has been established

Outline how you will investigate the effect of the variable on the equilibrium.

Mixtures will be made with identical amounts of ethanol, ethanoic acid and hydrochloric acid (catalyst), but with varying proportions of propanone and water as the solvent. To avoid problems with immiscibility the mixtures will contain at least 50% by volume propanone. The mixtures will be made up in tightly stoppered flasks and stored for one week to reach equilibrium. At the end of this time aliquots of the reaction mixtures will be titrated with aqueous sodium hydroxide to determine the concentration of the acid in the equilibrium mixture. This can be used to calculate the equilibrium concentrations of the other components and hence the equilibrium constant.

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

The volumes of the components, other than the solvent, are kept constant and the use of a volumetric flask will ensure the same volume of each mixture. They will all be stored in the same place and so will presumably be at the same temperature and because of the length of time the mixtures are left, coupled with the presence of a catalyst, it can be assumed to have reached equilibrium.

Method

The following mixtures are made up in a 50 cm^3 volumetric flask and then topped up to the mark with propanone. They are then left for one week.

Mixture	Volume of ethanoic acid /cm^3	Volume of ethanol /cm^3	Volume of conc. hydrochloric acid /cm^3	Volume of water /cm^3
A	4	4	2	0
B	4	4	2	1
C	4	4	2	2
D	4	4	2	3
E	4	4	2	4
F	4	4	2	5
G	4	4	2	10
H	4	4	2	15
I	4	4	2	20
J	0	0	2	48

At the end of this period 10 cm^3 aliquots of each mixture will be titrated with 1 mol dm^{-3} aqueous sodium hydroxide, using phenolphthalein as the indicator, until concordant results are obtained.

Data Collection

Mixture	Titre 1 /cm^3	Titre 2 /cm^3	Mean titre /cm^3	Volume reacting with CH_3COOH /cm^3
A	15.2	15.1	15.15	10.65
B	14.4	14.3	14.35	9.85
C	14.3	14.3	14.30	9.80
D	14.3	14.4	14.35	9.85
E	14.1	14.0	14.05	9.55
F	15.7	15.8	15.75	11.25
G	16.0	15.9	15.95	11.45
H	16.2	16.3	16.25	11.75
I	16.0	16.1	16.05	11.55
J	4.5	4.5	4.50	-

Note the final two columns are processed data, but it is convenient to record them here.

The mixtures all remained clear and colourless, with no sign of an immiscible layer forming. During the titration the change in colour of the indicator from colourless to pink gave a clear indication of the end point.

Data Analysis

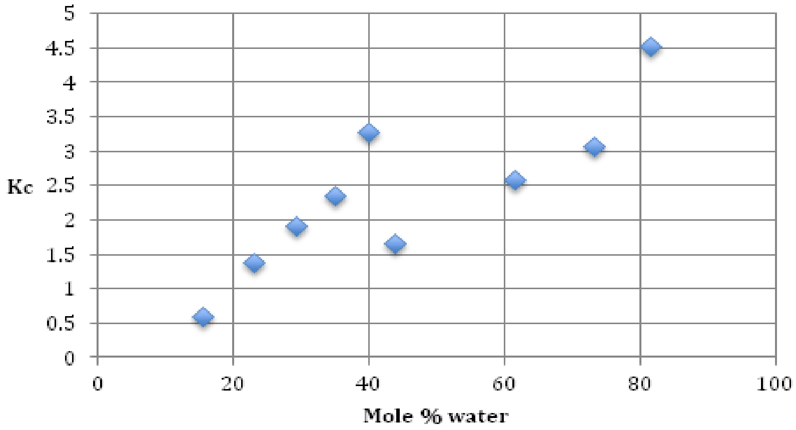
Initial concentrations (mol dm^{-3})

Mixture	Ethanoic acid	Ethanol	Water	Propanone	Mole % water
A	1.399	1.37	1.643	10.899	13.10
B	1.399	1.37	2.752	10.627	20.57
C	1.399	1.37	3.862	10.354	27.17
D	1.399	1.37	4.972	10.082	33.03
E	1.399	1.37	6.082	9.809	38.27
F	1.399	1.37	7.192	9.537	42.99
G	1.399	1.37	12.741	8.174	60.92
H	1.399	1.37	18.291	6.812	72.86
I	1.399	1.37	23.840	5.450	81.39

Equilibrium concentrations (mol dm^{-3})

Mixture	Ethanoic acid	Ethanol	Ethyl ethanoate	Water	K_c
A	1.065	1.036	0.334	1.977	0.598
B	0.985	0.956	0.414	3.166	1.392
C	0.98	0.951	0.419	4.281	1.925
D	0.985	0.956	0.414	5.386	2.368
E	0.955	0.926	0.444	6.526	3.277
F	1.125	1.096	0.274	7.466	1.659
G	1.145	1.116	0.254	12.995	2.583
H	1.175	1.146	0.224	18.515	3.080
I	1.155	1.126	0.244	24.084	4.519

If the equilibrium constant is plotted against the mole % water then the following graph results. It can be seen that overall the value of Kc increases as the mole % of water increases, but there is a discontinuity at about 40%. The values at high mole % water were measured on a different day to the lower mole % water and hence there may have been some variables that were not fully controlled. Nevertheless both sets of data show the same trend (see next page).



Conclusion & Evaluation

a) The conclusion that can be drawn is that as the amount of water in the solvent increases, the value of the equilibrium constant also increases. Extrapolating, the magnitude of this increase would probably be about a factor of 10 between the two pure solvents. The direction of the trend is quite certain as it is confirmed by every point with the exception of the discontinuity between the two data sets. The order of magnitude of the value of K_c in the water rich system is not inconsistent with values ~4 quoted by online sources that do not quote the solvent system. The difference between the two solvents is significantly less certain owing to this discontinuity.

b) It may have been expected that the presence of water might favour the alcohol and acid, that can hydrogen bond with water, but this would result in a lower value of the constant when more water was present, the opposite of the observed trend. It seems that the presence of water is stabilising the ester, or destabilising the acid and alcohol. Ethanoic acid is a weak acid and so in the presence of water will dissociate, thus decreasing the concentration of the undissociated acid. This would have a small effect as it is a weak acid and this would be expected to shift the equilibrium to the reactants as the water concentration increased. In brief it is not easy to explain the observed trend using simple theory.

c) The investigation went smoothly apart from having to split it into two sessions, one with higher and one with lower water concentrations, leading to discontinuous results. The discontinuity is also rather worrying, as it would seem to hint that there is some uncontrolled factor that has not been taken into account. One possibility is that the system had not reached equilibrium and that the higher water concentrations were further from equilibrium than the lower concentrations. This could be checked by using larger volumes of reagent and removing an aliquot for titration each day until the titre obtained in each case became constant. Another possibility is that because the "blank" to determine the volume of alkali reacting with the acid catalyst was only done once, the precise volume or the concentration of the acid may have varied slightly between the sets.

d) Obviously it would be good to carry out all determinations simultaneously or, if this was not possible, maybe the two sessions should have a wider range of mixtures. There was no temperature control and as the equilibrium constant varies with temperature, it would be good practice to keep the mixtures in a thermostatically controlled water bath so the temperature of equilibrium is known.

TEACHING NOTES for Investigation 18A
SOME MEASUREMENTS ON WEAK ACIDS AND BASES

Syllabus relevance; Topic 18.2

The properties of strong and weak acids could be investigated experimentally.

Experiments could include determination of the pK_a of a weak acid. The composition and action of buffer solutions.

Apparatus required

Per group

- Test tubes with rubber bungs (×6)
- Boiling tubes (×5)
- Burette
- Pipette
- Pipette filler
- Conical flask

Generally available

- pH meters
- Wide range pH paper

Chemicals required

About 20 cm^3 per group of

- Phenolphthalein indicator
- 0.05 mol dm^{-3} aqueous ammonia
- 0.002 mol dm^{-3} ethanoic acid
- 2 mol dm^{-3} hydrochloric acid
- 2 mol dm^{-3} aqueous sodium hydroxide
- 0.1 mol dm^{-3} aqueous ammonium sulfate
- 0.1 mol dm^{-3} aqueous sodium ethanoate
- 0.1 mol dm^{-3} aqueous ammonia
- 0.1 mol dm^{-3} ethanoic acid

About 50 cm^3 per group of

- "Acid X"–methanoic acid ~ 0.1 mol dm^{-3}
- 0.025 mol/dm^{-3} sodium dihydrogenphosphate
- 0.25 mol dm^{-3} disodium hydrogenphosphate

About 100 cm^3 per group of

- aqueous sodium hydroxide (~0.1 mol dm^{-3})

TEACHING NOTES for Investigation 18A
SOME MEASUREMENTS ON WEAK ACIDS AND BASES

Notes

Probable timing – 60 minutes laboratory time

It is important that students realise that all of the methods share the inherent weakness that they rely on pH measurements, which being logarithmic produces a large uncertainty, especially as most school pH meters cannot be relied on to more than one decimal place. Another thing they should consider is to what extent an uncertainty in making up the solution, or traces of acids or bases as impurities, is likely to lead to a significant change in the pH. The Investigation also contains an exercise looking at the qualitative effect of buffer solutions and a small challenge to see if students can work out how to use a weak acid and a strong base to produce a buffer solution with equal concentrations of the acid and its conjugate base, in order to determine the pK_a of the weak acid.

Sample data

1) pH of aqueous ethanoic acid = 3.03 pH of aqueous ammonia = 9.32

2) Water pH = 7 Neutral phosphate pH = 7

   Water + alkali pH = 10 Phosphate + alkali pH = 7

   Water + acid pH = 3 Phosphate + acid pH = 7

3) pH of ethanoic acid buffer = 4.41 pH of ammonia buffer = 9.16

4) pH of ammonium sulfate = 5.02 pH of sodium ethanoate = 8.04

5) Pipette out 25 cm^3 of Acid X into a conical flask and titrate it with aqueous sodium hydroxide from a burette until the phenolphthalein indicator just turns pink. Record the volume of alkali added. Pipette out a second 25 cm^3 sample of Acid X and add half the volume of alkali required for neutralisation. Measure the pH of this solution using a pH meter.

   Titre to change indicator = 25.0 cm^3 pH of "half neutralised" Acid X = 3.59

Data Analysis

a) If pH = 3.03, $[H^+] = 10^{-3.03} = 9.33 \times 10^{-4}$ mol dm^{-3}

$$K_a = \frac{x^2}{a-x} \approx \frac{x^2}{a} = \frac{(9.33\ x\ 10^{-4})^2}{0.002} = 4.35\ x\ 10^{-4}\ (pK_a = 3.36)$$

If pH = 9.32, $[H^+] = 10^{-9.32} = 4.79 \times 10^{-10}$ mol dm^{-3}, so $[OH^-] = 2.09 \times 10^{-5}$ mol dm^{-3}

$$K_b = \frac{y^2}{b-y} \approx \frac{y^2}{b} = \frac{(2.09\ x\ 10^{-5})^2}{0.05} = 8.73\ x\ 10^{-9}\ (pK_b = 8.06)$$

b) When the acid is added to water, the water dilutes it. If the dilution is by a factor of 1000 (10^3), then the pH will increase by 3 but, assuming it was initially quite small (~1?) the solution will still be quite acidic. Similar considerations apply when considering adding aqueous sodium hydroxide to water; the solution remains quite alkaline.

In the phosphate buffer solution however there is an equilibrium between the dihydrogenphosphate ions and the hydrogenphosphate ions:

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

When acid is added the above equilibrium is displaced to the left, converting hydrogenphosphate into dihydrogenphosphate, until the $[H^+]$ falls to a value almost equal to its original level. Similarly any alkali added will react with the hydrogen ions and the equilibrium shifts to the right, converting dihydrogenphosphate into hydrogenphosphate, until the $[H^+]$ increases to a value almost equal to its original level.

c) As the mixture contains 10 cm^3 of each solution, which have the same concentration, the concentration of both the ethanoic acid and the ethanoate ion are equal, hence $K_a = [H^+]$ so $pK_a = pH = 4.41$.

Similarly the concentrations of ammonia and the ammonium ion are equal, so again $pK_a = pH = 9.16$. Hence, as $pK_a + pK_b = 14$, $pK_b = 4.84$.

d) In aqueous sodium ethanoate the ethanoate ion is acting as a weak base, hence:

$pH = 8.04$, $[H^+] = 10^{-8.04} = 9.12 \times 10^{-9}$ mol dm^{-3}, so $[OH^-] = 1.10 \times 10^{-6}$ mol dm^{-3}

$$K_b = \frac{y^2}{b-y} \approx \frac{y^2}{b} = \frac{(1.10 \,x\, 10^{-6})^2}{0.1} = 1.20 \,x\, 10^{-11} \ (pK_b = 10.92)$$

As $pK_a + pK_b = 14$, $pK_a = 3.08$

In aqueous ammonium chloride the ammonium ion is acting as an acid, hence:

$pH = 5.02$, $[H^+] = 10^{-5.02} = 9.55 \times 10^{-6}$ mol dm^{-3}

$$K_a = \frac{x^2}{a-x} \approx \frac{x^2}{a} = \frac{(9.55 \,x\, 10^{-6})^2}{0.1} = 9.12 \,x\, 10^{-10} \ (pK_a = 9.04)$$

As $pK_a + pK_b = 14$, $pK_b = 4,96$

e) When the solution is half neutralised, then half of the acid has been converted to its conjugate base, hence their concentrations must be equal, so $pK_a = pH$. This means that the pK_a of Acid X is 3.59. It is therefore a stronger acid than ethanoic acid ($pK_a = 4.76$) as it has a smaller pK_a value.

Conclusion & Evaluation

f)

Method	pK_a ethanoic acid	pK_b ammonia
Solution of acid	3.36 (29% low)	8.06 (70% high)
Buffer solution	4.41 (7% low)	4.84 (2% high)
Solution of salt	3.08 (35% low)	4.96 (4% high)
Literature	4.76	4.75

g) It can be seen that the first method and third method, taking the pH of a solution of the weak acid or base or its salt, seems to produce much less reliable results than measuring the pH of a buffer solution, though the pK_b from ammonium chloride seems reasonably accurate. This is because in these methods any slight variation in the concentration of the acid or base, and/or the presence of any impurities which affect the pH of the solution, can have a significant effect on the result because the pH changes quite rapidly with the amount of acid/base. In a buffer solution any aberrations of this kind only have a minimal effect on the pH because the graph of the amount of acid/base against pH is quite flat, hence the results are less susceptible to error.

TEACHING NOTES for Investigation 18B pH CHANGES DURING ACID-BASE TITRATIONS

Syllabus relevance: Topic 18.3

Experiments could include investigation of pH curves.

Apparatus required

Per group

- Burette, stand & clamp
- 20 cm^3 pipette & filler
- Small funnel
- 100 cm^3 conical flask
- White tile
- pH meter

Chemicals required

~250 cm^3 per group of 0.1 mol dm^{-3} solutions of

- Sodium hydroxide (freshly made)
- Ammonia
- Ethanoic acid
- Hydrochloric acid
- Phenolphthalein indicator
- Methyl orange indicator

Notes

Probable timing – 90 minutes laboratory time

In this standard practical, rather than just getting students to plot pH against titre they were asked to plot all of the curves relative to the respective equivalence points. This avoids the problem of solutions (especially NH_3) not being quite the correct concentration, as well as allowing students to display judgement in determining the equivalence point. The question about pH at the equivalence point is perhaps best answered by considering the nature of the salt formed. Though less familiar than the "half-neutralisation point", a moments thought will show that in the ammonia titrations the "double neutralisation point" should give K_a for the ammonium ion. The requirement for fresh NaOH is that the presence of significant amounts of carbonate/hydrogencarbonate leads to observable buffering around the pH 8 region, spoiling the classic shapes of the curves.

Sample data

NaOH + HCl			NaOH + CH$_3$COOH			NH$_3$ + HCl			NH$_3$ + CH$_3$COOH		
Volume NaOH / cm^3	pH	Indicator change	Volume NaOH / cm^3	pH	Indicator change	Volume NH$_3$ / cm^3	pH	Indicator change	Volume NH$_3$ / cm^3	pH	Indicator change
0.00	1.05		0.00	2.68		0.00	0.94		0.00	2.61	
5.00	1.20		5.00	3.93	MO yellow	5.00	1.06		5.00	3.85	MO yellow
10.00	1.41		10.00	4.41		10.00	1.23		10.00	4.30	
15.00	1.72		15.00	4.91		15.00	1.42		15.00	4.67	
17.00	1.87		17.00	5.19		17.00	1.54		20.00	5.19	
18.00	1.98		18.00	5.39		18.00	1.59		22.00	5.50	
19.00	2.14		19.00	5.72		19.00	1.65		23.00	5.83	
19.50	2.21		19.40	6.04		20.00	1.72		23.50	6.16	
19.70	2.27		19.60	6.34		21.00	1.80		24.00	6.71	
19.90	2.33		19.80	7.21		22.00	1.89		24.50	7.40	
20.50	2.53		19.90	9.02	PP pink	23.00	2.02		25.00	7.70	
21.10	2.88		20.00	9.98		24.00	2.17		25.50	7.92	
21.50	3.80	MO yellow	20.20	10.46		25.00	2.39		26.00	8.06	
21.70	8.87	PP pink	20.50	10.78		26.00	3.00		27.00	8.22	
21.80	10.03		21.00	11.09		26.50	6.11	MO yellow	28.00	8.35	
21.90	10.40		23.00	11.57		26.70	6.84		30.00	8.53	
22.00	10.69		25.00	11.77		27.00	7.38		35.00	8.82	PP pink
22.50	11.08		30.00	12.08		27.50	7.78		40.00	8.97	
23.00	11.31		35.00	12.22		28.00	7.95		45.00	9.07	
23.50	11.47		40.00	12.32		29.00	8.17		50.00	9.16	
24.00	11.54					30.00	8.34		55.00	9.21	
25.00	11.62					32.00	8.52				
27.00	11.84					35.00	8.72	PP pink			
30.00	11.96					40.00	8.90				
35.00	12.15					45.00	9.02				
40.00	12.27					50.00	9.11				
						55.00	9.17				
						60.00	9.22				

Data Analysis

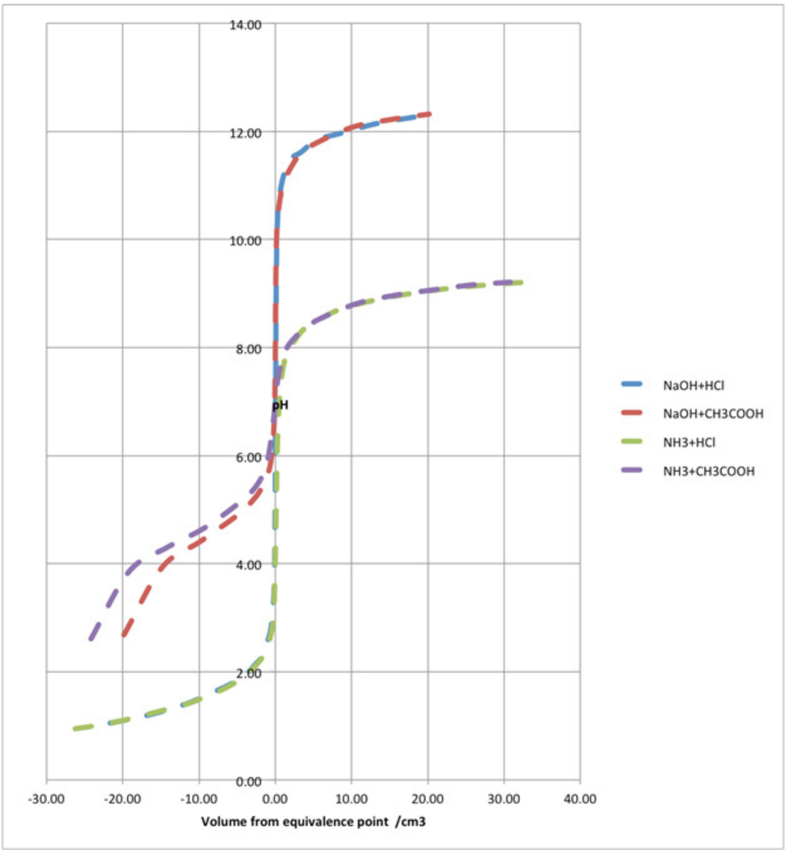
a)

Titration	NaOH + HCl	NaOH + CH$_3$COOH	NH$_3$ + HCl	NH$_3$ + CH$_3$COOH
Equivalence point /cm^3	21.60	19.85	26.25	24.20

b)

NaOH + HCl			NaOH + CH_3COOH			NH_3 + HCl			NH_3 + CH_3COOH		
Volume NaOH / cm^3	pH	Indicator change	Volume NaOH / cm^3	pH	Indicator change	Volume NH_3 / cm^3	pH	Indicator change	Volume NH_3 / cm^3	pH	Indicator change
-21.60	1.05		-19.85	2.68		-26.25	0.94		-24.20	2.61	
-16.60	1.20		-14.85	3.93	MO yellow	-21.25	1.06		-19.20	3.85	MO yellow
-11.60	1.41		-9.85	4.41		-16.25	1.23		-14.20	4.30	
-6.60	1.72		-4.85	4.91		-11.25	1.42		-9.20	4.67	
-4.60	1.87		-2.85	5.19		-9.25	1.54		-4.20	5.19	
-3.60	1.98		-1.85	5.39		-8.25	1.59		-2.20	5.50	
-2.60	2.14		-0.85	5.72		-7.25	1.65		-1.20	5.83	
-2.10	2.21		-0.45	6.04		-6.25	1.72		-0.70	6.16	
-1.90	2.27		-0.25	6.34		-5.25	1.80		-0.20	6.71	
-1.70	2.33		-0.05	7.21		-4.25	1.89		0.30	7.40	
-1.10	2.53		0.05	9.02	PP pink	-3.25	2.02		0.80	7.70	
-0.50	2.88		0.15	9.98		-2.25	2.17		1.30	7.92	
-0.10	3.80	MO yellow	0.35	10.46		-1.25	2.39		1.80	8.06	
0.10	8.87	PP pink	0.65	10.78		-0.25	3.00		2.80	8.22	
0.20	10.03		1.15	11.09		0.25	6.11	MO yellow	3.80	8.35	
0.30	10.40		3.15	11.57		0.45	6.84		5.80	8.53	
0.40	10.69		5.15	11.77		0.75	7.38		10.80	8.82	PP pink
0.90	11.08		10.15	12.08		1.25	7.78		15.80	8.97	
1.40	11.31		15.15	12.22		1.75	7.95		20.80	9.07	
1.90	11.47		20.15	12.32		2.75	8.17		25.80	9.16	
2.40	11.54					3.75	8.34		30.80	9.21	
3.40	11.62					5.75	8.52				
5.40	11.84					8.75	8.72	PP pink			
8.40	11.96					13.75	8.90				
13.40	12.15					18.75	9.02				
18.40	12.27					23.75	9.11				
						28.75	9.17				
						33.75	9.22				

c)



d) The curves are composed of four different quarters. The strong/weak acid giving the curves a characteristic form before the equivalence point and the strong/weak base determining the shape after it. The strong reagents have a pH very close to the values of the reagent except when close to the equivalence point. The weak reagents have values closer to pH 7, and throughout the titration they gradually increase in pH as more titrant is added.

e) At the equivalence point a solution of the salt is formed. The anions of strong acids and the cations of strong bases do not have any acid-base activity and hence do not affect the pH; if both of the reagents are strong there is no effect on the pH, which is therefore close to the pH 7 of water. The anions of weak acids act as weak bases and the cations of weak bases act as weak acids. If both reagents are weak, then the pH at the equivalence point will depend on their relative strengths; ammonia and ethanoic acid are similar, so again the salt solution has a pH close to 7. If the acid is strong (HCl) and the base weak (NH_3) the cation acting as an acid makes the solution acidic (pH ~5) at the equivalence point. Similarly if the acid is weak (CH_3COOH) and the base strong (NaOH), the anion from the acid acts as a base making the solution slightly alkaline (pH ~9) at the equivalence point.

f) These occur at a slightly acidic pH for a weak acid (CH_3COOH) that is partly neutralised and at a slightly alkaline pH for a weak base (NH_3) just after it has neutralised the acid. In these regions the solution acts as a buffer solution because the addition of a small volume of acid or base has very little effect on the pH. The solution has significant concentrations of both weak acid and weak base in equilibrium. Addition of small amounts of a strong acid or base causes a slight shift in the position of equilibrium, but this results in only a small change in $[H^+]$ and hence the pH.

g) When ethanoic acid is half neutralised by sodium hydroxide, the concentration of the acid and its conjugate base must be equal (the equivalence point corresponds to complete conversion to the conjugate base) so that the pH is equal to the pK_a. The pK_a of the acid is therefore 4.3. Similarly at the double neutralisation point of hydrochloric acid and ammonia the concentrations of ammonia and its conjugate acid must be equal, so that the pH is equal to pK_a of the conjugate acid. This is at pH = 8.9, so pK_b of the base will be 5.1 (14-8.9).

h) For the acid the pK_a can be found from the initial pH. For ethanoic acid this is 2.65, hence:

$[H^+] = 10^{-2.65} = 2.24 \times 10^{-3}$ mol dm^{-3}

$$K_a = \frac{x^2}{a-x} \approx \frac{x^2}{a} = \frac{(2.24 \, x \, 10^{-3})^2}{0.1} = 5.01 \, x \, 10^{-5} \ (pK_a = 4.30)$$

The pK_a can also be found from the pH at the equivalence point because the solution contains the salt, which acts as a weak base. The pK_b of the conjugate base can be found from the pH; as the volume is approximately doubled the concentration will be approximately halved. The pH at the equivalence point is ~8.5 so:

pH = 8.5, $[H^+] = 10^{-8.5} = 3.16 \times 10^{-9}$ mol dm^{-3}, so $[OH^-] = 3.16 \times 10^{-6}$ mol dm^{-3}

$$K_b = \frac{y^2}{b-y} \approx \frac{y^2}{b} = \frac{(3.16 \, x \, 10^{-6})^2}{0.05} = 2.00 \, x \, 10^{-10} \ (pK_b = 9.70)$$

As $pK_a + pK_b = 14$, $pK_a = 4.30$ (surprisingly in agreement with the first value!)

Similarly for the base the salt will act as a weak acid, hence the pH at the equivalence point can be used to calculate pK_a of the conjugate acid. Allowance must also be made for the ammonia having a significantly lower concentration than the 0.1 mol dm^{-3} of the aqueous hydrochloric acid. Taking the end point of this titration as 26.25 cm^3, the original concentration of the ammonia can be calculated as 0.0762 mol dm^{-3}. Using this along with the pH at the equivalence point of ~5.0:

$[H^+] = 10^{-5.0} = 1 \times 10^{-5}$ mol dm^{-3}

$$K_a = \frac{x^2}{a-x} \approx \frac{x^2}{a} = \frac{(1 \, x \, 10^{-5})^2}{0.0329} = 3.04 \, x \, 10^{-9} \ (pK_a = 8.52)$$

As $pK_a + pK_b = 14$, $pK_b = 5.48$

The pK_b of the base will determine the pH of the ammonia solution, but this is never measured and even when the volume added is 60 cm^3 the salt will still significantly affect the pH.

i) The values obtained for the pK_a of ethanoic acid are all 4.30, which is slightly lower than the value of 4.76 in the IB data booklet. The same source gives the pK_b of ammonia as 4.75, quite a bit lower than both the values found.

Determining the pH at the equivalence point is very imprecise as the gradient of the curve is at its greatest, therefore these values will have a high degree of uncertainty. Values based on the pH of the aqueous solution of acid (or base) will be susceptible to the presence of any impurities as there is no buffering action – the two initial values in the data are slightly different. The values based on the buffer regions have the advantage that the curves have a low gradient, so if the titre is not quite precise the effect on the calculated pH will only be small.

j) Methyl orange appears to change colour at just below pH 4, whereas phenolphthalein changes at just under pH 9. They change over different pH ranges because both are weak acids, but they have quite different pK_a values.

k) For an indicator to be effective the colour change (end point) must occur rapidly at the same titre as the equivalence point. With the strong acid and base both changed colour almost simultaneously and hence both would accurately indicate the equivalence point. With the weak acid and strong base the pH if the acid is slightly greater so that the methyl orange changes colour slowly well before the equivalence point. The phenolphthalein however accurately indicates the equivalence point because the colour change occurs when the pH rapidly rises to that of the excess strong base. The opposite is true with the strong acid and weak base because the methyl orange changes colour when the pH suddenly increases from that of the strong acid, accurately indicating the equivalence point whereas, because the excess base is only weak, the phenolphthalein changes colour slowly well after the equivalence point. For the titration of weak acid and weak base then, neither performs well, methyl orange changing well before the equivalence point, phenolphthalein well after. This titration really requires an indicator with pK_a ~7.

TEACHING NOTES for Investigation 18C DETERMINING THE pK$_a$ OF AN INDICATOR

Syllabus relevance: Topic 18.3

Experiments could include investigation of the pKa of an indicator.

Apparatus required

Per group

- ~15 test tubes
- 5 cm^3 measuring cylinder
- Dropper
- Colorimeter/spectrophotometer
- Supply of cuvettes

Shared

- 2 × burette (for the buffer solutions below)

Chemicals required

- 0.1 M hydrochloric acid (~5 cm^3 per group)
- 0.1 M aqueous sodium hydroxide (~5 cm^3 per group)
- 0.04% aqueous bromocresol purple indicator (~5 cm^3 per group)
- pH 7 buffer (~25 cm^3 per group, placed in a shared burette)
- pH 4 buffer (~25 cm^3 per group, placed in a shared burette)

(Note - these buffers need to be of the same concentration)

Notes

Probable timing – 60 minutes laboratory time

A colorimeter gives good results with an indigo filter (λ_{max} 430 nm) for HIn and a yellow filter (λ_{max} 580 nm) for In$^-$. With a spectrophotometer the optimum wavelengths are ~430 nm and 575 nm. In$^-$ absorbs to a moderate extent at the 430 nm maximum of HIn, so allowances for this need to be made. HIn has almost zero absorption at the very intense 375 nm In$^-$ peak making this the easier one to work with. Mixing the buffers gives a range of pH values, but not enough in the pH 5.5-6.5 region, something students ought to refer to in their evaluation.

Sample data

Part A The preparation of reference solutions

Wavelength /nm	Absorbance with HCl	Absorbance with NaOH
350	0.344	0.274
375	0.335	0.284
400	0.600	0.153
425	0.822	0.064
450	0.790	0.118
475	0.526	0.237
500	0.218	0.475
525	0.058	0.883
550	0.012	1.420
575	0.001	1.804
600	0.002	1.634
625	0.000	0.321
650	0.001	0.035
675	0.003	0.007
700	0.001	0.002
725	0.003	0.002
750	0.002	0.002
775	0.001	0.002
800	0.002	0.000

Part B Measuring the absorbance in solutions of known pH

Vol. pH 7 buffer / cm^3	Vol. pH 4 buffer / cm^3	pH	Absorbance at 425 nm	Absorbance at 575 nm
5.0	0	6.88	0.175	1.722
4.5	0.5	6.70	0.200	1.538
4.0	1.0	6.58	0.259	1.583
3.5	1.5	6.36	0.366	1.419
3.0	2.0	6.05	0.549	1.167
2.5	2.5	5.45	0.781	0.512
2.0	3.0	4.90	0.877	0.228
1.5	3.5	4.77	0.857	0.181
1.0	4.0	4.46	0.856	0.120
0.5	4.5	4.24	0.861	0.093
0	5.0	4.00	0.884	0.064

Data Analysis

As both the acidic (HIn) and basic (In^-) forms of the indicator absorb significantly at 425 nm, it is simpler to use the 575 nm data, where the absorption of HIn is negligible, to assess the fraction in the two forms. If the fraction present as In^- is x, then the absorption at 575 nm will be given by the formula:

Absorbance = 1.804 . x

The fraction present as HIn will be (1-x) and hence the ratio [HIn]/[In^-] is given by (1-x)/x. The equation governing the dissociation of the weak acid indicator is:

$$K_a = \frac{[H^+].[In^-]}{[HIn]} = [H^+].\frac{x}{1-x}$$

Values of K_a at each pH may be determined as indicated in the table below:

pH	Absorbance at 575 nm	x	1-x	x/(1-x)	[H^+]	K_a
6.88	1.722	0.955	0.045	21.000	1.32×10^{-7}	2.77×10^{-6}
6.70	1.538	0.853	0.147	5.782	2.00×10^{-7}	1.15×10^{-6}
6.58	1.583	0.877	0.123	7.163	2.63×10^{-7}	1.88×10^{-6}
6.36	1.419	0.787	0.213	3.686	4.37×10^{-7}	1.61×10^{-6}
6.05	1.167	0.647	0.353	1.832	8.91×10^{-7}	1.63×10^{-6}
5.45	0.512	0.284	0.716	0.396	3.55×10^{-6}	1.41×10^{-6}
4.90	0.228	0.126	0.874	0.145	1.26×10^{-5}	1.82×10^{-6}
4.77	0.181	0.100	0.900	0.112	1.70×10^{-5}	1.89×10^{-6}
4.46	0.12	0.067	0.933	0.071	3.47×10^{-5}	2.47×10^{-6}
4.24	0.093	0.052	0.948	0.054	5.75×10^{-5}	3.13×10^{-6}
4.00	0.064	0.035	0.965	0.037	1.00×10^{-4}	3.68×10^{-6}

This gives a mean value for K_a of 2.13×10^{-6}, equivalent to a pK_a of 5.67.

Using the data at 425 nm is more complicated because both forms of the indicator absorb and also the maximum value for the buffer solutions is greater than that in the acidic solution (different sized drops?). Applying a formula of:

Absorbance = 0.069 × + 0.885(1-x) provides a reasonable way of compensating for these aberrations.

Using this formula:

pH	Absorbance at 425 nm	x	1-x	x/(1-x)	$[H^+]$	K_a
6.88	0.175	0.870	0.130	6.698	1.32×10^{-7}	8.83×10^{-7}
6.70	0.200	0.839	0.161	5.229	2.00×10^{-7}	1.04×10^{-6}
6.58	0.259	0.767	0.233	3.295	2.63×10^{-7}	8.67×10^{-7}
6.36	0.366	0.636	0.364	1.747	4.37×10^{-7}	7.63×10^{-7}
6.05	0.549	0.412	0.588	0.700	8.91×10^{-7}	6.24×10^{-7}
5.45	0.781	0.127	0.873	0.146	3.55×10^{-6}	5.18×10^{-7}
4.90	0.877	0.010	0.990	0.010	1.26×10^{-5}	1.25×10^{-7}
4.77	0.857	0.034	0.966	0.036	1.70×10^{-5}	6.03×10^{-7}
4.46	0.856	0.036	0.964	0.037	3.47×10^{-5}	1.28×10^{-6}
4.24	0.861	0.029	0.971	0.030	5.75×10^{-5}	1.74×10^{-6}
4.00	0.884	0.001	0.999	0.001	1.00×10^{-4}	1.23×10^{-7}

This gives a mean value for K_a of 7.79×10^{-7}, equivalent to a pK_a of 6.11.

The two values differ considerably, but their mean is $K_a = 1.45 \times 10^{-6}$, equivalent to $pK_a = 5.84$.

Conclusion & Evaluation

a) The literature value for pK_a of bromocresol purple is 6.3, which converts to a K_a of 5.0×10^{-7}. This is smaller than both of the values determined above, though the value found using the 425 nm data is quite close (~50% greater, a factor of 1.56). The value found using the 575 nm data is more than a factor of 4 different and error of more than 300%. The range of values is quite large and some of those obtained at 425 nm (for example at pH 5.45) are quite close to the literature value.

The instrumental uncertainty is quite low with all readings being to 3 sig fig, so less than 1%. The pH is being converted to a hydrogen ion concentration, so because of the logarithmic scale, the difference between a pH of 6 ($[H^+] = 1 \times 10^{-6}$ mol dm^{-3}) and the next value at the limit of sensitivity, 6.01 ($[H^+] = 0.977 \times 10^{-6}$ mol dm^{-3}), is 2.3%.

At 575 nm the values for K_a range by more than a factor of 3 (1.15 – 3.68×10^{-6} mol dm^{-3}), and at 425 nm by a factor of more than 14 (1.23 – 17.4×10^{-7} mol dm^{-3}) so even though replicates were not done, the random variation of values found indicates a lack of reproducibility. Apart from some assumptions made (see below) a number of determinations involve quite low concentrations of one of the two species and finding a small difference between two large values always introduces significant uncertainties. The most reliable values should be those when there is a significant concentration of both species present, but unfortunately this is only the case for about 4 solutions with pH values from 5.45 to 6.58. These values show much less variation.

b) The instrumental uncertainties, discussed above, are probably significantly less than other sources of error. The major one of these would be considering the volume of a drop to be constant. The readings at 425 nm display the limitations of this because the reading in a buffer solution was higher than that in a strongly acidic solution. This is a logical impossibility if the absorption of a particular species (HIn or In^-) does not vary with the nature of the solution it is in (another assumption). When comparing the value obtained with a literature value it has to be remembered that dissociation constants are temperature dependent and in this investigation the temperature was neither measured nor controlled.

c) One major source of error would appear to be the assumption made about the size of a drop remaining constant. This could be counteracted by using a larger volume, measured using a pipette, of a more dilute solution. Another assumption made is that the Beer-Lambert law applies to this system and this could be verified by looking at solutions in acid and alkali with different concentrations of the indicator. The other major source of error was that many of the readings were at pH values where the concentration of one or other of the species was quite small and the calculation involved small differences between large numbers. It would be better to have a larger number of solutions between pH 5.5 and pH 6.5.

TEACHING NOTES for Investigation 19A
INVESTIGATING ELECTRODE POTENTIALS

Syllabus relevance: Topic 19.1

Calculation of cell potentials using standard electrode potentials.

Apparatus required

Per group

- 8 × 50 cm^3 beakers
- 4 × test tubes
- 50 cm^3 measuring cylinder
- Carbon electrode
- Filter paper
- Filter paper strips for salt bridges
- High resistance voltmeter/multimeter

Generally available

- Filter paper
- Crocodile clips
- Wire Scissors
- Sandpaper

Chemicals required

- Metal strips–magnesium, zinc, copper, lead (~1 cm × 3 cm)

~50 cm^3 per group of each of the following

- Aqueous magnesium sulfate (~0.1 mol dm^{-3})
- Aqueous zinc sulfate (~0.1 mol dm^{-3})
- Aqueous copper (II) sulfate (~0.1 mol dm^{-3})
- Aqueous lead (II) nitrate (~0.1 mol dm^{-3})
- Saturated aqueous potassium nitrate
- Saturated aqueous lead (II) chloride
- Aqueous iron(II) ammonium sulfate (0.1 mol dm^{-3} freshly made)
- Aqueous iron(III) chloride (0.1 mol dm^{-3})
- Dilute sulfuric acid
- iodine (~0.1 mol dm^{-3}) in aqueous potassium iodide
- Aqueous potassium iodide (~0.1 mol dm^{-3})
- Hydrogen peroxide (~10 volume)

Notes

Probable timing – 90 minutes laboratory time

The equipment in **Part A** is not the traditional arrangement of separate beakers and salt bridges, (which can be substituted if preferred), but I find this is a rapid way to measure a number of cell potentials quite quickly. The solutions are not the 1 mol dm^{-3} ones that should be used for standard conditions, but the tremendous discrepancy for magnesium results arises from the fact that the potential recorded is for the oxidation of water. In **Part C** the wording of the analysis is deliberately vague, in the hope that students will discover for themselves that they really need to plot log[Pb^{2+}] to produce a useful calibration graph for the range of concentrations used. In **Part D** students should come to the conclusion that H_2O_2 (in the presence of acid) should oxidise I^- to I_2 and then find a way of testing it. Unfortunately the activation energy is high and the reaction occurs very slowly unless a catalyst (a drop of aqueous Cu^{2+} or Fe^{2+}) is present.

Sample data

A Measuring electrode potentials

Metal	Copper		Magnesium		Lead		Zinc
Zinc	*Cu*	*1.07 V*	*Zn*	*0.72 V*	*Pb*	*0.61 V*	
Lead	*Cu*	*0.47 V*	*Pb*	*1.33 V*			
Magnesium	*Cu*	*1.87 V*					
Copper							

a) (i) The more reactive metal is always the negative terminal and the less reactive is the positive.

(ii)The greater the difference in reactivity, the greater the potential difference between the two metals.

b) Mg^{2+}/Mg -1.53 V Zn^{2+}/Zn -0.73 V Pb^{2+}/Pb -0.13 V

c) The Pb^{2+}/Pb is identical to the value in the IB Data Booklet, but the Zn^{2+}/Zn is slightly smaller (-0.73 V compared to -0.76 V). The value for Mg^{2+}/Mg is however very different (-1.53 V compared to -2.37 V).

d) There are slight differences to standard conditions. The concentrations of the solutions were 0.1 mol dm^{-3}, rather than 1 mol dm^{-3} and the temperature was probably not 298 K. However neither of these would have made a difference comparable to that observed for the Mg^{2+}/Mg half-cell. This is most likely because the potential at this electrode will correspond to the reduction of water to the hydroxide ion (-0.83 V) taking into account the very low concentration of ions present.

e)

Voltaic cell	Predicted potential /V	Measured potential /V	Difference /V
Magnesium–Zinc	0.80	0.72	0.8
Magnesium–Lead	1.40	1.33	0.7
Zinc–Lead	0.60	0.61	-0.1

There is good agreement in the case of the zinc-lead cell. In the case of the cells containing magnesium the result is not as good, but there is some consistency to the magnitude and direction of the discrepancy.

B Concentration effects on a voltaic cell not involving a metal

Ratio $[Fe^{2+}]:[Fe^{3+}]$	1:4	1:1	4:1
Potential difference	0.44 V	0.37 V	0.31 V

f) As the copper was the negative electrode, $E^{\theta} = 0.34 + 0.37 = +0.71$ V

g) As the proportion of Fe^{3+} decreased, the electrode potential became more negative.

h) The equilibrium in the solution is:

$$Fe^{3+}_{(aq)} + e^{-} \rightleftharpoons Fe^{2+}_{(aq)}$$

Decreasing the $[Fe^{3+}]$ would be predicted to shift the equilibrium to the left, generating more electrons and making the electrode more negative, hence the observations are in keeping with Le Chatelier's Principle.

i) Because it has a more positive electrode potential, Fe^{3+} is a more powerful oxidising agent than Cu^{2+}. As a result, Fe^{3+} will oxidise Cu to Cu^{2+}:

$$2\ Fe^{3+}_{(aq)} + Cu_{(s)} \rightarrow 2\ Fe^{2+}_{(aq)} + Cu^{2+}_{(aq)}$$

In addition, combining the electrode potentials, it can be see that the cell potential is positive indicating a spontaneous reaction:

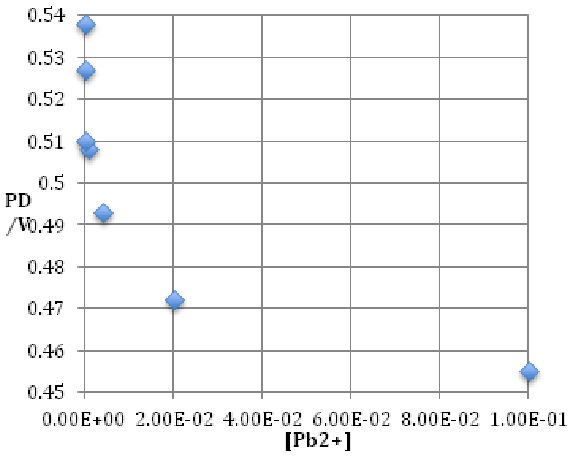
$$Eo_{cell} = +0.71 - (+0.34) = +0.37 \text{ V}$$

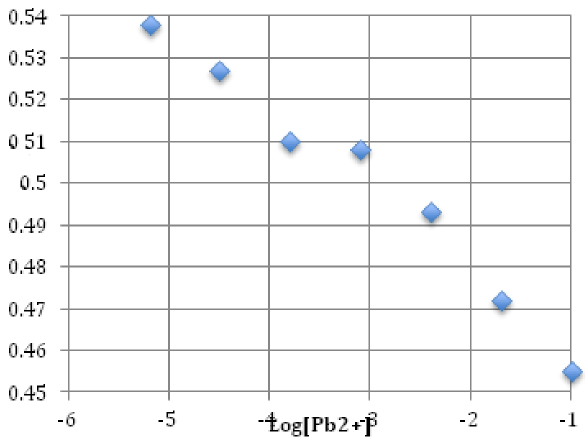
C Using electrode potentials to calculate solubility

Beaker	A	B	C	D	E	F	G	Sat. $PbCl_2$
Potential difference /V	0.455	0.472	0.493	0.508	0.510	0.527	0.538	0.481
$[Pb^{2+}]$ /mol dm^{-3}	1×10^{-1}	2×10^{-2}	4×10^{-3}	8×10^{-4}	1.6×10^{-4}	3.2×10^{-5}	6.4×10^{-6}	

j) The concentration of lead(II) ions in each of the diluted solutions has been calculated and entered into the table above.

k) Two graphs have been plotted, the first using concentration, the second using the logarithm of concentration. It can be seen that the latter is far more useful.





l) The potential difference is 0.481 V and this corresponds to $\log[Pb^{2+}] = -2.2$, so $[Pb^{2+}] = 6.31 \times 10^{-3}$ mol dm^{-3}. Converting this to g/100 g water, M_r ($PbCl_2$) = 278.1, so in 1 dm^3 there will be 1.75 g (= $278.1 \times 6.31 \times 10^{-3}$) dissolved, so the solubility is 0.175 g/100 g of water. This is considerably lower than the literature value of 1.2 g/100 g of water.

D Using electrode potentials to predict reactivity

1) There are two possible reactions:

$$H_2O_{2\,(aq)} + 2\,H^+_{(aq)} + 2\,I^-_{(aq)} \rightarrow 2\,H_2O_{(l)} + I_{2\,(aq)}$$

$$2\,H_2O_{(l)} + I_{2\,(aq)} \rightarrow H_2O_{2\,(aq)} + 2\,H^+_{(aq)} + 2\,I^-_{(aq)}$$

The E^θ of the first reaction would be +1.23 V (= +1.77−+0.54) and the second would be -1.23 V. As a positive E^θ corresponds to a negative value for ΔG (=−n.F. E^θ), the first reaction would be expected to be spontaneous.

2) If aqueous sodium iodide is added to a mixture of dilute sulfuric acid and aqueous hydrogen peroxide, then the mixture should become a yellow brown colour owing to the formation of iodine.

3) When the reaction is carried out the mixture remains clear and colourless.

m) The expected reaction did not occur – there was no sign of the iodine which should have been spontaneously formed.

n) The sign ΔG only indicates that the products are more stable than the reactants. It does not however give any indication of the rate of reaction, which will depend on other factors such as the activation energy. If the activation energy is quite high, then a spontaneous reaction will not occur (petrol does not catch fire until a match is applied). If a catalyst is added to the mixture proposed above, or the mixture left for some time, then a brown colouration can be observed.

TEACHING NOTES for Investigation 19B
INVESTIGATING THE ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE

Syllabus relevance: Topic 19.1

Explanation of the products formed during the electrolysis of aqueous solutions

As with any student planned practical, it is difficult to produce a precise list of requirements. The list below will however probably cover the major requirements.

Apparatus required

- Hofmann voltammeter (or similar apparatus for collecting gases produced during electrolysis)
- Power supplies and connecting wires
- Voltmeters
- Ammeters
- Gas syringes
- Water bath
- Thermometer
- Spectrophotometer/colorimeter
- Various glassware, such as measuring cylinders, beakers etc.

Chemicals required

- Saturated aqueous sodium chloride (~100 cm^3 per group?)
- 2 mol dm^{-3} aqueous sodium hydroxide
- 0.1 mol dm^{-3} aqueous potassium iodide

Notes

Probable timing–~60 minute homework + 60 minute lesson + 90 minutes laboratory time

This is an excellent final preparation for the Internal Assessment project. Students have to think about the underlying problem of a particular issue and come up with a practical solution – the Preliminary Exercises (may be best set as a homework assignment). Students then need to turn their ideas into a specific research question and devise a practical procedure (this may be best done in class). Finally they will have chance to carry out their planning and evaluate their results. Typical factors students will want to investigate are the effect of concentration, current and potential difference, though there is plenty of scope for varying other factors such as adding other electrolytes to increase the conductivity, or adding a buffer to the system to control the pH of the solution.

Sample results

i) Yes, if the current and the time it flows are known.

ii) $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ or $2\ H^+ + 2\ e^- \rightarrow H_2$

iii) The hydroxide ions formed, or left when the hydrogen ions are reduced, make the solution alkaline.

iv) $4\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ or $4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$

The volume of oxygen will be half the volume of hydrogen as 2 moles of electrons gives one mole of H_2, but only half a mol of O_2.

v) $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

The volume of chlorine will be equal to the volume of hydrogen as 2 moles of electrons gives one mole of both.

vi) It would make it acidic as aqueous chlorine is in an equilibrium forming hydrogen ions:

$$H_2O + Cl_2 \rightleftharpoons H^+ + Cl^- + HOCl$$

vii) Yes, the volume of gas at the anode should indicate whether it is pure oxygen (half the volume as at the anode), pure chlorine (the same as the volume at the anode – ignoring solubility) or the composition of the mixture from its exact volume between these limits.

viii) Using a Hofmann voltammeter (used for the 'electrolysis of water') the gas can be collected over each electrode and then transferred to a gas syringe.

ix) Aqueous sodium hydroxide (an alkali which reacts with the acidic chlorine) or aqueous potassium iodide (a reducing agent oxidized by the chlorine) would both react with chlorine but not with oxygen.

x) The amount of chlorine could be found using either of the above reagents. If a known excess amount of alkali was used the amount reacting with the chlorine could be found by back titration with a strong acid. If aqueous potassium iodide was used, the amount of iodine formed could be found by titrating with aqueous sodium thiosulfate.

Design

xi) Electrolyse until a given volume of hydrogen has been collected and note the volume of gas over the anode, as a rough indicator of the relative proportions of oxygen and chlorine. Pass the gas from over the anode into excess aqueous potassium iodide and titrate the iodine formed with aqueous sodium thiosulfate using aqueous starch as an indicator. 5 cm3 of chlorine will correspond to ~0.0002 mol, hence it will require twice this amount of thiosulfate to react with the liberated iodine. If an end point of ~40 cm3 is wanted (in most cases the gas will not be pure chlorine so the titre will be less), the concentration of the thiosulfate should be ~0.01 mol dm-3 (0.0004/0.04). The amounts are small so a spatula full of potassium iodide should provide a suitable excess (~0.07 g required).

xii) Does the current passing during the electrolysis of saturated sodium chloride, at room temperature, affect the proportion of oxygen and chlorine produced at the anode?

Independent variable	The current passing through the solution
Dependent variable	The chlorine:oxygen in the gas formed at the anode

xiii) The concentration of the solution would need to be controlled and, as the volume of a gas is being measured at one stage, the atmospheric pressure and the temperature should remain constant. It would have been convenient to have kept the potential difference constant, but as the electrode separation in the apparatus was fixed, the only realistic way to vary the current was to vary the potential difference.

xiv) The current will be varied and the time it is passed for, the volume of gas produced at both electrodes and the volume of aqueous sodium thiosulfate reacting with the oxidised potassium iodide will be recorded. The temperature and pressure in the laboratory will be measured at the start and end of the investigation to check they have remained constant. The ratio of the volume at the cathode to the volume of the anode will increase linearly between 1 and 2 as the proportion of oxygen increases. The amount of thiosulfate will indicate the amount of chlorine produced and hence the amount of the charge passed that oxidised chloride ions.

Method

1. Fill a Hofmann voltammeter with saturated aqueous sodium chloride.
2. Connect the voltammeter through an ammeter to a variable voltage power supply.
3. Start the stopwatch and electrolyse the mixture using a potential difference of 5 V, recording the mean current.
4. When 4-5 cm^3 of gas has collected over the cathode stop the electrolysis and record the time elapsed
5. Record the volume of gas collected over both electrodes.

6. Open the tap above the cathode limb to refill it with solution.
7. Add a spatula full of solid potassium iodide to a 250 cm^3 conical flask half filled with water and swirl until the solid dissolves.
8. Connect a tube from the jet at the top of the anode limb and place the other end in the flask containing the aqueous potassium iodide, then open the tap until the gas and the solution in the anode limb is displaced into the iodide solution.
9. Titrate the iodine formed in the flask with 0.01 mol dm^{-3} aqueous sodium thiosulfate, using starch indicator near the end point.
10. Repeat the above steps for voltages of 10,15, 20 and 25 V.

Data Collection

Potential difference	Current	Time	Volume of gas Cathode	Anode	Titre
/V	/A	/s	/cm^3	/cm^3	/cm^3
±0.1	±0.1	±1	±0.1	±0.1	±0.1
5.0	0.06	588	4.2	0.2	31.4
10.0	0.16	204	4.6	0.3	15.2
10.0	0.17	198	5.0	0.8	23.0
15.0	0.29	131	5.2	0.6	17.9
20.0	0.46	81	5.6	0.6	21.7
20.0	0.45	77	5.1	0.4	15.6
25.0	0.57	64	5.8	0.6	17.1

Note replicate data for 10 V and 20 V.

Laboratory temperature – 27°C (same at beginning and end)

Atmospheric pressure – 101.8 kPa (same at beginning and end)

Relevant qualitative observations

At low pd/current even though bubbles were produced quite rapidly from the cathode, very few bubbles could be seen at the anode, but the solution in that part of the apparatus had a distinct greenish tinge.

Data Analysis

The volume of gas at the anode should be between the volume at the cathode (if it were all Cl_2) and half the volume at the cathode (if it were all O_2). The volume observed is considerably less than that so it would appear that much of the product was chlorine and that this was dissolving in the solution rather than being liberated as a gas (the colour change in the solution would seem to confirm this). It was decided therefore to carry out one calculation on the assumption that the gas collected (which appeared colourless) was only oxygen. The volume of chlorine that had dissolved could then be calculated as the volume of hydrogen minus double the volume of oxygen, and this allowed the ratio of Cl_2:O_2 to be deduced. For the 5 V value this gave:

Volume of Cl_2 = Volume at cathode – (2 × Volume at anode)

$= 4.2 - (2 \times 0.2) = 3.8\ cm^3$

Ratio = 3.8/0.2 = 19.0

Applying this assumption to the rest of the data gives the following results:

Potential difference	Current	Volume of chlorine	Molar ratio Cl_2:O_2
/V	/A	/cm^3	
5	0.06	3.8	19.0
10	0.16	4.0	13.3
10	0.17	3.4	4.3
15	0.29	4.0	6.7
20	0.46	4.4	7.3
20	0.45	4.3	10.8
25	0.57	4.6	7.7

From the titration data the amount of chlorine could be calculated and the charge required to produce this amount of chlorine was calculated. For the 5 V value this gave:

Amount Cl_2 = ½ × amount of thiosulfate = ½ × titre × concentration

= ½ . 0.0314 . 0.01 = 1.57 × 10^{-4} mol (= 0.157 mmol)

The amount of hydrogen produced at the cathode can be calculated by multiplying the current by the time to calculate the charge passed and applying Faraday's Law. For the 5 V value:

Amount of hydrogen $= \frac{C}{z.F} = \frac{I.t}{z.F} = \frac{0.06\ x\ 588}{2\ x\ 96500} = 1.83x10^{-4}\ mol$ (= 0.183 mmol)

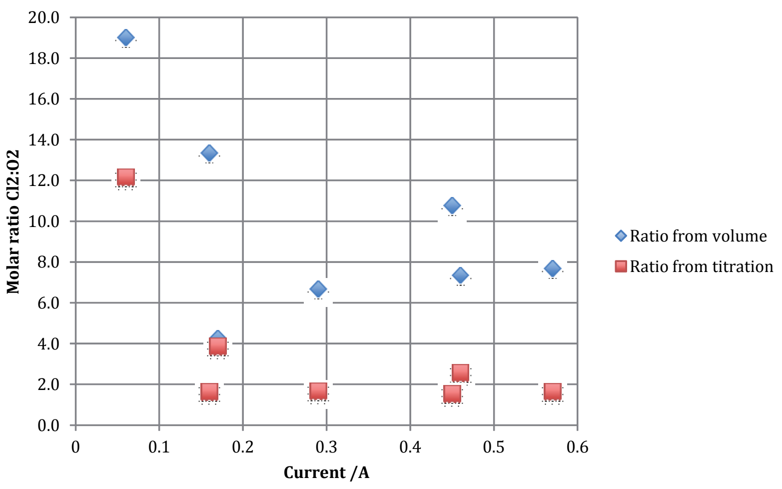
The amount of oxygen formed can be calculated by subtracting the amount of chlorine from the amount of hydrogen and dividing by 2. This can then be used to calculate the ratio of Cl_2:O_2. For the 5 V value:

Amount of oxygen = ½ (0.183 – 0.157) = 0.013 mmol Ratio = 0.157/0.013 = 12.1

Applying this method to the rest of the data gives the following results:

Potential difference	Current	Amount of hydrogen	Amount of chlorine	Amount of oxygen	Molar ratio Cl_2:O_2
/V	/A	mmol	mmol	mmol	
5	0.06	0.1828	0.157	0.0129	12.2
10	0.16	0.1691	0.076	0.0466	1.6
10	0.17	0.1744	0.115	0.0297	3.9
15	0.29	0.1968	0.0895	0.0537	1.7
20	0.46	0.1931	0.1085	0.0423	2.6
20	0.45	0.1795	0.078	0.0508	1.5
25	0.57	0.1890	0.0855	0.0518	1.7

Graphs can then be drawn of the ratio against current for the two methods:



At first sight, both graphs seem to indicate that the molar ratio of Cl_2:O_2 decreases as the current increases, but on closer examination this is very dependent on the single 0.06 A reading and if this is discounted, both sets of data would also be quite consistent with the current having no effect on the ratio.

The theoretical expectation might be that, as there is a high concentration of both water and chloride ions, then neither would become significantly depleted near the anode, even at a high current, so that having no effect would not be a surprising outcome. Water is however in a much greater concentration than chloride ion so any effect of current would be a reduction of the ratio with increased current, but it would be expected to be most noticeable at high currents rather than low currents.

Conclusion & Evaluation

a) In a couple of words the answer is "not really". The values at a low current give considerably greater values for the molar ratio of Cl_2:O_2 than the other data. Because of the significant uncertainties that the data displays it is unclear whether this indicates an effect at very low currents or whether the large ratio is just a random variation, especially for the gas volume method where the uncertainty in the volume at the anode is ±50%!. If these data are ignored then for both methods, a horizontal line could be drawn on the graph that would fall close to single data points and between replicates where these exist.

b) The method of the volumes of the gases at the two electrodes did not work as intended because of the significant solubility of chlorine in the electrolyte. The method was then modified using the assumption that the gas that was collected was oxygen because all of the chlorine dissolved. This assumption is quite questionable, but apart from the first data point it seems to yield results that are quite consistent within the considerable uncertainties. The variation between replicates, especially those at 10 V, are quite significant and indicate the presence of quite large experimental errors over and above the uncertainties resulting from the equipment.

The titration method also seemed to yield quite consistent results within the limits of the reproducibility of replicates. Interestingly a large value from one method seems to also correspond to a large value from the second method indicating that the source of error is probably affecting both methods. One possible source of this is the current passing through the system, which appeared to fluctuate quite significantly and the value recorded was an estimated mean value that attempts to take account of the fluctuations.

It is unclear why the current fluctuated, but this should not have affected the volume method as the charge passed is not used in the calculation of the result. If the charge required to produce 1 cm^3 of hydrogen is calculated for the different sets of data, then this too varies by about ±10%, showing some underlying source of error that has yet to be identified.

c) Firstly having more replicate data, for example carrying out each determination 5 times, should result in a significant improvement in the results. As the greatest uncertainty seems to be attached to the low current data then more data over a range of small currents (under 0.1 A) would be very helpful. The uncertainty in the volume of the gas at the anode is also quite high and using more precise data is not practicable, so the alternative would be to continue the electrolysis longer so that the volumes at both electrodes are significantly greater than the ones used – maybe a volume of ~25 cm^3 at the cathode. Ensuring that all the chlorine does dissolve in the electrolyte by adding an alkali to it, would reinforce the assumption made in this method, but it may also itself alter the ratio.

The titration method also displayed significant variations between replicates. It does suffer from the problem of ensuring all the dissolved chlorine is flushed from the voltammeter into the titration flask, but the fact that the fluctuations between the replicates match those in the other method might indicate a different source of error, namely variations in the current. Further work to try to identify the cause of the fluctuation in the charge required to produce 1 cm^3 of hydrogen is also something that should be undertaken.

TEACHING NOTES for Investigation 19C
SOME FACTORS AFFECTING ELECTROLYSIS

Syllabus relevance: Topic 19.1

Determination of the relative amounts of products formed during electrolytic processes.

Apparatus required

Per group

- Voltammeter in which the gases formed at the electrodes can be collected
- Hofmann voltammeter
- 4 × 100 cm^3 beakers
- 2 × test tubes
- Variable voltage power supply
- Ammeter

Generally available

- Splints
- Crocodile clips
- Connecting wires
- Thermometer (0-110°C)
- Barometer

Chemicals required

- Aqueous copper sulfate (~0.1 mol dm^{-3}, ~200 cm^3 per group)
- Sulfuric acid(~1.0 mol dm^{-3}, ~200 cm^3 per group)
- Sulfuric acid(~0.1 mol dm^{-3}, ~50 cm^3 per group)
- Propanone (~100 cm^3 in a shared beaker for rinsing electrodes)
- 2 copper electrodes (~1 cm × 5 cm) with scratch marks about 2 cm from one end
- 6 graphite electrodes

~100 cm^3 per group of each of the following (~0.1 mol dm^{-3})g

- Aqueous sodium sulfate
- Aqueous sodium bromide
- Aqueous lead (II) nitrate
- Aqueous silver nitrate

Notes

Probable timing – 90 minutes laboratory time

This is a fairly straightforward exercise designed to reinforce the basics of the electrolysis of aqueous solutions. In Part C, the resistance of Hofmann voltammeters varies tremendously dependent on their exact shape and the area of the electrodes. Choose an initial p.d. that will approximately ¼ fill the cathode limb in 5 minutes, then use double and triple this potential difference for the other runs.

TEACHING NOTES for Investigation 19C
SOME FACTORS AFFECTING ELECTROLYSIS

Sample data

A Products formed at the electrodes

Electrolyte	Observations at anode	Observations at cathode
Sodium sulfate	Bubbles of a colourless gas evolved, which supports combustion of splint	Bubbles of a colourless gas evolved, which gives a "pop" with lighted splint
Sodium bromide	The solution around the anode turns a yellow-brown colour	Bubbles of a colourless gas evolved, which gives a "pop" with lighted splint
Copper(II) sulfate	Bubbles of a colourless gas evolved, which supports combustion of splint	The electrode turns a reddish brown colour (if high current may be a loose blackish powder)

a) (i) Anode: $4\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ or $4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$

(ii) Cathode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ or $2\ H^+ + 2\ e^- \rightarrow H_2$

b) The solution near the anode turns brown owing to the formation of bromine: $2\ Br^- \rightarrow Br_2 + 2\ e^-$

c) The cathode turned brown owing to the formation of copper metal: $Cu^{2+} + 2\ e^- \rightarrow Cu$

d)

Reaction	E° /V
$S_2O_8^{2-}$ / 2 SO_4^{2-}	+2.01
½O_2, 2H^+ / H_2O	+1.23
½Br_2 / Br^-	+1.09

Reaction	E° /V
Cu^{2+} / Cu	+0.34
H_2O / ½H_2, OH^-	-0.83
Na^+ / Na	-2.71

e) At the anode the most easily oxidised species (the one with the least positive Eo) is changed. At the cathode the most easily reduced species (the one with the least negative Eo) is changed.

f) (i) At anode: I^-

(ii) At cathode: Ag^+, Pb^{2+}, Sn^{2+}

B Factors affecting the resistance of the voltammeter

Change to voltammeter	Effect on current
Increasing depth of immersion	Current increases as electrodes immersed deeper (25 → 40 mA)
Increasing angle to beaker wall	Current increases as electrodes rotated (40 → 60 mA)
Decreasing distance between electrodes	Current increases as electrodes moved closer together (40 → 120 mA)
Decreasing concentration of electrolyte	Current decreases as concentration decreases (40 → 25 mA as conc. halved)
Replacing Cu^{2+} by H^+	Current increases when H^+ replaces Cu^{2+}

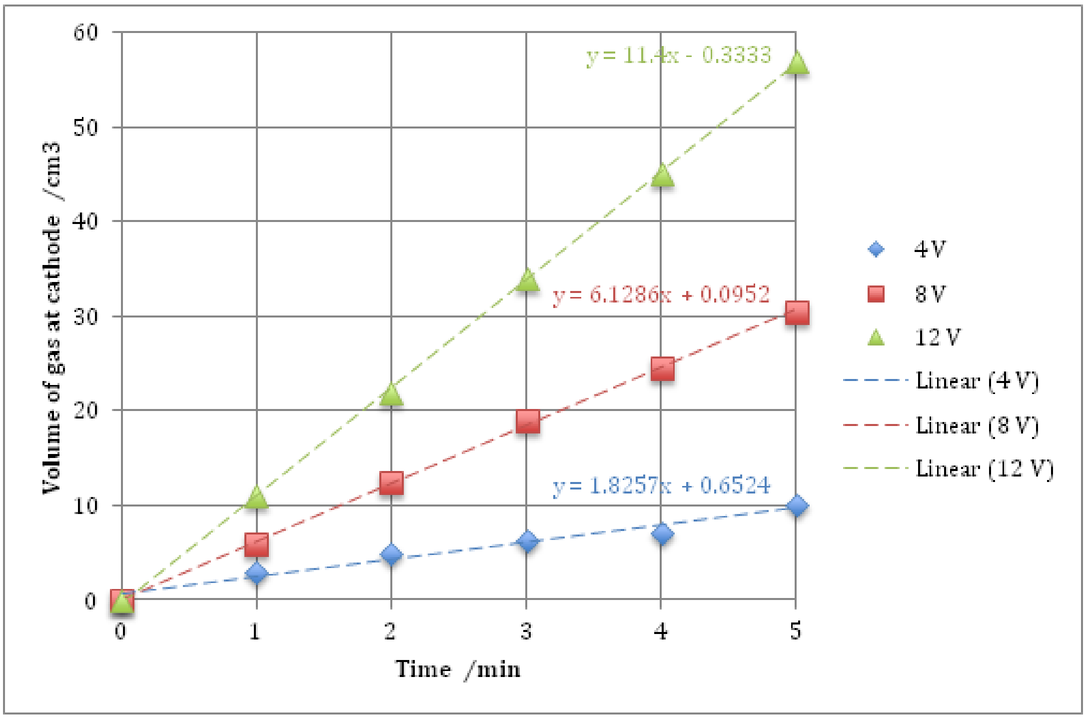
g) As the electrodes are immersed further a greater surface area is available for electron gain/loss, hence the resistance is reduced. When the electrodes are rotated both sides become equivalent thereby generating more effective surface area. When the electrodes are moved closer the ions have a shorter distance to move to carry the charge between the electrodes and so the resistance is less. When the solution is diluted there are less ions available to carry the charge, so the resistance is increased. H^+ can diffuse more rapidly than Cu^{2+}, so replacing Cu^{2+} with H^+ decreases resistance.

C Factors affecting the charge passed

Potential difference /V	**4**	**8**	**12**
Current /A	0.24	0.75	1.43
Time /min	**Volume of gas collected at cathode /cm^3**		
1	2.9	6.0	11.0
2	5.0	12.5	22.0
3	6.3	19.0	34.0
4	7.1	24.5	45.0
5	10.0	30.5	57.0
Volume of gas at anode (graphite) /cm^3	1.1	10.0	17.0

Temperature – 22.0 °C   Atmospheric pressure = 102.3 kPa

h)



i) As the potential difference is increased, the resistance remains constant and the current increases. As the current increases the rate at which the product is formed increases.

j) At the anode: $4\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ or $4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$

At the cathode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ or $2\ H^+ + 2\ e^- \rightarrow H_2$

It can be seen that 4 electrons are required to produce each gas molecule at the anode, but only two are required at the cathode. The same number of electrons pass through both electrodes so the volume of gas at the cathode is twice that at the anode. However in this case, as oxygen is produced on a graphite anode, the anode reacts to form carbon dioxide which is quite soluble in water.

k) P.V = n.R.T, so $V = \frac{n.R.T}{P} = \frac{1 \times 8.31 x 295}{102.3} = 23.963 dm^3$

½ mol (11.982 dm^3) of hydrogen would be produced by one Faraday (= 1 mol electrons)

For 4 V this would take $\frac{11982}{1.83} = 6547 minutes = 392842 s$

Charge passed = 392842 × 0.24 = 94282 C

For 8 V this would take $\frac{11982}{6.13} = 1955 minutes = 117276 s$

Charge passed = 117276 × 0.75 = 87957 C

For 12 V this would take $\frac{11982}{11.4} = 1051 minutes = 63061 s$

Charge passed = 63061 × 1.43 = 90178 C

Mean value for Faraday Constant = 90800 C mol^{-1}.

This is significantly less than the accepted value of 96500 C mol^{-1}.

D The effect of charge and molar mass on the mass of product

l)

Electrolyte	$CuSO_4$	$Pb(NO_3)_2$	$AgNO_3$
Initial mass of cathode /g	15.73	16.96	17.53
Final mass of cathode /g	15.89	17.32	18.01
Mass of metal formed /g	0.16	0.36	0.48
Ratio of masses	1	2.25	3.00
Theoretical ratio of masses	1	3.26	3.39

m) $Cu^{2+} + 2 e^- \rightarrow Cu$ so 1 mol of electrons forms ½ mol of Cu, which is ½ × 63.55 = 31.8 g

$Pb^{2+} + 2 e^- \rightarrow Pb$ so 1 mol of electrons forms ½ mol of Pb, which is ½ × 207.2 = 103.6 g

$Ag^+ + e^- \rightarrow Ag$ so 1 mol of electrons forms 1 mol of Ag, which is 107.9 g

Ratio = 1: 3.26: 3.39

It can be seen that there is a significant discrepancy between the experimental and theoretical values. This is probably a result of the differing extent to which the deposited metal flaked off the electrodes when they were rinsed – something that definitely occurred.

TEACHING NOTES for Investigation 20A
FACTORS AFFECTING THE HYDROLYSIS OF HALOGENOALKANES

Syllabus relevance: Topic 20.1

Explanation of how the rate depends on the identity of the halogen (i.e. the leaving group), whether the halogenoalkane is primary, secondary or tertiary and the choice of solvent.

Apparatus required

Per group

- 6 × test tubes
- 250 cm^3 beaker

Chemicals required

- Ethanol
- 1-chlorobutane
- 2-chlorobutane (*iso*-butyl chloride)
- 2-chloro-2-methylpropane (*tert*-butyl chloride)
- 1-bromobutane
- 1-iodobutane
- Aqueous sodium hydroxide (~1 mol dm^{-3})
- Aqueous silver nitrate (~0.01 mol dm^{-3})
- Dilute nitric acid
- Blue litmus paper

Notes

Probable timing – 40 minutes laboratory time

This is a short, fairly straightforward exercise designed to reinforce the factors that influence the rate of halogenoalkane hydrolysis and the mechanism by which the reactions occur.

Sample data

A Choice of nucleophile

Observations

When the 1-chlorobutane is added it forms a separate immiscible layer in both cases. The addition of ethanol causes the mixture to once again become homogenous. After acidification and the addition of aqueous silver nitrate, the tube containing the sodium hydroxide produced a white precipitate, where as there was only a slight cloudiness in the tube which had only water.

a) Halogenoalkanes cannot form hydrogen bonds to water, therefore mixing them with the water would involve the breaking of the hydrogen bonds in the water without any compensatory bonding to the solute. As a result halogenoalkanes are insoluble in water.

b) The ethanol allowed the two components to mix and this increases the reaction rate and if two layers are present then reaction could only occur at the interface between the two phases.

c) If silver ions are added to an alkali a grey-brown precipitate of silver oxide is formed:

$$Ag^+ (aq) + 2\ OH^- (aq) \rightarrow Ag_2O (s) + H_2O (l)$$

Hence the need to acidify before adding the silver nitrate.

d) The white precipitate formed was silver chloride:

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$$

e) The chloride ion in the above equation can only have resulted from the substitution of the chlorine on the 1-chlorobutane:

$C_4H_9Cl + OH^- \rightarrow C_4H_9OH + Cl^-$

f) A nucleophile is an ion or molecule that attacks a centre of positive charge within a molecule, such as the carbon atom that is bonded to the halogen in halogenoalkanes.

g) Whilst theoretically the same reaction can occur with water rather than the hydroxide ion it is much slower.

h) The slower reaction rate with water shows that it is a much weaker nucleophile than the hydroxide ion, because the hydroxide ion:

- has a negative charge and so is more attracted to the positive carbon
- has more lone pairs of electrons
- is smaller than the water molecule

B Effect of the halogen involved

Observations

The tube containing 1-iodobutane produced a pale yellow precipitate almost immediately. Over the next few minutes the tube containing the 1-bromobutane became cloudy and eventually formed a cream coloured precipitate. Even at the end of the ten minutes, the tube containing 1-chlorobutane only looked slightly milky.

i) The carbon-halogen bond is most polar for chlorine (electronegativity difference 0.6), less for bromine (electronegativity difference 0.4) and least for iodine (electronegativity difference 0.1). It might be expected that the more polar the bond the greater the rate of reaction as the charge on the carbon being attacked by the nucleophile is greater.

j) The carbon-halogen bond is strongest in chloroalkanes (324 kJ mol^{-1}), less in bromoalkanes (285 kJ mol^{-1}) and least in iodoalkanes (228 kJ mol^{-1}). It would be expected that a low carbon-halogen bond strength would favour a greater rate of reaction as the carbon-halogen bond fission is likely to dictate the activation energy of the reaction.

k) The reaction rate was considerably greater for the iodoalkane, so this would indicate that the second factor is more influential than the first factor, iodide ion being a good leaving group may also be an important factor, followed by bromide and then chloride.

C The effect of the hydrocarbon chain

Observations

The tube containing 2-chloro-2-methylpropane produced a white precipitate almost immediately. The tube containing the 2-chlorobutane became cloudy and eventually formed a white precipitate over the next few minutes. Even at the end of the ten minutes, the tube containing 1-chlorobutane only looked slightly milky.

l) It appears that halogenoalkanes in which the halogen is attached to a tertiary carbon atom are more reactive than those in which it is attached to a secondary carbon atom and these in turn are more reactive than primary halogenoalkanes.

m) In the S_N1 mechanism an intermediate carbocation is formed. The stability of carbocations increases as the charge density on the carbon decreases. Hydrocarbon chains are less electronegative than hydrogen atoms, hence they stabilise the charged carbon through an inductive effect. The result is that the stability of carbocations is in the order tertiary > secondary > primary, hence the observed effect on the reaction rate.

n) Factors that would predispose a halogenoalkane to react by a S_N1 mechanism seem to correlate with a greater rate of reaction, inferring that the go by this mechanism, rather than S_N2 increases the rate of reaction. As discussed above a weak carbon-halogen bond reduces the activation energy for the formation of the carbocation intermediate and the lower charge on the carbon atom in the tertiary carbocation, increases its stability.

o) The effect of solvents has not being investigated because hydrolysis reactions, of necessity, require water; a polar protic solvent. Polar aprotic solvents, such as propanone or DMSO favour the S_N2 mechanism as they do not solvate the nucleophile to the same extent that protic solvents do.

TEACHING NOTES for Investigation 20B
A TWO STAGE ORGANIC SYNTHESIS

Syllabus relevance; Topic 20.1 & 20.2

Multiple stage organic synthetic route series of experiments.

A range of experiments of organic synthetic reactions could be done.

Core techniques of organic chemistry could include reflux, distillation, filtration, purification (including chromatographic techniques), separations and extractions.

Apparatus required

Per group

- 250 cm^3 Quickfit flask
- 100 cm^3 Quickfit flask
- Condensers and adaptors for reflux and distillation
- Stopper for flasks
- 10 cm^3 measuring cylinder
- 25 cm^3 measuring cylinder
- 100 cm^3 measuring cylinder
- Thermometer
- 250 cm^3 separatory funnel
- 250 cm^3 beaker
- Glass vial
- Suction filtration apparatus (Buchner funnel, flask & pump)
- Melting point apparatus

Generally available

- Top pan balance
- Filter paper for Buchner funnels
- Melting point tubes
- Boiling chips

Chemicals required

- Benzoic acid (~25 g per student)
- Methanol (~150 cm^3 per student)
- Concentrated sulfuric acid (~20 cm^3 per student) **n.b. This must be very fresh for reasonable yields–if possible open a new bottle.**
- Dichloromethane (~100 cm^3 per student)
- 0.5 mol dm^{-3} aqueous sodium hydrogencarbonate (~50 cm^3 per student)
- Anhydrous calcium chloride (~5 g per student)
- Concentrated nitric acid (~15 cm^3 per student)
- Solid ice (~150 g per student)

TEACHING NOTES for Investigation 20B
A TWO STAGE ORGANIC SYNTHESIS

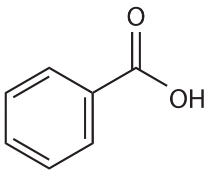
Notes

Probable timing–~4 × 90 minute practical periods, or better one day in the lab!

This is an excellent practical exercise as it involves lots of different organic techniques. The esterification followed by the nitration was chosen to give the student practice at isolating and purifying both a solid and a liquid product. As with most organic practicals there are a few tricky and hazardous aspects (conc. acids, volatile & flammable liquids) so consider whether your particular group of students is up to the challenge. If they are, students generally love to have an exercise where they produce their own product!

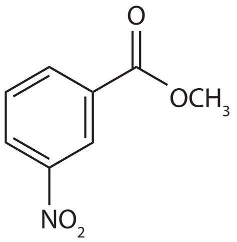
Planning

i)



ii) 3-nitrobenzoic acid, benzyl alcohol, benzoate esters

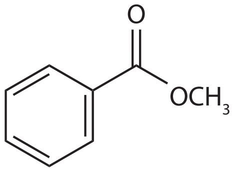
iii)

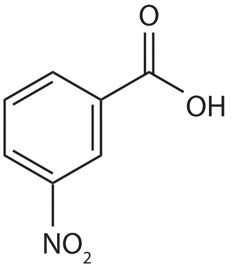


iv) methyl benzoate, 3-nitrobenzoic acid

v) methyl benzoate, 3-nitrobenzoic acid (also)

vi)





vii) The first compound could be produced by reacting benzoic acid with methanol in the presence of a strong acid catalyst.

viii) The first compound could be converted into the desired product by reacting with a mixture of concentrated nitric and sulfuric acids.

(Note: for the second intermediate the reagents for the two stages would just be reversed)

Data Collection

Relevant qualitative observations

The white, solid benzoic acid dissolves readily in methanol to give a colourless solution. The mixture formed on adding water and the immiscible organic solvent separated readily. The volatile solvent was readily removed to leave the almost colourless liquid product.

In the second stage adding the acid mixture produced quite a lot of heat and it had to be added very gradually. The ester and the mixed acids formed two separate phases and constant shaking was required to mix these to ensure an efficient reaction. The flask become noticeably warm in the early stages and cooling was required. On adding the ice the solid product separated readily, though on filtering globules of immiscible liquid came through into the flask – presumably un-nitrated ester. The m.p. of the crude product may be significantly lower than its real value as the heating was rather too rapid.

Mass of benzoic acid	= 25.00 g
Mass of crude intermediate	= 146.45–122.27 = 24.18 g (22 cm^3)
Mass of crude product	= 10.24 g (Actually 22.52 g from 22 cm^3)
Mass of recrystallised product	= 7.58 g (Actually 16.68 g from 22 cm^3)
Melting point range of crude product	= 50–54 °C
Melting point range of purified product	= 68–70 °C

Data Analysis, Conclusion & Evaluation

a)

Compound	Benzoic acid	Methyl benzoate	Methyl 3-nitrobenzoate
Molar mass /g mol^{-1}	122.13	136.16	181.16

Amount of benzoic acid = $\frac{25.00}{122.13} = 0.2047\,mol$

Theoretical mass of methyl benzoate = 0.2047 × 136.16 = 27.87 g

Theoretical mass of methyl 3-nitrobenzoate = 0.2047 × 181.16 = 37.08 g

Percentage yield of intermediate = $\frac{24.18}{27.87} \times 100 =$ 87%

Percentage yield of crude product = $\frac{10.28}{37.08} \times 100 =$ 28%

Percentage yield of recrystallised product = $\frac{7.58}{37.08} \times 100 =$ 20%

b) The main possible reasons for loss of product are:

- The esterification reaction may not have had time to reach equilibrium.
- Being an equilibrium the conversion of the acid to the ester would not have been complete.
- In the extraction some of the ester would still have been dissolved in the aqueous layer and hence lost.
- When the dichloromethane was distilled off, some ester may have been carried over.
- The nitration reaction may not have gone to completion.
- Some of the nitration product may not have crystallised before filtration.
- Some of the final product would have dissolved in the methanol both during the washing and during the recrystallisation.

Looking at the percentage yields and observations it would appear that the formation of the 2-isomer and incomplete nitration (old H_2SO_4?) probably occurred in this case.

c) In the same order as above, some possibilities are:

- The reflux time could have been increased.
- Some reagent (anhydrous $MgSO_4$?) could have been added to absorb water and shift the equilibrium.
- Salt could have been added to the aqueous layer to reduce the solubility of organic compounds.
- Fractional distillation might have reduced the loss of ester.
- The nitration reaction could have been carried out for longer and the mixture warmed near the end.
- Salt could have been added to the ice and the mixture further cooled.
- The methanol washings and recrystallisation liquor could have been saved and the solvent evaporated to try to isolate more product from the residue.
- In this case the single major improvement would be opening a fresh bottle of conc. H_2SO_4, which would have reduced the amount of water in the esterification equilibrium and have made the nitration process more efficient.

d) The melting point of the crude product is very low, implying a high degree of impurity. The purified product similarly has a rather low melting point, though better than the crude product. In both cases the product was maybe not dried for long enough to remove the last traces of the solvent. As would be expected, the melting point range for the crude product is greater than that of the purified one.

e) The intermediate probably had benzoic acid dissolved in it, so this would have been converted to 3-nitrobenzoic acid in the second stage. Further washing of the intermediate with sodium hydrogencarbonate, or distillation of the intermediate would almost certainly have reduced the amount of it present. Nitration gives predominantly the 3-nitro compound, but the method specifically mentions the 2-nitro compound, which presumably is an impurity as well as maybe traces of the 4-nitro one.

f) The dissociation reaction of sulfuric acid in methanol, like that in water, is very exothermic and methanol has a low boiling point, so if the temperature rose too high it would be vapourised.

g) As well as being a strong acid to catalyse the reaction, the acid would react with the water produced and displace the position of equilibrium to create more product.

h) The ester can only form weak H-bonds to the water through the ester group, but the benzene ring provides a large hydrophobic hydrocarbon section that will break many H-bonds in water, rendering the solution very endothermic.

i) The final stage of purification of a liquid product is distillation and so the methyl benzoate should be distilled to further purify it.

j) The electrophile is the nitronium ion (NO_2^+). It is produced in the equilibrium:

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2\,HSO_4^-$$

k) Impurities are either less soluble in methanol than the product, in which case they will not dissolve in the methanol and be removed as an insoluble residue, or they will be more soluble in which case they will remain dissolved in the cold methanol and separated from the solid product.

l) Chromatography techniques (maybe HPLC on a solution of the product?) could be used to see if the product comprised only a single compound and this would also give some indication of the extent of the impurities. These impurities could be identified by spectroscopic techniques such as IR, UV and NMR. One particularly powerful technique is to use mass spectrometry to analyse the impurities as they elute from a chromatography column.

TEACHING NOTES for Investigation 22B
MEASURING K_{sp} FOR A SPARINGLY SOLUBLE SALT

Syllabus relevance: Topic A.10

Experiments could include investigations of K_{sp}.

Apparatus required

- 10 × 250 cm^3 conical flasks with bungs
- 100 cm^3 measuring cylinder
- 25 cm^3 measuring cylinder
- 25 cm^3 pipette & pipette filler
- 2 × burette

Chemicals required

- 0.005 mol dm^{-3} $AgNO_3$ (~1 dm^3)
- 0.005 mol dm^{-3} KIO_3 (~1 dm^3)
- Aqueous KI (0.004, 0.002 & 0.001 mol dm^{-3}; ~250 cm^3 of each)
- Aqueous $Na_2S_2O_3$ (0.02, 0.004, 0.002 & 0.001 mol dm^{-3}; ~250 cm^3 of each)
- 2 mol dm^{-3} sulfuric acid (~200 cm^3)
- 1% starch indicator (~20 cm^3)
- Solid KI

Notes

Probable timing – ~30 minutes to make up solutions & ~90 minutes for the titrations

This is a nice elegant method for measuring the solubility of a product and provides some useful revision of redox ideas. The reagents unfortunately are not cheap so it may be a good idea to assign one mixture to a particular student, or group of students, and then share the results after the titrations have been carried out. This would also substantially reduce the time needed for the second lesson (~30 minutes?).

Sample data

Mixture	Titre / cm^3	KI $[I^-]$ /mol dm^{-3}	$[Ag^+]$ /mol dm^{-3}	Titre /cm^3	$Na_2S_2O_3$ $[S_2O_3^{2-}]$ / mol dm^{-3}	$[IO_3^-]$ /mol dm^{-3}	K_{sp} $\times 10^8$
A	35.8	0.004	0.001909	4.1	0.001	0.000009	1.74
B	26.9	0.004	0.001435	7.0	0.001	0.000016	2.23
C	18.8	0.004	0.001003	5.2	0.002	0.000023	2.32
D	10.0	0.002	0.000267	8.4	0.002	0.000037	1.00
E	6.3	0.002	0.000168	16.5	0.004	0.000147	2.46
F	5.2	0.002	0.000139	28.9	0.004	0.000257	3.56
G	7.4	0.001	0.000099	22.1	0.020	0.000982	9.69
H	8.0	0.001	0.000107	32.2	0.020	0.001431	15.27
I	7.9	0.001	0.000105	43.3	0.020	0.001924	20.27

Uncertainty in burette readings = ± 0.05 cm^3

Uncertainty in pipette volume = ± 0.06 cm^3

Relevant qualitative observations

When the solutions were mixed together the mixture became cloudy owing to the formation of a white solid. On standing this settled out to leave a solid residue on the bottom of the flask and a colourless liquid above it. On titrating with aqueous potassium iodide the formation of a white precipitate made the solution opaque, nevertheless the end point was indicated by a clear transition from colourless to blue. Similarly in the second titration the transition from blue to colourless gave a good indication of the end point.

Data Analysis

a) $Ag^+_{(aq)} + IO_3^-{}_{(aq)} \rightleftharpoons AgIO_{3\,(s)}$

$$K_{sp} = [Ag^+].[IO_3^-]$$

b) $Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}$

The mixture turns blue at the end point because when all the silver ions have been consumed, there will be excess iodide ions in the solution. These are oxidised by the iodate ions present (see equation in c) to form iodine, which reacts with starch to produce the blue colour.

c) $IO_3^-{}_{(aq)} + 6\,H^+_{(aq)} + 5\,I^-_{(aq)} \rightarrow 3\,I_{2\,(aq)} + 3\,H_2O_{(l)}$

$I_{2\,(aq)} + 2\,S_2O_3^{2-}{}_{(aq)} \rightarrow 2\,I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

The mixture is initially turns blue because the iodine produced reacts with starch to produce the blue colour. At the end point the thiosulfate has reacted with all the iodine, hence the solution turns colourless.

d) **For mixture A**

Amount of I^- = c . V = 0.004 × 0.0358 = 0.0001432 mol

As a 1:1 reaction, $[Ag^+] = \frac{n}{V} = \frac{0.0001432}{0.075} = 0.001909$

Amount of $S_2O_3^{2-}$ = c . V = 0.001 × 0.0041 = 0.0000041 mol

As a 1:6 reaction, amount of IO_3^- = $= \frac{n}{6} = \frac{0.0000041}{6} = 0.0000006833$

$$[IO_3^-] = \frac{n}{V} = \frac{0.0000006833}{0.075} = 0.000009111$$

$$K_{sp} = [Ag^+].[IO_3^-] = 1.909x10^{-3}\ x\ 9.111x10^{-6} =$$

$= 1.739 \times 10^{-8}$

e) **For mixture A**

Uncertainty in volume of pipette = ±0.06 in 25 = 0.24%

Uncertainty in titre 1 = ±0.1 in 35.8 = 0.28%

Uncertainty in titre 2 = ±0.1 in 4.1 = 2.44%

Uncertainty in $[Ag^+]$ = 0.24 + 0.28 = ±0.52%

Uncertainty in $[IO_3^-]$ = 0.24 + 2.44 = ±2.68%

Uncertainty in K_{sp} = 0.52 + 2.68 = 3.2% = ±0.06 × 10^{-8}

f)

Ion	Initial amount = c.V /mol	Equilibrium amount = c.V /mol	Amount precipitated /mol	Percentage precipitated %
Ag^+ in A	= 0.005 × 0.14 = 0.0007	= 0.001909 × 0.2 = 0.0003818	0.0007 – 0.0003818 = 0.0003182	45.4
IO_3^- in A	= 0.005 × 0.06 = 0.0003	= 0.000009 × 0.2 = 0.0000018	0.00003 – 0.0000018 = 0.0000282	94.0
Ag^+ in E	= 0.005 × 0.1 = 0.0005	= 0.000168 × 0.2 = 0.0000336	0.0005 – 0.0000336 = 0.0000466	93.3
IO_3^- in E	= 0.005 × 0.1 = 0.0005	= 0.000147 × 0.2 = 0.0000294	0.0005 – 0.0000294 = 0.0000471	88.8
Ag^+ in I	= 0.005 × 0.06 = 0.0003	= 0.000105 × 0.2 = 0.000021	0.0003 – 0.000021 = 0.000279	93.0
IO_3^- in I	= 0.005 × 0.14 = 0.0007	= 0. 001924 × 0.2 = 0.0003848	0.0007 – 0.0003848 = 0.0003152	45.0

Comparing the systems to E; when the initial amounts of both ions are equal, in A, when $[Ag^+]$ is high this displaces the equilibrium to the right and the percentage of IO_3^- precipitated should be high. This is reflected in the increase from 88.8% to 94.0%.and the percentage of Ag^+ precipitated decreases from 93.3% to 45.4%. In 'I' the reverse is true and the excess IO_3^- should have caused the percentage of Ag^+ precipitated to increase, but instead there is a very slight decrease (93.3% to 93.0%). The percentage of IO_3^- precipitated does however decrease, as expected, from 88.8% to 45.0%. These results show that the variations are overall as would be predicted by Le Chatelier's Principle.

Conclusion & Evaluation

g) The mean value of the solubility product is 7.10×10^{-8}, slightly greater than the literature value of 3.0×10^{-8}. The values in G, H and I are much greater than the preceding values and, if these are omitted the mean is 2.2×10^{-8}.

h) The variation in the results, even the values for A to F, which have a degree of consistency, is much greater than the calculated uncertainty implying the presence of systematic errors. One source of error could be some of the solid silver iodate remaining in the solution or being drawn up in the pipette. This would lead to an increase in the value of the solubility product and this may be the explanation for the anomalously high results in G, H and I. The steady increase through these mixtures would however imply some regular change as the amount of iodate is increased, rather than a random variation caused by precipitate being drawn up. A closer examination of the figures shows that for H and I in particular, the $[Ag^+]$ did not decrease as might have been predicted and hence suspicion must rest on the accuracy of the first titration for these solutions.

i) The potential problem of drawing up precipitate into the pipette could have been avoided either by filtering off the solid or allowing it to settle in a taller deeper container, such as a measuring cylinder in which the solid could be kept further from the pipette. As the solubility of salts is quite temperature dependent, the solutions should also have been left in a thermostatically controlled water bath when reaching equilibrium.

TEACHING NOTES for Investigation 23B
ENZYME ACTIVITY AND THE MICHAELIS CONSTANT

Syllabus relevance: Topic B.7

Determination of the maximum rate of reaction (V_{max}) and the value of the Michaelis constant (K_m) for an enzyme by graphical means, and explanation of its significance.

Apparatus required

- 100 cm^3 beaker
- 25 cm^3 measuring cylinder
- 10 cm^3 measuring cylinder
- Balance connected to data-logger

Chemicals required

- 1 mol dm^{-3} hydrogen peroxide (~100 cm^3 per group)
- Potato juice (~30 cm^3 per group)

The potato juice is obtained by feeding potato pieces into a domestic juice extractor (used for preparing carrot juice, apple juice etc.). It needs to be freshly prepared as it rapidly denatures on standing. When the juice from a large potato is left to stand it gives about 100 cm^3 of juice and about half that amount of starchy sediment, which is rejected.

Notes

Probable timing – ~60 minutes laboratory time

This allows students to generate data that permits them to investigate *Michaelis-Menten* kinetics and the extension of this into the reciprocal (*Lineweaver-Burk*) plot.

The formation of froth on the reaction mixture can be a problem, but it can be turned into an advantage. An alternative method for rate determination is to carry out the reaction in a measuring cylinder (100 cm^3?) and to record the level of froth against time.

Sample data

Time /s	Mass A /g	Mass B /g	Mass C /g	Mass D /g	Mass E /g
0	62.90	62.70	62.35	62.05	61.86
10	62.87	62.69	62.35	62.05	61.85
20	62.86	62.68	62.34	62.05	61.85
30	62.85	62.67	62.34	62.04	61.85
40	62.84	62.67	62.31	62.03	61.85
50	62.83	62.64	62.31	62.03	61.85
60	62.81	62.63	62.29	62.01	61.83
70	62.80	62.62	62.26	62.01	61.83
80	62.79	62.61	62.26	62.00	61.83
90	62.78	62.59	62.26	62.00	61.83
100	62.77	62.59	62.26	61.99	61.81
110	62.75	62.58	62.26	61.98	61.81
120	62.75	62.58	62.26	61.98	61.81
150		62.56	62.23	61.96	61.81
180		62.55	62.22	61.95	61.79
210			62.20	61.94	61.78
240			62.19	61.92	61.78
270				61.91	61.77
300				61.90	61.76

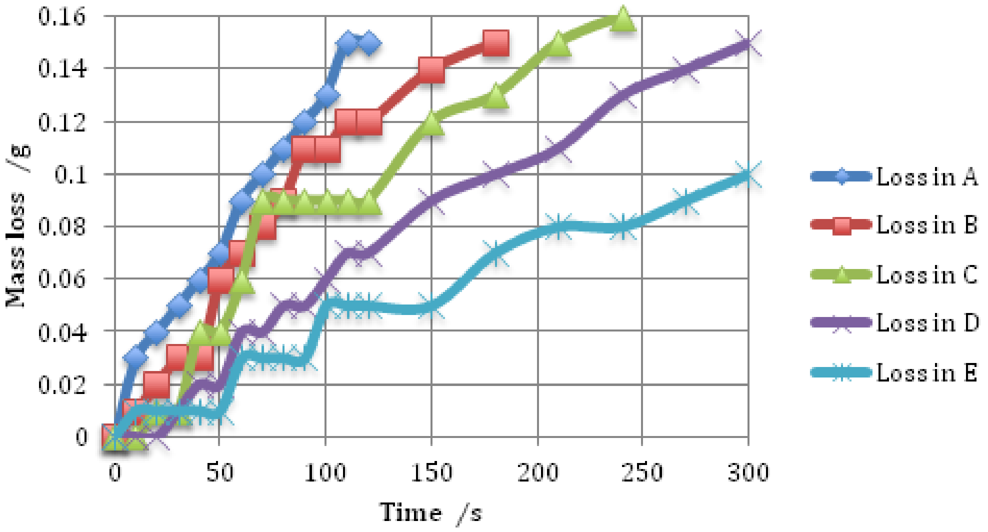
Uncertainty in time = ± 1 s   Uncertainty in mass = ± 0.005 g

Relevant qualitative observations

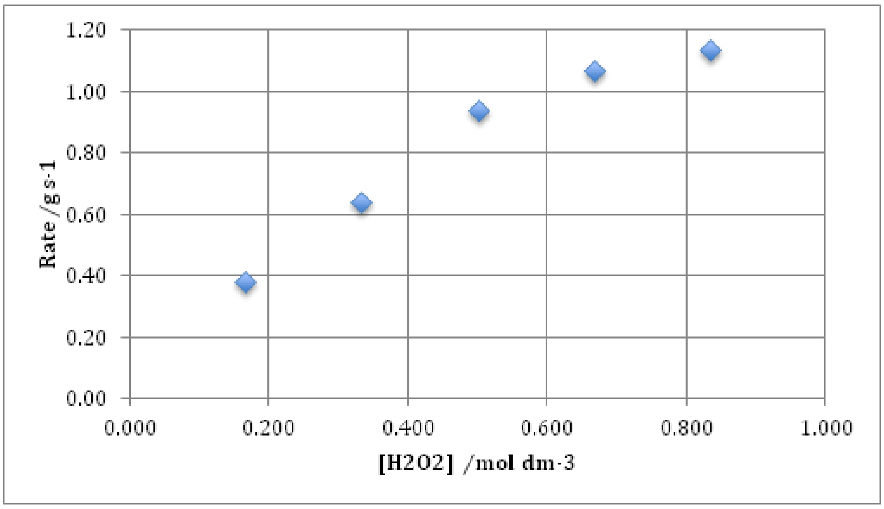
When the reaction occurred there was rapid effervescence and as a result a layer of foam formed on the surface of the liquid causing it to froth up. Measurements were ceased when this would have caused the contents of the beaker to overflow.

Data Analysis

a)



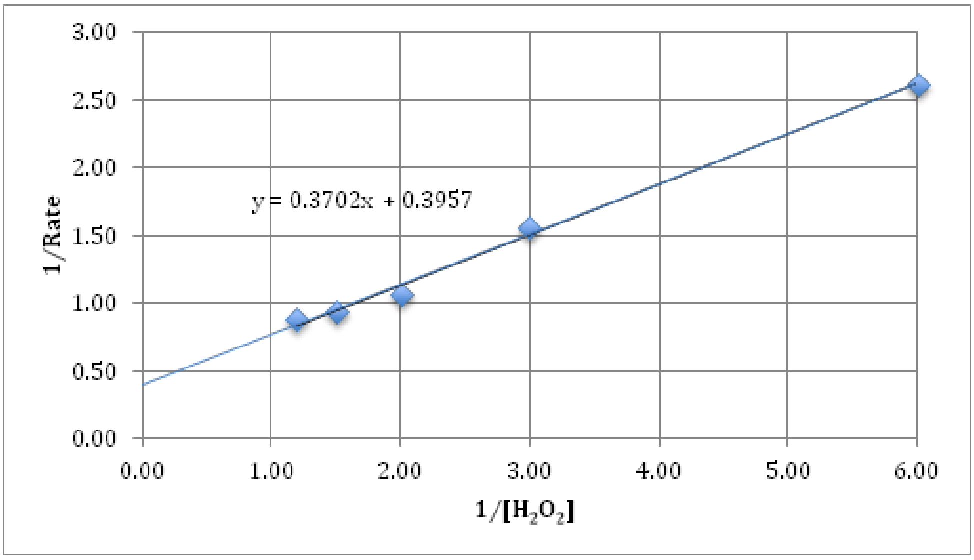
b)



It can be seen that as the concentration of hydrogen peroxide increases initially the rate appears to increase linearly, but at higher hydrogen peroxide concentrations it seems to be tending towards a maximum value.

Mixture	A	B	C	D	E
$[H_2O_2]$ /mol dm^{-3}	0.833	0.667	0.500	0.333	0.167
Rate /mg s^{-1}	1.14	1.07	0.94	0.64	0.38
$^1/[H_2O_2]$ /dm^3 mol^{-1}	1.20	1.50	2.00	3.00	6.00
$^1/$Rate /s mg^{-1}	0.88	0.94	1.06	1.56	2.61

c)



The intercept on the y-axis (0.3957) is equal to $^{1}/_{V_{max}}$, giving V_{max} as 2.53 mg s^{-1}.

The intercept on the x-axis (calculated as -1.069) is equal to -$^{1}/_{K_m}$, giving K_m as 0.936 mol dm^{-3}.

The gradient should be to $^{K_m}/_{V_{max}}$ and the value using the results calculated above of 0.37 is consistent with the gradient of the equation of the best-fit line.

Conclusion & Evaluation

d) Yes the data does support this hypothesis. At low concentration the rate of collision between the enzyme (catalase) and the substrate (hydrogen peroxide) is rate determining, but at high substrate concentrations all the active sites are occupied and the rate at which the complex is converted to the products and becomes rate determining.

e) The reaction produced data that seems to fit well with the kinetics that would be expected to arise from the formation of an enzyme-substrate complex. The major practical difficulty encountered was the formation of froth on the reaction mixture. The uncertainty in the loss of mass (~10%) was also significantly larger than ideal. The greatest rate in the experiment was also significantly below the maximum velocity (~50%) and never clearly indicated that a maximum velocity is attained, hence the theory was never tested in this region.

f) Using a more accurate balance (3 dp) would have greatly improved the precision of the results. In the absence of this, using a greater [H_2O_2], at the same time as a lower [catalase] so as to keep the rate approximately the same, would have given a greater mass loss. This would also have the advantage of producing conditions (high [substrate] and low [enzyme]) that would more clearly display the maximum velocity.

TEACHING NOTES for Investigation 24B
SOME FACTORS AFFECTING VOLTAIC CELLS

Syllabus relevance; Topic C.6

The factors that affect the voltage of a cell and the lead–acid battery could be investigated experimentally.

Apparatus required

Per group

- 8 × 100 cm^3 beakers
- 100 cm^3 measuring cylinder
- Variable resistance (~1 MΩ maximum) or a well spaced series of fixed resistors in the 1 kΩ–1 MΩ range
- Variable voltage power supply
- High resistance voltmeter
- Ammeter
- 1.5 V torch bulb
- Thermometer

Generally available

- Strips of filter paper
- Crocodile clips
- Connecting wires

Chemicals required

- Aqueous zinc sulfate (1 mol dm^{-3}, ~100 cm^3 per group)
- Aqueous zinc sulfate (0.00001 mol dm^{-3}, ~100 cm^3 per group)
- Aqueous copper(II) sulfate (1 mol dm^{-3}, ~200 cm^3 per group)
- Sulfuric acid (1 mol dm^{-3}, ~100 cm^3 per group)
- Saturated aqueous potassium nitrate (~10 cm^3 per group)
- 4 × copper electrodes
- Zinc electrode
- 2 × lead electrodes

Notes

Probable timing – 90 minutes laboratory time

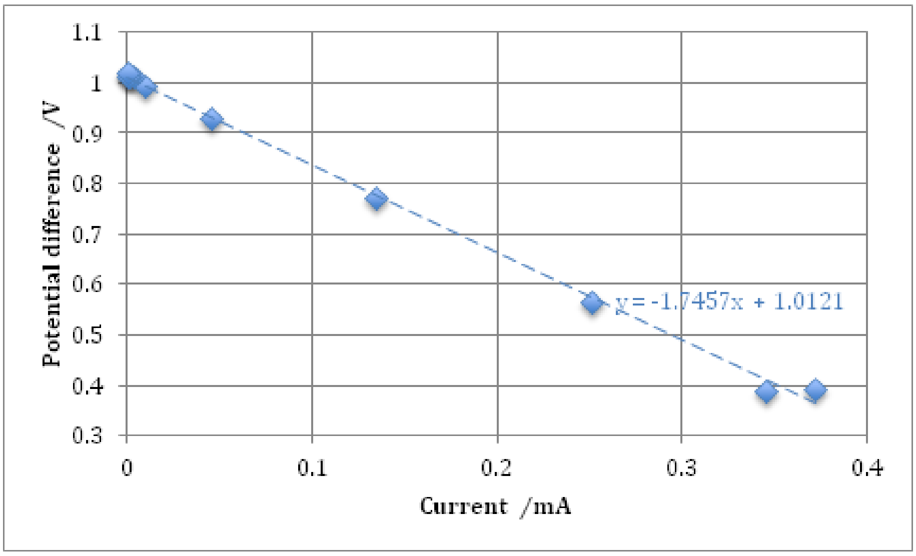
This investigation reinforces some of the more advanced concepts of voltaic cells and the associated thermodynamics, including the Nernst equation. It also demonstrates the basic reactions that occur in the lead-acid storage battery.

Sample data

Part A The internal resistance of a voltaic cell

Potential difference /V	Current /mA	Resistance /kΩ
0.391	0.372	1.0
0.387	0.345	1.0
0.567	0.250	2.2
0.773	0.134	5.0
0.929	0.045	20
0.993	0.009	100
1.011	0.003	330
1.012	0.001	560
1.014	0	∞
1.019	0	∞

a)



The emf is the potential difference when zero current is being drawn = 1.012 V

The internal resistance is the gradient with the sign changed = 1.75 V mA^{-1} = 1750 Ω (V A^{-1})

b) There is very good agreement between the graph and the theory, the data points are close to a straight line. The emf is slightly low (accepted value = 1.10 V). The duplicate values for a 1 kΩ resistor also differ by about 10% showing the presence of some experimental error. This could be a result of minor movements of the components of the cell causing a variation in the internal resistance.

c) A current of about 0.29 mA, quite low for many applications, causes the potential difference across the terminals to fall to half the emf, hence the cell is not going to be useful for practical applications.

d) Internal resistance would be decreased by:

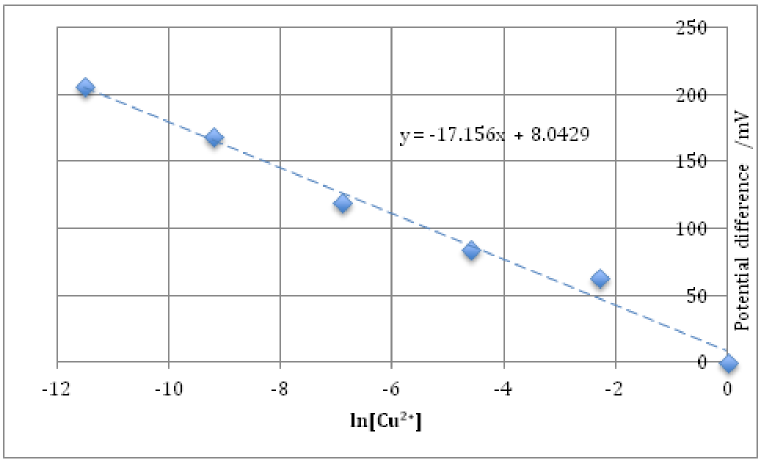
- increasing the surface area of the electrodes and the salt bridge
- bringing the electrodes closer together
- increasing the concentration of the electrolytes

Part B The effects of concentration

$[CuSO_4]$ /mol dm^{-3}	0.1	0.01	0.001	0.0001	0.00001
Potential difference /mV	63.1	83.7	119.5	168.2	206.3

Laboratory temperature = 22.0 °C

e)



Gradient of the line = $\left(\frac{RT}{nF}\right) = -0.0172$

$\left(\frac{8.31 \times 295}{2 \times F}\right) = 0.0172$ so $F = \left(\frac{8.31 \times 295}{2 \times 0.0172}\right) = 71{,}263\ C$

The value for the Faraday Constant is a little low, being about 25% less than the accepted value of 96,500 C.

f) The concentration of the more dilute solution would increase, through the anode dissolving and concentration of the more concentrated solution would decrease through copper being deposited on the cathode. These processes would continue until the two concentrations became equal.

g) The equilibrium at a metal/metal ion electrode is:

$M_{(s)} \rightleftharpoons M^{2+}_{(aq)} + 2\ e^-$

If the metal ion concentration is increased the equilibrium is displaced to the left and the electrode becomes more positive (less electrons present). The zinc is the negative electrode, so to maximise the potential this needs to be as negative as possible, hence a low concentration is required. The opposite is true of the copper electrode, which is the positive electrode. The greatest cell potential would therefore result from a high $[Cu^{2+}]$ and low $[Zn^{2+}]$.

	E° /V	
$[Cu^{2+}]$ $[Zn^{2+}]$	1 mol dm^{-3}	0.001 mol dm^{-3}
1 mol dm^{-3}	1.015	0.934
0.001 mol dm^{-3}	1.042	

h) The Nernst equation would predict that the effect of reducing the concentration of the zinc ions from 1 mol dm^{-3} to 0.001 mol dm^{-3} would be:

$$E = -0.76 + \left(\frac{8.31\ x\ 298}{2\ x\ 96500}\right) ln(1\ x\ 10^{-3}) = -0.76 - 0.09 = -0.85\ V$$

The cell potential would therefore be predicted as 1.18 V (0.34 + 0.85).

Conversely with 1 mol dm^{-3} Zn^{2+} and to 0.001 mol dm^{-3} Cu^{2+} the cell potential would be

1.01 V (0.34 – 0.09 + 0.76).

Quantitatively the results do not show good agreement with the predictions of the Nernst equation.

C The effect of temperature

Temperature /°C	12	32	52	72	92
E° /mV	987	891	844	798	823

i) Combining the equations:

$\Delta G = \Delta H - T.\Delta S = -n.F.E^\circ$

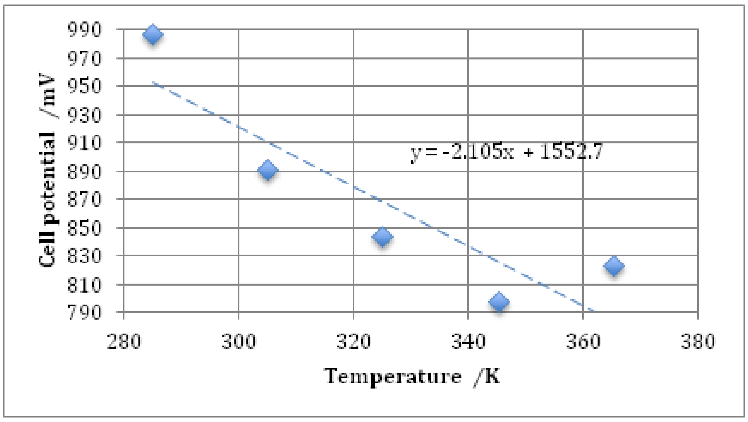
$n.F.Eo = T.\Delta S - \Delta H$

$$E^{\ominus} = \frac{\Delta S}{n.F}.T - \frac{\Delta H}{n.F}$$

Part C The effect of temperature

j) Temperature did not have a large effect. This is because it depends on the entropy change for the reaction and, as copper and zinc are both divalent metals, the entropy of their solids and the solutions of their salts are quite similar, so ΔS is small.

k) A graph of $E^{\ominus}$ against temperature (in K) should be linear with a gradient $\frac{\Delta S}{n.F}$ and an intercept $\frac{\Delta H}{n.F}$:



It can be seen that the data are not good; the cell potentials are all too low and the linear fit is poor. From the equation for the best line:

$$-\frac{\Delta H}{n.F} = 1553\,mV$$

Hence ΔH = -2 × 96500 × 1.553 = -300 kJ, a value at least of a similar order of magnitude to the accepted value for ΔH (-219 kJ).

$$\frac{\Delta S}{n.F} = -2.105\,mV$$

ΔS = 2 × 96500 × 0.0021 = 405 J mol^{-1} K^{-1}

This entropy change seems rather high, again casting doubt on the validity of the data.

Part D The lead-sulfuric acid cell.

Initial potential difference: 0 V Final potential difference: 1.968 V

The negative terminal goes a uniform matt grey. The positive terminal bubbles for a while, then a dark brown layer forms on the surface. The bulb lights up when connected across terminals.

l) $Pb_{(s)} + H_2SO_{4\,(aq)} \rightarrow PbSO_{4\,(s)} + H_{2\,(g)}$

The layer of insoluble lead(II) sulfate protects the lead electrode from further reaction.

m) The anode turned a brown colour owing to the formation of a layer of lead(IV) oxide:

$PbSO_{4\,(s)} + 2\,H_2O_{(l)} \rightarrow PbO_{2\,(s)} + H_2SO_{4\,(aq)} + 2H^+_{(aq)} + 2\,e^-$

The cathode turned a grey colour owing to the formation of lead metal:

$PbSO_{4\,(s)} + 2H^+_{(aq)} + 2\,e^- \rightarrow Pb_{(s)} + H_2SO_{4\,(aq)}$

n) At the positive electrode:

$PbO_{2\,(s)} + H_2SO_{4\,(aq)} + 2H^+_{(aq)} + 2\,e^- \rightarrow PbSO_{4\,(s)} + 2\,H_2O_{(l)}$

At the negative electrode:

$Pb_{(s)} + H_2SO_{4\,(aq)} \rightarrow PbSO_{4\,(s)} + 2H^+_{(aq)} + 2\,e^-$

o) The charging reactions both form sulfuric acid as a product so charging increases the concentration of the acid. Conversely discharging decreases the acid concentration.

TEACHING NOTES for Investigation 25B
RAOULT'S LAW AND FRACTIONAL DISTILLATION

Syllabus relevance: Topic D.9

Consider the use of fractional distillation, Raoult's Law and the properties on which extractions are based.

Apparatus required

- 100 cm^3 flask equipped for reflux , with a thermometer in the liquid, and distillation with a thermometer.
- 25 cm^3 measuring cylinder
- Boiling chips

Chemicals required

- Cyclohexane (~50 cm^3)
- Methylbenzene (toluene, ~50 cm^3)

Notes

Probable timing – 90 minutes laboratory time

This investigation allows students to produce a liquid-vapour composition diagram and use it to investigate separation by distillation and fractional distillation.

If a Y-tube or twin-neck flask is not available to allow the temperature of a refluxing liquid to be taken, take the **liquid** temperature as it distils and collect a small volume of distillate. Measure the boiling point of the distillate before returning it to the flask.

If other equipment is available, more sensitive techniques for determining the composition of the distillate could be used, such as a refractometer (refractive indices are 1.426 and 1.497) or vapour phase chromatography.

For reference the densities of cyclohexane and methylbenzene are 0.779 and 0.867 g cm^{-3} respectively.

Sample data

Volume cyclohexane /cm^3	Volume methylbenzene /cm^3	Boiling point of liquid /°C	Temperature at distillation /°C
20	0	79	-
20	5	84	80
20	10	86	81
20	15	90	83
20	20	92	84
		91	84
15	20	95	85
10	20	97	86
5	20	102	90
0	20	108	-

Uncertainty of volume measurements = ± 0.5 cm^3

Uncertainty of temperature measurements = ± 0.5 °C

Relevant qualitative observations

Apparatus to measure the liquid temperature when it was refluxing was not available and so these data involve taking the liquid temperature as it distilled, then collecting a small volume of distillate and taking its boiling point. The colourless liquid mixture distilled smoothly to give a colourless distillate.

Data Analysis

a)

Volume cyclohexane /cm^3	Volume methylbenzene /cm^3	Mole percentage methylbenzene in liquid	Mole percentage methylbenzene in distillate
0	0	0	0
20	5	20	8
20	10	34	12
20	15	43	19
20	20	50 50	22
			22
15	20	58	25
10	20	67	29
5	20	80	42
0	20	100	100

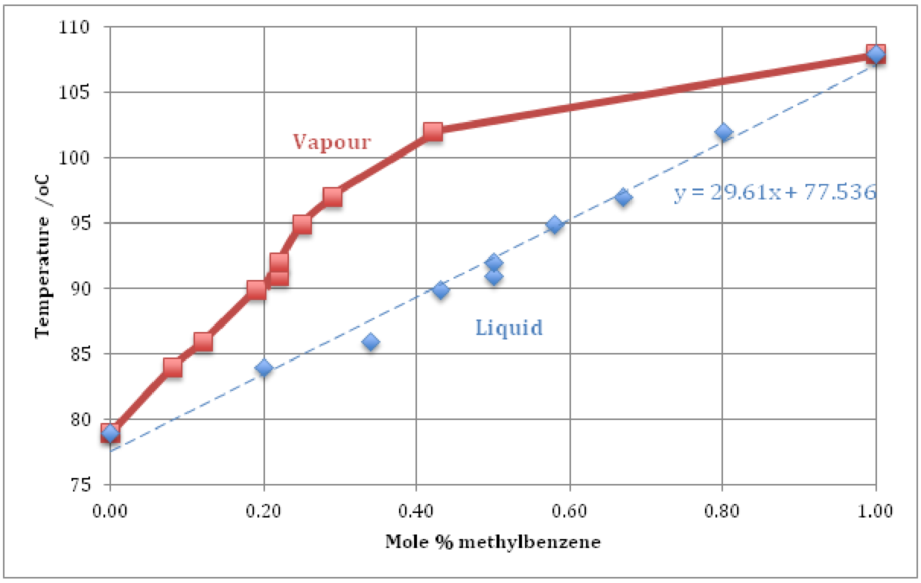
Amount = $\frac{volume \times density}{molar\ mass}$ so for 20:20 mixture:

Amount of methylbenzene = $\frac{20 \times 0.867}{92.15} = 0.1882\ mol$

Amount of cyclohexane = $\frac{20 \times 0.779}{84.18} = 0.1851\ mol$

Mol% methylbenzene = $100 \times \frac{1.882}{(0.1882 + 0.1851)} = 50.42\%$

b) & c)



d) The mixture can be seen to obey Raoult's law because the boiling point of the liquid varies linearly with its molar composition. This indicates that the forces between the two different molecules are similar to those between molecules of the same type.

Conclusion and Evaluation

e) Because cyclohexane has the lower boiling point, a lower temperature is required for its vapour pressure to equal atmospheric pressure, hence it must have the greater vapour pressure.

f) Assuming Raoult's Law, the vapour pressure of a liquid in a mixture is equal to the vapour pressure of the pure liquid, at that temperature, multiplied by the mole fraction of that liquid in the mixture.

g) The mixture starts to distil when the sum of the vapour pressures of its components are equal to the atmospheric pressure.

h) No, the mixture will be richer in cyclohexane, the more volatile component. This is because at any temperature the vapour pressure of cyclohexane will be greater than that of methylbenzene and the composition of the distillate is determined by the composition of the vapour.

i) When the liquid boils the vapour will pass into the fractionating column. As it passes up the column it will condense, the equivalent of one distillation. Under the influence of gravity, the liquid runs down the column and meets more hot vapour, which causes it to boil again and rise higher up the column, where it again cools and condenses – a second distillation cycle. This process continues with the mixture getting richer in the more volatile component, the higher up the column it travels.

j) i) The distillate would contain about 67 mol% cyclohexane (33 mol% methylbenzene).

ii) The distillate would contain about 95 mol% cyclohexane (5 mol% methylbenzene).

iii) 4 or 5 distillations would produce cyclohexane of this purity

k) i) The greater the difference in boiling point the easier the mixture is to separate. Mixtures of components with very similar boiling points require sophisticated distillation apparatus for their efficient separation.

ii) The greater the length of the column the more efficient the separation because the mixture will undergo more evaporation-condensation cycles before reaching the top of the column.

iii) The packing in the column must allow the vapour to pass upwards and the liquid to trickle down, so some space is required. That being said heat must be transferred from the hot vapour rising to the cooler liquid running down. In order to do this efficiently, there must be a large surface area of contact between liquid and vapour and the packing is designed to ensure this.