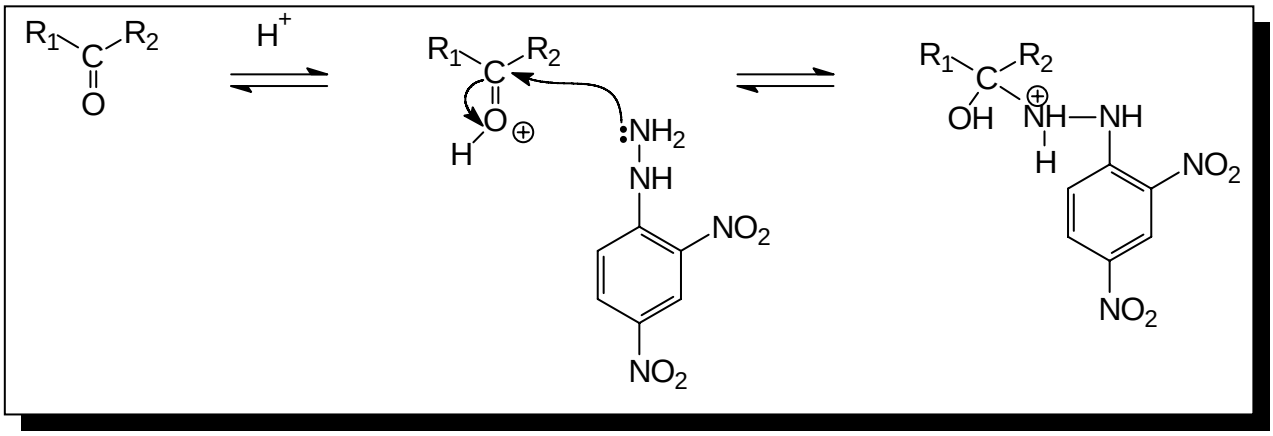
JAMES COOK UNIVERSITY
OF NORTH QUEENSLAND

Department of Chemistry
Cairns Edition



CH1012
LABORATORY NOTES
2007

Name:

Partner:

DEPARTMENT OF CHEMISTRY

CH1012 PRACTICAL COURSE

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GENERAL INTRODUCTION

1. INTRODUCTION

This course involves aspects of organic, inorganic and physical chemistry. Some of it is qualitative, other parts are quantitative. As far as is possible the laboratory work is organised to correspond with the lectures but a perfect match is not possible.

2. WORK INVOLVED

a. **Before you come into the laboratory**, check the LearnJCU timetable to find out which assignment you will be doing then read over, understand and prepare for that assignment. Sort out any queries before the lab class by the use of textbooks and tutorial staff. Where possible, complete equations in the "REPORTS" book.

b. **You should arrive on time** for the session. Once in the laboratory, before beginning your lab work, you should collect last week's report. Often there will be a tutor-led discussion before the practical work begins.

c. **If you are late** you must ask your demonstrator about any safety matters associated with the experimental work before commencing the practical session.

d. **When you have finished** the lab work you should clean up your work space and return any borrowed apparatus to the preparative laboratory. Glassware and other apparatus are to be cleaned and replaced (ready for use by the next student) in your allocated bin. Usually there will be a tutor-led discussion on treatment of results. If you have finished early you should begin (and often complete) your calculations and begin to write up your report. The class finishes either at 12am or at 5pm. All experimental work must be completed by 11.45pm or by 4.45pm, anyone leaving early will be marked **absent** unless all of the lab work is completed AND **a completed report is presented to your tutor.**

e. **After the practical session** you should complete your report and prepare for the next session.

f. **If you are absent** for a medical reason you should present a medical certificate to your tutor in the next lab session and ensure that it is noted on your record. Absence for any other valid reason should be explained in writing or preferably by a certificate from the University student councillor and must be recorded with your tutor.
*If you miss **3 or more practicals** without a valid reason you will have failed the practical component and will have to repeat the course.*

3. REPORTS

A "REPORTS" book must be obtained from the Medicine, Health and Molecular Sciences Faculty office and used to write up your reports. Reports are submitted by placing them in the Chemistry Department (locked) box along from the first year A2.114 laboratory after completion of the practical component of the course.

Make sure that your **name, day and demonstrator** are clearly recorded on the front of your "REPORTS" book.

Late reports will be penalised unless the student has made a prior arrangement **with the tutor responsible for marking the report.** Normally, late reports will incur a penalty of 10% per day.

4. ASSESSMENT

The details are the same for each assignment as shown below.

Assignment	Lab*	Report	Total
1	5	15	20
2	5	15	20
3	5	15	20
4	5	15	20
5	5	15	20
6	5	15	20
7	5	15	20
8	5	15	20
9	5	15	20

* Failure to clean-up will result in a loss of marks!

5. ITEMS NEEDED

1. One copy of the "CH1012 REPORTS" book.
2. One copy of "CH1012 CHEMISTRY LABORATORY NOTES" (this book!).
3. A breakage deposit must be paid to the Medicine, Health and Molecular Sciences Faculty Office and the receipt number entered on your card by the third week of the second semester. **Deductions will be made from refunds for breakages and special equipment damaged and a small amount for laboratory coat cleaning.**
4. A laboratory coat (provided), safety glasses (provided) and protective footwear (ordinary shoes but not thongs) must be worn at all times in the laboratory.

6. SAFETY

SAFETY MANUAL.

As part of the practical component of this course you are required to read the Safety Manual that accompanies this course. THIS IS COMPUSLORY and a record is kept electronically that indicates that you have downloaded the Safety Manual for reading.

To access the Safety Manual the WEB address is :
http://cnsfse01.jcu.edu.au/Schools/Chemistry/SafetyManual/manual.htm
At the prompt enter your student login name and password and then download the Safety Manual for reading.
Alternatively the manual may be addressed from the CH1012 LearnJCU web site under **Find More..**

6.1 Accidents

Accidents do happen in chemical laboratories, usually through thoughtlessness. You are therefore requested, for your own sake and that of your neighbours, to read the **Safety Manual** and to **THINK** before you act. Remember to heat organic solvents on a water bath or hot plate - **NOT OVER A BUNSEN BURNER**.

6.2 Fire

Many organic solvents are highly flammable and require cautious handling. If a fire starts, turn out all adjacent burners and remove everything that may ignite. Water should not be used on fires involving organic chemicals. Smother fires by covering with any suitable object (e.g. bunsen mat) to exclude air. Fire extinguishers are available in all laboratories and should be used for larger fires.

6.3 Handling chemicals

Many chemicals are **TOXIC** and should be handled with caution. Chemicals spilt on the skin should be washed off **immediately** with plenty of water followed by soap and warm water. Gloves are provided for some experiments. Care should be taken not to leave chemicals where others may come into contact with them. Any liquid running down the side of a container should be wiped off with a piece of paper towel.

All experiments involving the use or generation of irritating or corrosive substances e.g. Br_2, HNO_3 etc., should be carried out in a fume cupboard.

In many cases bottles are provided for waste chemicals and must be used for this purpose.

6.4 Pregnant Women

Many chemicals are teratogenic and should not be handled by pregnant women. If any student is pregnant then they should inform their laboratory supervisor and they will be directed to perform only those practical experiments which it is safe for them to undertake.

7. DATA RECORDING

Measurements and observations should normally be recorded in your "REPORTS" book or separate notebook. Whenever it is possible and appropriate, data should be plotted as it is obtained.

NOTES ON ORGANIC CHEMISTRY ASSIGNMENTS

The four practical assignments (2 - 5) are designed to illustrate some of the common manipulative techniques used in organic chemistry. Assignments 2 and 3 are preparative experiments in which you will carry out simple reactions, isolate the products from reaction mixtures and purify them. Each of these experiments is set down for a single week, but you may find it impossible to isolate reaction products and characterise them on the same day. In such cases, you will need to come back to the lab on another day to finish the experiment. This may involve **suction filtration and the recording of melting points only**. You will *not be allowed to use bunsens or any other heating devices* unless you are supervised by a **tutor.** Assignments 4 and 5, 'Qualitative Analysis of Organic Compounds", are designed to be carried out over a two week period.

Flow sheets*:* Before you commence preparative experiments (Assignments 2 and 3) you will be required to submit to your demonstrator a flow sheet summarising the experimental procedure. It should indicate the techniques to be used, in what order, and where the desired compound is at each stage of the experiment. Although you should not discard anything until you have finally isolated the purified product, the flow sheet should tell you which flask can be set aside and which contains the compound you require. It is hoped that by writing out a flow sheet, you will understand the purpose of each experimental step before you commence the experiment. Your flow sheet will be marked and will constitute 10% of the assessment of each experiment. As a guide to what a good flow sheet looks like, a flow sheet for the second part of Assignment 2 is appended.

Reports*:* You should fill in the boxes in your report book according to the way the sample write-up for the second part of Assignment 2 has been written. Under "Reaction:" you should write out the relevant **balanced** equation, **NOT THE MECHANISM** (i.e. no arrows or intermediates) specific for the reaction you have performed. You may be asked questions about mechanisms, in which case arrows and intermediates should be included. In general, the **"Discussion"** should **briefly** mention any departures you made from the procedure indicated in the laboratory notes, **only**. It should not be a rewrite of the laboratory notes. The "Description" should be of the purified product i.e. appearance, odour etc. when answering the questions, be prepared to consult your textbook or other source. When requested to hand in your samples, you should submit them clearly labelled with the following information.

Name Sample Name wt g m.p or b.p. range

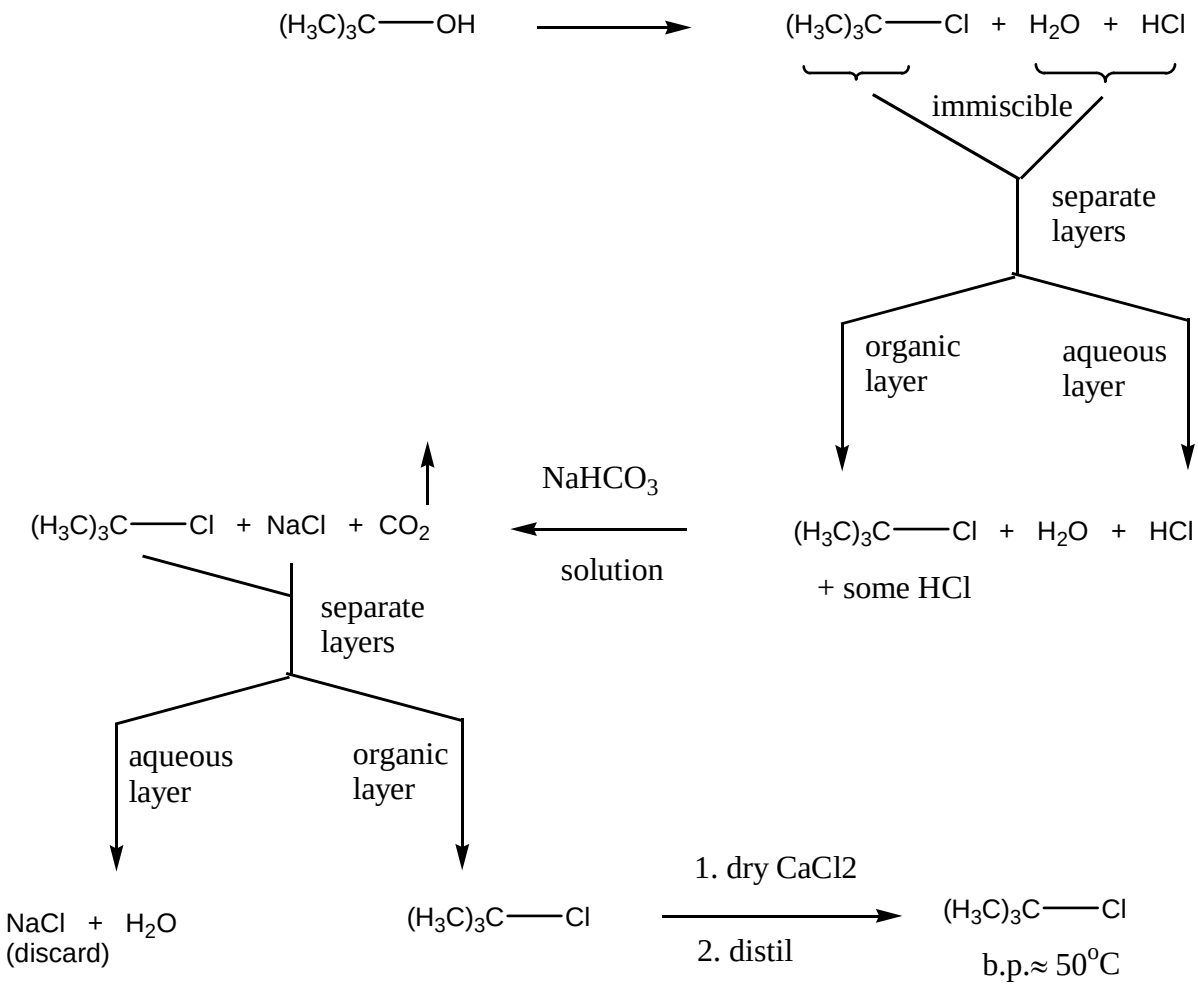
Care should be taken to ensure that liquids are dry and that solids are free from the recrystallisation solvent before submission.

Your report book must be submitted along with your marked flow sheet and any requested products.

SAMPLE FLOW SHEET

Assignment 2 , Part 2: **Nucleophilic substitution at saturated carbon**

Preparation of tertiary-butyl chloride (2-chloro-2-methylpropane)



SAMPLE REPORT

Assignment 2 Part 2: Nucleophilic substitution at saturated carbon.

Preparation of tertiary-butyl chloride (2-chloro-2-methylpropane)

2. Preparation of *t*-butyl chloride

Reaction:

$(CH_3)_3C\text{-}OH + HCl \rightarrow (CH_3)_3C\text{-}Cl + H_2O$

Discussion:

t-Butyl chloride was prepared from *t*-butanol (2-methylpropan-2-ol) (20mL) and concentrated hydrochloric acid (60mL) as instructed. Some difficulty was experienced in separating the organic and aqueous layers in the final 5% sodium bicarbonate washing. The dried product was combined with that of student X, stored in a stoppered flask until the next practical session and distilled as instructed.

Description of product:

The product *t*-butyl chloride was a clear colourless liquid.

b.p. range	
Comparison with literature	

TECHNIQUES OF ORGANIC CHEMISTRY

Two of the experiments in the organic section are organic preparations. In general, an organic preparation involves the combination of a reagent with an organic substrate so that a reaction occurs, and once the reaction is complete, the isolation of the required product from the reaction mixture.

Substrate + Reagent ⟶ Product + By-products

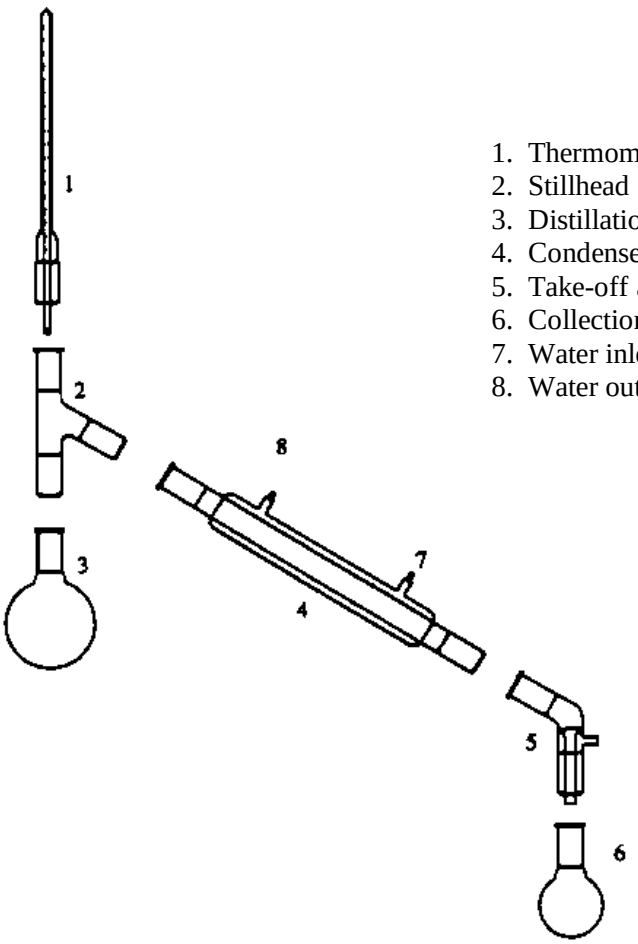
↓ "Purification"

Pure Product

Apart from the desired product, however, the reaction mixture may also contain inorganic and organic by-products, and side products resulting from unwanted side reactions**.** "Purification" involves the separation of the **pure** product from this reaction mixture.

DISTILLATION:

If the product is a liquid with a boiling point significantly different from the other components of the reaction mixture, the best method of purification involves the distillation of the product out of the mixture. The apparatus used for distillation is shown below.



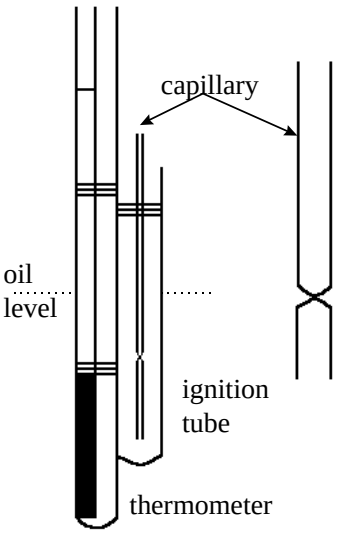
1. Thermometer
2. Stillhead
3. Distillation flask
4. Condenser
5. Take-off adaptor
6. Collection flask
7. Water inlet
8. Water outlet

The distillation procedure involves gradually increasing the temperature of the distillation flask until the compound boils at such a rate that it condenses in the top of the condenser, and then flows down into the collection flask. (N.B. If the liquid only condenses at the lower end of the condenser, near the take-off adaptor, the distillation flask is too hot, and the heating should be reduced.)

The thermometer is fitted in such a way that its bulb is slightly below the level of side arm. This ensures that the thermometer registers the temperature of the vapour before it enters the side arm. The temperature observed as the liquid distils is the boiling point and is a unique property of a compound at a given pressure. In practice, the liquid will distil over a range of temperatures, and it is this temperature range that should be recorded. The boiling point range determined in this way can be used to help identify the compound, by comparison with a list of known boiling points. The boiling point alone is usually not sufficient to unambiguously identify a given compound, and must be used in conjunction with other measurements (e.g. IR spectrum).

DETERMINATION OF BOILING POINT USING SIWOLOBOFF'S METHOD:

When there is not enough liquid available to perform a conventional distillation, a boiling point can be determined using Siwoloboff's method:



A sample of the liquid is placed in an ignition tube (small test tube), together with a capillary that has been sealed in the middle. The ignition tube is clipped to a thermometer and heated in an oil bath The boiling point is found by observing the following events. As the temperature rises, bubbles begin to escape from the lower end of the capillary tube. The release of bubbles is at first slow, but as the boiling point of the test liquid is reached the bubbling becomes rapid. At this stage the heating device is removed and the oil in the beaker is allowed to cool. The boiling point is taken to be the temperature at which the evolution of bubbles ceases, and the test liquid begins to rise up the capillary tube. Since the beginning of the rise of the liquid up the capillary occurs at a single instant, this technique gives a boiling point, not a boiling range. To avoid the formation of local "hot spots" and "cold spots" in the oil, it should be well mixed throughout the whole exercise. This is especially important as the liquid cools, as this is when the actual boiling point is recorded**.**

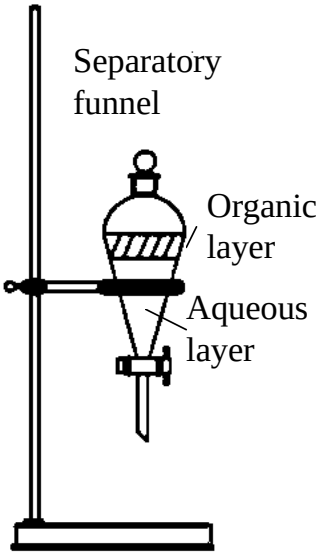
Explanation: During the initial heating, the air that was originally in the lower part of the capillary tube is replaced by the vapour of the test liquid. When the liquid is heated above its boiling point and then allowed to cool at atmospheric pressure, it enters the capillary tube only where its vapour pressure has become equal to atmospheric pressure. Since the boiling point of a liquid is defined as the temperature at which its vapour pressure is equal to atmospheric pressure, the entry of the liquid into the capillary occurs at the boiling point of the liquid.

Experimental Procedure

Place one mL or less of the liquid in an ignition tube and attach this tube to the thermometer using two stainless steel springs. Ensure that the liquid in the ignition tube and the bulb of the thermometer are at the same level. Place a capillary that has been sealed in the middle, in the ignition tube, with the shorter end downwards. Clamp the thermometer in the oil bath so that the open end of the ignition tube is above the level of the oil (see diagram). At no time should oil be allowed to enter the ignition tube. Heat the oil bath with a bunsen or hot plate and record the boiling point of the liquid by observing the events described above. Remember to mix the oil thoroughly throughout the entire procedure. Note that if a very small quantity of liquid is used, or if the oil bath is heated to a much higher temperature than the boiling point, the liquid may all boil away before the boiling point can be determined.

EXTRACTION PROCEDURES:

When a reaction is complete the resulting mixture is usually "quenched" by pouring it into an equal volume of water. It is then not possible to distil the product directly from such a mixture. The usual isolation procedure involves the addition of a quantity of low boiling solvent such as diethyl ether (b.p.35ºC) [which is normally referred to as simply "ether"] or petroleum ether (b.p ~30-40^{0}C) and the organic material separated from the water soluble components using a separatory funnel (see diagram).



A consideration of the expression "like dissolves like" is used to decide which layer the product is likely to be found in. This means that a *non-polar* organic product will transfer almost exclusively into the *non-polar* organic solvent while the *polar* inorganic salts will be confirmed to the *polar* water (aqueous) layer. Both diethyl ether (ρ 0.71 g.cm-^{3}) and petroleum ether (ρ 0.66 g.cm^{-3}) are less dense than water so when these solvents are used, the organic layer will be above the aqueous layer. Occasionally chloroform (ρ 1.48 g.cm^{-3}, b.p. 62^{0}C) or dichloromethane (ρ 1.33 g.cm-^{3}**,** b.p. 41^{0}C) are used as the extraction solvent, in which case the organic layer will be below the aqueous layer.

The organic layer is separated from the aqueous layer by running the lower layer out of the bottom of the funnel. If the organic layer is on top of the aqueous layer, a *little* of the organic layer is run out with the aqueous, the tap closed and the organic layer tipped into a dry flask through the top of the funnel. This limits the amount of water that is put into the flask with the organic layer. Small quantities will remain suspended in it however, and they can to be removed by use of an anhydrous inorganic salt such as sodium sulphate, calcium chloride or magnesium sulphate. The wet organic solvent will often appear cloudy but will become clear (meaning "see through" not colourless) when dry. Most organic compounds boil at a higher temperature than the extraction solvents, so the solvent can be removed by distillation on a steam bath. (Note that a bunsen is not used for the distillation. This is because both ether and petroleum ether have very low flash points and are highly flammable). The organic product, if a liquid, is then distilled and its boiling point determined as described above.

If the organic product is a solid it will remain in the distillation flask after the solvent is removed and will most likely crystallise on cooling. It can then be recrystallised from a suitable solvent.

RECRYSTALLISATION

Occasionally, when a reaction is complete, the product crystallises out of the mixture and can be filtered off. More often, the above extraction procedure must be adopted. In either case the resulting solid or semisolid product must then be purified. Recrystallisation is a very effective method of purifying organic solids. This process may be divided into a number of distinct steps:

1. The solid to be recrystallised is dissolved in a **minimum volume** of a suitable solvent (e.g. water, ethanol, etc.) at or near its boiling point, then a slight excess (**~10 %**) of hot solvent is added.

2. A fluted filter paper and a short stemmed funnel are preheated by pouring a few mls of pure boiling solvent through them. Before they are allowed to cool, the boiling solution containing the compound to be recrystallised is poured rapidly through them. The filtrate is them returned to the heat to ensure complete solution at the boiling point. The filtration removes insoluble contaminants like dust etc. as well as organic impurities which are not soluble in the chosen solvent. It is important to do the preheating process properly otherwise large quantities of the product will crystallise out on the filter paper.

3. The funnel is then removed, the flask covered and allowed to cool to room temperature (or cooler if instructed). The pure organic compound should crystallise in the flask as it cools. The best crystals, and hence the purest material, are obtained if the solution is allowed to cool slowly without disturbance.

4. When crystallisation is complete, the pure crystals are separated from the mother liquor (Recrystallisation solvent containing impurities) by vacuum filtration, using a small amount of the mother liquor or a spatula to assist in the transfer of the crystal to the filter. The crystals should be gently pressed down onto the filter paper so that a rapid flow of air passes through them.

5. The crystals should be washed with a **few** mL of chilled pure recrystallisation solvent to remove all traces of mother liquor adsorbed on the surface of the crystals, and sucked **dry.**

Experimental Procedure

The following instructions give details for recrystallisation of a solid from (a) water, and (b) from a flammable solvent such as ethanol.

(a) Recrystallisation of a compound from water

Heat some water to boiling point in a large conical flask* over a bunsen or hotplate. Place the compound in another dry conical flask. Add some boiling water to the solid together with several boiling chips (crushed tile) or sticks,# and try to dissolve the solid with heating. Add small amounts of hot water to the crystals until they just dissolve, then add about a 10% excess**.**

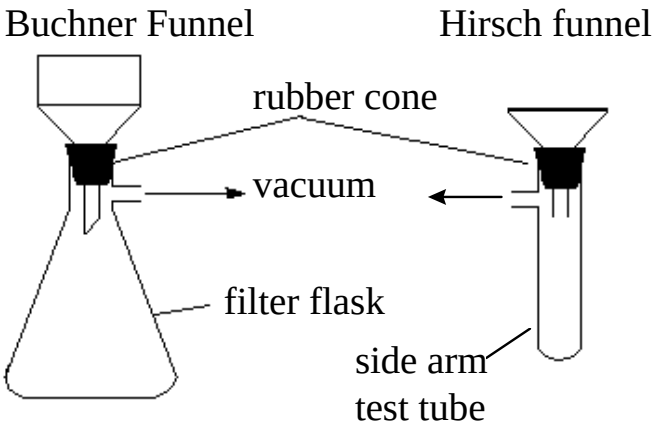
Allow the solution to boil very gently while you prepare a fluted filter paper. Place the filter paper in a glass funnel and preheat both paper and funnel by pouring boiling water through them. While still hot, quickly pour the solution containing your compound through the filter and collect the filtrate in a clean vessel.

Briefly return the filtered solution to the heat to redissolve any solid material that may have prematurely crystallised, then cover the vessel and allow it to cool slowly without disturbance.

* Conical flasks NOT beakers should be used for recrystallisations because; (a) it is easier to rinse the inner walls of a conical flask, (b) when heated, the solvent will reflux on the inside of the flask with minimal evaporation and (c) the narrow neck of the conical flask makes it easier to handle than a beaker, especially when hot.

Boiling chips or sticks provide sharp points on which bubbles can easily form. In their absence, large bubbles form over the entire bottom of the flask and cause the mixture to "bump".

Filtration and Collection of Crystals



(See apparatus in diagram) When the solution is quite cool and crystallisation is complete the crystals must be collected by **vacuum (suction) filtration**. Select a suitably sized Hirsch or Buchner funnel and place it in your side arm test tube or filter flask. You will notice that these funnels have perforated ceramic bases with large holes in them. Unlike a sintered glass disk, these funnels must be used in conjunction with a suitably sized filter paper. The filter paper is placed on the funnel and moistened with a little of the recrystallisation solvent (water in this case) and the vacuum applied. With a moistened finger, ensure that the paper is flat and that all the holes are covered. Swirl the crystals in the mother liquor, and pour the mixture quickly and carefully into the funnel**.** In some cases the volume of solvent may be too great for the side arm test tube and it will be necessary to drain it half way through the filtration. Do not discard the filtrate until you are sure you have a reasonable yield of crystals (consult your demonstrator if unsure). Crystals left in the flask may be helped out with a spatula or with a little of the mother liquor. Gently press the crystals down on the filter paper and carefully wash them with a mL or two of cold recrystallisation solvent (iced water). Use the vacuum to suck them dry, covering the top of the funnel with a larger filter paper to keep dust out. When the crystals seem fairly dry, transfer them to a larger filter paper. The filter paper should be folded to prevent loss while still allowing the crystals to dry. Place them in your cupboard and record their melting point once they are completely dry (usually the next day).

(b) *Recrystallisation of a sample from ethanol*

NO BUNSENS SHOULD BE USED NEAR ETHANOL.
You will do all recrystallisations from **organic solvents** over **a steam bath** or on a **hotplate in a fume cupboard.**

Warm some ethanol in a conical flask to near boiling on a steam bath or hot plate. Place the compound to be recrystallised in another dry conical flask and warm it in the same way. If you are using a hot plate, be careful not to over-heat the compound before adding the solvent. Add a boiling chip or stick then hot ethanol, a little at a time, until the compound completely dissolves. Add a ≈ 10% excess of hot ethanol and keep the solution gently boiling**.** Quickly warm a fluted filter paper and funnel by pouring some boiling ethanol through it. Filter the solution into a clean dry vessel by quickly pouring it through the filter paper and funnel. Warm the filtrate briefly to redissolve any material which may have crystallised during filtration and then cover it and set it aside to cool slowly without disturbance.

Filter the crystals using vacuum filtration as described above and leave them to dry in air, before recording their melting point.

DETERMINATION OF PURITY

Since, in most areas of chemistry it is vital that we work with pure substances, various ways of characterising compounds and determining their purity have been developed.

Two important properties used for this purpose are the boiling point or range of a liquid and the melting point or range of a solid**.** If a compound is pure and crystalline, and if it doesn't decompose on heating, it will have a sharp (range $\leq 2^{o}$) and characteristic melting point. As with a boiling point, the melting point of a pure solid can be used to help identify it, if used in conjunction with other measurements. In addition, if one has an idea of the identity of a recrystallised compound, and an authentic sample of the proposed compound is available, unambiguous structural proof can be obtained by recording a "mixed melting point". This is

done by making a 1:1 mixture of the unknown and the authentic sample (by grinding them together on a watch glass) and recording the melting point of the resulting mixture. All three melting points (unknown, authentic and mixed) will only be the same if the two compounds are identical. The technique relies on the fact that impurities lower or depress the melting point of a compound. If the compounds are identical and have a melting range of e.g. l49-l51ºC, we report "m.p. and mixed m.p. 149 - l5l ºC, unaffected by admixture with authentic sample." It should be noted that solvent can also be considered to be an impurity, hence a compound must be **COMPLETELY DRY** before its melting point is recorded.

Experimental Procedure for the Determination of a Melting Point:
Seal one end of a melting point capillary by rotating the end **in a** bunsen flame (**NB**: Before you light the bunsen, ensure there are **no organic solvents** in the vicinity) until a small bead of molten glass closes off the end. Allow the capillary to cool. Now take a small sample of the solid to be tested (or 1:1 mixture for a mixed m.p.) and crush it on a watch glass, using a spatula. Scrape a small quantity of the powder into the open end of the sealed melting point capillary and, while holding the bottom of the tube, tap it on the bench until the compound falls down into the end that is sealed. Alternatively the capillary may be dropped down a length of glass tubing several times. If the powder inside the melting point tube is clearly visible, you have added enough. Do not add more than is necessary. Place the tube in the electrically heated m.p. apparatus and heat slowly. Record the temperature **range** over which the solid melts, i.e. the temperature range from when you see the first crystal melt to when the whole sample is molten. A temperature range of more than 3^0 C suggests that the sample is not pure.

It is vital that the sample is heated slowly, so that the melting point tube and the thermometer are as close to the same temperature as possible. The melting point should always be recorded with rising temperature (sample going from solid to liquid), rather than with falling temperature (sample going from liquid to solid) because in the latter case, supercooling of the liquefied test substance can lead to large errors.

Other Purity Criteria:
In modern organic laboratories a range of techniques are used to confirm structural assignments and purifies of organic compounds. These include refractive index, elemental analysis (which gives the % C, H, O, N etc), mass spectrometer, infrared and ultraviolet spectroscopy and NMR spectrometry. In this course we will concentrate on the more simple techniques of boiling point and melting point determination, and examine some basic aspects of the interpretation of infrared and ultraviolet spectra.

ASSIGNMENT 1
LABORATORY SAFETY

AIMS

Safety is an important issue when experimental work is carried out in a laboratory situation. This practical is concerned with identifying and minimizing the risks in common laboratory procedures, becoming familiar with Material Safety Data Sheets and working out what to do in the event of a dangerous situation or an accident in a laboratory.

1. INTRODUCTION

Chemicals are found in nearly all laboratory situations. Each chemical has associated with it some degree of risk (eg. corrosive, carcinogenic, flammable). The information on the risk associated with the use of a chemical may be found in the Material Safety Data Sheet (MSDS) for that chemical. These MSDS sheets accompany every chemical that enters a laboratory. Each laboratory is required to have, near the doorway to the laboratory, a folder that contains the MSDS sheets for all the chemicals in the laboratory.

Workplace Health and Safety is managed at the University by the Workplace Health & Safety Officer. The Workplace Health & Safety Act requires that all members of an organisation maintain safe work practices. In the event of an accident the laboratory supervisor will report to the Workplace Health & Safety Representative who then reports back to the Workplace Health & Safety Officer. In the laboratory each student must act in a safe manner and if they are doing something that is hazardous then they are required to notify others in their vicinity that they are carrying out a hazardous operation. This is a requirement of the Act and is generally applicable to all laboratory environments.

Prevention of accidents is the key to maintaining a safe laboratory. In each operation carried out in a practical experiment the various hazards associated with the chemicals being manipulated need to be assessed. The level of risk is then determined in a Risk Assessment procedure and if any area of the procedure has a high risk then measures are taken to lower the risk. All practical experiments in the Chemistry courses in Cairns have had Risk Assessments carried out and they fit within the Safety Guidelines laid down within the WH & S Act.

A SAFETY VIDEO will be shown illustrating how to work safely in a laboratory.

2. EXPERIMENTAL

You will do this experiment **In Pairs**

2.1 Material Safety Data Sheets

You will be given a set of reagents with their accompanying MSDS sheets. A hypothetical accident situation is presented to you in your report book and you are asked to suggest how to deal with the accident situation on the basis of the information from the MSDS sheets.

2.2 Obtaining Safety Information

This section you will complete after the practical. You will need to go to the library and familiarise yourself with how to obtain MSDS information from the WEB and how to find safety information from the literature.

2.3 Laboratory Awareness

You will be instructed on how to work safely in the laboratory by anticipating standard hazards. A familiarisation trip around the lab will cover the location and use of equipment such as spill kits, fire

extinguishers and eye wash stations.

References

Vermont SIRI searchable MSDS site : http://hazard.com/msds/
Australian alternative site : http://www.msds.com.au/
Chemwatch: http://max.chemwatch.net/cg2/

SAFETY MANUAL.

As part of the practical component of this course you are required to read the Safety Manual that accompanies this course. THIS IS COMPUSLORY and a record is kept electronically that indicates that you have downloaded the Safety Manual for reading.

To access the Safety Manual the WEB address is :
http://cnsfse01.jcu.edu.au/Schools/Chemistry/SafetyManual/manual.htm
At the prompt enter your student login name and password and then download the Safety Manual for reading.
Alternatively the manual may be addressed from the CH1012 LearnJCU web site under **Find More..** .

ASSIGNMENT 2
COLLOIDS

AIMS

This experiment involves the preparation of several common emulsions, gels and colloids (sols). The properties of each sample prepared are discussed including factors such as the stability and the charge on the colloids prepared. A dialysis experiment is carried out to determine the efficiency of the dialysis process using a cellophane membrane.

1. INTRODUCTION

A colloidal system consists of a homogeneous medium (dispersion medium) containing dispersed particles (disperse phase). The latter, although not necessarily spherical, have approximate diameters in the range 10-1000 nm (1 nm = 10^{-9}m), so that the particle is intermediate between those in a coarse dispersion (e.g. sand particles suspended in water) and those in a normal true solution (e.g. sugar, salt solution).

There are various types of colloidal systems depending on the nature of the disperse phase and dispersion medium. These are described in Table 1.

TABLE 1

General Name	Dispersion Medium	Disperse Phase	Examples
Aerosol	Gas	Liquid	Hairspray, fog, mist
Aerosol	Gas	Solid	smoke, dust
Foam	Liquid	Gas	Fire-extinguisher foam, whipped cream, beer froth
Emulsion	Liquid	Liquid	Milk, mayonnaise
Colloidal Solution (or Sol)	Liquid	Solid	printing ink, paint
Gel or Solid Emulsion	Solid	Liquid	Ice cream, bituminous road paving, jelly, skin, muscle
Solid Dispersion	Solid	Solid	Ruby glass (gold metal in glass), some alloys
Solid Foam	Solid	Gas	Insulating foam

In this experiment we are concerned with the study of colloidal solutions, emulsions and gels.

Colloidal Solutions (Sols)

In colloidal solutions the particles can be either aggregates of small particles insoluble in the medium (a two phase system) or single molecules of very high molecular weight in true solution. Regardless of the nature of the particles a distribution of particle size exists and the sols are said to be **polydisperse.** Associated with the size of the particles, sols exhibit certain special properties. Thus the particles cannot be seen in an ordinary microscope and pass through ordinary filter papers. However, unlike small molecules in true solution, they show remarkable optical properties and are retained by special filters, called ultrafilters. In addition they exhibit Brownian Movement. (Further information on these properties will be supplied in lectures.)

Sols can be conveniently classified into two types, lyophobic and lyophilic. The properties of these are compared in Table 2. Lyophobic colloids are thermodynamically unstable systems; lyophilic colloids are thermodynamically stable systems.

TABLE 2

Lyophobic (Hydrophobic)	**Lyophilic** (Hydrophilic)
No affinity between particle and medium "Solvent Hating"	Particles solvated by medium "Solvent Liking"
Stability due to charge	May carry charge, but stability due to solvation
Particles usually aggregates of inorganic materials insoluble in the dispersion medium	Particles usually high molecular weight molecules of organic origin, soluble in the medium
Low viscosity	High viscosity
Stable only at low concentrations	Stable at high concentrations
Easily precipitated by electrolytes	Unaffected by electrolytes though large quantities can "salt out" particles
Unstable on prolonged dialysis	Stable on prolonged dialysis
Coagulation produces definite granules	Coagulation produces a gel
Coagulation difficult to reverse	Coagulation easily reversed
Strong Tyndall Effect	Weak Tyndall Effect
Surface Tension similar to medium	Surface Tension lower than medium

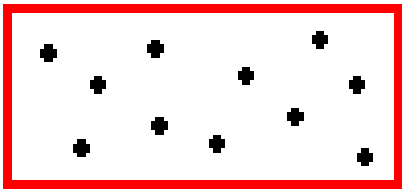
The particles in a lyophobic sol carry a charge which originates either through the adsorption of trace ions from the medium onto the surface of the particle or through the ionisation of chemical groups at the surface. As a result of this charge an **electrical double layer** is formed around the particles and they are prevented from coagulating because of electrostatic repulsion. The sols, however, are unstable in the presence of relatively large amounts of electrolytes since the repulsive force between the electrical double layers is reduced, allowing coagulation to occur. Coagulation is induced by the ion of opposite charge to the colloid and the efficiency of precipitation increases markedly with the valency of the ion (Hardy-Schulze Rule).
(Na^+ monovalent ion, Ca^{2+} divalent ion). Although lyophilic sols may carry a charge, due to the ionisation of certain groups in the molecules, it is not essential to their stability and consequently they are not affected by the addition of electrolytes unless the latter are at a very high concentration.

Effect of Lyophilic Colloids on the Stability of Lyophobic Colloids

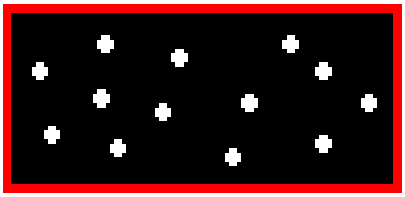
The presence of very high molecular weight molecules (macromolecules, polymers) in solution can markedly affect the stability of lyophobic colloids. In some cases the stability is enhanced so that more electrolyte is required to induce coagulation of the particles (protective effect). In other cases coagulation occurs more readily (sensitizing effect). The later process is referred to as **flocculation** to distinguish it from the coagulation process induced by the addition of electrolytes alone. In both the protective and sensitizing processes segments of polymer chains are adsorbed at the surface of the particles. Which effect is operative depends on the degree of adsorption and the molecular weight and concentration of the polymer.

Emulsions

An emulsion is a dispersion of one liquid in another. Usually one of the liquids is water and the other an organic substance (generally referred to as an 'oil'). Thus two types of emulsion are known.



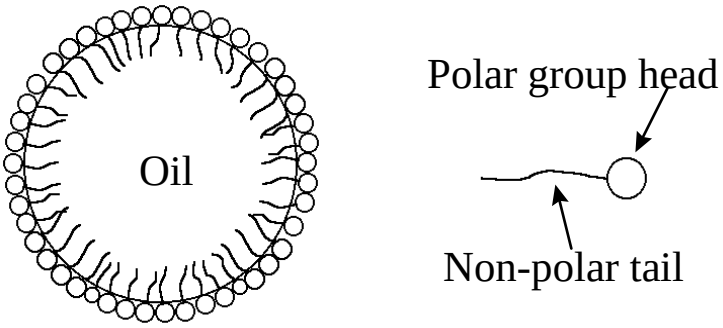
Organic dispersion in water ie. 'oil' in water emulsion (O/W)



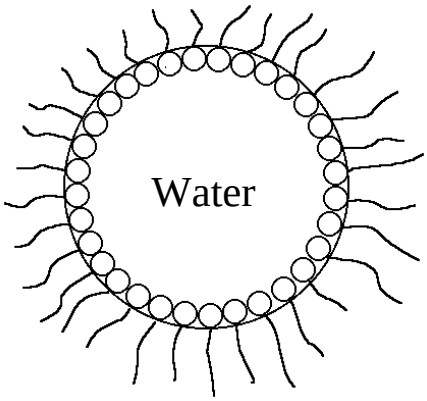
Water dispersion in organic ie. water in 'oil' emulsion (W/O)

Clearly if water is carefully added to an O/W emulsion it should mix more readily with the emulsion than if it were added to a W/O type, since in the latter case water is not the continuous phase. Observation of this mixing process can thus be used to determine an emulsion type.

The stability of an emulsion depends on the presence of a third component (approximately 0.5-2%), called an **emulsifying agent**. The latter is an **amphipathic** compound, that is a substance whose molecules consist of a long non-polar group (soluble in 'oil', insoluble in water) attached to a polar group (soluble in water, insoluble in 'oil'). These molecules form a monomolecular layer around the particles preventing coagulation. Sodium stearate ($C_{17}H_{35}COO^-\ Na^+$), a component of ordinary household soap, is an emulsifying agent which stabilises O/W emulsions.



On the other hand calcium and magnesium stearate tend to stabilise W/O type emulsions (Why?)



Gels

A gel consists of a network of solid molecules in the pores of which a liquid is dispersed. Although possessing a rigid structure the gel can contain up to 99% of liquid, so that it behaves like a molecular sponge.

Reference

R.J. Hunter "Introduction to Modern Colloid Science"

2. EXPERIMENTAL

To be done in pairs.
For each experiment you will note down observations as you proceed and develop explanations with the help of your demonstrator. For each explanation you must indicate the dispersion medium and the disperse phase where a colloidal system is involved.

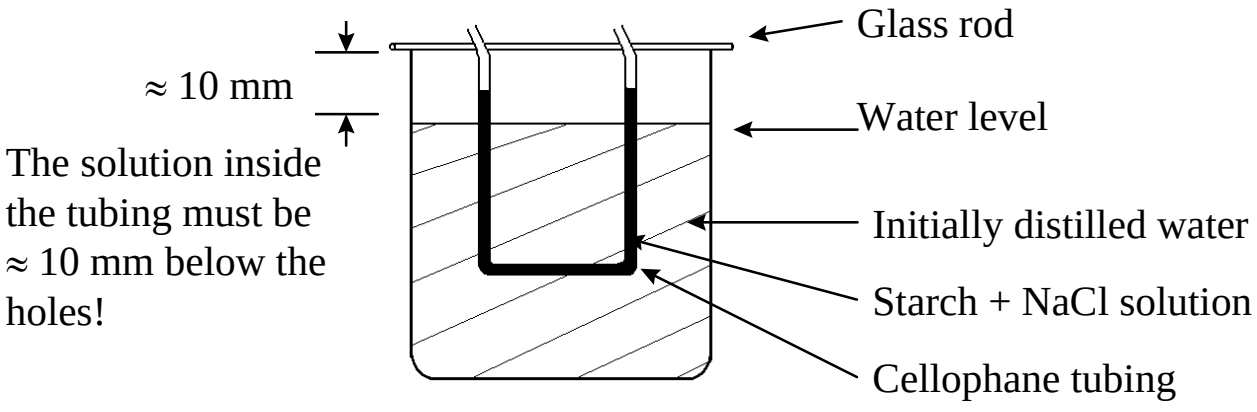
2.1 Experimental Dialysis

In this experiment, in the process of dialysis, colloidal solutions are freed from any electrolytes or low molecular weight particles present in the medium using an ultrafilter.

Here a starch colloid is to be separated from a NaCl solution using cellophane as the semipermeable membrane.

Prepare a piece of cellophane tubing by soaking in distilled water in a beaker for 2-3 minutes.
Take a prepared length of cellophane tubing, gently close the holes at one end with your thumb and forefinger and blow compressed air into the tubing to open it up.

Push a glass rod through the holes at both ends of the tubing as shown in the diagram.



Mix together 10 cm^3 of a 1% sodium chloride solution and 10 cm^3 of a 0.1% solution of starch. Using a funnel transfer the mixture to the cellophane tubing being careful to avoid the mixture coming in contact with the outside of the tubing. Do not overfill your tubing.

Take of few drops of the mixture and test for the presence of starch using the iodine solution and the presence of Cl^- using the $AgNO_3$ solution - these are your positive test results. Carry out the same tests on distilled water - these are your blank results.

Then suspend the tubing on a glass rod in a beaker (250 mL) of distilled water for at least one hour. Make sure that most of the tubing is below the water level.

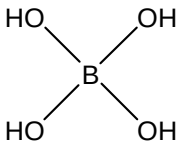
While waiting, go on to other experiments.

When an hour has elapsed, test a sample of the distilled water for both starch (iodine solution $\rightarrow$ blue), and chloride ion (0.1M $AgNO_3 \rightarrow$ white ppt). Note and explain the result.

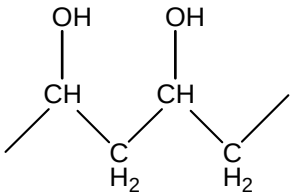
2.2 Preparation of an Water / Organic Gel - SLIME

Polyvinyl alcohol solution and borax solution are found in separate containers.
One drop of food colouring is added to the borax solution. The borax is then added to the PVA solution slowly while stirring with a stirring stick. After sufficient stirring the material becomes quite an elastic, semi-rigid mass and at this stage it can be removed from the container. You should investigate stretching the material slowly and quickly. The gel formed comprises 96% water.

Borax (sodium tetraborate, $Na_2B_2O_7.10H_2O$) hydrolyses in water to form a borate ion which is tetra functional in it's interaction with the hydroxyl groups of the PVA.



The borate ion $B(OH)_4^-$ interacts with PVA which is a polymer with a normal repeating unit of $[CH(OH)CH_2CH(OH)CH_2]_n$.



Suggest a possible structure for the slime incorporating hydrogen bonding as a feature.

Question 1. Is the structure of slime consistent with the observed behaviour - why?

2.3 Preparation of Colloidal $Fe(OH)_3$

Reaction of Fe(III) ions with hot water results in the formation of the colloid $Fe(OH)_3$.

Heat 100 cm^3 of water to boiling and while boiling add 1 cm^3 of the provided iron(III) chloride (32%) solution drop by drop. Boil further 1 minute and filter. Retain the filtrate. Take 8 x 5 cm^3 samples of filtrate in 8 test tubes arranged in order in a test tube rack.

Take 5 cm^3 of the $Fe(OH)_3$ filtrate and try the effect of centrifugation.

Do not cap the tubes, use parafilm.

Take 4 x 5 cm^3 samples of filtrate in the test tube rack (Tubes 1 – 4) and treat as follows:

Add the following solutions dropwise, counting the drops until the colloid turns cloudy or up to maximum of 25 drops.

Use the following solutions:

	Add to:
0.06M NaCl	Test tube 1
0.03M $BaCl_2$	Test tube 2
0.03M Na_2SO_4	Test tube 3
0.03M $Na_4\ P_2O_7$	Test tube 4

In your report you must deduce the charge of the $Fe(OH)_3$ colloid particles.

2.4 Protective Colloids

Nowadays stabilisation by either natural or synthetic polymers (often referred to as steric stabilisation) is exploited in a diverse range of industrial products: paints, glues, inks, pharmaceutical and food emulsions, detergents, lubricants, etc. Furthermore, polymeric stabilization is operative in many biological systems, such as blood and milk. It is also important in a wide range of industrial and agricultural processes (e.g. water treatment, soil stability, coal washing, oil recovery, etc.).

Take 4 test tubes, each containing 5 cm^3 of the $Fe(OH)_3$ colloid filtrate, in a suitable rack. Number the test tubes 1-4.

To test tube 5 add 6 cm^3 of distilled water, then 6 drops of 0.03M Na_2SO_4 solution.

To test tube 6 add 6 cm^3 of 0.1% starch solution, then 6 drops of 0.03M Na_2SO_4.

To test tube 7 add 6 cm^3 of 0.1% starch solution, then 1 cm^3 of distilled water.

To test tube 8 add 6 cm^3 of 0.05M sucrose solution, then 6 drops of 0.03M Na_2SO_4.

Each solution should be stirred thoroughly and then left to settle until the end of the practical period. Note any results.

2.5 Flocculation of a Clay Mineral Sol

The use of small concentrations of synthetic polyelectrolytes to induce the flocculation of hydrophobic colloids is of widespread industrial importance. For example, these materials are used in the mining industry, in the recovery of metals and metal ores from slimes and suspensions, in the treatment of petroleum refinery and electro-plating wastes, in sewage disposal, in the pulp and paper industry, and in the treatment of cane juice in sugar mills. The process is distinguished from the coagulation or precipitation effect resulting from the addition of low-molecular-weight electrolytes to colloidal systems.

The most common and successful synthetic flocculants are random copolymers of acrylamide (A) and sodium acrylate (B) with molecular weights of ~ 1 x 10^7.

Copolymer = -AABABB-

where A = $-CH_2CH-$ ($CONH_2$) and B = $-CH_2CH-$ ($COO^-\ Na^+$)

The effect of such a polymer on a clay mineral sol will be demonstrated.

2.6 Preparation of an Emulsion

To be carried out in the fumecupboard.
Place 3 clean test tubes in a suitable rack and number the test tubes 1-3.

To test tube 1 add 3 cm^3 distilled water and 3 cm^3 kerosene.

To test tube 2 add 3 cm^3 2% sodium oleate solution and 3 cm^3 kerosene.

To test tube 3 add 3 cm^3 2% sodium oleate solution and 50 mg of magnesium sulphate. Shake the test tube until dissolved. Then add 3 cm^3 kerosene.

Take test tubes 1 and 2. Shake both test tubes vigorously up and down (close the test tube with your thumb) for 15 seconds. Replace them in the rack and observe the resulting emulsions for their stability. After 5 minutes gently invert test tube 2 ten times. Make a sketch of your results.

Take test tube 2 and 3. Shake both test tubes vigorously up and down for 15 seconds. Replace them in the rack and add one drop of methylene blue dye to both test tubes. Note the results after 2-3 minutes. Make a sketch of your results.

Question 2. Since organic substances are generally worse conductors of electricity than water, based on this suggest an alternative method of determining the emulsion type.

Discuss the observations you have noted in the experiment with the demonstrator.

ASSIGNMENT 3
CHEMICAL EQUILIBRIUM, SOLUBILITY PRODUCTS, FORMATION CONSTANTS AND COMPLEX FORMATION

AIMS

Complex formation is used as a method for qualitatively and quantitatively examining the behaviour of equilibrium mixtures of transition metal ions. In the qualitative tests you will determine the effects of varying the equilibrium mixture concentrations on complex formation according to Le Chatalier's principle. For the quantitative test you will determine the molarity of an unknown nickel salt solution using complex formation and gravimetric techniques.

1. INTRODUCTION

1.1 Chemical equilibrium

While many chemical reactions proceed to completion, many others do not. For example, in the gaseous mixture of hydrogen and iodine vapour at 400^{o}C some reaction occurs with the formation of hydrogen iodide

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)} \qquad ....(1)$$

But, if pure HI is heated to 400^{o}C it decomposes partly

$$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)} \qquad ...(2)$$

Thus in a closed system at 400^{o}C both reactions (1) and (2) are taking place and the reaction can be written as

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \qquad ...(3)$$

The rates of the two reactions (1) and (2) depend on the concentrations of the reacting substances - this is one way of stating the Law of Mass Action. If hydrogen and iodine are mixed at 400^{o}C, reaction (1) proceeds rapidly at first, then more slowly as the hydrogen and iodine are consumed. The rate of the reverse reaction (2), on the other hand, increases as more and more HI is formed. Eventually a state is reached when both (1) and (2) are proceeding at the same rate and the system is then in DYNAMIC EQUILIBRIUM at 400^{o}.

1.2 Law of Mass Action

For a reaction, in solution, that can be expressed as

$$A + B \rightleftharpoons C$$

the Law of Mass Action gives the condition of equilibrium as

$$\frac{[C]}{[A][B]} = K_c$$

where K_c is a constant (dependent on temperature) known as the EQUILIBRIUM CONSTANT and the square-bracket denotes concentration of A, B, C, respectively, in mol/dm^3.

The equilibrium system is quantitatively described by K_c (changed only by temperature) from the Law of Mass Action. The system is qualitatively described by Le Chatelier's Principle. If a change in conditions is made to a system in equilibrium, the position of equilibrium will alter in an endeavour to counteract the change so that the original conditions tend to be restored.

Thus in the case of the reaction expressed by equation (3), if the concentration of either H_2 or I_2 were increased, the concentration of HI would also increase and the position of equilibrium would shift to the left.

1.3 Solubility Products $K_{S.P.}$

For a slightly soluble salt MX in contact with its saturated solution, an equilibrium exists between the solid and the ions in solution.

The reversible reaction is

$$MX_{(solid)} \rightleftharpoons M^+_{(aq)} + X^-_{(aq)}$$

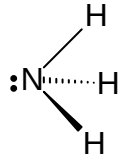
Since the concentration of the MX solid is constant by definition, the condition for equilibrium at a given temperature is

$$[M^+][X^-] = K_{S.P.}$$

where $K_{S.P.}$ is a constant called the SOLUBILITY PRODUCT, affected only by temperature changes.

1.4 Coordination Compounds - Metal Complexes

Coordination compounds are substances which contain coordinate bonds. This is the bond formed between atoms when one atom provides both electrons for a shared pair. Consider the ammonia molecule



Ammonia is a **ligand** (*ligo* = "I bind") and can attach itself to certain metal ions via the nitrogen atom (donor atom) by the donation of its lone pair of electrons with the formation of a **coordinate bond**, resulting in a complex ammine ion. Many metals form such ammines, particularly those in the central region of the Periodic Table. The property is characteristic of weakly basic elements. Transition elements are particularly liable to act in this way.

Some examples are:

$$[Ag^{I}(NH_3)_2]^+, \ [Cu^{II}(NH_3)_4]^{2+}, \ [Co^{III}(NH_3)_6]^{3+}$$

On evaporation or crystallisation, the complex amine is obtained as a salt (chloride, sulphate etc.).

1.5 Complex Compounds

There are four types.

(A) Anionic complexes. There is a metal present in the anion of the salt as well as a number of anionic ligands, but the usual properties of the metal ion and of the anions are partly or almost

completely suppressed.

Examples:

$K_4Fe^{II}(CN)_6$ containing $[Fe^{II}(CN)_6]^{4-}$, the hexacyanoferrate(II) ion
$K_3Fe^{III}(CN)_6$ containing $[Fe^{III}(CN)_6]^{3-}$, the hexacyanoferrate(III) ion

The properties of the cation K^+ are normal, but the cyanide and metal in the complex have lost partly or completely the properties of the simple ions and behave like anions such as SO_4^{2-}. With a solution of $K_3Fe^{III}(CN)_6$ for example, ammonia or sodium hydroxide fail to precipitate any iron(III) hydroxide. Similarly, additions of strong acid fails to produce any hydrogen cyanide.

(B) Cationic complexes. Examples are the well-known metallic ammines or compounds with ammonia. The metal is in the cation and in solution there is present a complex cation e.g. $[Ag(NH_3)_2]^+$ or $[Cu(NH_3)_4]^{2+}$. Many salts can be prepared from a complex cation, which behaves like a single metallic ion. As before, the properties of the metal ion in the complex may be partly or almost completely suppressed. For example addition of chloride ions to a solution containing the diamminesilver ion fails to precipitate silver chloride, unless either a very small excess of ammonia has been used, or a great excess of chloride ion is used.

Examples:

$[Ag(NH_3)_2]^+$ the diamminesilver(I) ion
$[Cu(NH_3)_4]^{2+}$ the tetramminecopper(II) ion
$[Cu(H_2O)_4]^{2+}$ the tetraquacopper(II) ion

(C) Neutral complexes. These are uncharged species.

Examples:

$[Ni(dmg)_2]$ - bis(dimethylglyoximato)nickel(II) dmg = dimethylglyoximate anion
$[Co(NH_3)_3(NO_2)_3]$ - triamminetrinitrocobalt(III)

(D) Double complexes.

Examples:

$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$ diamminesilver(I) dicyanoargentate(I)

1.6 Effects of Complex Formation

Coordination is accompanied by a number of effects. Coordination compounds are quite often, but not invariably, deeply coloured. This is due to the effect of the electric field produced by the ligands on the outer electrons of the metal ion. Again, the properties of a particular metal ion may be profoundly modified by coordination. Thus while Ag^+ is precipitated by Cl^-, this is not normally true of $[Ag(NH_3)_2]^+$. Simple copper(I) salts are unstable and simple copper(III) salts are unknown, but both oxidation states are stabilised by complex formation.

1.7 Solutions of Complex Ions

A PROPERTY OF ALL COMPLEX IONS IN SOLUTION - ANION OR CATION - IS THAT THE COMPLEX ION IS IN EQUILIBRIUM WITH ITS CONSTITUENTS.

Thus $Ag(NH_3)_2^{+}{}_{(aq)} \rightleftharpoons Ag^+{}_{(aq)} + 2NH_{3(aq)}$ ...(4)

and $Fe(CN)_6^{4-}{}_{(aq)} \rightleftharpoons Fe^{2+}{}_{(aq)} + 6CN^-{}_{(aq)}$ ...(5)

The tendency towards formation of such a complex is shown by writing the equilibrium in the opposite direction. The equilibrium constant for (4) would then be

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

where K_f = formation constant of the complex. K_f is a large number, increasing with increasing complex stability.

Complex ions offer a convenient medium for producing small concentrations of a particular ion, and are valuable in analytical work and in such operations as electroplating and photography.

1.8 Analytical Applications

If a metal is to be precipitated from a solution containing a complex of that metal, the following must be considered:

The magnitude of K_f, the formation-constant of the complex.
The magnitude of $K_{S.P.}$ (solubility product of the intended precipitate).
The concentrations of the species present in solution.

For example to precipitate Ag as AgCl from a solution containing $Ag(NH_3)^{2+}$ we must recall:

$Ag(NH_3)_2^+{}_{(aq)} \rightleftharpoons Ag^+ + 2NH_{3(aq)}$ (i.e. some Ag^+ is present)

$[Ag^+][Cl^-] = K_{S.P.}$ ($K_{S.P.}$ = solubility product)

For any concentration of ammonia, the $[Ag^+]$ is determined by *K*.

To initiate precipitation of AgCl, a concentration of Cl^- must be added such that

$$[Ag^+] \times [Cl^-] > K_{S.P.(AgCl)}$$

Silver iodide is much less "soluble" in ammonia solution than silver chloride because its solubility product is so much less. However, because of the great stability of the $Ag(CN)_2^-$ complex even silver iodide is readily soluble in excess KCN.

TABLE OF SOLUBILITY PRODUCTS

Compound	Solubility product

AgCl	1.6×10^{-10}	(25^oC)
AgI	1.5×10^{-16}	(25^oC)
$Ni(OH)_2$	1.6×10^{-16}	(25^oC)
$Zn(OH)_2$	4.5×10^{-17}	(25^oC)
$Cu(OH)_2$	1.6×10^{-19}	(25^oC)
$Fe(OH)_3$	4.0×10^{-38}	(25^oC)
$BaCrO_4$	8.5×10^{-11}	(25^oC)
$PbCrO_4$	2.0×10^{-16}	(25^oC)
Hg_2Cl_2	1.1×10^{-18}	(25^oC)

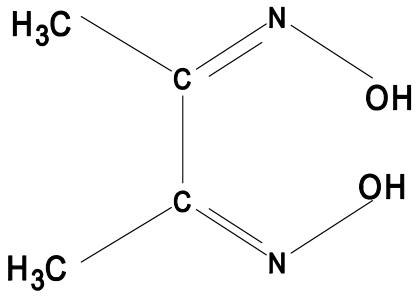
TABLE OF FORMATION CONSTANTS

Complex	Formation Constant
$[Ag(NH_3)_2]^+$	2×10^7
$[Co(NH_3)_6]^{3+}$	6×10^{34}
$[Cu(NH_3)_4]^{2+}$	4×10^{13}
$[Ni(NH_3)_6]^{2+}$	6×10^9
$[Zn(NH_3)_4]^{2+}$	4×10^9
$[CuBr_4]^{2-}$	- to arrive
$[Fe(Cr_2O_7)]^+$	- to arrive
$[Fe(CrO_4)]^+$	- to arrive

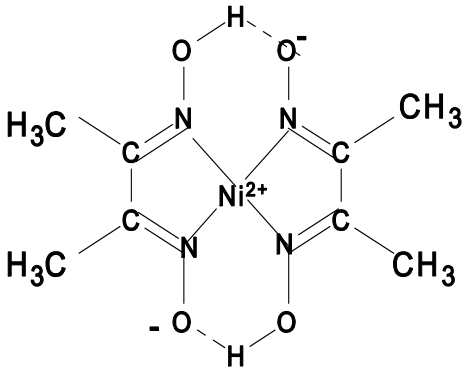
2. EXPERIMENTAL

To be done in pairs.

In this section of the practical you will be investigating the interaction of nickel ions (Ni^{2+}) with the complexing agent dimethylglyoxime referred to as dmgH and looking at a series of complexation reactions.



dmgH



$[Ni(dmg)_2]$

Dimethylglyoxime forms a red precipitate $[Ni(dmg)_2]$ with neutral solutions containing nickel ions. The red precipitate may be collected and weighed to quantitatively determine the amount of nickel in a solution.

When a solution of dimethylglyoxine is added to a solution of nickel ions the following equilibria are established

$2dmgH_{(aq)} + Ni^{2+}_{(aq)} \rightleftharpoons 2H^{+} + Ni(dmg)_{2(aq)}$ ...(6)

$Ni(dmg)_{2(aq)} \rightleftharpoons Ni(dmg)_{2(s)}$ (red pt) ...(7)

Removal of $Ni(dmg)_{2(s)}$ by filtration leaves the single equilibrium (6).

NOTE: The experimental section of this week's practical consists of two distinct parts
(a) the QUALITATIVE examination of equilibrium (6), and
(b) the QUANTITATIVE analysis of a nickel salt solution.
The QUANTITATIVE section must be started first; there is ample opportunity to do the QUALITATIVE section later in the practical.

2.1 Qualitative Examination of Equilibrium - (6)

2.1.1 Preparation of the Ni + DMG Equilibrium Mixture

Take 25mL of nickel sulphate solution (bottle labelled "equilibrium studies") and add 10 mL of dimethylglyoxime solution (**Caution: you should have gloves on while manipulating this reagent**) in a beaker or conical flask. Heat the mixture to 60-70^{o}C (to coagulate the precipitate). **Stir** during the heating as this mixture will otherwise "**bump" dangerously**. After the precipitate has formed take out 5 mL of the suspension place in a flask and label this **A – DO NOT USE PLASTIC PIPETTES for the transfer**. Remember at 60-70^{o}C the container can no longer be comfortably held in the hand and you should **use an insulated glove to make the transfer**. Filter using a fluted filter paper the remainder of the material while hot and keep the filtrate **B**.

To the unfiltered material **A** add a little dilute sulphuric acid. Explain the result.

2.1.2 Study of Ni + DMG Equilibrium (7)

Place small amounts of the filtrate **B** obtained in 2.1.1 (approx. 1 cm depth) in three test tubes add and shake with the following reagents.

(i) Dimethylglyoxime solution, 5 mL.
(ii) A drop of dilute ammonia (2 mol dm^{-3}).
(iii) A few drops of sodium acetate solution.

2.1.3 Metal ammine complexes

In the following tests use only a small amount of the metal salt solution (about 1 cm. length in a test-tube) and shake well during the addition of other solutions. When the initial reaction has occurred and been recorded, tip out most of the contents and then add further ammonia.

Add dropwise ammonia solution. (bench reagent; 2 mol dm^{-3}) to solutions of Zn^{2+}, Cu^{2+}, Fe^{3+}, respectively. Count and note carefully the drops added and the colour of precipitate, solubility in excess NH_3 and colour of final solution. Write equations for all reactions and comment on any ion that behaves differently to the rest of those tested.

2.1.4 Silver Complexes

(a) Take equal amounts (1cm depth) of silver nitrate solution in two separate test tubes,
(i) to one add excess ammonia solution (5 mol dm^{-3}) and
(ii) to the other add a similar amount of distilled water.
What ions you would now expect to be present in appreciable amount in each test-tube?

To each tube, add dropwise a sodium chloride solution (0.1M).
(Shake the tubes after each drop has been added). Explain your observations.

(b) Repeat 2(a) substituting a solution of potassium iodide for the sodium chloride solution. Explain your observations. Compare 2(a) and 2(b) explaining any differences.

2.2 Quantitative Analysis of a Nickel Salt Solution

(a) Collect a sample of the unknown nickel solution in a clean dry 100 mL beaker from the end bench (your demonstrator will tell you which unknown (A to E) to use, and will allocate a sintered glass crucible number to you. The crucible will be found in the desiccator, marked with your practical day.

(b) Rinse a pipette (25 mL) with a small volume of the unknown nickel sample. If the pipette is clean (no droplets adhered to the glass) take a 25 mL aliquot by pipette of your nickel solution and place it in a clean 400 mL beaker Add 5 mL of 1:1 hydrochloric acid, dilute to a total volume of about 200 mL with distilled water and heat to 70-80^{o}C. Add a slight excess (40 mL) of dimethylglyoxime reagent with stirring while keeping the reaction at 70-80^{o}C. Continue stirring and add dilute ammonia solution rapidly (pasteur pipette) until a faint permanent pink precipitate forms. Continue to stir and add dilute ammonia solution dropwise until complete precipitation occurs. Now add about 5 mL (pasteur pipette 5 squirts) more of ammonia solution to ensure that the solution contains a slight excess of ammonia. Cover the beaker with a clean watch glass and heat just to boiling) (do not boil vigorously) for 45 minutes.

NOTE: At the end of the 45 minute heating period you will require a large amount of hot distilled water (about 500 mL). This should be put on to heat during the 45 minute waiting period.

(**c)** During this heating period remove the crucible from the oven and place it in the desiccator to cool. Always use tongs not fingers and leave the desiccator lid slightly open. Do not place the crucible in contact with the desiccator gauze as this often gathers dust which can transfer to the crucible. When cool weigh the crucible and return it to the dessicator, weigh again after 5 min. If the weighings agree to the nearest milligram proceed with the chemistry otherwise repeat the last step until constant mass is achieved.

(d) Filter the hot solution through the weighed crucible, wash with hot distilled water until free of chloride (test samples of filtrate with silver nitrate) and dry the precipitate at 110^{o} - 120^{o}C overnight.

(e) Return after 10 am the following day and collect sample from desiccator and weigh as $Ni(C_4H_7O_2N_2)_2$ which contains 20.31% nickel.
(To clean the crucible after weighing remove the bulk of the material with a jet of water and place in the crucible conc. HCl in the fume cupboard carefully).

(f) From the mass of your precipitate calculate the mass of nickel in 25 mL of the original unknown nickel solution and hence calculate the molarity of this nickel solution (At. Wt. Ni = 58.70).

2.1 Metal ammine complexes

In the following tests use only a small amount of the metal salt solution (about 1 cm. length in a test-tube) and shake well during the addition of other solutions. When the initial reaction has occurred and been recorded, tip out most of the contents and then add further ammonia.

Add dropwise ammonia solution. (bench reagent; 2 mol dm^{-3}) to solution of Ni^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+} respectively. Count and note carefully the drops added and the colour of precipitate, solubility in excess NH_3 and colour of final solution. Write equations for all reactions and comment on any ion that behaves differently to the rest of those tested.

2.2 Silver Complexes

(a) Take equal amounts (1cm depth) of silver nitrate solution in two separate test tubes,
(i) to one add excess ammonia solution (5 mol dm^{-3}) and
(ii) to the other add a similar amount of distilled water.
What ions you would now expect to be present in appreciable amount in each test-tube?

To each tube, add dropwise a sodium chloride solution (0.1M). (Shake the tubes after each drop has been added). Explain your observations.

(b) Repeat 2(a) substituting a solution of potassium iodide for the sodium chloride solution. Explain your observations. Compare 2(a) and 2(b) explaining any differences.

ASSIGNMENT 4
CHEMICAL REACTIVITY - THE COPPER CYCLE

AIMS

This experiment is designed to introduce you to the practical aspects of recognizing redox and metathesis reactions. A quantity of copper is passed through a series of redox and metathesis reactions which culminate in a cycle where the starting metal is recovered.

1. INTRODUCTION

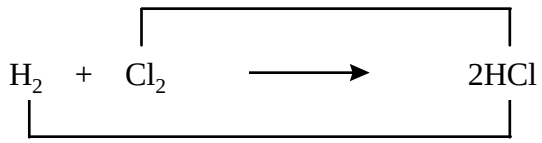
Chemical reactions can be divided into two general categories: **REDOX** or **METATHESIS** processes.

1.1 In a **REDOX** reaction, there is a transfer of electron(s) from one atom to another. Oxidation refers to a loss of electrons by one reactant, and reduction to a gain of electrons by another: accordingly oxidation and reduction occur together (and hence the name ***redox*** reaction).

e.g.	2Na	+	Cl_2	$\rightarrow$	2NaCl	
where	2Na	-	$2e^-$	$\rightarrow$	$2Na^+$	i.e. Na is oxidised to Na^+
	Cl_2	+	$2e^-$	$\rightarrow$	$2Cl^-$	i.e. Cl_2 is reduced

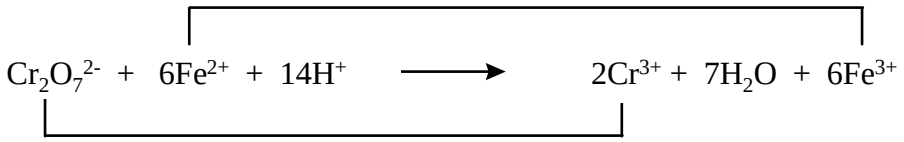
Redox reactions may therefore be recognised by the fact that oxidation states of atoms/ions will be changed in the stoichiometric or ionic equation in going from reactants to products.

oxidation state of Cl changes from 0 to -I **ie. reduction**



oxidation state of H changes from 0 to +I **ie. oxidation**

oxidation state of Fe changes from +II to +III **ie. oxidation**



oxidation state of Cr changes from +VI to +III **ie. reduction**

1.2 In **METATHESIS** reactions on the other hand, there are no net electron transfers, although there may well be exchange of ions or groups. Generally, a metathesis process will be driven by one of three factors, or a combination of them, which removes molecules from the solution:

(a) ***formation of a precipitate*** -

e.g. $CaCl_{2(aq)} + Na_2CO_{3(a)} \rightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$
because $CaCO_3$ is insoluble.

i.e. $Ca^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)}$

(b) ***formation of a weak electrolyte*** -

e.g. $HCl_{(aq)} + NaOH_{(aq)} \rightarrow HOH_{(1)} + NaCl_{(aq)}$

i.e. $H^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \rightarrow H_2O_{(1)}$

The analogous process of <u>metal complex formation</u> fits into this category

e.g. $Al^{3+}{}_{(aq)} + 3ox^{2-}{}_{(aq)} \rightarrow Al(ox)_3{}^{3-}{}_{(aq)}$ (ox^{2-} = oxalate ion)

(c) ***formation of a gas*** -

e.g. $Na_2S_{(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2S_{(g)}$

i.e. $S^{2-}{}_{(aq)} + 2H^{+}{}_{(aq)} \rightarrow H_2S_{(g)}$

This experiment provides a number of reactions of all the above types, and requires each student to discriminate between them. It also involves reactions of metals with acids and the activity series. All of these aspects are treated in the text "*Chemistry - The Central Science"* (8th edition) by Brown, Le May, Bursten as detailed below.

1. ***Metathesis reactions, ionic equations*** (pp. 111-119)
2. ***Redox reactions*** (pp. 120-122)
3. ***Reactions of metals with acids*** (pp. 122-124)
4. ***Activity series*** (pp. 124-125)

Some coloured compounds that you need to be aware of for this prac:

$Cu(NH_3)_4{}^{2+}{}_{(aq)}$ - dark blue solution
$Cu(NO_3)_{2(aq)}$ - light blue solution
$Cu(OH)_{2(s)}$ - light blue precipitate
$CuO_{(s)}$ - black precipitate

2. EXPERIMENTAL

To be done **in pairs**.
All manipulations to be carried out in the fumecupboards.
Make notes on all reactions that occur as you do the experiment.

2.1 Place a piece of pre-cut copper wire (about 0.3 g, weighed to the nearest 0.01g), 1 mL of water and a small amount of urea (tip of spoon) in a 250 mL beaker in the fume hood. Add 5 mL of concentrated nitric acid* carefully (with gentle swirling) to the beaker using the dispenser. Keep the beaker in the fume hood and wait until the reaction is complete (~ 2 mins), then add 100 mL distilled water.

2.2 Add slowly with stirring, 8 mL of 5M ammonia* solution from the dispenser in the fumecupboard. If necessary, carefully add further ammonia until the deep blue colour just persists on stirring.

2.3 To the solution from (2.2), add 30 mL of 3M NaOH*. Check the pH is 10 or greater, if not add a further 5mL of NaOH. Heat the solution formed in (2.3) with continuous stirring just to boiling and test for the liberation of ammonia with a piece of filter paper moistened with HCl.

2.4 Heat the solution for 5 – 10 minutes. If the colour of the solution does not change, adjust the pH to ~10 using NaOH and reheat. Allow the precipitate to settle, and decant the supernatant liquid. Add 100 mL of very hot distilled water, allow the precipitate to settle, and decant. Repeat the washing procedure.

2.5 To the precipitate remaining from (2.4), add 15 mL of 6M H_2SO_4* from the dispenser in the fumecupboard.

2.6 To the resultant solution, add 1.5 g of zinc mesh and stir until the supernatant liquid is colourless. After gas evolution has become slow, decant.

2.7 While waiting for gas evolution to diminish in (2.6), obtain a sintered glass crucible from the desiccator and weigh it.

2.8 To the solid remaining from (2.6), add 5 mL of distilled water and then 10 mL of concentrated HCl*. When gas evolution has become very slow, warm on a hot plate set on low heat.

2.9 When gas evolution has ceased, decant and transfer the solid quantitatively to the weighed sintered glass crucible [see (2.7)]. Filter, using a Buchner flask and then wash the precipitate twice with 5 mL of distilled water, then 5 mL of ethanol and then twice with 5 mL of acetone.

2.10 Dry the crucible in the oven for 10 minutes, cool and weigh.

---

*Concentrated nitric acid, 5M aqueous ammonia, 3M NaOH, 6M H_2SO_4 and concentrated HCl are all extremely corrosive. DO NOT SPILL ON CLOTHING, and if accidentally spilt on the skin wash area immediately with copious amounts of water. Report any major spills to the tutor.

3. CALCULATIONS AND QUESTIONS

Complete the following questions in your report book.

A. Detail observation of chemical reactions involved in steps 2.1[**] , 2.2, 2.3, 2.4, 2.5, 2.6 and 2.8. Write balanced ionic equations for each of these steps.

B. Classify each of these reactions as either a redox or metathesis reaction. For the metathesis reactions, identify the driving force for each reaction.

C. Why do you wash the precipitate as described?

D. Why do H_2SO_4 and HCl react with zinc but not the precipitated copper?

E. What other metals could be used in step 6 instead of zinc?

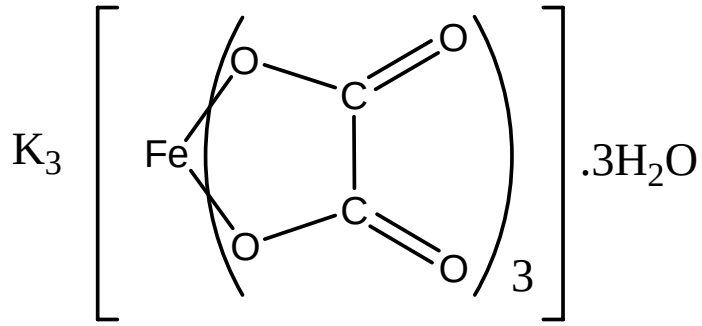
F. Report the percentage reclamation of copper for the experiment.

[**] *Ignore the presence of the urea in this reaction. It is present to diminish the quantity of toxic brown gaseous nitrogen dioxide liberated in the reaction*

ASSIGNMENT 5
PREPARATION OF A TRANSITION METAL COMPLEX, POTASSIUM TRIS(OXALATO)FERRATE(III) TRIHYDRATE

AIMS

This experiment introduces you to the standard techniques used in preparative inorganic chemistry of coordination compounds. Purification will be achieved by means of crystallization.



1. INTRODUCTION

There exist a large number and variety of compounds of transition metal in which the metal ion is surrounded by a number of bonded groups called **ligands**: such species are called **coordination compounds** or **complexes**. For example, for the tri-valent iron atom, the best known example with six ligands is potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$. Potassium tris(oxalato)ferrate(III), which will be synthesized in the practical experiment, is another member of this class, with each oxalate ion ligand occupying two of the six coordination positions around the iron centre forming a ring known as a **chelate ring** (see structure above).

The complex, which may be a charged ion, or neutral, is shown in a formula within square brackets emphasizing the fact that the metal ion with its ligands has independent existence both in solution and in the solid state.

This experiment illustrates and gives practice in certain simple procedures of practical chemistry: *viz.* weighing, filtering, concentrating solutions, crystallizing, etc. A preparation involves three steps -

(A) - forming the required substance;
(B) - isolating it in pure condition; and
(C) - checking its identity and purity (e.g. analysis, spectrum, etc.)

Potassium tris(oxalato)ferrate(III) is made by mixing ferrous oxalate (prepared by precipitation from solutions containing ferrous ions {Fe(II)} and oxalate ion $\{C_2O_4^{2-}\}$) with potassium oxalate, then oxidizing the iron to the trivalent state with hydrogen peroxide $\{H_2O_2\}$ and adding oxalic acid.

1. $Fe^{2+} + C_2O_4^{2-} \rightleftharpoons FeC_2O_{4(s)}\downarrow$
2. $2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$
   $Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(s)}\downarrow$
   $Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$
3. $[Fe(C_2O_4)_3]^{3-} + 3K^+ + 3H_2O \rightleftharpoons K_3[Fe(C_2O_4)_3]\ 3H_2O$

The complex salt is made less soluble by adding ethanol to the aqueous solution while hot: the complex salt precipitates out of solution on cooling.

Step (B) in this experiment is achieved by means of **crystallization**, the theory of which may be summarized

briefly as follows. The growing crystals selectively incorporate the pure substance and reject (though not always completely) impurity molecules, which thus remain in solution: separation of the pure crystals from impure solution is then easy. The purification is achieved at some sacrifice in material. Suppose that the substance is soluble in hot water to the extent of p grams/100 cm^3 and in cold water only to the extent of q grams/100 cm^3. (Most substances are more soluble in hot than in cold solution). It follows that 100 cm^3 of hot saturated solution yields (p-q) grams of crystals on cooling and standing. Thus only the fraction (p-q)/p of the substance is recovered as the purified crystals, the rest remaining in the mother liquor together with the impurities. The reason that the impurities themselves do not crystallize out of solution is that they are not present in sufficient amount to exceed their solubility.

Potassium tris(oxalato)ferrate(III) is stable in the solid state provided it is kept in darkness or subdued light. Exposed to strong light on the surface, the bright green crystals soon become covered with yellow powdery ferrous oxalate. Therefore the compound should be stored in darkness.

Step (C) which is checking the purity of your preparation might be carried out by spectral measurements (mass spectroscopy, NMR) or by elemental analysis (C,H,N,Fe) – which are beyond this practical session.

2. EXPERIMENTAL

To be done in pairs.

2.1 Preparation of Potassium Tris(oxalato)ferrate(III)

(i) Preparation of Ferrous Oxalate

(a) Heat 50 mL of distilled water on a hotplate in a 250 mL conical flask (fumecupboard). In a 250 cm^3 conical flask, dissolve 15.0 g of ferrous ammonium sulphate $\{(NH_4)_2SO_4.FeSO_4.6H_2O\}$ in 50 cm^3 of the warm water to which 1 cm^3 of dilute (2M) sulphuric acid has been added.

(b) Dissolve 7.5 g of oxalic acid (**toxic**) in 75 cm^3 of warm water, and add to the solution in the conical flask.

(c) Heat the mixture to boiling ((fumecupboard), stirring **continuously** using a large stirred bar to prevent "bumping" (you can cover the top of the flask with aluminium foil with holes punched in it), then stop heating and stirring and allow the granular yellow precipitate of ferrous oxalate to settle to the bottom of the flask.

(d) Separate the solid by decanting and discarding the clear supernatant solution, **taking care to do this without appreciable loss of solid**. Wash the ferrous oxalate free of other ions by stirring with 50 cm^3 of hot water and again decanting, remove the stirred bar using the "flea remover". The wet ferrous oxalate so obtained is pure enough for use in the next step.

(ii) Oxidation with Hydrogen Peroxide

(a) Dissolve 10 gram of potassium oxalate ($K_2C_2O_4.H_2O$) in 30 cm^3 of warm water. Add this solution to the previously prepared ferrous oxalate and mix thoroughly.

(b) Add <u>slowly</u> from a burette 25 cm^3 of 6% hydrogen peroxide, stirring the mixture continuously during the addition. The temperature of the mixture should be kept between 35°C and 50°C (DO NOT EXCEED 50°C). After all the hydrogen peroxide has been added heat the mixture **<u>just</u>** to boiling to destroy any excess hydrogen peroxide. During the addition of the hydrogen peroxide a **dark red-brown precipitate** will have formed. This is ferric hydroxide, which must be dissolved as set out below.

(c) Add (conveniently from a burette) 20 cm^3 of 10% oxalic acid rapidly with stirring. Then add **slowly with stirring** more 10% oxalic acid solution until all the ferric hydroxide dissolves. The solution at this stage will be a **clear lime green**. DO NOT ADD EXCESS OXALIC ACID.

(iii) Crystallization

Filter the hot solution obtained into a 250mL conical flask. Stir ethanol into the solution until precipitation occurs (approx. 30 cm^3) then heat on a hot plate or water bath until the solids just dissolve. Add a seed crystal of $K_3[Fe(C_2O_4)_3].3H_2O$ and allow to stand. About thirty minutes before leaving the laboratory collect the crystals by vacuum filtration. Wash the crystals on the filter with 10 cm^3 of 50% aqueous ethanol (i.e. a mixture of equal volumes of ethanol and water), then with 10 cm^3 of acetone. Weigh and label a large watch glass, add a filter paper to the watch glass and re-weigh. Spread the crystals onto the filter paper on the watch glass and allow them to dry in an oven at 50^oC for 10 minutes and at this stage record a melting point for the sample. Place your crystals in a labelled bottle (name of compound, your name, date of lab experiment) and hand in with your report.

3. CALCULATIONS AND QUESTIONS

Complete the sections in your report book for each step of the preparation with balanced equations for the reactions and an explanation in words for what happened.
Calculate the theoretical and percentage yields of your product. The percentage yield is defined as

$$\frac{Actual\ Yield}{Theoretical\ Yield}\ x\ 100$$

The theoretical yield is obtained from the balanced equation for the preparation, and the number of grams of a suitable starting material. The starting material chosen should preferably be a solid and must be one that is all consumed in the reaction. In the experiment the theoretical yield should be based on the potassium ions added as potassium oxalate ($K_2C_2O_4.H_2O$).

Question.
Why is oxalic acid or ferrous ammonium sulphate unsuitable for the theoretical yield calculation?

Draw a structure of the iron oxalate complex in your report book.

ASSIGNMENT 6
SPECTROSCOPY

NOTE A full report with gaps for you to fill in is **provided**. The purpose in doing this is to illustrate what is required in a full report. You should therefore read it carefully not just fill in the boxes. In most cases data may be entered directly into this report.

AIMS

This experiment is designed to:
(i) Introduce you to basic spectrophotometric theory.
(ii) Allow you to become familiar with a simple spectrometer.
(iii) To use spectroscopy to evaluate an equilibrium constant.

1. INTRODUCTION

Spectroscopy is an extremely important analytical technique which may be used to identify or to find the concentration of a wide range of substances. The range of applications is enormous, including such varied analyses as the determination of haemoglobin levels in blood and manganese levels in steel. In this assignment it is used to
allow determination of the equilibrium constant for the reaction.

$$2CrO_4^{2-} + 2H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O \qquad (\mathbf{1})$$

This constant, K_c, which is given by

$$K_c = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2} \qquad (\mathbf{2})$$

is difficult to evaluate by other means.
The object of this experiment is to determine the value of K_c.

1.1 The Absorption of Radiation

Many chemical substances are coloured. The colour of a substance arises when white light impinges on this substance and certain wavelengths are absorbed by the constituent molecules; the light which is transmitted to the eyes is therefore deficient in the absorbed wavelengths. Thus a substance which appears red to the eye is absorbing in the blue end of the visible spectrum.

Normally the absorption of a quantum of light excites an electron from its 'ground' state to a higher-energy 'excited' state within the absorbing molecule or ion. The energy difference between these two states, ΔE, must be supplied to the electron by the light quantum which will have a definite frequency ν, or wavelength, λ, given by the equation:

$$\Delta E = h\nu = hc/\lambda \qquad (\mathbf{3})$$

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

We might expect, then, that light absorption in the molecule or ion would occur at a characteristic wavelength (or frequency). In practice, the absorption occurs, not at a single wavelength, but over a small range of wavelengths (called an "absorption band"). This is centred about one wavelength, where maximum absorption occurs - the "absorption maximum", λ_{max} (Figure 1).

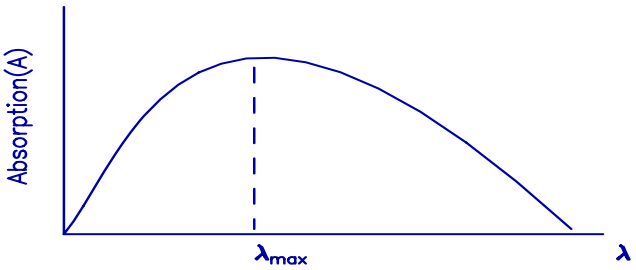


Figure 1. Absorption maximum.

The broadening of an absorption line to a band is due primarily to the fact that the ground and the excited electronic states each have associated with them a number of energy sub-levels within the molecule. Excitation of an electron to a range of levels is thus possible (Figure 2). The most likely excitation (corresponding to the absorption maximum) is usually that between the lowest vibrational sub-levels in the ground and in the excited electronic states. At room temperature most molecules are in the lowest vibrational level in the ground state. Inspection of Figure 2 will reveal that some transitions involve more, and some less, energy than that corresponding to maximum (most probable) absorption.

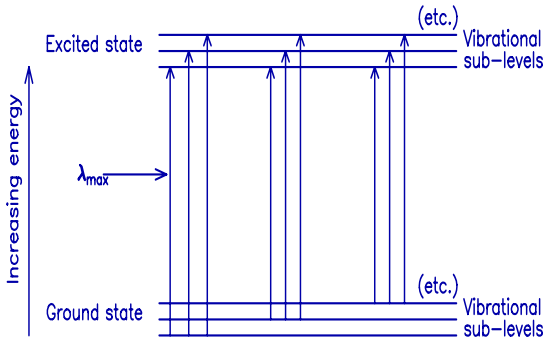


Figure 2. Possible electronic transitions.

1.2 The Beer-Lambert Law

The basic laws governing the absorption of light were formulated by Lambert (1760) and Beer (1852). The two laws have been combined to give a fundamental equation for the study of the absorption of light by solutions which is usually referred to as the **Beer-Lambert Law.** Since an absorption band involves a range of wavelengths, the **Beer-Lambert Absorption Law,** which relates quantitatively the extent of absorption to the concentration of the absorbing species, **must refer to a stated wavelength**; the law cannot refer to the absorption band as a whole.

$$A = log_{10}\frac{I_o}{I_t} = \varepsilon c l \qquad (4)$$

The Beer-Lambert Law may be expressed in the following form:

where A is the absorbance of the solution,

I_o is the incident intensity of light of a definite wavelength,

I_t is the transmitted intensity of light of the **same** wavelength,

ε is the **molar absorption coefficient** (sometimes called the molar extinction coefficient) at the stated wavelength and is a constant for a pure substance,
c is the concentration of the absorbing substance, and
l is the optical path length of the absorbing solution.

The experimental arrangement is shown in Figure 3.

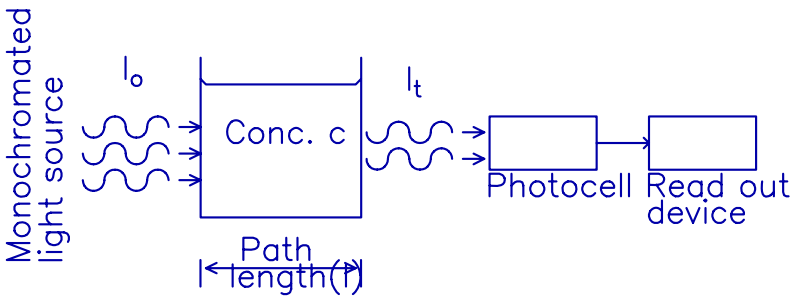


Figure 3. Schematic representation of spectrophotometer.

For a mixture of two absorbing substances, the observed absorbance A_{obs} is equal to the sum of the two individual absorbances A_1 and A_2, i.e.

$$A_{obs} = A_1 + A_2 = (\varepsilon_1 c_1 + \varepsilon_2 c_2)l \qquad (5)$$

Equation (5) enables a mixture to be analysed, provided one concentration is known. It also indicates that if the two absorption bands overlap, i.e. occur in the same wavelength region the observed "absorption band" is compounded from the two individual bands. Thus chromate ion has an absorption maximum at around 360 nm and its absorption band can overlap with the absorption band of dichromate ion which has an absorption maximum around 430 nm.

1.2.1 Applications of the Beer-Lambert Law: Spectroscopy

If the absorbance, A, is measured at a definite wavelength in a cell of known optical path length, then the Beer-lambert Law may be exploited for three important purposes.

(1) Measuring the **concentration of a substance** whose absorption coefficient is known or can be measured. The absorption coefficient, ε, is normally determined from the measured absorbances of a series of solutions of known concentrations (Part II of this experiment). Because the optical quality of instruments varies, ε should be determined with the same spectrophotometer which is to be used in any analysis based on an ε value.

(2) If a substance of known concentration is known to react stoichiometrically with a substance for which ε is known at a definite wavelength, then the former substance may often be quantitatively analysed by means of its reaction with the latter substance. For example, **alcohol** can be determined by reacting it with standard **dichromate**; the analysis involves measurement of the absorbance of the dichromate solution before and after reaction with alcohol.

(3) **Identifying an unknown substance** by means of its absorption spectrum by measuring ε for a range of wavelengths. Many physical and biological analyses exploit this possibility.

1.3 The Spectrometer

A **spectrometer** is an instrument designed to measure the radiation absorbed by substances. The analysis of solutions based on the quantity of light absorbed is called **spectrophotometry.**

A light source emitting a range of wavelengths shines into a monochromator which selects one wavelength - or a very small wavelength range - and allows the monochromatic light beam to pass through a sample contained in a vessel of accurately known path length. The incident light beam is absorbed somewhat in the sample and the transmitted light (**of the same wavelength** as the **incident light**) impinges on a suitable photoelectric device to measure the transmitted light intensity. The circuitry can be designed so that the reading of the instrument is **calibrated directly** in absorbance (and often percentage transmission).

The spectrophotometer used in this experiment is the Spectronic 21D. The instrument operates over the wavelength range at least 400-700 nm. White light passes through an interference glass filter, called a spectrum wedge, which selects a narrow range of wavelengths. This monochromatic light beam passes through a cell, which contains the sample, and then impinges on a photoelectric cell coupled to a meter. The measurement of absorbance involves a measurement of the **ratio of incident to transmitted light intensity** (see equation 4). In the spectrometer a cell containing only the solvent is first introduced into the light beam and the galvanometer attached to the photocell is balanced to zero. This procedure corrects for any **absorption by the solvent itself**. When the sample is moved into the light beam, the meter deflects since the light intensity transmitted by the sample, I_t, is less than I_o. In the Spectronic 21D the scale is calibrated directly in Absorbance.

2. EXPERIMENTAL

You will do this experiment **In Pairs**
Two pairs will work together on parts **2.1** and **2.2** (only on these 2 parts).
Pair A will complete **2.1**, Pair B will complete **2.2** and the results of these two parts will then be shared by both pairs.

This experiment consists of five sections:

(1) Measurement of the absorption spectrum of potassium dichromate.
(2) Measurement of the absorption spectrum of potassium chromate.
(3) Determination of a Suitable Wavelength for Determination of Dichromate
(4) Confirmation of the Beer-Lambert Law for potassium dichromate.
(5) Determination of the equilibrium constant for the chromate-dichromate equilibrium.

2.1 The Absorption Spectrum of Potassium Dichromate ($K_2Cr_2O_7$)

(1) Rinse and fill one cell with **2M sulphuric acid** and rinse and fill a second cell with **0.0016M potassium dichromate in 2M sulphuric acid.**

(2) Using the **2M sulphuric acid** as the reference, measure the absorbance of the potassium dichromate solution at intervals of 20 nm from 400 nm to 560 nm.

(3) Take several more measurements in the region of the absorption maximum For example if the absorption maximum occurs at about 500 nm, then take measurements every 10 nm for 480 nm to 520 nm.

(4) Enter the data in Table 1 of your Report book.

(5) Prepare a graphical plot of absorbance (as ordinate or Y-axis) versus wavelength (as abscissa or x-axis) Enter in Figure 1 of your Report book. THIS PLOT MUST BE PREPARED AND CHECKED WITH THE DEMONSTRATOR BEFORE GOING ON TO THE NEXT PART.

2.2 The Absorption Spectrum of Potassium Chromate (K_2CrO_4)

(1) Fill one cell with **1M sodium hydroxide** solution and fill another cell with a solution of **0.0004M potassium chromate in 1M NaOH.**

(2) Measure the absorbance of the chromate solution, using the 1M NaOH as reference, at intervals of 20 nm from 400 nm to 560 nm.

(3) Enter the data in Table 1 of your Report book.

(4) Prepare a graphical plot of absorbance (ordinate) versus wavelength (abscissa), also in Figure 1 of your Report book. THIS PLOT MUST BE ALSO BE CHECKED WITH THE DEMONSTRATOR BEFORE GOING ON.

2.3 Determination of a Suitable Wavelength for Determination of Dichromate

(1) Using the absorption curves obtained in 2.1 (potassium dichromate) and 2.2 (potassium chromate) select a wavelength at which the absorbance of the **chromate ion** is almost zero (less than 0.05) but where the **dichromate ion** still has appreciable absorbance. DISCUSS YOUR CHOICE WITH YOUR DEMONSTRATOR BEFORE PROCEEDING.

At this wavelength it is possible to determine the concentration of **dichromate ion** in a mixture of chromate and dichromate ions without interference from the **chromate** ion. Discuss your results in your Report book.

2.4 Confirmation of the Beer-Lambert Absorption Law

(1) Fill a reference cell with 2M sulphuric acid and fill four other cells separately with 0.4000, 0.8000, 1.200 and 1.600 mmol dm^{-3} potassium dichromate in 2M sulphuric acid.

(2) Using the 2M sulphuric acid as the reference, measure the absorbance of the four potassium dichromate solutions at the wavelength determined in 2.3. (**NOTE:** IN ORDER TO OBTAIN MEANINGFUL RESULTS THE CELLS MUST BE CLEAN AND THEIR OUTSIDES DRY).

(3) Enter the data in Table 2 of your Report book.

(4) Prepare a graphical plot of absorbance (as ordinate) at the wavelength determined in 2.3 versus dichromate concentration (abscissa) in Figure 2 of your Report book.
THIS PLOT MUST ALSO BE CHECKED WITH THE DEMONSTRATOR
BEFORE GOING ON.

(5) From the graph, determine whether the Beer-Lambert Law holds for your solutions, within the limits of experimental error. Discuss in your Report book.

(6) Assuming the law holds, calculate the molar absorption coefficient ε (unitless) for $Cr_2O_7^{2}$ at the wavelength determined in 2.3 and estimate the uncertainty in the answer.

2.5 Determination of the Equilibrium Constant

(1) Prepare a CHROMATE-DICHROMATE EQUILIBRIUM mixture as follows: Pipette 5 cm^3 of 0.0032M K_2CrO_4 in 1M NaOH into a **clean dry test tube.** Add (pipette) 5 cm^3 of 1.23M acetic acid and mix thoroughly by shaking. Transfer some of the resultant solution to a spectrophotometer cell The pH of this solution is 5.4.

(2) Using buffer pH 5.4 as the reference, measure the absorbance of the equilibrium mixture (i.e. the solution prepared in step 1) at the wavelength selected in 2.3. Remember that at this wavelength the measured absorption is due entirely to any **dichromate** ions present.

THIS VALUE MUST BE CHECKED WITH THE DEMONSTRATOR BEFORE LEAVING - IF INCORRECT THE WHOLE EXPERIMENT WILL FAIL.

(3) Using the absorbance measured in step 2, calculate the concentration of **dichromate** ion present in the equilibrium mixture. For this purpose use the value of ε (the molar absorption coefficient) calculated in 2.4.6 .

(4) From the concentration of **dichromate** ion measured in the equilibrium mixture and knowing the original concentration of **potassium chromate** used, together with appropriate dilution factors, calculate the concentration of **chromate ions** remaining in the equilibrium mixture. Enter the results in your report book.

(5) Calculate the hydrogen ion concentration ($pH = -\log_{10}[H]^+$). Enter in your report book.

(6) Using the value of dichromate, chromate and hydrogen ion concentrations calculated in steps 3, 4 and 5 respectively, and equation (2) calculate the value (INCLUDING UNITS) of the equilibrium constant for the chromate-dichromate equilibrium. Enter this in your report book as the value for K_c .

References

VOGEL, A.I. *Vogel's textbook of quantitative chemical analysis* (5th ed., 1989) Chapter 17 (or any other comprehensive textbook on quantitative analysis)

ASSIGNMENT 7
QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

AIMS

Experimental techniques are developed in this practical to characterise an organic compound on the basis of standard chemical tests and physical properties with emphasis on finding the functional group type.

1. INTRODUCTION

This experiment will illustrate how one can identify an organic compound on the basis of it's solubility, elemental composition, infrared spectrum and chemical reactivity. Most of the compounds examined will be relatively simple mono-functional species. The general procedure is outlined below:

2. EXPERIMENTAL

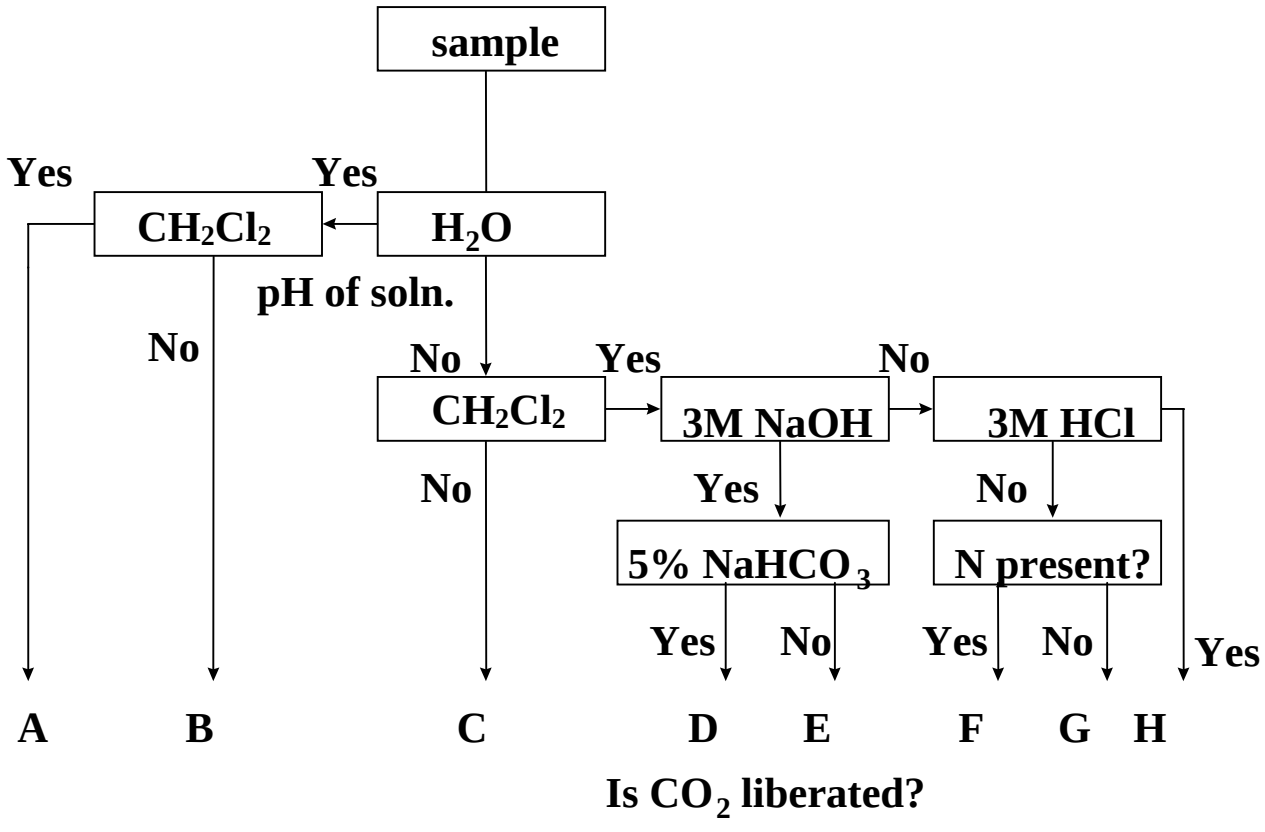
All sections will be carried out **in pairs**.

All operations will be carried out in a fumecupboard.

2.1 Determine the *melting point or boiling point* of the compound. Use the tables provided to narrow down the possible structure to about 4 possibilities. NB. Do not assume that your technique is good enough to obtain the exact literature melting point or boiling point!!!

2.2 Observe the *colour and odour* of the compound. Comment.

2.3 Solubility. Test the solubility of small amounts of the compound in a mL or two of the relevant solvents, as indicated in the following scheme:



For key A – H see over page.

KEY

A. Lower members of: Alcohols, Aldehydes, Ketones, Acids & Phenols (pH<7), Amines (pH>7).
B. Amino acids, Sugars, Salts of Acids or Amines, Some Amides.
C. Some Sugars and Amides.
D. Acids, Sulphonic Acids.
E. Phenols.
F. Nitro Compounds, Amides, Sulphonamides.
G. Hydrocarbons, Alcohols, Aldehydes, Ketones, Esters, Halo Compounds.
H. Amines.

2.4 Elements Present

It is possible to carry out chemical tests (e.g. Lassaigne tests) to determine whether the test substance contains the elements S, N or halogen (Cl, Br, I). However, such tests can be hazardous under the conditions of the *first* year laboratory and therefore will not be performed. Instead, you will be told what elements are present in a particular compound.

2.5 Infrared (IR) spectroscopy: Determination of functional groups present

As indicated in the lecture course, infrared spectroscopy may be considered as a "functional group detector". This is because particular functional groups show infrared absorptions at characteristic frequencies. Typical absorption frequencies for the major functional groups are summarised in Chart 1.

Use the tables provided to predict the major functional group(s) present in the compound. In some cases you will now have narrowed the possibilities down to one compound. In other cases, the compound may still be one of two or three possibilities. In any case, you must test your conclusions by carrying out some of the chemical tests indicated below.

3. Specific chemical tests for functional groups:

The following reactions will establish the presence or absence of specific functional groups.

3.1 Alkenes

The presence of double (and triple) carbon-carbon bonds can be detected by their addition reactions with bromine. Alkenes decolourise bromine instantly at 0º without the evolution of HBr (i.e. no white fumes when the stopper of an ammonia bottle is held at the top of the tube). Many other groups decolourise bromine but with the evolution of HBr. The latter reactions are substitutions not additions. Compounds that decolourise bromine with the evolution of HBr include phenols, aldehydes, ketones, aniline and others.

If the compound is organic soluble, add it (0.1 g or 3 drops) to dichloromethane dropwise with shaking, so that it dissolves. Now add a few drops of Br_2 / CH_2Cl_2 solution. **Do this under the fumehood, as Br_2 is corrosive, toxic and has a CHOKING ODOUR.** Take the NH_3 stopper and hold above the test tube.

If the compound is water soluble, test with bromine water. Take the NH_3 stopper and hold above the test tube.

3.2 Phenols: (Solutions of water soluble phenols have pH <7).

Phenols form coloured coordination complexes with Fe^{3+}.

Add the **test compound** to 2 mL of water and treat with 2 drops of ferric chloride solution. Repeat with ethanol as solvent. If a transient or permanent coloration is produced, the compound is a phenol. The colour may be characteristic of a particular phenol.

3.3 Carbonyl Groups in Aldehydes and Ketones

As you know from Assignment 3 a characteristic reaction of aldehydes and ketones is their conversion to a bright yellow or orange insoluble hydrazone in acidic dinitrophenylhydrazine solution. This has a well defined melting point that may be used to characterize the parent aldehyde or ketone more readily than a boiling point.

Add the DNP reagent (2 mL) to a small sample of the test substance (dissolved in a minimum volume of ethanol if it is a solid), and shake. if no precipitate forms immediately, warm and allow to stand 5 minutes. (NB Amines sometimes give a precipitate!).

3.4 Distinction between aldehydes and ketones:

Aldehydes are oxidised rapidly (to carboxylic acids) and thus are reducing agents. Ketones cannot be oxidised easily and are not reducing agents.

Schiff's Reagent This is a dye which is a pinkish-purple colour in its oxidised form, and colourless (often pale pink) in its reduced form. Sulphur dioxide is used to keep the dye in the reduced form. Aldehydes remove the sulphur dioxide (through the formation of bisulphite addition compounds) and the coloured form of the dye is generated through atmospheric oxidation. Ketones do not react with sulphur dioxide (neither do some aromatic aldehydes) and the solution remains colourless.

Shake the test substance with a few mL of Schiff's Reagent (do not heat). Development of a pinkish-purple colour in the aqueous layer within a minute indicates that the substance is an aldehyde. For compounds that give a negative test and appear to be insoluble, repeat the test using a small quantity dissolved in a minimum volume of alcohol. Run a blank test using alcohol alone for comparison.

3.5 Amines

The presence of an amino group will be indicated by solubility in aqueous acid (already tested in **2.3**) and one of the elements present being nitrogen (part **2.4**). May also fall in solubility group A, with the pH of water solution >7. Low molecular weight amines have a characteristic fishy odour which also helps in the identification of this class of compound.

3.6 Carboxylic Acids

A carboxylic acid will fall into solubility group D (already tested in **2.3**) and will give a negative phenol test. May also fall in solubility group A, with the pH of water solution <7.

The common test for a carboxylic acid is to react a solution of the acid with sodium bicarbonate solution. The reaction of bicarbonate with an acid will generate CO_2.

3.7 Esters

Esters can be converted to hydroxamic acids by treatment with hydroxylamine. The hydroxamic acids thus produced form violet coloured coordination complexes with Fe^{3+}.

Treat about 0.1 g (or < 0.5 mL) of the compound with 1 mL of 5% hydroxylamine hydrochloride solution in methanol. Add enough methanolic KOH to make the mixture alkaline. Heat on a water bath until hot (steaming) and then allow to cool. Acidify with dilute HC1. Add a drop of ferric chloride. A violet (or claret) coloration indicates that the test substance is an ester.

3.8 Amides

Primary amides ($RCONH_2$) are hydrolysed to ammonia and a sodium salt of a carboxylic acid in hot sodium hydroxide solution.

Heat on a water bath a sample of the test compound with a few mL of 3M sodium hydroxide solution. Test for ammonia by gently smelling and by placing moist red litmus paper near the mouth of the tube. The carboxylic acid will remain in solution as the sodium salt, but in some cases can be precipitated by acidification with 3M hydrochloric acid. (NB The latter step will only produce a precipitate if the carboxylic acid is not very water soluble)

4. Investigation of Known compounds:

The following compounds have been chosen so that you can observe what a positive result looks like for each test. Take a few drops (or tip of a spatula if it is a solid) of the compound to be tested, place it in a test tube and carry out the following tests. (N.B. **carry out only those tests that are needed for that class of compound**). Note down reasonably detailed observations of what happened in your report book. Afterwards wash your test tube into the organic residues jar using acetone to wash it out - **keep all smelly test tubes in the fume cupboard**.

(i) Test for an amine: Test the solubility of aniline in water and in 3M HCl.

(ii) Test for a carboxylic acid: Test a solution of benzoic acid with sodium bicarbonate solution.

(iii) Test for the presence of multiple bonds: Carry out test 3.1 on 1 mL or so of a solution of cholesterol, and on 3 drops of aniline.

(iv) Test for a phenol: Carry out test 3.2 on 3 drops of o-methoxyphenol.

(v) Test for aldehydes and ketones: Carry out tests 3.3 & 3.4 on acetone and on aqueous benzaldehyde solution.

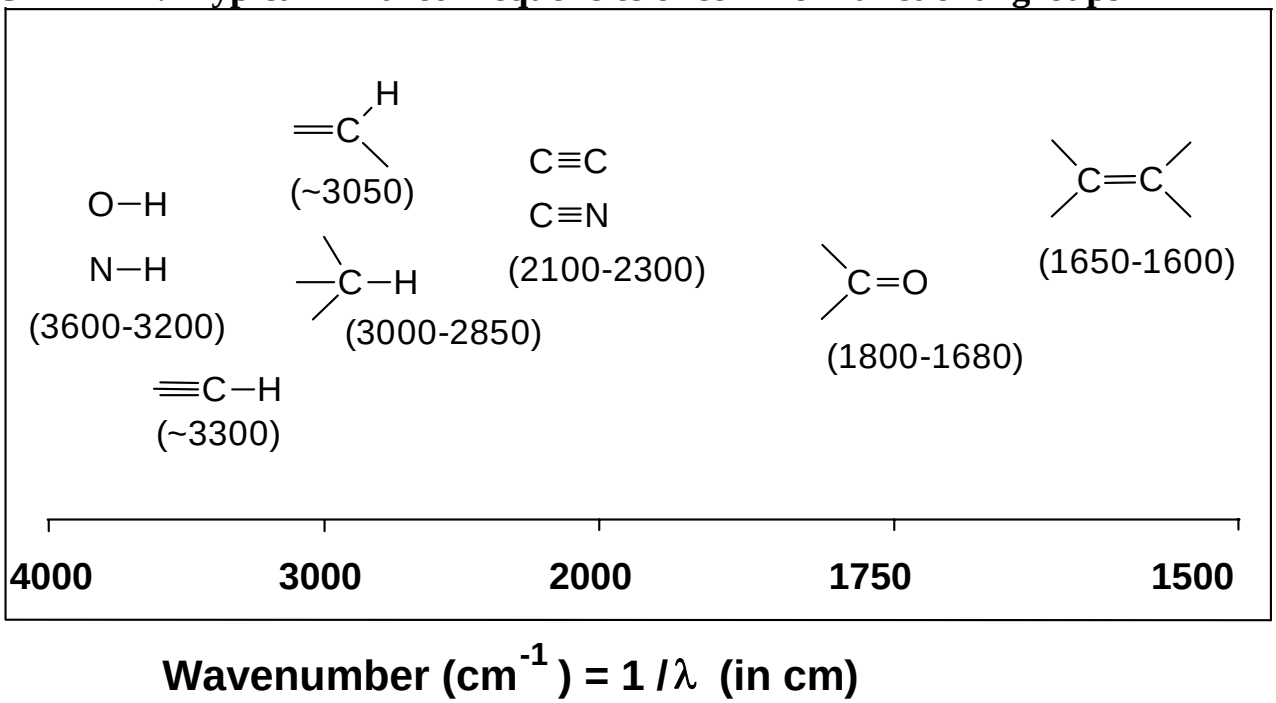
(vi) Test for an ester: Carry out test 3.7 on ethyl acetate.

(vii) Test for an amide: Carry out test 3.8 on acetamide.

Report your experimental observations and chemical equations for the tests (i) - (vii).
The equations should serve as explanations for your observations.

You will not be allowed to leave the laboratory until your tutor has examined your results and equations. if you have failed to observe important features of a particular positive test result, you will be required to repeat the test.

CHART 1. Typical Infrared frequencies of common functional groups



Wavenumber (cm^{-1}) = 1 / λ (in cm)

5. Unknowns:

After the completion of Part 4 you will be familiar with all the chemical tests required to qualitatively identify an organic compound within the range of functional groups that you were presented with and you will know what a positive test result looks like for each functional group.

You will now be assigned an unknown compound, either a solid or a liquid, and you will then be asked to identify this unknown compound by determining each compound's functional groups (carrying out the diagnostic tests) and using this information in conjunction with the tabulated data below and the tables displayed in the laboratory.
You should do this without discussion with anyone but your partner.

Chemical information on the unknowns is provided in the tables below and an approximate m.p. or b.p. value is given in the tables for each unknown (within a couple of degrees Celcius).
Begin with tests 2.1 to 2.5 and then use the tables provided to narrow down the structure of the unknown to a few possibilities.
Now carry out selected tests (from 3.1 - 3.8) to confirm the identity of your unknown.

Record your results in your report book.

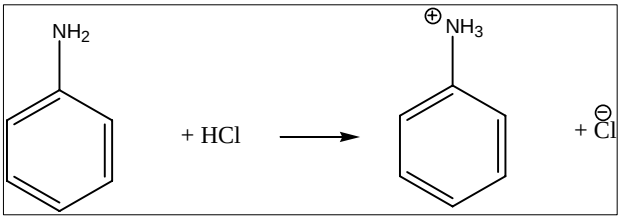
Table 1 Additional elemental, boiling point and IR data for liquid samples

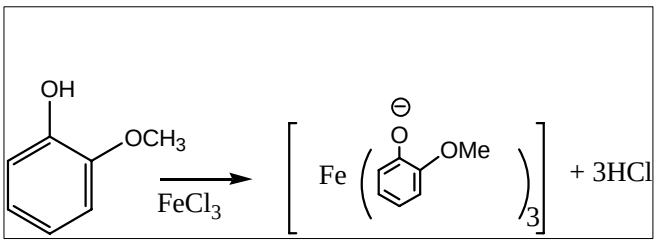
Liquid no	**Elements present**	**Infra-red absorptions cm^{-1}**	**Boiling Point(^oC) - approx**
1	C, H, O	1745, 1150	76
2	C, H, O	3500 broad, 1700	-18
3	C, H, Br	3050, 1605	150
4	C, H, O	1710	154
5	C, H, O	3050, 1695, 1600	177
6	C, H, N	3300, 3050, 1602	180

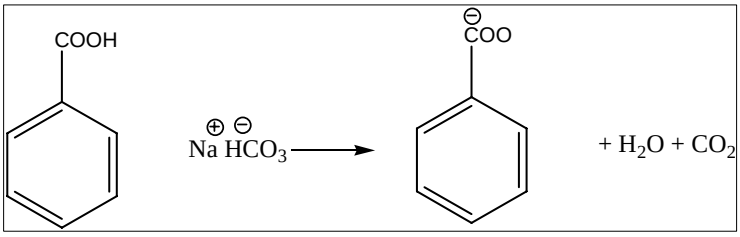
Table 2 Additional elemental, melting point and IR data for solid samples

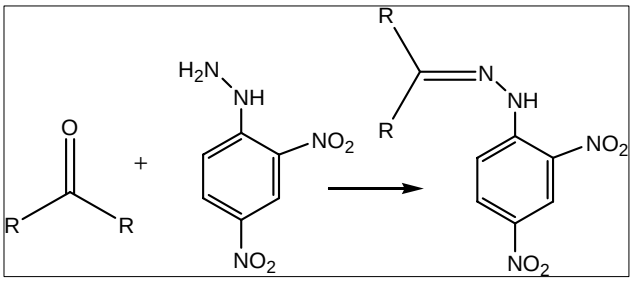
Solid no	**Elements present**	**Infra-red absorptions cm^{-1}**	**Melting Point (^oC) - approx**
1	C, H, Cl	3050, 1603	52
2	C, H, N, Cl	3300, 3050, 1600	71
3	C, H, N, O	3050, 1693, 1602	105
4	C, H, O	3500 broad, 3050, 1675 1630, 1600	131
5	C, H, O	3500 broad, 3050, 1675 1600	121
6	C, H, N, O	3050, 1602	53
7	C, H, O	3300 broad, 1630, 1600	122

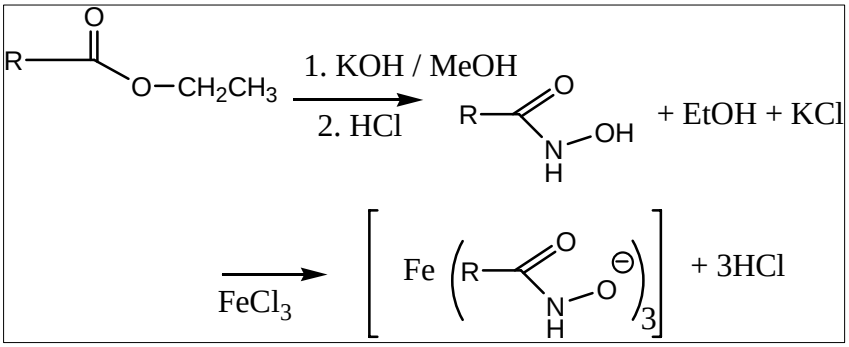
Relevant Equations

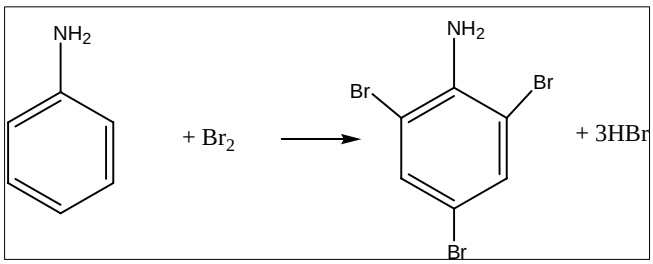


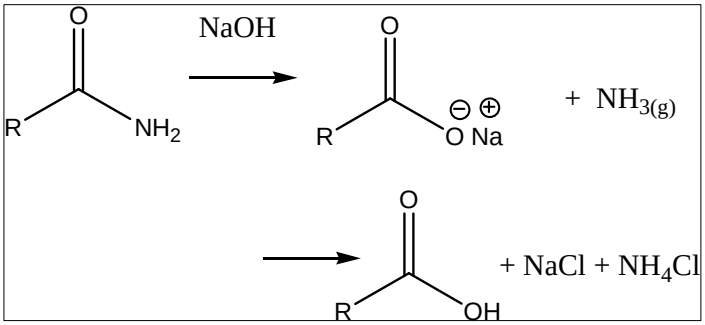


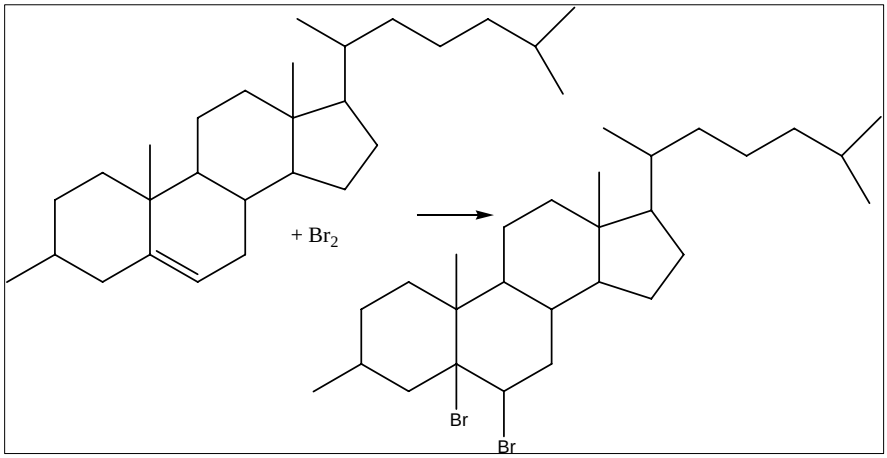












ASSIGNMENT 8
ELECTROPHILIC AROMATIC SUBSTITUTION AND NUCLEOPHILIC SUBSTITUTION AT SATURATED CARBON

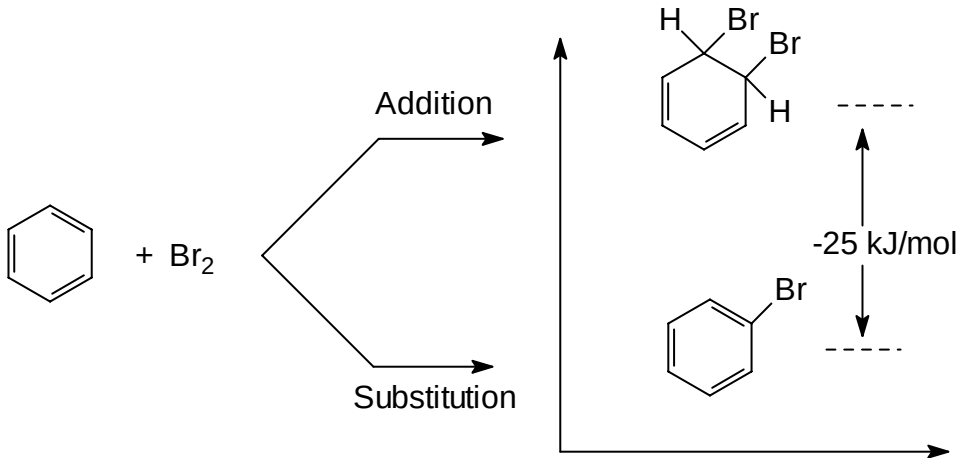
AIMS

Familiarization with standard electrophilic aromatic substitution and nucleophilic substitution reactions of preparative organic chemistry.

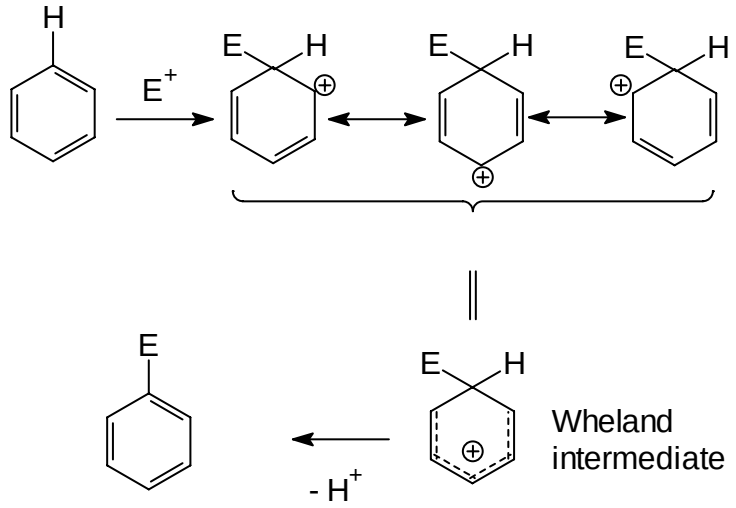
Part 1. Electrophilic Aromatic Substitution: Preparation of 2,4,6- tribromoaniline.

1. INTRODUCTION

Aromatic compounds have a characteristic closed shell of (4n + 2) π electrons. They are typified by an elemental composition indicating many degrees of unsaturation, but their reactions are not those of normal alkenes or other unsaturated compounds. In particular, aromatic compounds undergo electrophilic substitution rather than addition reactions. Addition is unfavourable with aromatic compounds because it would lead to a loss of aromatic stabilisation energy, whereas substitution allows the resonance stabilisation to be maintained:



The mechanism of electrophilic substitution is well understood and is generally portrayed as indicated below.



Substituents on the benzene ring have a marked effect on the outcome of electrophilic substitution reactions. Substituents which are capable of pushing electron density into the ring (e.g. NH_2), make the ring increasingly susceptible to electrophilic substitution, especially at the *ortho* and *para* positions. By contrast, groups which withdraw electron density from the ring (e.g. NO_2) deactivate the ring towards electrophilic aromatic substitution. This is demonstrated by the observation that nitrobenzene will only undergo electrophilic substitution under forcing conditions and then only at the *meta* position.

Aniline ($C_6H_5NH_2$) has a highly activated aromatic ring and bromination proceeds at low temperature to give 2, 4, 6-tribromoaniline, with only extremely low quantities of mono and dibrominated aniline being produced.

2. EXPERIMENTAL You will do this experiment **In Pairs**.

All operations will be carried out in a fumecupboard.

Half the class will start on 2.1 and the other half on 4.1.

2.1 2,4,6- Tribromoaniline: Electrophilic substitution on an activated aromatic ring

Complete the flow sheet before commencing experimental work (see Notes on Organic Chemistry at the front of this book for an example of format) and have this checked by your demonstrator.

WARNING: Take care with bromine and aniline as they are volatile & toxic. Check the MSDS!

Dissolve aniline (1 mL, from a dispenser) in glacial acetic acid (17 M, 6 mL, from a dispenser) in the fumecupboard and add dropwise (over 2 minutes) with shaking and cooling (in ice water) a solution of bromine in acetic acid (30% V/V, 7.0 mL, from a dispenser) in a 150 mL conical flask. Dilute the reaction mixture with water (15 mL). In the fumecupboard and quickly vacuum filter off the product using suction and wash it well with water, transfer the washings to the residues container in the fumecupboard. Recrystallise the product from a minimum volume of boiling ethanol (N.B. you must use bumping chips in the ethanol flask). Vacuum filter the cooled product after around 1/2 hour has passed. Transfer the product to a weighed petri dish. Once the purified product is completely dry (this will take at least overnight in the drying oven) weigh it and record its melting point (ca. 120^0 C).

Using the density of aniline (ρ = 1.02 g/mL) calculate the theoretical yield for the reaction and the % yield you obtained, aniline is the limiting reagent in this reaction. Hand in your product with your report book.

2.2 CALCULATIONS AND QUESTIONS

Complete the reactions and discussions required in your report book.

Question 1. Write an equation for the bromination of cyclohexene and comment on the difference between this and the bromination of aniline.

Part 2. Nucleophilic Substitution Reaction: Preparation of *t*-butyl chloride and distillation.

3. Introduction

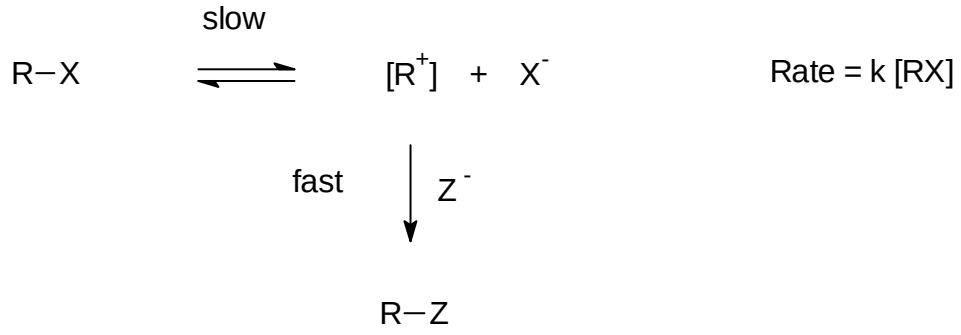
Nucleophilic substitution at saturated carbon is one of the most widely studied classes of organic reactions

$$R\text{-}X + Z^- \rightarrow R\text{-}Z + X^-$$

Two major mechanisms for such reactions have been identified:

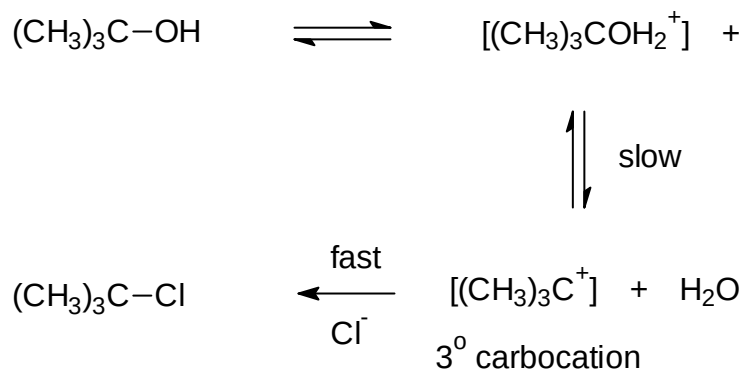
S_N^1 Reactions: These are characterised by first order kinetics in which the rate of substitution is proportional only to the concentration of the substrate [RX] and not to that of the nucleophile [Z].

The mechanism proposed to account for these kinetics and other experimental observations, involves a rate determining, unimolecular ionisation of the substrate to give a carbocation intermediate, which then reacts rapidly with the nucleophile to give the substitution products.

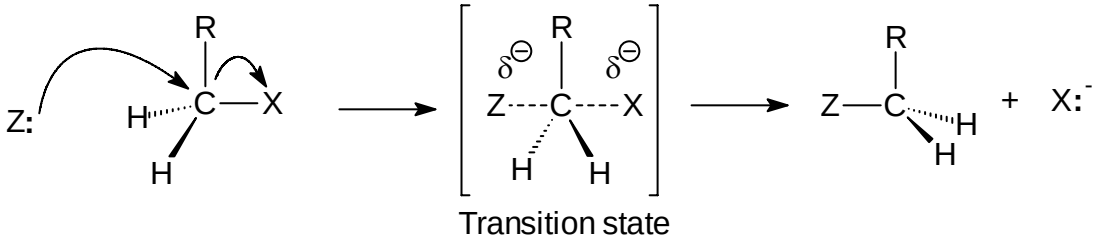


The carbocation intermediate is stabilised by alkyl substitution and for this reason the S_N1 mechanism is most often observed for tertiary substrates R_3CX (e.g. alkyl halides, sulphonate esters, etc.).

In this experiment you will prepare *t*-butyl chloride from *t*-butyl alcohol. The reaction proceeds *via* the protonated alcohol, which is formed when the alcohol is treated with concentrated hydrochloric acid. This intermediate then dissociates to give water and a tertiary cation, which is quickly trapped by a chloride ion to give the final product, *t*-butyl chloride.



S_N2 Reactions: These are characterised by second order kinetics, i.e. the rate of substitution is proportional to the concentrations of both the substrate [RX] and the nucleophile [Z^-]. The mechanism proposed to account for these kinetics is indicated below. The mechanism shown also accounts for the fact that when optically active substrates undergo this reaction, an inversion of configuration is observed.



In contrast to the S_N1 case, the S_N2 mechanism involves rate-determining bimolecular attack of the nucleophile on the substrate in a single step reaction. This mechanism is most often observed for primary substrates (i.e. RCH_2X) which offer little steric hindrance to attack by the nucleophile and form carbocations much less readily than tertiary substrates. Secondary substrates (i.e. R_2CHX) can undergo substitution by either mechanism depending on the conditions of the reaction.

4. EXPERIMENTAL You will do this experiment **In Pairs**.

All operations will be carried out in a fumecupboard.

4.1 Preparation of t-butyl chloride

WARNING: ***t-butyl chloride boils at 51ºC (i.e. it is more volatile than acetone or methanol) and should be stored in a sealed container when it is prepared.***

Carry out the following manipulation in the fume cupboard.
In a 500 mL separatory funnel place *t*-butanol (2-methyl-2-propanol) (20 mL, from a dispenser) and concentrated hydrochloric acid (60 mL, from a dispenser). Carefully swirl the funnel for a few minutes with the stopper off so that no pressure builds up in it. Stopper the funnel and carefully invert it and open the tap to relieve the pressure. Shake the funnel over a 15 min period, relieving the pressure more frequently at the start and then every 5 minutes as time goes on (N.B. this whole operation is carried out in the fumecupboard). Return the funnel to its stand or clamp and remove the stopper. Allow the layers to separate completely and run off the lower acid layer. Add 40 mL of water and again shake carefully, relieving pressure until no further fizz or hiss is heard on opening the tap. Run off the lower water layer. Carefully wash the t-butyl chloride remaining in the funnel with 25 mL of 5% sodium bicarbonate solution to remove any residual acid and again run off the lower aqueous layer. Swirl the funnel so that the remaining water droplets fall to the bottom; the sides of the funnel should appear dry of water. Run off this water, and allow a few drops of your product to enter the tap. The t-butyl chloride is then poured out of the funnel through the top (not through the tap!) into a clean, dry conical flask. Add a few pieces of calcium chloride to dry the halide and stopper the flask. Once dry the liquid should appear clear.

Combine your product with that of one other student and purify it by distillation. Before you do this you should have read the "Distillation" part of the section "Techniques of Organic Chemistry" Collect a box of distillation apparatus and seek advice from your tutor on how to set it up. Be careful, "Quickfit" apparatus is fragile and expensive. Place the liquid sample in the distillation flask, add a few boiling chips and then assemble the remainder of the apparatus. Use a sand bath or a water bath (But not a bunsen!!) to supply the heat. Remember to make sure that the distillation flask is secure and that a stream of water is passing through the condenser, from the bottom to the top. Record the boiling point *(ca.* 50 ^{0}C) in your report book, measure the volume of sample using a measuring cylinder and submit the purified sample of *t*-butyl chloride to your tutor for inspection. Once the tutor has seen your purified product, discard it by pouring it into the appropriate waste bottle.

Using the density of t-butanol (ρ = 0.786 g/mL) and the density of of t-butyl chloride (ρ = 0.851 g/mL) calculate the theoretical yield for the reaction and the % yield you obtained, t-butanol is the limiting reagent in this reaction

4.2 CALCULATIONS AND QUESTIONS

Complete the reactions and discussions required in your report book.

We have seen how facile a reaction t-BuOH $\xrightarrow{HCl}$ t-BuCl is; by contrast the preparation of *n*-butyl bromide from *n*-butanol requires more drastic reaction conditions:

viz $CH_3CH_2CH_2CH_2OH + NaBr \xrightarrow[80^o]{H_2SO_4(conc.)} CH_3CH_2CH_2CH_2Br$

Question 2. Explain the difference in the relative ease of these two reactions.

ASSIGNMENT 9
REACTIONS OF CARBONYL COMPOUNDS

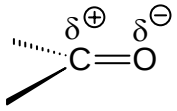
Part 1. Nucleophilic addition to Ketones and Aldehydes

AIMS

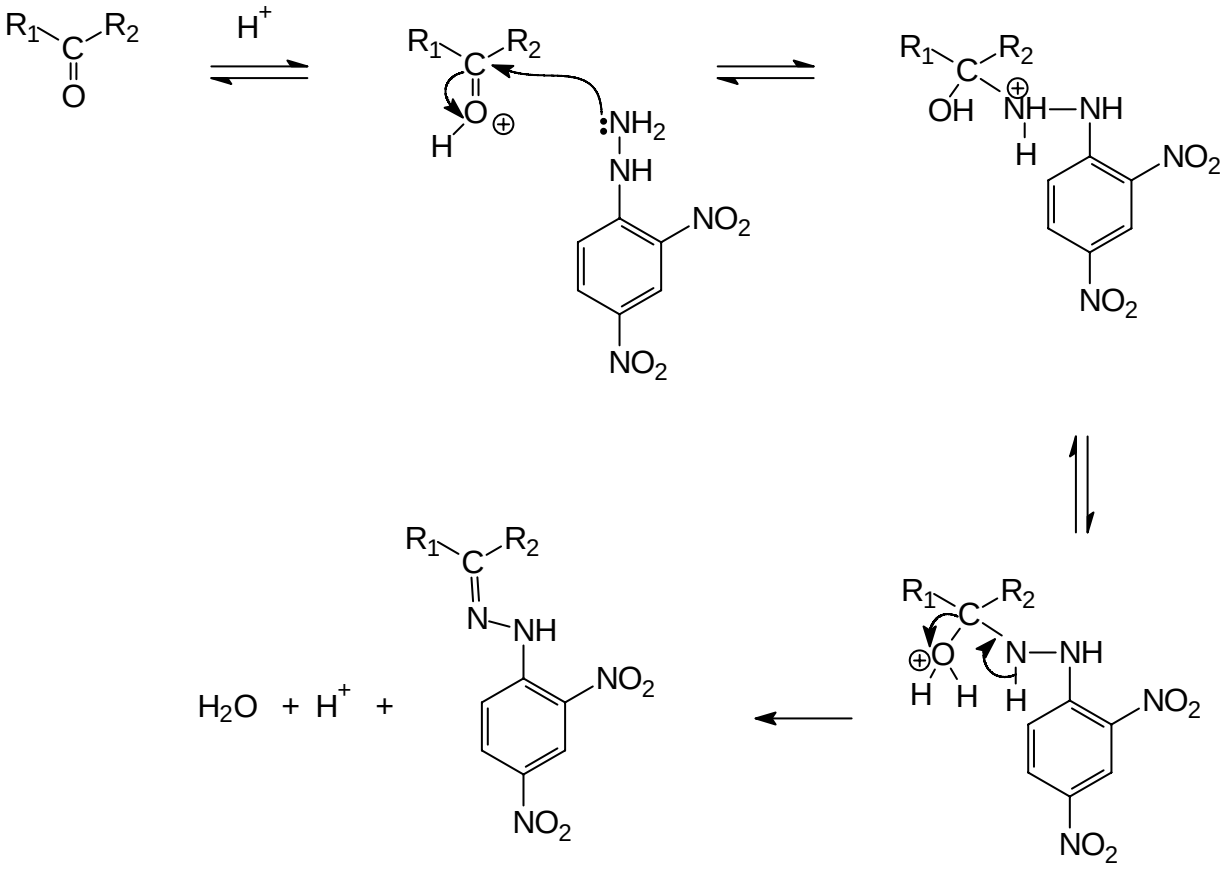
An introduction to the practical aspects of nucleophilic addition to ketones and nucleophilic substitution of carboxylic acids. New techniques such as making derivatives and boiling point determinations will be used.

1. INTRODUCTION

As indicated in the diagram below, the carbonyl group is polarised such that the carbon carries a partial positive charge and the oxygen a partial negative charge.



This makes the carbon atom susceptible to nucleophilic attack. However, since the carbonyl group is unsaturated, the actual reaction that occurs is a nucleophilic addition. This process is sometimes aided by protonation of the carbonyl oxygen. In the case of ketones and aldehydes, DNP derivative formation is a very good example of this. The DNP reagent consists of 2,4-dinitrophenylhydrazine in a sulphuric acid solution. The acid protonates the carbonyl oxygen of the ketone or aldehyde and the nucleophilic hydrazine nitrogen attacks the carbonyl carbon. Elimination of water then leads to the hydrazone or DNP derivative.



2. EXPERIMENTAL

You will do this experiment **In Pairs**.

You will be provided with a sample (ca. 1 mL) of an unknown carbonyl compound (either A, B or C). Note down in your report book which sample you have. Complete and have checked your flow chart before starting the experimental section proper. You will work **in pairs**.

2.1 Boiling Point Determination

Take approximately 0.5 mL of the sample and determine the boiling point by the Siwoloboff technique (consult the notes on "Techniques of Organic Chemistry" for detailed instructions). For Sample A place oil bath on the bench for the other samples place the oil bath in the fumecupboard.

2.2 Preparation of 2,4-dinitrophenylhydrazone (DNP) derivative

Handle the DNP reagent carefully is a suspected carcinogen.

To 20 mL of DNP reagent (from a dispenser) in a test tube or small conical flask add your unknown carbonyl compound. For unknown A add 50-60 drops; for B and C use 25-30 drops. Allow the mixture to stand for 5 min and filter off the derivative by suction filtration. The residues are transfered to the residues beaker in the fumecupboard. Recrystallise the crude derivative from ethanol, wash with ethanol (see the notes on "Techniques of Organic Chemistry" for detailed instructions on how to recrystallise a sample from a flammable solvent). Once the purified product is completely dry, determine its m.p.

Use the chart of literature values below to identify the unknown carbonyl compound. Check your conclusions with your demonstrator and submit the derivative with your report book.

Carbonyl Compound	b.p.	m.p. of DNP Derivative
propanal (propionaldehyde)	49	155
propanone (acetone)	56	128
2-methylpropanal (*iso*-butyraldehyde)	64	187
butanal	75	123
butanone	80	115
pentan-3-one	102	156
cyclopentanone	131	146
cyclohexanone	156	162
benzaldehyde	179	237
cycloheptanone	180	148
salicylaldehyde	197	252

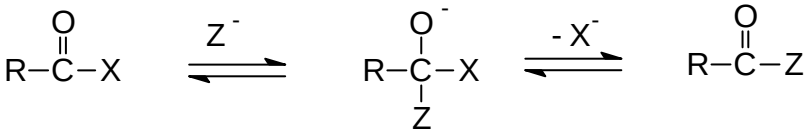
3. CALCULATIONS AND QUESTIONS

1. Write equations for three other reactions involving nucleophilic addition to the carbonyl group of an aldehyde or ketone.

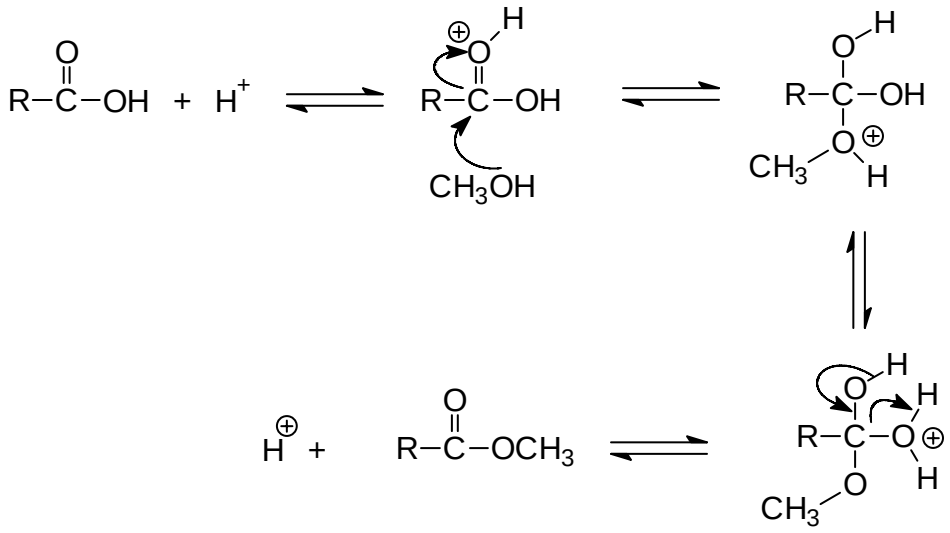
Part 2. Nucleophilic substitution of Carboxylic Acids & Esters: Esterification & ester hydrolysis

4. INTRODUCTION

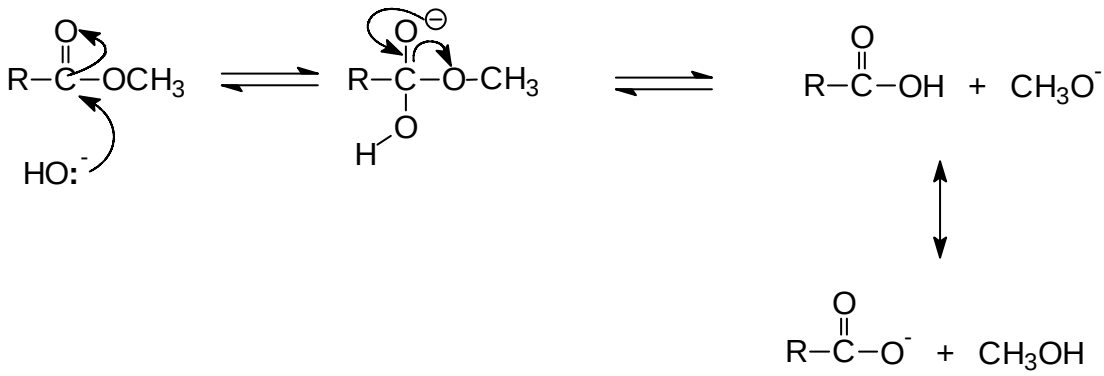
Even though carboxylic acids and their derivatives (acid chlorides, esters etc.) of the general structure R-C(O)X contain a carbonyl group, they show quite different reactivates to those of aldehydes and ketones. Carboxylic acids and their derivatives **are** susceptible to nucleophilic attack, but after the initial attachment of the nucleophile, an alternative reaction, namely the loss of X-, can occur. The **overall** process is thus a **substitution reaction**.



An example of this is the acid catalysed esterification of a carboxylic acid with methanol, shown below**.**



The reverse reaction, ester hydrolysis, can be carried out under basic conditions:



As an illustration of these processes you will prepare methyl salicylate (active ingredient of Dencorub and many heat treatment creams for sore muscles) and carry out its hydrolysis to salicylic acid.

5. EXPERIMENTAL

All operations will be carried out in a fumecupboard.

5.1 Qualitative esterification of salicylic acid:

Place methyl alcohol (≈ 1 mL, from a dispenser) in a test tube and add to it a little solid salicylic acid, $C_6H_4(OH)(COOH)$. Then add a few drops of concentrated sulphuric acid and shake gently to dissolve the salicylic acid. Stand the test tube in hot water for ten minutes. Do not boil the liquid in the test tube. Pour the contents into water in a 100mL beaker, and note the characteristic odour of methyl salicylate.

5.2 Preparative alkaline hydrolysis of methyl salicylate:

Now perform the reverse reaction of esterification. Add 20 mL of 10% sodium hydroxide to 1 mL of methyl salicylate (*N.B. this is the pure reagent it is NOT from 5.1*) in a 100mL conical flask. Boil the mixture very gently in a small flask until any solid matter which may have formed has dissolved. Cool the flask in ice and add concentrated hydrochloric acid dropwise until all the liquid appears to have been replaced by a thick white paste (-5 mL of conc. HCl should be required). Filter off the sparingly soluble salicylic acid and wash it with a little cold water. Suck the precipitate dry using vacuum filtration as well as possible, and recrystallise it from a minimum volume of boiling water. Oven dry the material at 50oC for 1 day (no more than 1 day). Once the purified product is completely dry, weigh it and record its melting point. Compare the melting point (range) you obtained with the literature melting point**.**

Using the density of methyl salicylate (ρ = 1.17 g/mL), calculate the theoretical yield for the reaction and the % yield you obtained. Hand in your product with your report book.

5.3 QUESTIONS

2. Draw the formulae of salicylic acid and methyl salicylate.

3. Can you suggest another method of preparing methyl salicylate from salicylic acid? (Consult your textbook - McMurray).

4. Describe briefly how **pure** methyl salicylate could be obtained from your preparation.

Hint: Consultation of the "Extraction Procedures" section of the "Techniques of Organic Chemistry" may be of help.

RIP OUT SECTION

These notes are intended as a work book for this part of the course.

Please make comments on any part of the course here as you go along and then at the end of the course make sure you rip out this section and return it to the Chemistry Department box. This will enable the course to be improved with time and at the same time ensures that THIS IS NOT A RE-SALEABLE ITEM.