UNIVERSITY OF NAIROBI DEPARTMENT OF CHEMISTRY

CHEMISTRY 2

ORGANIC CHEMISTRY PRACTICALS FOR ENGINEERING STUDENTS

Academic year: 2015

Prepared by:
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LABORATORY RULES

1.   Laboratory overalls (coats must be worn at all times by persons while in the laboratory.

2.   Students are fully responsible for the security of their locker of apparatus and will be charged for broken or missing apparatus and glassware that has been issued to them.

3.   Benches, lockers and apparatus must be put away and bench tops left clean and tidy. All apparatus must be put away and bench tops left clean at the end of each laboratory period. Apparatus left on the bench top at the end of a class (or found dirty in lockers at the end of the course) will be charged for as though broken.

4.   Many organic liquids and their vapours are highly flammable. They must not be handled near, or heated in an open vessel by, a Bunsen burner flame for fear of causing a fire.

5.   Waste must be put into a suitable container. (some solvents can be purified for re-use and should be put in the recovery bottles provided). Other liquids should be poured down the sink and washed away with plenty of water. Solids, including waste paper, must be put in the boxes provided. Broken glass must never be put in the sink: it causes blockage of pipes and can give serious cuts to the hands.

6.   Smoking, eating and drinking while in the laboratory are prohibited.

Practical Organic Chemistry deals with the reactions of carbon compounds whose molecules are mainly covalent in character. Single (two electron, sigma) bonds between carbon atoms, and between carbon and hydrogen atoms are relatively strong and relatively difficult to break in a chemical reaction. Organic molecules can therefore usually be regarded as having a stable carbon skeleton e.g. as in the molecule propane a typical alkane.

Bonds between carbon or hydrogen and other atoms present in the molecule (hetero-atoms) are often weaker and partially polarized: they are therefore more easily broken in a chemical reaction. Common hetero-atoms are O, R, Halogens, less common ones are S and P (all of which are to the right of carbon in the periodic table and therefore more electronegative than carbon). The presence of one or more hetero-atoms usually results in a more reactive centre in the molecule known as the **functional group.**

Many liquid covalent compounds also have a characteristic boiling point, which combined with a knowledge of the chemical reaction (i.e. of the functional group present) can assist in determining the approximate molecular structure and complexity:

THE PRACTICAL COURSE

This course will consist of a series of exercise which will introduce and apply several operations; or techniques, which are frequently used in practical organic chemistry, e.g.

1. **Determination of the Melting Point of a solid.**
2. **Investigation of monofuctional organic compounds containing the elements carbon, hydrogen and (probably) oxygen only**
3. **Boiling point of a liquid using Siwoloboff method**
4. **Crystallization of a solid from a solvent,**
5. **Synthesis of Aspirin.**

(Other techniques used for separating mixtures of organic compounds, such as fractional distillation, steam distillation, chromatography, etc will be introduced at a later date).

In addition, practice will be give in the identification of hetero-atoms in organic molecules and in the recognition of functional groups by their characteristic chemical reactions. Procedures for transforming one functional group into another (a process known as preparation or synthesis) will also be introduced.

Identification of unknown compounds will become possible by investigation of their chemical reactions, thereby identifying the functional group present and by

determination of physical properties and comparing these with the "literature", i.e. data in textbooks, handbooks and collected copies of information on organic compounds.

The group of atoms the hydroxyl functional group has characteristic reaction, which are largely independent of the carbon skeleton to which it is attached and for which tests can be made whereby it can be recognized..

In this way a class of organic compounds, the alcohols, can be recognized as having a common set of chemical reactions. Because of the presence of the –OH group, the class of alcohols can also be the presence of –OH group, the class of alcohols can also be identified by having similar interactions with infra-red radiation as measured by the infrared absorption spectrium. Interpretation of this physical measurement is now an important guide to the functionality of organic molecules.

Molecular environment can alter the chemical reactivity of a functional group. A good example is when the –OH group is attached **directly** to a benzene ring, as in phenol, PhOH, which is much more acidic than propanol, and is chemically easily recognizable because of this acidity. However, in benzyl alcohol, $PhCH_2OH$, where the benzene ring and the OH group are separated by CH_3 (a group of atoms called the methylene group) the properties of –OH group are again much more like those of propanol, because the immediate attachement is to a sign bonded carbon atom.

Carbon – carbon double and triple bonds (containing pi electrons and characteristic of the classes alkene and alkyne) also represent reactive centres in a molecule and although within the carbon skeleton have some of the properties of a functional group with specific diagnostic reactions. Note however, that the benzene ring, although also containing pi electrons, is much less reactive than would be expected for alkenes owing to its special property of "aromaticity" (resonance stability)
Solid convalent compounds (in contrast to most ionic compounds) have relatively low melting points (usually below 250^0C), which are characteristic and reproducible for a particular molecular structure. Determination of melting point of a solid is therefore a useful operation in organic chemistry.

"Unknowns" will in general be restricted to substances with a molecular complexity of not more than ten carbon atoms and possessing one functional group only.

EXPERIMENT 1: DETERMINATION OF MELTING POINT RANGE

Determination of melting point range (usually shortened to m.p.) can give information on

    a.   The purity of a compound
    b.   The identity of a compound

a.   Pure compounds melt rapidly over a narrow temperature range of not more than $1 - 2^0C$. Impure compounds melt slowly over a **wide** temperature range **below** the melting point of the pure substance. The **range** of melting is from the onset of melting, as shown by the collapse of the crystals (i– ii) to complete melting (iii) – Figure 1. the observed temperature **range** of melting is recorded, although usually referred to as the melting **point.**

(i) Powdered crystals

(ii) Partially melted crystals

(iii) Melting Complete
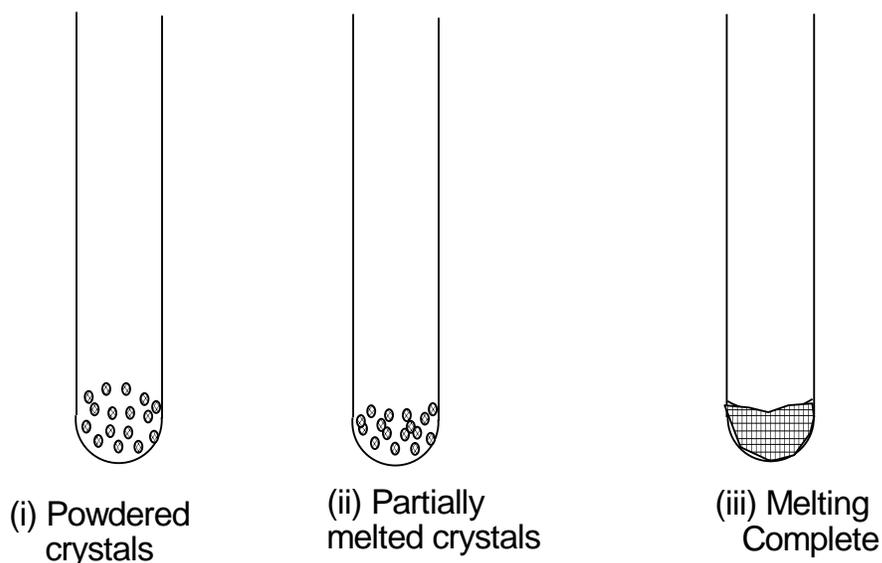
    b.   Knowing the melting point of a compound narrows down the possibilities as to its identity, e.g. if it is known to be an acid and has a m.p. $120^0 - 22^0$, it is more likely to be benzoic acid. (literature m.p. $121 - 122^0$) than the similar (lit. m.p. $109 - 110^0$). But because most solid organic compounds have m.p's within the temperature limits $20 - 300^0C$, quite a large number will by chance have a m.p. of about 120˚, so m.p. alone is not a good proof of identity.

A simple test the mixed melting point can confirm a suspected identity. If the "suspected benzoic acid (above) is mixed with equal amount of "know" benzoic acid (obtained from a stock bottle) and a melting point of the mixture is determined two possible circumstances can result:

i. The mixture contains only benzoic acid and melts over the narrow range of 121 - 122˚ characteristic of benzoic acid and showing that the "suspected" benzoic acid is benzoic acid.

ii. The mixture is now a very impure sample of benzoic acid and melts over a wide range of temperature and well below 122˚, (see a. above) because the "suspected" benzoic acid is not benzoic acid at all but some other molecular structure.

This test, like many others used later in the course, is in effect asking a question "is the unknown sample benzoic acid?" and obtaining the answer by an experimental observation, which can only be interpreted in one or two ways – "Yes, it is benzoic acid (because there is no lowering or depression) of melting point in the mixed melting point experiment) or – "No it is not benzoic acid (because there is a depression at melting point.

EXPERIMENTAL

Determination of Melting and Mixed Melting Points

Apparatus

The melting point apparatus consists of a small beaker containing liquid paraffin (which can be safely heated about 200˚C) and a glass chimney which allows mixing by convection currents when the bath is heated.

The sample to investigated is contained in a small capillary tube sealed at one end, which is attached to a thermometer with a rubber band. The thermometer bulb and the sample are immersed in the bath as shown in the diagram (figure 2)
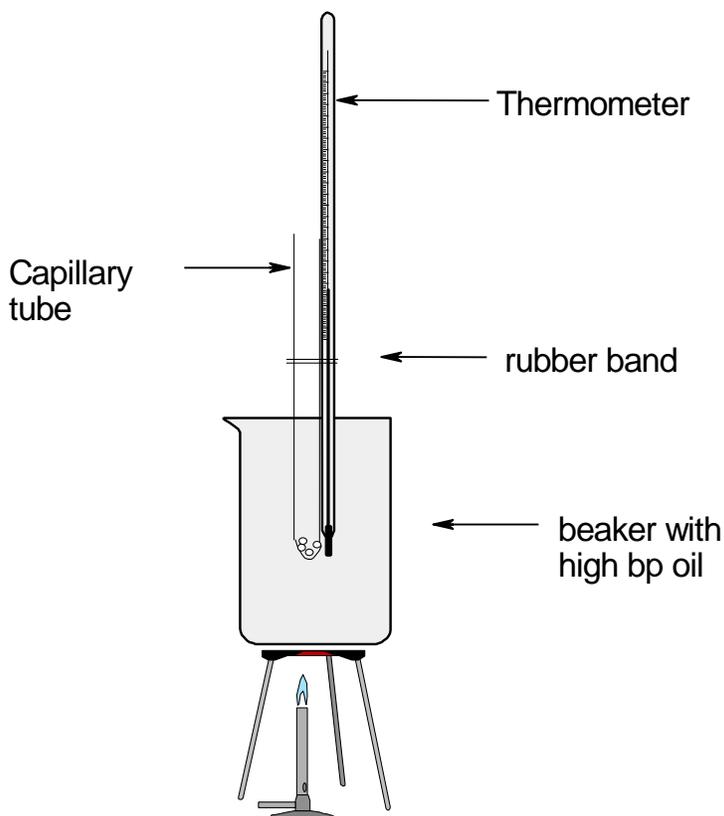
Other designs of melting point apparatus include some with mechanical stirring devices or with a different liquid to allow higher temperatures to be used. Also useful for higher temperatures are designs in which the thermometer and sample are in a metal block instead of a liquid bath the block being heated electrically or by gas. For very small samples a special heated microscope stage can be used and the sample observed through the microscope.

Procedure

For each determination take a fresh capillary tube, which is supplied open at both ends. First close one end by heating the tip of the tube in the edge of a Bunsen burner flame until glass just melts, while rotating the tube between thumb and first finger.

Crush a small quantity (1-2 mg. Is sufficient) of the solid substance on a clean hard surface such as a watch glass or microscope pressing against the end of metal spatula. Then, holding the closed end of the tuve against the bench surface to shake down the powder. Repeat the operation if necessary until you get a column of about 5 mm in length in the capillary tube.. The open top end of the capillary tube may be then sealed by careful heating if required.

Attach the capillary tube to the thermometer and place in the melting point bath as shown in Figure 2. **The rubber band must be above the level of the paraffin** or it will be destroyed by the hot liquid.

Heat the beaker with a **small** Bunsen burner flame until the temperature is about 20˚ **below** the expected melting range (a first "rough" determination may be necessary to find the approximate temperature) and the **very slowly** (4˚ per minute – which means that you must take the flame away fro under the bath and just wave it back and forward under the wire gauze) until the changes from (i) to (ii) take place. Record the temperature at which the changes form (i) to (ii) take place. Record the temperature at which the changes from (i) to (ii) to (iii) occur. These temperature represent melting point or melting range.

For a mixed melting point, crush the two samples separately as in Figure 3a, then mix approproximately equal amounts and **crush** again before filling the capillary tube. It is possible to heat more than one sample at a time in a melting point bath by attaching the capillary tubes side by side to the thermometer with one rubber band but take care that you note which is which and do not muddle up your results. Use a new capillary tube for each determination and do not remelt the same sample for a second reading – irreversible chemical changes may have occurred in the first melt**. Put used capillary tubes into the solid waste box**. Do not leave them on the bench or throw them into the sink.

EXPERIMENT ONE

a.   Determine for practice the m.p. of the benzoic acid ($C_6H_{15}COOH$) benzoic acid has very narrow range of melting about 122˚C. heat your melting point bath very slowly as you approach this temperature and see how rapidly the melding phenomenon occurs in this case. (the sharp m.p. of pure benzoic acid can be used as calibration point for a melting point apparatus which uses methods other than direct reading of a thermometer to measure temperature.

b.   Determine the m.p.'s of the three given samples A,B and C which have m.p.'s of approximately 80, 120 and 160˚ respectively. Do them in the order given so that you will not have to wait for the bath to cool right down to room temperature each time, as is necessary for a determination on a completely unknown sample. Record the results on the experimental record sheet.

c.   Unknown X, with a m.p. (of about 130˚ may e either urea (NH_2CONH_2) or cinnamic acid ($C_6H_6(CH+CHCOOH)$), both of which have m.p.'s of about the same temperature, but which have as you can see by inspection of their molecular formulae, very different structures samples are provided of each of these. Use m.p.'s and mixed m.p.'s to determine whether X is identical

with either of these two substances. Record your results on the experimental record sheet, complete the question section and hand it in **before you** leave the laboratory.

DATE:………………………………… NAME:………………………………….

<div align="right">REGN. NO.:…………………………</div>

EXPERIMENTAL RECORD SHEET ONE – MELTING POINTS AND RANGES

Melting of Benzoic Acid starts (fig. 1 i- ii) …………………………………………˚C

Finishes (fig. 1 – (iii ……………. ˚C)

Therefore m.p. of benzoic acid is …………………………………………………………

Melting of A starts ………………………………. finishes …………………………………..

m.p. of A is ………………..

m.p. of B is …………………

m.p. of C is …………………..

Mixed Melting Points (Ranges)

X   m.p. …………………………………………

Cinnamic Acid   m.p. …………………………………………

Mixture of X and cinnamic acid   m.p. …………………………………………

Urea   m.p. …………………………………………

Mixture of X and urea   m.p. …………………………………………..

Complete the following section

I consider that X is ………………………………… and is not ……………………………..

Because ………………………………………………………………………………………

…………………………………………………………………………………………

Write the full structural formulae of benzoic acid, cinnamic acid and urea below. **Condensed** formulae are given in the text. (can cinnamic acid be written in more than one way?).

EXPERIMENT 1 - POST LAB QUESTIONS

1. Why is it misleading to identify a solid compound just from a lone m.p. determination?

2. Why is it not a good idea to do m.p. determinations on large sample?

3. What are some of the reasons for not using resolidified sample for confirmation of melting point?

EXPERIMENT 2: THE INVESTIGATION OF MONOFUCTIONAL ORGANIC COMPOUNDS CONTAINING THE ELEMENTS CARBON, HYDROGEN AND (PROBABLY) OXYGEN ONLY.

Although tests for the presence of the hetero-atoms nitrogen, sulphur and halogen can be applied to unknown compounds (and will be the subject of a later exercise) there is no simple test for the presence of the element oxygen in an organic compound. Since oxygen is the commonest of the heteroatoms and is present in several important functional groups, one normally assumes it is present until contrary evidence is obtained. The next experiment will involve the investigation of unknown compounds which do not contain any of the heteroatoms N, S or Halogen but which may well contain no oxygen and therefore is a hydrocarbon.

N.B. remember that these tests are being carried out with the fore-knowledge that the heteroatoms N, S, and Halogen are absent. As you will see later in the course, the examination of an unknown for the presence or absence of these elements is an essential preliminary test before starting on the search for functional groups. This is because some functional groups containing N and S may show parallel reactions to O-containing groups e.g. most amines will give a coloured precipitate with Brady's reagent, thus giving a false positive test for a carbonyl compound. (the precipitate is the reagent itself, because it is weaker base than most amines and so is displaced from a solution of its soluble salt.)

Oxygen is the only heteroatom in the functional group of the following classes of compounds:

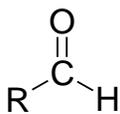Carboxylic acids (alkanoic and arenoic acids) (where R- is any carbon skeleton)
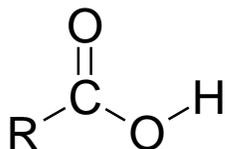
Alcohols (alkanols) R-OH
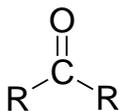(where R – is an laknae or cycloalkane)

Phenols Ar-OH

(Ar- indicates that the carbon skeleton s specifically a benzene –like skeleton, aryl)
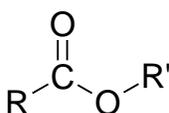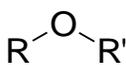

Carbonyl compounds

Aldehydes

$$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-H$$

Ketones

$$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-R$$

Esters of carboxylic acids

$$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-R'$$

Ethers

$$R-O-R'$$

As will be seen later, oxygen also occurs combined with other heteroatoms in a number of functional groups, e.g. the nitor group $-NO_2$. these will be identified by the presence of other heteroatoms.

If a compound is suspected of having an oxygen-containing functional group; a series of chemical classification tests can be applied to try to identify that functional group by its characteristic chemical reactions. The tests can be divided into two grades – the first can be considered as **preliminary** and may give a clue as to which of the more **specific** and **confirmatory** tests should then be applied. The tests must be carried out in an ordered succession, because each one designed to eliminate certain possibilities, which can subsequently be accepted as "impossible" (provided that you have done the test correctly and made an accurate observation and deduction from it).

Each chemical reaction can be considered as a question :Is it or is it not …? And the observation should lead to clear answer "Yes or "No". Rembember that this course of practical organic chemistry is specifically limiting "unknowns" to relatively small organic molecules with one functional group only (simple compounds). Obviously the presence of more than one functional group in a complicating factor, which will have to be considered in more advanced course, and is specifically excluded from the experimental scheme used here for simple compounds.

As an alternative to chemical tests for functional groups one can use infra red absorption spectroscopy. The following characteristic absorption frequency regions are used to identify oxygen containing functional groups.

- OH   3200 – 3400 cm^{-1} (broad band, due to hydrogen bonding)

C = O   1650 – 1800 cm^{-1} (sharp strong absorption bonds with frequencies

As characteristic for each type of environment of

the C = O group, e.g. aldehyde (saturated).1720-1740 cm^{-1}

(together with a band at around 2720 cm^{-1} for the C-H).

ketone (alicyclic satd)   1705-1725   cm^{-1}

Ketone (five membered ring)   1740-1750 cm^{-1}

Carboxylic acid (satd   1700-1720 cm^{-1}
And 2500-3000 cm^{-1}for –OH)

Esters (saturated)   1735-1750 cm^{-1}
Anhydrides – two bands   1800-1550 cm^{-1}

The interpretation of spectral evidence for the identification of unknown will be a later exercise. At present chemical tests will be used.

PRELIMINARY TESTS

a.   One simple test, solubility in cold water, can give some information about monofuntional compounds. Easy solubility in cold water is confined to carboxylic acids, alcohols and carbonyl compounds with not more than four carbon atoms, together with one or two of the simpler phenols (which must have a minimum of six carbon atoms in the benzene ring). Most of the simpler esters and ethers (and also all hydrocarbons) are insoluble in cold water, while anhydrides are initially insoluble but may react to form water soluble products (which are acidic); with the production of heat of reaction.
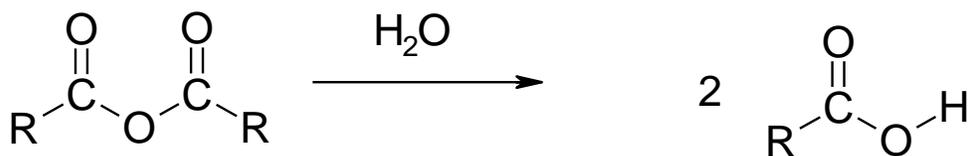

Solubilities increase with temperature (see the crystallization experiment) and rates of chemical reaction also increase with temperature solubility in hot water, but not in cold, may mean increased solubility (as for benzoic acid) or more rapid reaction (acid anhydrides and some esters) and is not a very useful test.

If a substance is soluble in cold water, the solution my be acidic, neutral or basic. In general basicity is to be associated with the class of compounds containing the amino group, -NH$_2$, and so ca be left aside for the time being since only oxygen-containing functional groups are being considered.

Acidity can be tested for with litmus paper or universal indicator. Water solubility, combined with acidity means that the compound is almost certainly a simple carboxylic acid, or a phenol.

     b.   If a substance is not soluble in cold water, but is acidic, this property can now be tested for by finding if it is soluble in aqueous NaOH, either cold or after heating. (substances that are soluble in water will also be soluble in aqueous solutions of NaOH, whether they are acidic or not, and there is no point in applying this test to a substance known to be water soluble).

Almost all carboxylic acids and phenols, if not soluble in water, will dissolve in aqueous NaOH, due to the formation of the corresponding sodium salt of the acid or phenol e.g.
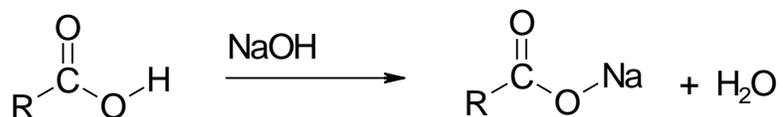

Warming may be necessary to speed up the rate of solution, but there is then the possiblilty of non-acidic compounds reacting with NaOH e.g. acid anhydrides and esters may dissolve by reaction, aldehydes may polymerize to form gummy solids. To check that simple solution in NaOH to form the anion, is the only reaction that has occurred, acidify the solution when the original acid substance will be precipitated unchanged.

By the application of one (or for water insoluble substances two) preliminary tests, the unknown can now be classified as acidic or non-acidic (i.e. the first question, "is it or is it not acidic," has been answered). If it is acidic, further tests can now be applied of a more specific nature to gain more information.

ACIDIC COMPOUNDS

Acidic compounds (with oxygen as the only heteroatom) are likely to be carboxylic acids or phenols (a further class – the "enols" are also acidic but are not monofuctional). These two can be distinguished by their different levels of acidity (a measure of the ease of ionization in the reversible reaction.

$$AH + H_2O \longleftrightarrow A^- + H_3O^+$$
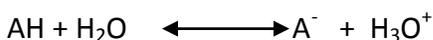
Carboxylic acids relatively strong acids (through weaker than sulphuric acids RSO$_3$H and the familiar "mineral acids" viz. sulphuric, hydrochloric and nitric acids). In particular they are stronger than carbonic acid, whereas simple phenols are weaker than carbonic

acid. this forms the basis of the next test, with sodium or potassium bicarbonate solution, in which carboxylic acids react with displacement of **visible bubbles** of carbon dioxide gas while simple phenols do not react. (The question, therefore is "Is the acidic substance a stronger or a weaker acid than carbonic acid?" and the answer "Yes" or "No" is interpreted to decide between carboxylic acid and phenol). The presence of a phenol can now be confirmed by a special test, the ferric chloride colour test, to be described in detail later.

FURTHER TESTS FOR CLASSIFYING NON-ACIDIC COMPOUNDS

If the characteristic property, acidity, has been found to be absent, there till remain the possible functional groups carbonyl C = O, hydroxyl – OH (in an alcohol but not a phenol) and the class of compounds containing the ester, acid anhydride and other groups. Finally there is always the possibility that no oxygen containing functional group is present i.e. that the compound is a hydrocarbon.

For the carbonyl group, present in either an aldehyde R-C $\overset{H}{\underset{}{O}}$ or a ketone ($R_2C=O$) there is a general test, using Brandy's reagent (an acidic solution of 2,4-dinitrophenylhydrazxine in aqueous alcohol) with the reagent to give a product which is of low solubility in the aqueous alcoholic solvent and is coloured yellow, orange or red, so that the appearance or non-appearance of a coloured precipitate answers the question "Is it a carbonyl compound or not?"
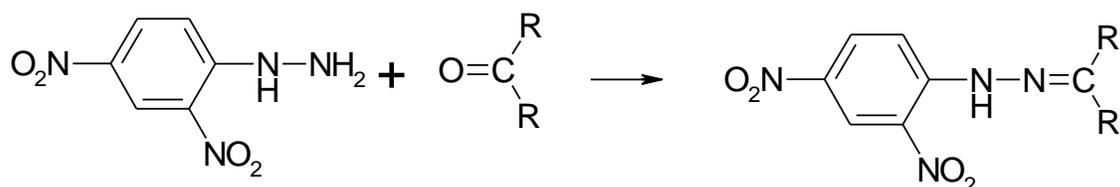
The classification of carbonyl compounds into aldehydes and ketones, as described later, can be carried out if a positive test has been obtained.

If the possibility of a carbonyl group has been ruled out (and acidic groups, such as carboxylic acid and phenol have also been eliminated earlier) a test for the very weakly acidic hydroxyl group can now be carried out. Alkanols in general are weaker acids even than water (which has a H^+ ion concentration of 10^{-7}) but, like water will react with very reactive metals such as sodium with the evolution of H_2 gas.

$$2 \text{ ROH} + 2Na \rightarrow 2RONa + H_2$$
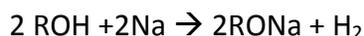
Their similarity to water in this test means that a **completely dry** test tube must be used for the test to avoid a false result. (equally a false test would be given by carboxylic acids and phenols, both of which will give H_2 gas with sodium metal – but these should have been identified earlier provided the tests have been carried out in the correct

order). A positive test with metallic sodium can be followed up with a confirmatory test with acetyl chloride (see experimental details page 32).

If the test for hydroxyl group is negative, the remaining possilbities are being very few. A test for the acyloxy grouping of atoms ISSI DRAW present both in esters and acid anhydrides, can be carried out. It is known as the **hydroxamic acid** test, and involves warming the unknown with hydroxamic acid of formula RC NHOC which can be recognized by the deep red colour that it gives on treatmentwith ferric chloride solution. Full details of the test are given in the experimental description later.
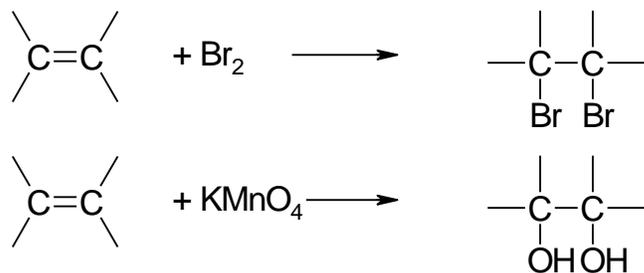
A negative hydroxamic acid test leaves only the class of ethers among the oxygen containing compounds or the possibility a hydrocarbon which will also have failed to give any positive up to now. The hydrocarbon might be a saturated alkane or cycloalkane an unsaturated alkene or alkyne, or have a benzenoid ring structure. Some further information can be obtained by the action of concentrated sulphuric acid, by the burning test, and by tests for unsaturation. Infra red spectroscopy is the best approach for distinguishing this group of compounds.

Saturated alkanes and cyloalkanes are insoluble in either cold or warm concentrated sulphuric acid. ethers and unsaturated hydrocarbons will dissolve, without any darkening of colour, in cold concentrated sulphuric acid, but benzenoid hydrocarbons will usually only dissolve in warm or hot sulphuric acid, again without any darkening of colour. If the unknown reacts with cold or warm concentrated sulphuric acid with the formation of a dark brown or black colour it is probable that a functional group is present which has been missed in the earlier tests. A yellow or pale brown colour may however merely indicate that the sample is slightly impure hydrocarbon or ether.

Ethers dissolve in sulphuric acid by the formation of an unstable oxonium salt (i.e. they act as very weak bases). The salt formation is reversed on dilution with water, and the ether is recovered unchanged.

Unsaturated hydrocarbons react with sulphuric acid to give acid sulphate ester $ROSO_3H$ which may remain in solution if the acid is diluted with water or may hydrolyze to give an alcohol, a change in smell will be detectable. Benzenoid compounds react with warm concentrated sulphuric acid to form sulphuric acids, $ArSO_3H$ which are soluble in water. However dilution of the concentrated sulphuric acid may cause a partial reversal of the sulphonic acid formation and the regeneration of some of the hydrocarbon.

"unsaturation", i.e. the presence of double or triple carbon-carbon bonds can be tested for by the ability of these bonds to undergo addition reactons using bromine or a dilute solution of potassium permanganate. In each case decolourization of the reagent will be observed if addition takes place. Benzenoid hydrocarbons do not react in either of these tests.

$$\diagdown C = C \diagdown \quad + Br_2 \longrightarrow \quad -\overset{|}{\underset{Br}{C}} - \overset{|}{\underset{Br}{C}} -$$

$$\diagdown C = C \diagdown \quad + KMnO_4 \longrightarrow \quad -\overset{|}{\underset{OH}{C}} - \overset{|}{\underset{OH}{C}} -$$

The presence of benzenoid ring system in a hydrocarbon (or in any other organic molecule) can usually be detected by the **burning test.** If one or two drops of the unknown are put on an upturned crucible lid and ignited with a Bunsen burner flame, benzenoid compounds will burn with a characteristic yellow flame, at the top of which a cloud of black sooty particles can be seen. Simple aliphatic compounds tend to burn with a clean blue flame or if the flame is yellow no sooty particles are visible above it.

It is often useful to carry out this burning test as a routine preliminary test on an unknown to see the general nature of the carbon skeleton. However, if a benzenoid skeleton is suspected as a result of the burning test, you must not assume that any functional group later detected is necessarily attached directly to the benzenoic ring (see page 2).

METHODS OF INVESTIGATION

A general scheme for the examination of an unknown believed to contain C_3H and O only can be summarized in the chart below. First the unknown should be examined visually and a note made of its physical state (solid or liquid) colour and smell.

The burning test can be carried out to check for possible benzenoid structures. The solubility in water or aqueous NaOH to determine acid or non-acid reaction is carried out and according to the result the appropriate arm of the chart below is followed.

Preliminary Solubility Test with Water or Aqueous NaOH

Acidic
    NaHCO$_3$(aq)

Non-Acidic

Brady'
reagent

Carboxylic acid

Non-carboxylic acid

Carbonyl
compound

Not carbonyl
compound

Phenol
Confirm with FeCl$_3$
TEST

(differentiate
Aldehydes and
Ketones)

Metallic
sodium
H$_2$ gas evolved

Hydroxyl group present

Non hydroxyl
present

confirm with acetyl
chloride present

hydroxamic
acid test

Red Fe salt of Hdroxamic acid formed

Esters or acid
Anhydride present

ether or hydro-
Carbon present

TESTS
   a) Solubility in concentrated sulphuric acid (and dilution with water)

b) Unsaturated tests

c) Burning test (if not already done as a preliminary test)

EXPERIMENTAL: FIRST WEEK PART 1

Examine the four unknowns supplied, which contain C, H and (probably) only, according to the scheme described above and report on the nature of the compound present and the probable functional group present. For this week the unknowns may be carbonyl compounds or alcohols only and the tests carried out should be limited to those required to identify these functional groups.

Use the experimental record sheet for recording your tests, observations and interferences. It is not necessary to copy out the experimental details of each test on to the record sheet, but the test should be clearly identifiable by a brief phase e.g. "solubility in NaOH(aq)" of "Brady's Reagent". The observations column should record what you actually see, e.g. "Bubbles or gas evolves". ("positive" and "negative" are **not** observation).

Each test and observations has a meaning and leads to an interference i.e. what you believe to be the reason for what you have. Do not leave a blank space in the third column. If nothing can be deduced from the test say so.

For each test follow carefully the experimental details and conditions given below. Tests should be done in a **small** test tube unless otherwise instructed.

Do not use more than the indicated quantities for each test. The sample of unknown tube are supplied which contains sufficient for all the required tests and **no more material will be issued**. Use a dropping pipette with a rubber teat to measure liquid samples for tests.

<u>**Burning test**</u>

Use an upturned crucible lid supported on a tripod and pipe clay triangle. Put one or two drops of a liquid sample (or a few small crystals of a solid) onto the lid and heat from above with a small bunsen burner flame until the substance lights. Remove the burner flame and observe the burning sample.

If in doubt about the appearance of the sooty flame obtained from benzenoid compounds try the test on two drops of benzene.

Solubility tests

a. **In water:** Add two drops of a liquid unknown only, or a few crystals on the tip of a small spatula, to 2ml of cold water. Shake well.

If the unknown does not dissolve, try test (b).

b. In NaOH (aq): Add two drops, or a few crystals (as above) to 2 ml of 5% (1.25M) NaOH solution. Shake well. If the unknown dissolves acidify with a few drops of concentrated hydrochloric acid and look for reprecipitation. If the unknown does not dissolve in cold NaOH solution, warm gently, but **do not boil**. Testagain for reprecipitation with acid if the unknown dissolves.

Reaction with Sodium or Potassium Bicarbonate (aqueous)

If the preliminary solubility tests indicate an acidic add 2 drops, or a few crystals to 2ml of aqueous bicarbonate solution. Look carefully for the evolution of gas bubbles. With insoluble solid samples these may be quite small, but will apperar around the edges of the solid particles. (the solid will slowly dissolve as it reacts). There is no need to test the gas evolved – it can only be carbon dioxide:

Reaction with Brady's Reagent

If the preliminary solubility tests indicate a non-acidic reaction, add 2 drops (or a few crystals dissolved in 2 drops of methylated spirit) to 2ml of Brady's reagen, mix well and allow to stand for a minute. Look for a **coloured** precipitate. If nothing appears, warm and cool again. If a coloured precipitate is obtained the unknown is either a ketone or an aldehyde. Carry out the differentiating test. If no coloured precipitate is obtained proceed to the next test.
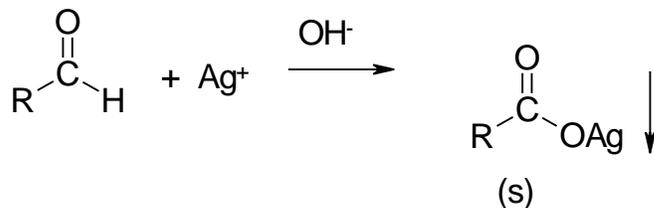
Reaction with Metallic Sodium

Put 0.5ml (10 drops) of the unknown (most simple alkanols are liquids) into a **dry** test tube. take a pea-sized piece of metallic sodium form the bottle where it is stored in an inert solvent, dry it quickly on a small piece of filter paper and put it into the unknown. Watch carefully for a steady evolution of gas bubbles. If none are seen after half a minute warm but do not boil and again look for bubbles.

IMPORTANT: At the end of this test, half fill the test tube with methylated spirit to dissolve residual sodium. Wait until all the sodium has dissolved before washing out the with water.

Differentiation Test for Aldehydes and Ketones

Aldehydes cn be differentiated from ketones (both respond to the general carbonyl group tests) by their ability to act as mild reducing agents. The best genral test is the reduction of complexed silver ions in alkaline solution to metallic silver in tollen's silver mirror test.

$$\underset{R}{\overset{O}{\underset{}{\parallel}}}\overset{}{C}\diagdown{H} \quad + \text{ Ag}^+ \quad \xrightarrow{\text{ OH}^-} \quad \underset{R}{\overset{O}{\parallel}}C\diagdown{OAg} \downarrow$$

(s)

However, owing to the high cost of silver salts, it is not possible to use this test in a class exercise. Other general test for aldehyes are less reliable and it is recommended that result of two of the following tests should agree before a definite decision is made on the presence or absence of an aldehyde.
Schiff's test is a colour test and the exact chemical reaction which occurs is not known.

Fehling's test, like Tollen's test, relies on the reducing power of the aldehyde towards metal ion, in this case converting blue Cu^{2+}ions (complexed in alkaline solution) to insoluble, yellow or red Cu^+ oxide.

The permanganate reduction test is given by many oxidisable organic molecules, (and is used on as a test for unsaturation). It, like Fehling's tes, should be doen in parellel with blank test.

Procedure

a) **Schiff's test.** Add about 1 ml of schiff's reagent to a few drops of the carbonyl compound. A magenta (bluish-red) colour develops within a few minutes form simple aliphatic aldehydes. Benzenoid examples are much slower and require shaking. Carry out a blank if the colour only develops very slowly.

b) **Fehling's test**. To a few drops of the carbonyl compound, add 1 ml of 10% Na_2CO_3 and then a few drops of Fehling's solution and boil the mixture gently for one minute. The appearance of a yellow or red precipitate of cuprous oxide is a positive test, provided that the blank test does not give any such precipitate.

c) **Permanganate reduction test.** Warm a few drops of the carbonyl compound with 2-3ml of dilute potassium permanganate solution and 1 ml of 10% Na_2CO_3. The discharge of the colour and formation of a precipitate of MnO_2 indicates the presence of a reducing agent. A blank test should be carried out.

Confirmatory Test for Alcohols

Carry out this test in the fume cupboard. Add a few drops of the unknown **slowly and cautiously** to a few drops of acetyl chloride in a **dry** test tube. A vigorous evolution of hydrogen chloride (fume in most air) and heat will be observed. Add 2 ml of water, when the formation of a pleasant smelling product – an acetate ester – indicates that the unknown was an alcohol, (familiarize yourself with the smell of acetate esters by smelling some ethyl acetate).

$$ROH \ + \ CH_3COCl \ \longrightarrow ROCOCH_3 \ + \ HCl$$

Solubility in Concentrated Sulphuric Acid

To 1 ml of concentrated sulphuric acid in a test tube add 2 drops or a few crystals of the unknown. Shake carefully and observe whether the substance dissolve, whether any colour change occurs and whether any heat is evolved.

If solution occurs, pour the sulphuric acid into another test tube containing 3 ml of water and mix well. Look for the separation of solid or liquid droplets. Smell cautiously and compare the smell with that of the original unknown. A change in smell is significant, but if the precipitated material has the smell as the unknown, an ether may be suspected.

If no solution occurs in the cold, warm gently for about one minute and cool the tube under the tap. If solution has now taken place, pour into water as above. Record any changes in appearance and smell.

Tests for Unsaturation

Carbon-carbon double and triple bonds respond positively to **both** of the following tests. Do not rely on a positive result from one test only because the test can react with other functional groups, as shown below.

   a.   Addition of bromine. To a solution or suspension of 2 drops or a few crystals
          in 2 ml of water add bromine water dropwise with shaking. The
          decolourisation of more than a few drops of the reagent indicates
          unsaturation, or that an easily compound is present such as a phenol.
   b.   Reaction with dilute potassium permanganate. Add 2 drops of a few small
          crystals of the unknown to 2 ml of dilute aqueous potassium permanganate
          solution and shake. Discharge of the colour and the formation of a brown
          precipitate of manganese dioxide indicates unsaturation, or the presence of
          an easily oxidisable compound, such as secondary alcohol or an aldehyde.

EXPERIMENTAL: SECOND WEEK – PART II

This week the four unknowns again contain C, H and (probably) O and may be acidic or non-acidic. The acidic compounds may be **either** carboxylic acids **or** phenols and must be examined for their distinguishing reactions. Phenols can be confirmed by the test with ferrin chloride (below)

Non-acidic unknowns may be carbonyl compounds or alcohols, (as before) but may also be esters ethers or carbon-carbon double bond (unsaturated) compounds. Proceed as in the first week, but if no carbonyl or hydroxyl group reaction found, test in turn for esters by the hydroxamic acid test (below) for ethers and for unsaturation of **both** of the tests given.

Confirmatory Test for Phenols

For water soluble phenols, dissolve 2 drops or a few crystals in 2 ml of water nd add one drop of neutral ferric chloride solution. A violet, blue or green colour indicates a phenol. The colour may help on identifying the phenol (see text book)

For **water insoluble** phenols, dissolve 2 drops or a few crystals in 2ml of cold methylated spirit and then add one drop of ferric chloride solution. Watch carefully as the colour may form and fade away rapidly.

The Hydroxamic Acid Test

Add 2 drops of the unknown to 0.5 ml of a solution of hydroxylamine hydrochloride in methanol (5%) and follow it by a dilute solution of methanolic potassium hydroxide until the solution is just alkaline (test with litmus). Boil the solution for one minute. Cool and just acidify with dilute hydrochloric acid. Add a few drops of ferric chloride solution. A red colour indicates the presence of a hydroxamic acid, and therefore that the unknown was an ester (or an acid anhydride).

DATE …………………………………NAME …………………………………………

REGN. NO …………………………………..

EXPERIMENTAL RECORD SHEET THREE

The Investigation of Unknowns Containing C_2 H and O only

Substance No. …………………………………………………………………………..

Appearance

TEST	OBSERVATION	REFERENCE
Soluble in Water?		

Conclusion   Substance No.   is

Because

(Make up your own report sheet for each additional substance)

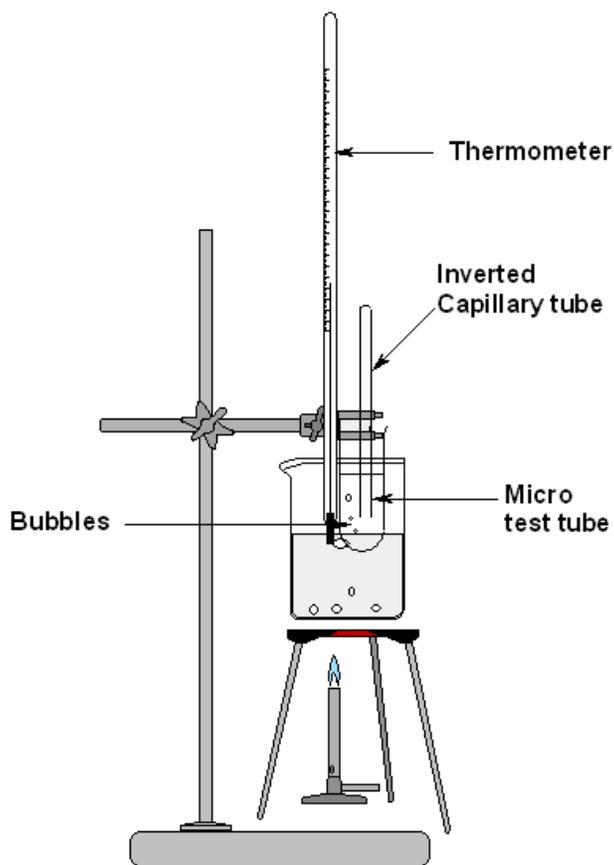# EXPERIMENT 3: BOILING POINT DETERMINATION BY SIWOLOBOFF's MICRO-METHOD

Introduction

Boiling points can be determined on a large scale by distilling the liquid and measuring the temperature of the vapour. A pure liquid will boil (and distill) at a very exact temperature under constant pressure. When only a small sample is available a micro-method can be used as described below.

The phenomen of boiling is observed when the vapour pressure of a liquid (which rises with temperature) becomes equal to that of the surrounding atmosphere. Since at the altitude of Nairobi the atmospheric pressure averages 630 mm Hg (as compared with the standard "sea level" atmosphere of 760 mm) boiling points determined here are appreciably lower than the figures given in reference books, which normally refer to 760 mm 1 g: e.g. water, Nairobi b.p. 94.5˚C. Corrections have to be applied to obtain values at 760 mm Hg which can be compared with the literature . Corrections vary with the temperature and with the nature of individual liquid, so that only a very approximate general correction factor can be given, as in the table below.

Observed b.p./630 mm Hg*	Add	Approx. corrected b.p. 760 mm Hg
	1 - 2˚	
75˚	3- 4˚	78- 9˚
100˚	5˚	105˚
150˚	6 - 7˚	156 - 7˚
200˚	8 - 9˚	208 - 9˚

* for intermediate values of observed b.p.'s a "guesstimate" probable correction must be made, to the nearest whole number. The boiling point of a liquid, while useful in assisting identification is not such a geed criterion as melting point partly because it is so considerably affected by changes in atmospheric pressure and also because there is no equivalent test to a mixed melting point that can be used to prove the identity of two liquids. **Melting points are unaffected by the** relative small pressure changes such as occur in the atmosphere and only changes in pressure of several atmospheres are able to affect melting point significantly.

Thermometer

Inverted Capillary tube

Micro test tube

Bubbles

EXPERIMENTAL

Determine the boiling points of the three samples A, B and C which are in order of rising boiling point – so carry out the determinations in that order. Record yur observations on the experimental Record Sheet and hand it in before leaving the laboratory.

Seal one end of a melting point capillary. Place a small sample of the liquid, between 0.5 and 1 cm in depth, in a special micro-test tube provided, fasten the test tube to the thermometer of a melting point bath with a rubber band and insert the open end of the capillary in the liquid. Insert the test tube and thermometer into the paraffin of the melting point bath so that all the liquid sample is just below the surface but the rubber band is well above. Heat the bath slowly and observe that as the temperature rises small bubbles of air escape from time to time from the open end of the capillary, due to the expansion of the air trapped inside it. At the boiling point of the liquid the rate of escape of bubbles rises rapidly and becomes a continuous stream. Immediately note the temperature and remove the flame. Now as the temperature begins to fall, a second and probably more accurate reading can be taken. The rapid stream of bubbles will stop quite suddenly usually the last bubble tries to escape but is sucked up into the lower part of the capillary. Note the temperature at this point, which is the temperature at which the atmospheric pressure just becomes greater than the vapour

pressure of the liquid. Use an average of the two values (to the nearest whole number), which should not differ by more than one or two degrees after a little practice, as the observed boiling point at the current atmospheric pressure. Empty out dry and reuse the micro-test but use a new capillary tube for each determination. Put used capillary tubes in the solid waste box.

DATE:………………………………………… NAME:……………………………

REG. NO. ………………………..

EXPERIMENTAL RECORD SHEET FOUR – DETERMINATION OF BOILING POINTS

Sample A

Rising temperature (appearance of continuous stream of bubbles) ˚C

Falling temperature (last bubble sucked back)   ˚C

Mean of two readings   ˚C

Observed boiling point of sample A

Observed boiling point of sample A   ˚C/630 mm Hg

Corrected boiling point of sample a   ˚C/760 mm Hg

Sample B

Sample C

EXPERIMENT 4: SELECTION OF A SUITABLE SOLVENT FOR CRYSTALLIZATION OF A SOLID COMPOUND

In the preparation of N-phenylacetamide (experiment 2) you were given the necessary information about a suitable solvent to use for the crystallization of the product. However from time to time it will be necessary to find this out by experiment, since there are no reliable rules that can be used, except that it is often the case that "like dissolves like" – meaning that a compound with one or more hydrophilic groups (-OH, -COOH, C = O) tends to be more soluble in solvents with similar functional groups (e.g. water, ethanol, acetic acid) while compounds lacking these groups, and therefore with solubility properties more controlled by their carbon skeleton, tend to be more soluble in non-polar solvents such as petroleum ether, benzene, etc)

As mentioned in the section on crystallization, mixed solvents may be necessary when a substance is very soluble in one and very little soluble in the other so that a mixture may have just the right solvent properties, (the two solvents must be completely miscible). When using a mixed solvent either a premixed solvent of the right proportions is used as was the case in the N-phenylacetamide experiment – the proportions having been found by experiment, or more usually, the substance is dissolved in the minimum volume of the boiling solvent in which it is very soluble, and then the second solvent, in which it is less soluble, is added drop wise under refluxing conditions, until precipitation is just beginning as indicated by a cloudiness in the solution. A few drops of the first solvent are then added to give a clear solution, and the solution is set aside for crystallization to occur as it cools. Remember that all solvents except water, are expensive and many are flammable and the vapours may be toxic.

Since the rate of solution of a solid in a solvent may be affected by the size of the crystals or particles powdered compounds should be used in these tests – the sample to be used should be crushed on a watch glass or microscope slide with the end of a spatula before use.

NOTE:

    a.   Ethanol is usually supplied as the constant boiling mixture (azeotrope) rectified spirit, which contains 85% ethanol and 5% water, industrial methylated spirit is rectified spirit containing some added methanol, which is poisonous to drink. Rectified spirit is not completely miscible with benzene but pure ethanol (dry or absolute alcohol) will mix with benzene in all proportions.

b.   Petroleum ether is a mixture of alkane from petroleum and is supplied in various boiling ranges, e.g. 60 - 80˚ or 80 - 100˚. It is miscible with benzene and with pure ethanol but not with rectified spirit.

EXPERIMENTAL

Place about 0.1 kg of the powdered solid in a small test tube and just cover it with the cold solvent. Shake if it dissolves you can report the substance as being very soluble. If it does not dissolve in the cold, heat gently in a boiling water bath (or over a small Bunsen burner flame if using the non-flammable water as solvent and if it still does not dissolve add more solvent drop wise until either it dissolve or it does not dissolve in 3 ml of hot solvent. In the latter case it can be regarded as virtually insoluble.

If the compound has dissolved in the hot solvent the tube must now be cooled to see if crystalisation occurs. Sometimes solutions remain supersaturated and scratching the inside of the test tube with a glass rod may be necessary to induce crystallization.

Summarize the results, in tabular form, for each substance examined on the experimental record sheet provided.

DATE: …………………………………… NAME:……………………………………………

REG. NO……………………………………………

EXPERIMENTAL RECORD SHEET FIVE – SOLVENT SELECTION TESTS

State which of the solvent would be the most suitable for the crystallization of each substance (there may be more than one – or none). If you think a mixed solvent might be more suitable, suggest one **and try it out.**

Substance …………………………………………………………

Solvent	solubility Cold	solubility hot	crystallization
Water			
Ethanol (Ind. Meths)			
Benzene			
Petroleum Ether 80 - 100˚			

The most suitable solvent for crystallization of ……………………………………..
Would be:

Make up your own report form for each of the other two given substances

EXPERIMENT 5: SYNTHESIS OF ASPIRIN

Salicylic acid
(2-hydroxy-benzoic acid)

Molecular Weight =138.12
Exact Mass =138
Molecular Formula =$C_7H_6O_3$

Aspirin
(2-Acetoxy-benzoic acid)

Molecular Weight =180.16
Exact Mass =180
Molecular Formula =$C_9H_8O_4$

Ethanoic acid
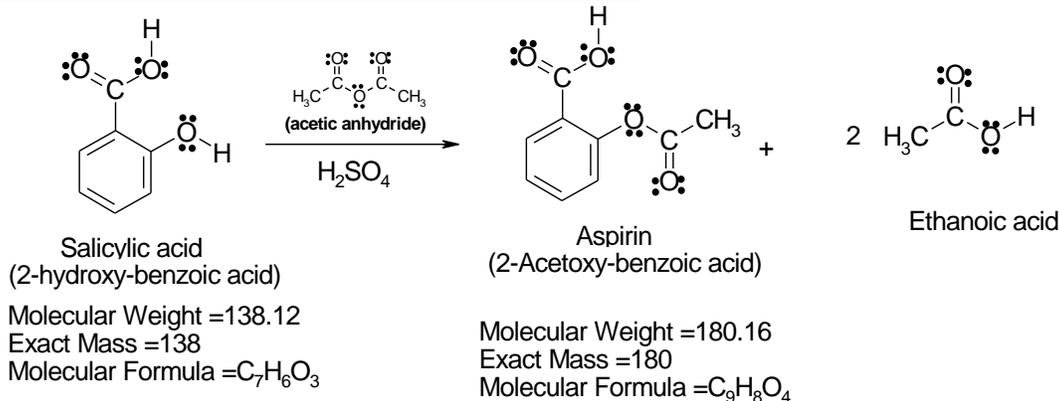
Procedure:

Combine 2.5g of salicylic acid and 5ml of acetic anhydride in a 100ml conical flask. Add 3 drops of concentrated sulphuric acid and swirl. When the reaction starts, heat will be liberated. After the initial reaction is over, heat the mixture at between 50-60°C for 15 minutes to complete the reaction (use a steam bath and a thermometer).

Cool the solution to room temperature (approx 25 ^{o}C), add 40 ml of water and stir until the solid is well dispersed. Collect the product by vacuum filtration and was it twice with 3ml of cold water.

To recrystallize, dissolve the crude aspirin in the minimum volume of 25% aqueous ethanol and pour this solution into 15ml of water at 45°C. If a solid separates, warm the mixture on a steam bath until solution is complete, then allow the solution to cool slowly. Filter the crystals by vacuum suction, and dry by pressing between filter papers.

Determine the yield, percentage yield and melting point. Test your product as follows:

1. To about 100mg of salicylic acid, add 1-2 drops of 1% ferric chloride solution. Record your observations.

2. Repeat the test with the aspirin you have prepared.

Note: Most phenols react with ferric chloride to produce red, purple, blue or green coloured complexes.