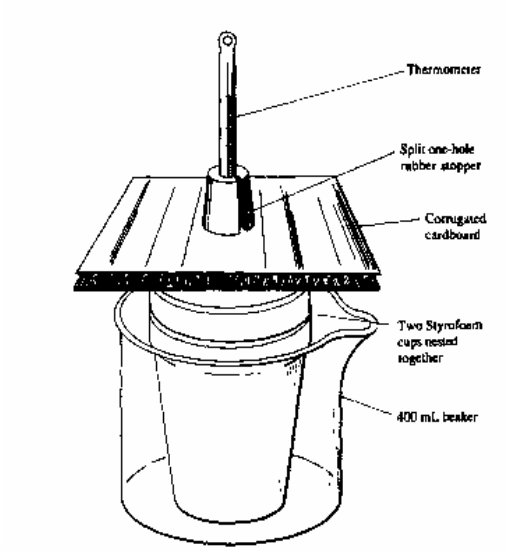
JAMES COOK UNIVERSITY
OF NORTH QUEENSLAND

Department of Chemistry
Cairns Edition



CH1011
LABORATORY NOTES
2007

Name:

Partner:

DEPARTMENT OF CHEMISTRY

CH1011 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 use of text books and tutorial staff. Where possible, complete equations in the "REPORTS" book. You should collect last week's report from the Faculty office.

b. **You should arrive on time** for the session. 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. **Plagiarism** in your practical work write-ups is not allowed. You will usually work in pairs obtaining the experimental data. The write-ups however are individual efforts. Any indication of collaborative write-ups will in the first instance result in the allocation of 1 practical experiments worth of marks across the group of students involved. (ie. if a pair of students collaboratively prepare a report your individual maximum mark will be 10/20)

e. **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 complete your calculations and finish the write up of your report. The classes finish either at 12am or at 5pm. All experimental work should be completed half an hour before the end of the practical session, anyone leaving early will be marked **absent** unless all of the lab work is completed AND **the completed report is presented to your tutor.**

f. **Report books** will be handed in for marking at the end of the practical session. Marks will be put up on LearnJCU 2 days before your next practical session at which time the report books will be available in the Faculty office.

g. **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. The only exception is Assignment 7, for which you are required to write a report without the guidance provided in the "REPORTS" book. All reports other than Assignment 7 will be handed in at the end of the practical session. Assignment 7 will be handed in at the Faculty office (mornings until 3pm).

4. ASSESSMENT

The details vary from one assignment to the next as shown below.

Assignment	Lab*	Report	Total
1	4	16	20
2	4	16	20
3	4	16	20
4	4	16	20
5	5	15	20
6	3	17	20
7	5	15	20
8	5	15	20
9	5	15	20
10	5	15	20
11	5	15	20
12	5	15	20

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

Assessment of the reports is made essentially according to the following formula:

1) Practical performance	≈ 5	you must perform moderately well.
2) Structure & Logic	≈ 5	
3) Specifics	≈ 5	answering any questions correctly
4) Quality	≈ 5	ie. generating an easy to follow report.

5. ITEMS NEEDED

1. One copy of the "CH1011 REPORTS" book.
2. One copy of the "CH1011 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 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

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 Handbook** 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.

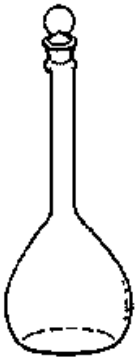
7. DATA RECORDING

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.

USE OF VOLUMETRIC GLASSWARE

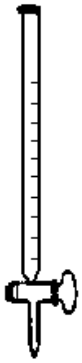
1. INTRODUCTION

Volumetric glassware consists of *bulb pipettes, burettes and volumetric flasks*. All must be cleaned thoroughly before use. This means that water must flow smoothly off the glass and not leave any adhering drops.



Volumetric flask

bulb pipette



burette

Measuring cylinders and graduated pipettes are **NOT** sufficiently accurate for quantitative work and are used for measuring out approximate volumes of liquids.

measuring cylinder

graduated pipette

2. BULB PIPETTES

In using a bulb pipette:

- **rinse** the pipette at least three times with the solution to be delivered;
- **fill** the pipette to about 1-2 cm above the mark (using a 'pipette filler");
- **wipe** any adhering liquid from the outside of the lower stem;
- with the pipette vertical and the tip of the pipette in contact with a discharge vessel, run the liquid out of the pipette until the <u>bottom</u> of the meniscus is level with the graduation mark, which must be at eye level;
- run the liquid into the receiving vessel with the tip of the pipette <u>in contact with the wall</u> <u>of the vessel</u>;
- when the continuous discharge has ceased, a **drainage time** (usually 15s) is allowed before the pipette is removed from contact with the wall. A pipette will not deliver constant volumes of liquids if discharged too rapidly.

3. BURETTES

Burettes are employed to deliver variable volumes of liquid accurately and are used in titrations.

- Rinse the burette thoroughly (at least three times) with the liquid it is to deliver.
- Fill the burette to above the zero mark with this liquid. If a funnel is used it should be removed immediately.
- Open the tap and release liquid until the jet is **filled**.
- To measure the volume of liquid delivered, the position of the bottom of the meniscus is read before and after delivery - the *difference* is the volume delivered. In reading the burette the smallest division should be divided into 5 divisions by eye. For a 50 cm^3 burette the readings will be to ±0.02 cm^3. To achieve this accuracy in the addition of solution from a burette requires the ability to add **one drop or less** from the burette. This can be done by allowing a small drop to form on the tip of the burette and then removing it by touching the receiving vessel against the tip of the burette. In a titration the drop must then be washed down into the bulk of the receiving solution. If a drop of liquid adheres to the tip of the burette after delivery, then it has been included in the volume delivered and should be detached by touching the receiving vessel against the tip.

4. VOLUMETRIC FLASKS

Volumetric flasks are used to prepare solutions of accurately known concentration, or to accurately dilute a concentrated solution.

- Rinse the flask thoroughly with the solvent; usually distilled water;
- Add a weighed quantity of the substance (if making up a solution) or add an aliquot of a solution using a pipette (if doing a dilution) to the flask;
- add water (or other solvent) to make up the total volume to the mark on the neck of the flask. The last few drops of water needed to achieve this **must** be added with a Pasteur pipette until the bottom of the meniscus is level with this mark;
- mix the solution by firmly stoppering the flask, and inverting several times and shaking vigorously.

5. CONCENTRATIONS

For calculations, all concentrations must be taken from the **bottle** or be provided by the Tutor, not assumed from the laboratory notes!

6. USE OF REAGENTS

1. Do not remove the reagent bottles from the side benches. Get what you need in a clean beaker. If the beaker is wet rinse it with a **small** amount of the solution (at least three times) first.
2. Clean up any spills immediately.

7. ANALYTICAL BALANCES

The operation of these balances will be demonstrated during the second week of the semester. They must be kept clean at all times. Clean up any spills immediately with a tissue.

REPORT WRITING

1. INTRODUCTION

For many assignments in this course, report writing requires no more than filling in a number of gaps or boxes. Obviously there is much more to report writing than this and it is important to know how to write reports. In a number of cases a complete report is presented with gaps which you fill in to complete the report. These are intended to illustrate what is required in a full report. In other cases the outline is that of an abbreviated report. In a few cases you will be expected to write a full report yourselves.

You may have to write reports for various reasons after you have finished your studies here. For instance, your report may be intended to do one of the following:

- to explain your work to other scientists, and to enable them to compare their work with yours (eg. a report to a scientific journal);

- to enable a manager in industry to make decisions of economic or marketing importance based on your work (eg. a report to your superior in industry);

- to help you remember and understand your own work, and plan further work (eg. a progress report).

These and other types of reports are required in the work of most professional scientists. In notes we explain how to write a good report. In your "REPORTS" book much of the write-up has already been completed in order to illustrate how this is done in a way which is relevant to work that you have actually done in the laboratory. Other parts are left blank for you to finish. To obtain the most benefit from this course it is important that you clearly understand why the completed sections contain the information which is in them.

In any report you set out to show what you have accomplished. It should give a clear, complete and **readable** account of what you have done. All of your work will be wasted effort if no one reads it and so the report is written for the convenience of the **reader.** The basic features of a well written report are its:

(a) structure
(b) content
(c) style

Each of these will be considered in turn. In addition, where quantitative work is involved, correct use of units and experimental precision need to be considered.

2. STRUCTURE OF A REPORT

To cater for the reader's convenience and, at the same time, ease of writing for the author, reports are usually divided into sections as follows:

Title / Authors / Date / Abstract
1. Introduction
2. Experimental
3. Results
4. Discussion

References
Appendices (optional)

In some cases the order may be different, in others two sections may be combined (eg. results and discussion) or one of these sections may be expanded (eg. introduction and theory). The one given here is probably the most common arrangement.

3. CONTENT OF A REPORT

In deciding the content of a report a good general guide is to include all information relevant to the report, as briefly as possible, and include nothing else. The aim should be, while including all essential information, to make the report as brief AND AS READABLE as possible. The content of each section is as follows.

3.1 Heading

This consists of the following:

1. the title of the report (taken from the lab notes),
2. the NAME of the author (along with the DAY and GROUP),
3. the date on which the experiment was performed,
4. an **abstract**.

The first three require no explanation except that it is worthwhile stressing that the date of **performance** of the experiment (not date of writing report, for instance) is required, since some results may be affected by ambient conditions (eg. atmospheric pressure), which vary from day to day.

In the abstract should be a brief and clear account of **what is accomplished** by the work presented in your report. It should include:

1. the method used eg. "the method of Ramsey and Young",
2. the important results (in the case of numerical results this should include the "error" in those results), and
3. any conclusions drawn from the work.

It should not normally present what was hoped to be accomplished but what **was** accomplished.

3.2 Introductory Section

This serves to introduce the reader to the topic and content of the report. In doing this it should also present those equations or concepts which are needed in the subsequent sections and explain the aims of the work which is being reported. It should explain the relevance and importance of this work to chemistry. Equations should be numbered sequentially. Unlike the introductions in these notes, introductions for the reports should NOT include detailed derivations of equations. Instead a reference should be given in which the derivation may be found. Usually this will be your textbook.

3.3 Experimental Section

The experimental details in the laboratory notebook are not to be simply copied out. Instead, you should use the brief description of what you did in your report book as the basis for this section. The experimental section will be written in the past tense and must be in your own words. The focus of this section is on the equipment and techniques used. Whenever possible the manufacturer and model of any equipment should be quoted. Where volumetric glassware is used it is sufficient to give the grade (A or B) of apparatus used.

3.4 Results Section

Here you describe your observations and measurements. In some cases it is appropriate to combine this with another section eg. "Results and Discussion".

In the **results section** you should:

(i) describe your observations and measurements,
(ii) present any (raw) experimental data,
(iii) explain, where appropriate, how any data was treated to obtain numerical results (referring back to equations presented in the Introduction and to Appendices for details of the calculations),
(iv) present any results calculated from experimental data, and
(v) describe your results.

Where numerical data is involved (quantitative work), it should most often be presented in the form of a table. Note, however, that a table of data by itself is neither sufficient or satisfactory. You **MUST WRITE** a description of your results and refer to the table in which they are presented. An example of how to present tabulated data is given over page.

Example

Table 1. Crystallization temperatures of naphthalene from toluene solution

V_{tol}/cm^3	T/K	kK/T	ln x_{naph}
6.00 ± 0.04	333.65 ± 0.5	2.997 ± 0.004	-0.394 ± 0.004
8.00 ± 0.08	328.65 ± 0.5	3.043 ± 0.005	-0.502 ± 0.006
10.00 ± 0.12	323.95 ± 0.5	3.087 ± 0.005	-0.591 ± 0.006
12.00 ± 0.16	319.85 ± 0.5	3.126 ± 0.005	-0.675 ± 0.006
14.00 ± 0.20	316.45 ± 0.5	3.160 ± 0.005	-0.755 ± 0.008
16.00 ± 0.24	313.25 ± 0.5	3.192 ± 0.005	-0.828 ± 0.011

Sometimes a graph, as well as a table is needed. In plotting a graph it is essential to make an appropriate choice of **scale.** Examples of a poor choice of scale in Fig. 1 (b) and (c) are compared with a good choice in Fig. 1 (a).

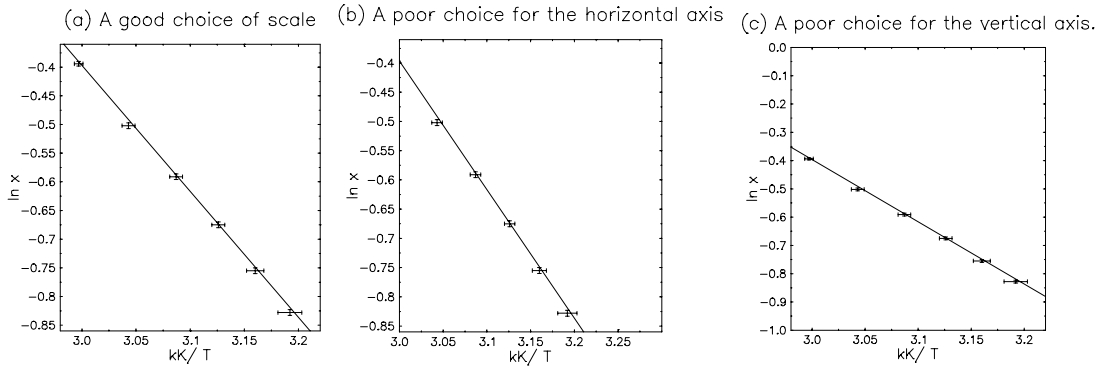
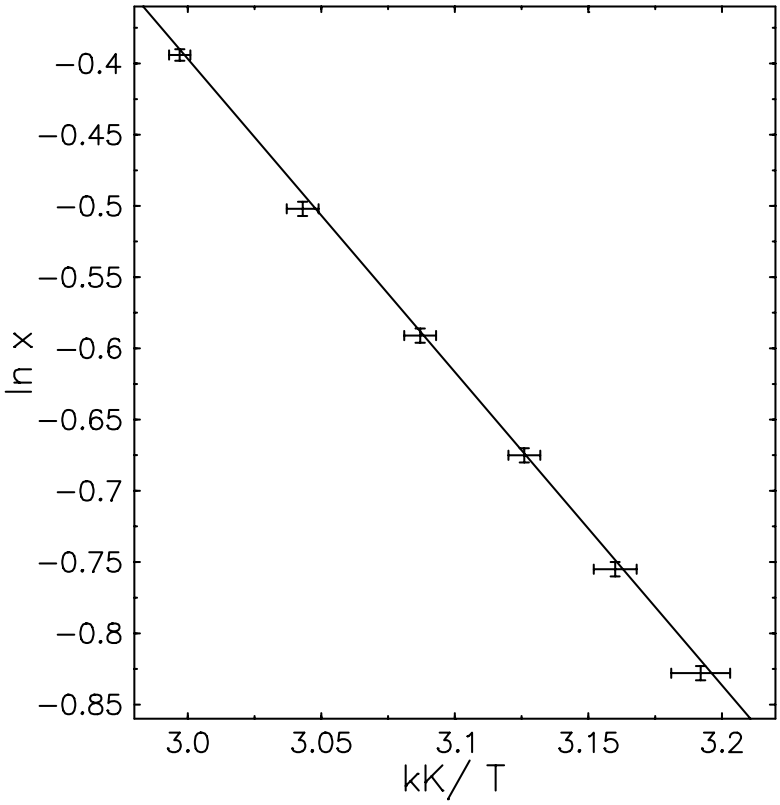


Figure 1. The importance of a good choice of scale for both axes

Tables and graphs must be numbered and carry an appropriate caption (as shown in Figure 2) and must be clearly and correctly labelled. Correct labelling is illustrated here and will be fully explained in a later section ('Presentation and Treatment of Data').

Figure 2. Variation of crystallization temperature (T) with mole fraction (x) for solutions of naphthalene in toluene



In quantitative work, error estimates should be included with your values, as shown in Table 1. The treatment of errors is described in a later section entitled 'Errors of Observation and their Treatment'.

Lengthy, detailed calculations have **no place** in the results section of a report; they belong in an appendix.
It is obvious that such calculations are needed before the results section can be completed and that the different sections, often, will not be written in the order in which they appear in the final report. It may be convenient therefore to begin each section on a new page, and later, to combine them together to complete the report.

In the report the **primary data** and **results** obtained from them will be presented in the results section. The **methods** by which the primary data and results were obtained will be given in the introduction or in a theory section and should be referred to when writing the results section. Any apparatus used to obtain the data is to be described in the experimental section.

3.5 Discussion section

Here you discuss the **significance** of your results. Since these are set experiments and not original research your scope is somewhat limited but there are certain (minimum) basic points you must cover.

Sometimes you will have a result which can be compared to a literature result. If that is possible it must be done. Where the result includes a numerical value the comparison MUST involve consideration of the experimental error. It is also necessary to comment on this comparison.

Wherever possible try to interpret your results in terms of some physical, chemical or theoretical model.

In some cases it is difficult or inappropriate to separate the results and discussion. In such cases a "combined" section "Results and Discussion" is presented.

3.6 List of references

In the text, reference to other parts of the report should be made by section (or equation) number, not by page number. References to other works (e.g. papers) should be consecutively numbered in the text and should be listed by number in a list of references at the end of the article. Each reference to another work is given a superscript number directly after it is mentioned in the text. These references should be as complete as possible and presented as follows.

(a) For a book give the following information, in the order shown, author(s) book title, volume, publisher, city, year.

Example
S.E. Manahan, Environmental Chemistry, Sixth Edition, Boca Raton, Florida 1994.

(b) For a paper in a journal the required information is author(s), journal, year, volume, page.

Example
H. Wu and L.S. Wang, *J. Chem. Phys.*, 1997, **107**, 8221.

An example of the use of the referencing method follows.

Example
There have been many approaches introduced, such as multiple time scale techniques[1] and linear scaling methods,[2,3] to increase the efficiency of Car-Parrinello[4] based ab initio molecular dynamics simulations to treat extended systems.

References
1. Tuckerman, M.E.; Parrinello, M. *J. Chem. Phys.* 1994, **101**, 1316.
2. Galli, G.; Parrinello, M. *Phys. Rev. Lett.* 1992, **69**, 3547.
3. Mauri, F.; Galli, G.; Car, R. *Phys. Rev. B* 1993, **47**, 9973.
4. Car, R. Parrinello, M. *Phys. Rev. Lett.* 1985, **55**, 2471.

3.7 Appendices

Generally any essential material which does not belong in the main body of the report is put in an Appendix. It is often detail whose omission will not present a good general understanding of the work but is essential for a detailed understanding.

For this course it is suggested that all lengthy calculations be presented in an appendix. Each appendix should have a title and be numbered. Also each appendix may be broken into sections.

4. STYLE

Style means simply how you or I write. In our approach to report-writing, we will divide style into two components: "English" and "Science". In the English component, we shall include aspects of vocabulary and grammar, sentence and paragraph structure, brevity, etc; by contrast, the Science component shall deal with items such as the correctness and clarity of results and their discussion.

In scientific reports, which tend to deal with "hard" facts and often numerical data, attention to style is important. Poor style can make a report confusing, boring, frustrating, or can even convey to the reader incorrect information. A general rule is **"the 3 C's".** A report should be

Correct, **C**lear and **C**oncise

The above considerations of structure and content will help to eliminate problems. By breaking the report into sections you know clearly what sort of material should be included in each section. The content for each section is therefore made clear, given that it must be chosen to include everything which is relevant and nothing else. Your writing style then will be chosen so as to present this content as briefly and as clearly as possible.

Finally it is NEVER adequate to simply present a series of tables and graphs; you must WRITE about your results! Your report should give a **complete** and **readable** account of what you have done. It should be written for someone who is a competent chemist. It SHOULD NOT be written for someone who is already familiar with the experiment!

DEMO REPORT

This demo report is for your use as a model of how to write up a practical report so that they do not take unnecessary time and yet still convey sufficient information to the reader. This is a mixture of several student reports from the second year Environmental Chemistry subject CH2041 and is intended to be illustrative rather than rigorously correct.

CH2041

Author: Mike Liddell
Partner : Les Various
Date : 31 / 5 / 99

ASSIGNMENT 21
IDENTIFICATION OF GASES

ABSTRACT
The qualitative analysis of food dyes in jellybeans and the quantitative level of benzoic acid in the soft drink *Sprite* were obtained by spectrophotometry. The dyes found the jellybeans (Red10, Blue10, Yellow10) and the benzoic acid concentration in the soft drink (10mg / L) were all within the Australian standards.

1.0 INTRODUCTION

1.1 Toxicology
Toxicology is the science of poisons or toxicants, as they are otherwise known. Toxicants are chemical substances that are harmful to living organisms through their effects on tissues, organs or the biological processes of the organism being studied. The physiological effect of the toxicant on an organism and the toxicant required to cause that effect are the two important aspects which are observed in toxicology. By observing these effects, we can establish the concentration of toxicant which causes the harmful effects (LC_{50}, lethal concentration), a concentration below which there are no harmful effects. This is otherwise known as a Dose-Response relationship.[1]

1.2 Gaseous pollutants
Some of the major gaseous pollutants are the oxides of nitrogen, collectively called NO_x, these refer to NO and NO_2. These are produced in car exhaust and from subsequent reaction in the atmosphere.

$$N_2 + O_2 \leftrightarrows 2NO \qquad (1)$$
$$2NO + O_2 \leftrightarrows 2NO_2 \qquad (2)$$

The method of analysis used for NO_x was based on the fact that NO_x dissolves in aqueous solutions to form nitrite ions. The nitrite ion collected from cigarette smoke and diesel exhaust was analysed spectrophotometrically by the distinctly coloured azo dye that forms when NO_x reacts with sulfanilic acid and 1-napthylamine in acetic acid by the following reaction:

$$2NO_2 + H_2O \leftrightarrows 2H^+ + NO_3^- + NO_2^- \qquad (3)$$

2.0 EXPERIMENTAL

2.1 pH Determination
Using a pH meter (Beckman 10H), which was calibrated in a pH = 7.0 buffer solution, then rinsed and placed in a pH = 4.01 buffer solution (and adjusted accordingly), we took pH readings from the four water samples obtained, as well as three other samples provided (vinegar, soft drink, washing powder). We placed the electrode into the sample, stirring it around gently and recording the pH meter reading once the meter had became static in it's measurement. The electrode was then rinsed thoroughly and placed in the next sample.

2.2 Hardness of water
50 mL of the two freshwater samples and sewage sample, and 5 mL of the seawater sample were each transferred via pipette into their respective 250 mL flasks. To these, 2 mL of buffer solution was added,

and 3-4 drops of EBT indicator. This solution was then titrated with EDTA until the colour changed from wine red to blue. This gave us the total Ca^{2+} and Mg^{2+} concentration

3.0 RESULTS

3.1 Analysis of dyes in jellybeans

Table1 shows the correlation between the expected and observed spectra found in the jelly bean food dyes extracted from the violet and amber jellybeans.

Jellybean	Name	Expected Absorption Maxima (nm)	Observed Absorption Maxima (nm)
Violet	**Green10**	**625**	**625**
	Red10	**530**	**531**
Amber	**Yellow10**	**440**	**439**
	Red10	**530**	**530**

Table 1. Expected and Observed absorption spectra for food dyes in jellybeans.

The food dye experiment was only carried out on the violet and amber jellybeans as there was insufficient time to conduct the experiment on the purple jellybeans. The green and red dyes of the violet jellybeans were visibly separated on the SepPak cartridge. The red dye was the first to be released followed by the green. Comparison of the spectrophotometric absorbance maxima of the dyes (Figures 1 and 2) to those of known dyes (Appendix I) identified the dyes and red10 and green10 in the violet jellybeans.

3.2 Analysis of benzoic acid in soft drink

The data reported in Table 2 show the variation in absorbance of the standard solutions of benzoic acid at various concentrations. From the calibration curve (Figure 3) it was found that the soft drink (absorbance of 0.280) contained 50.1 mg / L in the diluted sample. This figure was multiplied by four to allow for the dilution (25 mL of sample was made up finally in 100 mL of solution) to give a final value of 198.8 mg / L of benzoic acid in the soft drink.

4.0 DISCUSSION

4.1 Standard NaOH

The actual titre values of the prepared NaOH solution were larger than the calculated values and the calculated concentrations of NaOH were larger than the actual values. This may be due to Na_2CO_3 being present. Standard deviations and relative standard deviations were small, indicating either superior analytical skills or more likely too few samples for the statistics to be significant.

4.2 'tris' buffer

The calculated volume of 0.188 M NaOH required to reach a pH of 7.60 (33.37 mL) was lower than the actual volume used (33.96 mL) due to human error (NaOH concentration) and the deficiencies in the calculation of the pH using the Henderson-Hasselbach equation.

REFERENCES

1. S.E. Manahan, Environmental Chemistry, 6th Edition, Lewis, Boca Raton, 1994, pp 102-120.

APPENDIX I

- **Calculation for concentration of NaOH required for titration with KHP samples**

Sample 1: c = n / V = 4.29e-3 mol / 24.95e-3 L = 0.1880 M

PRESENTATION AND TREATMENT OF DATA

To a large extent experimental chemistry involves accurate measurements made on chemical systems. It is important that the measurements be made accurately, recorded accurately and that calculations using them be carried out correctly. To do this and to present the data and the results calculated from that data correctly requires care and understanding in the use of quantities, units and symbols.

1. PHYSICAL QUANTITIES AND UNITS

The value of a *physical quantity* is equal to the product of a *numerical value* and a *unit*, that is

$$\text{physical quantity} = \text{numerical value} \times \text{unit}.$$

This is the essential rule from which everything else follows. Neither any physical quantity nor the symbol used to denote it should imply a particular choice of unit. Operations on equations involving physical quantities, units, and numerical values should follow the ordinary rules of algebra.

Thus the physical quantity called the melting point of water, as the temperature of water at its freezing point has the value

$$T = 273.15\ \text{K}$$

where K is the symbol for the unit of temperature called the Kelvin This may equally well be written in the form

$$T/\text{K} = 273.15$$

or in any of the other ways of expressing the equality of T and 273.15 multiplied by K.

2. TABLES AND GRAPHS

Although for some quantities only a single measurement (say room temperature T = 300.5K) might be taken; in general, there will be a series of measurements such as the vapour pressure of a liquid at different temperatures or the variation of some other property as a function of time. Such data should be recorded and presented in a table or tabulation.

It follows from the above discussion that when numerical values of a physical quantity are tabulated, the expression to be placed at the head of a column should be the symbol for the physical quantity and the symbol for the unit used.

In the following table *T* denotes thermodynamic temperature and K the unit of thermodynamic temperature called the kelvin. Expressions such as '*T*(K)' or '*T*,K' do not denote *T* divided by K and should be abandoned in favour of ' *T*/K' or ' $T\ \text{K}^{-1}$'.

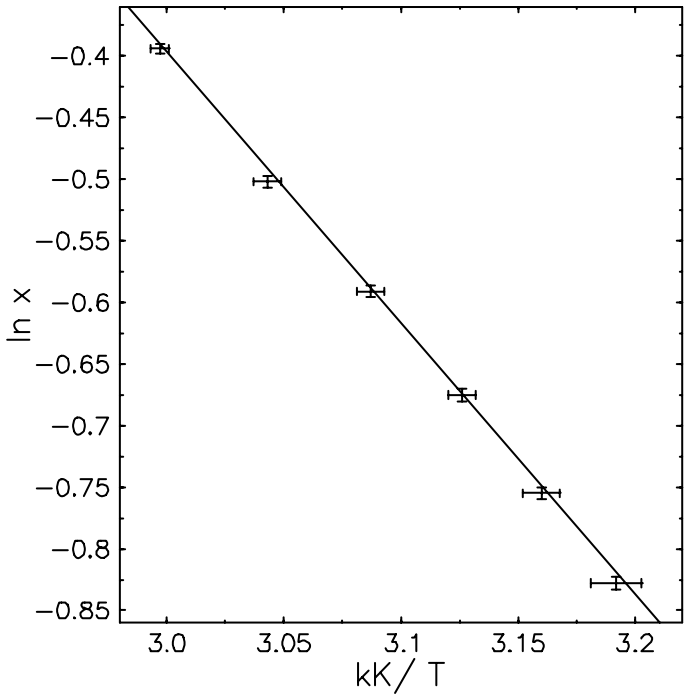
Example

Table 2. The variation of the vapour pressure (p) of some substance with temperature (T)

T/K	kK/T	p/MPa	ln(p/MPa)*	V_m^g/cm^{3}mol^{-1}	pV_m^g/RT
216.55	4.6179	0.5180	-0.6578	3177.600	0.9142
273.15	3.6610	3.4853	1.2486	456.970	0.7013
304.19	3.2874	7.3815	1.9990	94.060	0.2745

Often a graph of the results is needed. When numerical values of a physical quantity are plotted on a graph, the expression chosen to label the axis should be the symbol for the physical quantity and the symbol for the unit used.

Figure 3. Variation of crystallization temperature (T) with mole faction (x) for solutions of naphthalene in toluene



While it is desirable to maintain the above principle, its use should be flexible. For example, algebraically equivalent forms such as kK/T or 10^3K/T, may of course be used in place of T^{-1}/(kK)$^{-1}$.

* Note **ln** refers to natural logarithms, that is logarithms to the base e (where e = 2.718….)

4. SI PREFIXES

These are used to construct decimal multiples of units. A combination of prefix and symbol for a unit **is regarded as a single symbol** which may be raised to a power without the use of brackets. Thus $kK^{-1} = 10^{-3}K^{-1}$ NOT $10^{3}K^{-1}$! A list of prefixes is given in Table 3.

Table 3. SI prefixes used to construct decimal multiples of units

MULTIPLE	PREFIX	SYMBOL	MULTIPLE	PREFIX	SYMBOL
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^{2}	hecto	h
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

Calculations

In calculations involving physical quantities, the units (m, nm, K, etc.), being an **essential part** of any such quantity, **must** be included.

Example
Titration of 10 cm^3 of a NaOH solution with a 0.1024 mol dm^{-3} HCl solution gives a titre of 9.24 cm^3. Then the amount of HCl in the titre = 0.1024 mol dm^{-3} x 9.24 cm^3

$$= 0.1024 \times 9.24 \times \frac{10^{-3}\ \text{mol}\ dm^{-3}\ dm^{3}}{}$$

Notice that unless the units are included the result will be wrong by a factor of 1000!
Inclusion of units is of even greater importance where more complex calculations are involved.

5. SI UNITS

Wherever possible SI units should be used.

The SI units are of two basic kinds: *base* and *derived*. There are seven base units (see Table 4.), one for each of the seven physical quantities: Length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity which are regarded as dimensionally independent. The derived unit for any other physical quantity is that obtained by the dimensionally appropriate multiplication and division of the base units. Fourteen of the derived units have special names and symbols (Table 5.). There is one and only one SI unit for each physical quantity, although a derived unit may be denoted by more than one combination of symbols. Decimal multiples of any of the units may be constructed by means of the SI prefixes.

The seven base SI units are defined as follows:

METRE: The metre is the length equal to 1 650 763.73 wavelengths in vacuum of the radiation

corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton-86 atom.

KILOGRAM: The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

SECOND: The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.

KELVIN: The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

MOLE: The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

AMPERE: The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.

CANDELA: The candela is the luminous intensity, in the perpendicular direction of a surface of 1/600 000 square metre of a black body at the temperature of freezing platinum under a pressure of 101 325 newtons per square metre.

Table 4. Names and symbols for the SI base units

PHYSICAL QUANTITIES	NAME OF SI UNIT	SYMBOL FOR SI UNIT
length	metre	m
mass	kilogram	kg
time	second	s
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

Table 5. Special names and symbols for some SI derived units

PHYSICAL QUANTITY	NAME OF SI UNIT	SYMBOL FOR SI UNIT	EQUIVALENT DEFINITION OF SI UNIT	FORM(S) OF SI UNIT
energy	joule	J	$m^2 kg\ s^{-2}$	N m
force	newton	N	$m\ kg\ s^{-2}$	$J\ m^{-1}$
pressure	pascal	Pa	$m^{-1} kg\ s^{-2}$	$N\ m^{-2}$, $J\ m^{-3}$
power	watt	W	$m^2 kg\ s^{-3}$	$J\ s^{1}$
electric charge	coulomb	C	sA	A s
electric potential difference	volt	V	$m^2 kg\ s^{-3} A^{-1}$	$J\ A^{-1} s^{-1}$, $J\ C^{-1}$
electric resistance	ohm	Ω	$m^2 kg\ s^{-3} A^{-2}$	VA^{-1}
electric conductance	siemens	S	$m^{-2} kg^{-1} s^3 A^2$	Ω^{-1}, $A\ V^{-1}$
electric capacitance	farad	F	$m^{-2} kg^{-1} s^4 A^2$	$A\ s\ V^{-1}$, $C\ V^{-1}$
magnetic flux	weber	Wb	$m^2 kg\ s^{-2} A^{-1}$	V s
magnetic flux density	tesla	T	$kg\ s^{-2}\ A^{-1}$	$V\ s\ m^{-2}$, $Wb\ m^{-2}$
frequency	hertz	Hz	s^{-1}	
(radio)activity	becquerel	Bq	s^{-1}	
absorbed dose	gray	Gy	$J\ kg^{-1}$	

References

1. "Quantities, units, and symbols", The Symbols Committee of The Royal Society, London, 1975.

ERRORS OF OBSERVATION AND THEIR TREATMENT

In taking a scientific measurement it is essential to know the precision of that measurement. For example the statement that the distance between two points on a map is 30 km might mean (amongst other possibilities) that:

a) the distance lies somewhere between 25 and 35 km
or b) the distance lies between 29.999 and 30.001 km.

Clearly (b) reflects a more precise evaluation of the distance between the two points.

For everyday use this difference may not be of much importance but in scientific work it is of critical importance. Therefore, it is a waste of time to make a measurement without also determining is precision. This is then presented by quoting an "error" in that measurement. In the example above this is done by writing

a) distance = 30 ± 5 km
or b) distance = 30.000 ± 0.001 km.

What this means should become clearer as we look at 'errors' in more detail.

1. ERROR IN A SINGLE MEASURED QUANTITY

Let us begin by looking at the error in a single quantity such as the distance between two points. In measuring any particular property or quantity x, the observed value, x_{obs}, is always slightly different from the true value x_t. Although it may be impossible to know the true value it is possible to set limits within which the true value must lie and, in this case, to determine that x_t, lies between x_{obs}-E(x) and x_{obs} + E(X). The quantity E(x) which defines the region about x_{obs} is called the error in x. Since the true value lies within this region the value of x is written as

$$x = x_{obs} \pm E(x)$$

or, including the units, as

$$x = [x_{obs} \pm E(x)] \text{ units}$$
$$e.g.\ T = (245.3 \pm 0.3)K$$

1.1 Estimated error

One way of determining E(x) is by estimation and this is frequently used. Take, for example, reading the liquid level in a burette. My best estimate of this reading (V) is 13.22 cm^3 but I believe the value could be as low as 13.20 cm^3 or as high as 13.24 cm^3. Therefore

$$V = (13.22 \pm 0.02)\ cm^3$$

Note that the value of the estimated error is **half** the difference between the extreme values!

1.2 Statistical evaluation of the error

A better approach is to repeat the measurement a large number of times. If the measurement is repeated several times as honestly and as accurately as possible a number of different values will be obtained. The best estimate of the (true) value of x is the average (x_{av}) of all of these measurements.

$$x_{av} = (\sum_{i=1}^{N} x_i) / N$$

Instead of an estimated error it is now possible to calculate a better defined but related quantity, the standard deviation σ given by

$$\sigma^2 = \{\sum_{i=1}^{N} (x_i - x_{av})^2\} / N$$

When it is necessary to compare estimated errors and standard deviations a good rule is to take a standard deviation to be about half of an estimated error. You must, therefore, say if you are using estimated errors or standard deviations (statistically derived errors).

Sometimes, particularly where the error is a standard deviation, a measurement is written not as

$$T = (245.3 \pm 0.3)K$$

$$or\ p = (101.4 \pm 1.1)kPa$$

but, instead, as

$$T = 245.3(3)K$$

$$or\ p = 101.4(11)\ kPa$$

NOTE the lack of decimal points in the later cases; the numbers in brackets refer to the last figures in the value itself!

1.3 Significant figures in the error

In the examples above the errors are to one (e.g. 0.2 and 0.3) or two (e.g. 1.1) significant figures. This practise is universal. **Errors are approximate** (we do not try to find the error in the error and so on) **and are quoted to one, or AT MOST two, significant figures.**

2. ORIGIN AND NATURE OF ERRORS

Errors are of two basic types **random** and **systematic** errors. Random errors are revealed by repeated measurement and can be estimated, or evaluated, as described above. Systematic errors are introduced by the measuring device and are not revealed by repeated measurement. They may be quite difficult to detect.

Take the measurement of a length using a ruler. As usual repeated measurement of the distance between points will give slightly different results; due to a 'random error' in measurement. However, if the ruler was marked at one temperature and used at another all the measurements

will be in error due to thermal expansion or contraction of the ruler. This additional error is a systematic error. The ruler should be recalibrated at the new temperature. (Of course any calibration is not perfect but the error involved in calibration is a measurable random error not an unknown systematic error). Systematic errors are best dealt with by calibration. Alternatively they may be estimated in some way (often from the manufacturer's specifications).

3. ERROR IN A CALCULATED QUANTITY

Now consider the error in a quantity *calculated* from other quantities in which the error is known. (So far only the error of a particular measured quantity has been considered). There are a few simple rules which may be used. In using these rules it must be kept in mind that errors are only calculated to 1 (at most 2) significant figures. This means that any contribution which is less than one tenth of any other contribution may be neglected! It also means that such calculations, being approximate, may, with practise, be carried out very quickly.

1) Sums and differences

If a quantity A is given by

$$A = B + C \quad \text{or} \quad A = B - C$$

where the errors E(B) in B and E(C) in C are known, then the error E(A) in A is given by

$$E(A) = E(B) + E(C).$$

This may be extended to any number of sums and differences as long as *only* sums and differences are involved.

Example:
In a titration the initial liquid level in the burette is read as $V_i = (5.44 \pm 0.02)\ cm^3$ and the final level as $V_f = (23.68 \pm 0.02) cm^3$ so that if the titre is V then

$$V = V_f - V_i = (18.24 \pm 0.04) cm^3$$

since

$$E(V) = E(V_f) + E(V_i) = 0.02\ cm^3 + 0.02 cm^3 = 0.04\ cm^3.$$

2) Products and quotients

If

$$A = BxC, \text{ or if } A = B/C, \text{ or if } A = C/B$$

then

$$E(A)/A = E(B)/B + E(C)/C.$$

This may be extended to any number of products and quotients as long as *only* products and quotients are involved.

The ratio E(A)/A is called the **relative error** (RE) in A. Since the relative error is so important

the error (in this case E(A)) is sometimes called the **absolute error** to avoid confusion.

Example:
If a solution contains n_x = (0.135 ± 0.003)mol of solute X in V = (1.104 ± 0.002)dm^3 of solution then the concentration [X] is

$$[X] = n_x/V = 0.122282608 \text{ mol } dm^3$$

To find the error in this value apply rule (2) to give

$$\begin{aligned} RE([X]) = E([X])/[X] &= E(n_x)/n_x + E(V)/V \\ &= 3/135 + 2/1104 \\ &= 3/140 + 2/1100 \\ &= 1/47 + 1/550 \end{aligned}$$

This looks very messy and it becomes important at this stage to introduce a couple of rules concerning error calculations:

RULE 1: It is never necessary to keep more than 2 significant figures in error calculations.
RULE 2: If any single contribution is less than one tenth of another contribution then it is neglected.

In the present example, since then denominator in the second term is more than ten times the denominator in the first term, then it should be neglected giving

$$RE([X]) = E([X])/[X] = 1/47.$$

To obtain E([X]), the error in [X], rearrange the expression for RE([X])

$$E([X]) = X.RE([X])$$

so that

$$E([X]) = 0.12228x1/47 = 0.0026 = 0.003$$

giving $[X] = (0.122 \pm 0.003) \text{ mol } dm^{-3}$.

3) Natural logarithms

If $Y = \ln(X)$

then $E(Y) = E(X)/X$ or $E(\ln X) = E(X)/X$,

so that the error in ln X equals the relative error in X!
Example:
If $x = 0.104 \pm 0.006$ then $\ln x = -2.26 \pm 0.06$

since $E(\ln x) = E(x)/x = 0.006/0.104 = 0.06.$

4) Logarithms to base 10

If $Y = \log_{10}(X)$ then $E(Y) = (1/2.3)E(X)/X$ or $E(\log_{10}X) = (1/2.303)E(X)/X$.

5) General rule

If $Y = f(X)$

then $E(Y)/E(X) = dY/dX$ or $E(Y) = E(X).dY/dX$

Example:
If $Y = \ln X$

then $dY/dX = 1/X \Rightarrow E(Y) = E(X).1/X$

4. SIGNIFICANT FIGURES

The way in which a value is quoted, the number of significant figures, is determined by its error
e.g. $T = (259.28 \pm 0.03)K$
but **not**
$T = (259.2834621 \pm 0.03)K$ (too many significant figures)
and **not**
$T = (259.3 \pm 0.03)K$ (too few significant figures).

The temperature
$T = (259.28 \pm 0.03)K$

is known to **five** significant figures.

Although expressions such as:

$p = (235{,}000 \pm 2{,}000)Pa$ and $l = (0.00334 \pm 0.00005)m$

are not incorrect, they are clumsy and forms such as

$p = (235 \pm 2)kPa$ or $p = (0.235 \pm 0.002)MPa$ and $l = (3.34 \pm 0.05)mm$

should be used.

Finally forms such as
$p = (2.35 \times 10^{5} \pm 2 \times 10^{3})Pa$ and $l = (3.34 \times 10^{-3} \pm 5 \times 10^{-5})m$,

in which different exponents are used for the quantity and error, should NOT be used.

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 :

LearnJCU/CH1011/FindMore /CH1011 Safety Booklet

or

http://cnsfse01.jcu.edu.au/Schools/Chemistry/SafetyManual/manual.htm

At the prompt enter student login name and password then download the Safety Manual for reading.

ASSIGNMENT 2
BASIC VOLUMETRIC ANALYSIS

AIMS

To become familiar with the use of two basic analytical techniques: calibration of a pipette and an acid-base titration.

1. INTRODUCTION

This assignment deals with chemical analysis and provides the opportunity to develop certain fundamental quantitative laboratory skills. You will conduct an acid-base titration and calibrate a pipette.

The experiments involve the use of accurate volumetric glassware and the analytical balance. Use of the balance will be demonstrated during the laboratory sessions. The correct technique for using volumetric glassware will be demonstrated prior to your commencing the assignment, and is explained in "Use of Volumetric Glassware" (see previous Section).

The calibration of a pipette is based on the fact that masses can be measured much more accurately than volumes. For any substance, its density (ρ) is related to its mass (m) and volume (V) by

$$\rho = m/V$$

Provided accurate values are available for the density of water, the volume of aqueous solution delivered by a pipette can be accurately determined by measuring the mass of water delivered by that pipette.

Titration techniques are used to determine the quantity of a substance (X) in a solution. The determination is done by taking an accurately known volume (called an "aliquot") of that solution and adding just enough of a solution containing a known concentration of another substance Y (with which X undergoes a chemical reaction) to completely react with it. This precise point in the reaction is called the "end point" or "equivalence point", and one of the skills of the titration technique - besides accuracy in the use of the volumetric glassware - is the detection of this point. By determining the volume of the second solution, the amount of X in the first solution can be calculated.

Chemical reactions between substances occur in proportions given by the balanced chemical equation. For example, if substance Y reacts with substance X according to

$$xX + yY \rightarrow \text{products}$$

where x and y are coefficients, then this stoichiometry tells us that x moles of X react with exactly y moles of Y. Thus at the "equivalence point" the amounts of X (n_X) and Y (n_Y) in moles are such that:

$$\frac{n_X}{n_Y} = \frac{x}{y} \qquad \ldots (1)$$

The concentration of a substance in solution (represented by C_X or [X], as e.g. [NaOH]) is the quantity (number of moles) of that substance in 1 dm^3 (or 1 litre) of solution. In our example above, C_X is unknown but C_Y is known. In our titration, the volume of the solution of X is accurately measured (V_X), and the volume of the solution of Y to completely react with it (V_Y) is determined by titration.

Now $n_X = C_X.V_X$ and $n_Y = C_Y.V_Y$. Accordingly, from Eq. 1,

$$\frac{C_X.V_X}{C_Y.V_Y} = \frac{x}{y} \qquad \ldots (2)$$

or

$$\frac{C_X.V_X}{x} = \frac{C_Y.V_Y}{y} \qquad \ldots (3)$$

Since the stoichiometry (i.e. x and y) is known, V_X and V_Y are measured and C_Y is known, then C_X can be calculated.

[NOTE: Once some solution, of known volume and concentration, has been added to the reaction mixture the addition of water will NOT alter the amount which has been added! This means, at least in principle, that any amount of water can be added to the reaction vessel at any time; the only limitation being the size or volume of the vessel.]

2. EXPERIMENTAL

There are two parts to this experiment. Half the class will be assigned to start on 2.1 and half on 2.2. After you have completed the part assigned to you then commence on the remaining part.

2.1 Calibration of a pipette

A 10 cm^3 "B" grade pipette has a tolerance of ±0.04 cm^3, i.e. the volume it will deliver will be in the range 9.96 to 10.04 cm^3. The volume delivered by a given pipette will, however, show much better reproducibility than this. For accurate work it is often necessary to find accurately the volume delivered by a given pipette. The pipette is then said to be <u>calibrated</u>. Do the experiment in duplicate, or until your calibrations agree to ±0.02 cm^3.

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

1. Accurately weigh a clean dry weighing bottle (plastic) on the analytical balance.
2. <u>Pipette</u> 10 cm^3 of distilled water into the bottle.
3. Accurately weigh the bottle plus the 10 cm^3 of water.
4. Immediately measure the temperature of the water.
5. Calculate the volume delivered by the pipette, as indicated below.

CALCULATIONS AND QUESTIONS

See your REPORT book. Complete the calculations and questions in Appendix 1 and then the Results and Discussion section 3.1.

2.2 A Neutralisation Reaction: Determination of acetic acid concentration in vinegars

All vinegars contain acetic acid, CH_3COOH, formed by oxidation of ethyl alcohol in their manufacture. Like all Brønsted-Lowry acids, acetic acid reacts with hydroxide ion, OH^-, in a *neutralisation* reaction:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

By reaction of an aliquot of vinegar with a standard solution of sodium hydroxide ion of known concentration, and determining the volume at the point of neutralisation, the acetic acid solution concentration can be determined. The "end point" of the titration is determined by using an *indicator* which undergoes a rapid colour change at the neutralisation point.

In this experiment, the practical class will determine the variation of acetic acid concentrations in a number of commercial vinegars. Each student pair will titrate two of the 4 different vinegars.

At the end of the session a class list will be placed on the board and each pair will enter their results. Class averages should then be taken down from this list for entry into Table 1 of your REPORT book.

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

SAFETY NOTE: Use safety bulbs with the pipettes

1. Fill the burette with the supplied standard sodium hydroxide solution, note down the concentration in your report book (eg. 0.1698 M).

2. Pipette 5 cm^3 of the vinegar into a 100 cm^3 conical flask. Note down the vinegar you have used in your report book. Add approximately 20 cm^3 of distilled water and 3 drops of phenolphthalein indicator solution.

3. Titrate the sodium hydroxide solution into the vinegar solution, swirling after each addition, until the first permanent red colouration of the indicator. The last few additions will need to be made very carefully to determine this "end point" precisely: you should be able to read to **± 0.02 cm^3** by estimating between the 0.1 cm^3 divisions on the burette. **Your start point and your end point need to be signed in your report book by your demonstrator.**

4. Record the titre value.

5. Repeat the titration until concordant results are obtained (**titrations should agree to within ±0.05 cm^3**).

Repeat Steps 1 – 5 using a second vinegar (<u>both partners</u> must practice the titration step).

CALCULATIONS AND QUESTIONS

See your REPORT book. Complete the calculations and questions in Appendix 2 and then the Results and Discussion section 3.2.

ASSIGNMENT 3
GEOMETRIC MODELS
Valence Share Electron-Pair Repulsion (VSEPR) Method

AIMS

Familiarisation with a simple theory (VSEPR) used to predict molecular geometries .

1. INTRODUCTION

Number of valence electrons

1	**2**											**3**	**4**	**5**	**6**	**7**	**8**
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nd	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

For compounds of non-transition elements, it is often possible to predict stereochemistries by considering the number of electron pairs, both bonding and lone pairs, in the valence shell of the central atom.

The theory is due to Sidgwick and Powell, and was later extended by Gillespie and Nyholm. Rule #1 : It proposed that regions of electron density around the central atom will arrange themselves so that the maximum symmetry is achieved, since in this configuration the repulsions will be minimised.

The method will work by using only a very crude description of the electronic structure of the molecule, so called **Lewis Structures**: e.g. as provided by the Lewis Theory of electron sharing between atoms to form covalent bonds (the "Octet Rule"). The **Octet Rule** says that for the elements C – F when molecules are formed that involved covalent bonds there must be **8 electrons** around these main group atoms for the molecule to have a stable structure (eg. In CO_2 there must be 8 electrons around C and 8 electrons around each O). N.B the octet rule holds strictly for period 2 atoms(C-F) but not for **period 3** atoms where up to **12 electrons** may be found around an atom, it also does not hold for Group 3 where lower counts may be accepted. The Lewis Theory does NOT require a knowledge of the geometric structure. When creating reasonable Lewis structures it is important to realise that all atoms must have only pairs of electrons either in bonds or in non-bonding pairs – there should **never be a single unpaired electron** in a reasonable Lewis structure for a relatively stable molecule.

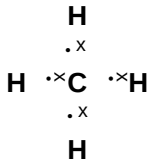
1.1 Electron-pair repulsion

Rule #1: *Electron pairs (electron domains) orient themselves in space so as to minimise their mutual repulsions*

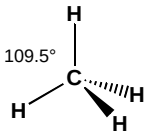
This allows prediction of geometry of regular structures - as shown in Table 1.

Example 1: Methane CH_4

The Lewis structure shows the carbon atoms to be surrounded by four bonding electron pairs, so that the electronic structure as well as the molecular structure are *tetrahedral.*



• Lewis structure



• Electronic geometry & Molecular geometry

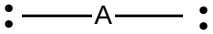
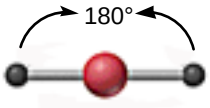
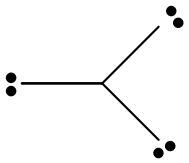
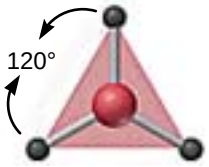
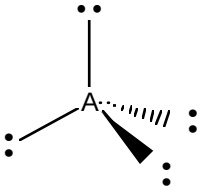
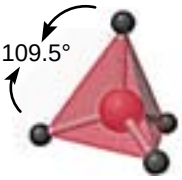
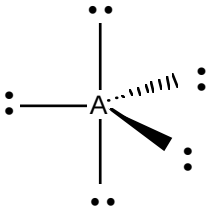
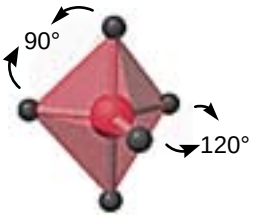
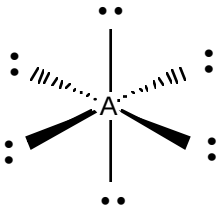
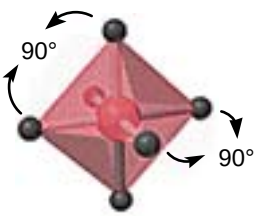
Number of electron domains (central atom)	Electronic Geometry	Molecular Geometry
2		 linear
3		 trigonal planar
4		 tetrahedral
5		 trigonal bipyramidal
6		 octahedral

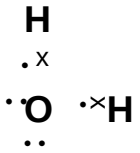
Table 1. Configuration for number of electron domains

1.2 Size of repulsions

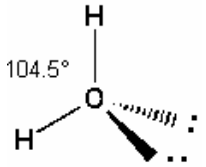
Rule #2: *Lone pair-lone pair (lp/lp) repulsions are greater than lone pair-bond pair (lp/bp) repulsions, which are in turn greater than bond pair-bond pair (bp/bp) repulsions.*

Example 2: Water H_2O

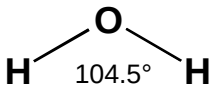
The Lewis structure shows two bonding electron pairs and two lone pairs about the central oxygen atom. Accordingly there are four regions of electron density and the electronic geometry will be *tetrahedral.* However, two of those regions are lone pairs, so the molecular geometry is essentially part of the tetrahedral structure: i.e. *bent,* with the H-O-H angle being tetrahedral (109.5°). In fact, the angle is less than that (*viz.* 104.5°), because the *lp/lp* and *lp/bp* repulsions exceeds that of *bp/bp* resulting in a contraction of the bond angle.



Lewis structure



Electronic structure



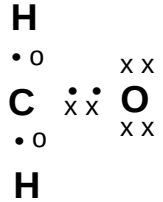
Molecular structure

1.3 Multiple bonds

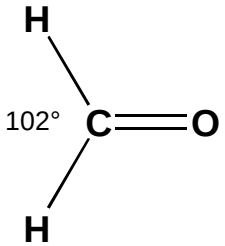
Rule #3: *The electron pairs of a multiple bond are considered as a single electron domain: however, they take up more room that a bonding electron pair, but less than a lone pair.*

To find a reasonable structure with double or triple bonds we first look to see if 2 or more of the elements **C, N, O, P or S** are present. If this is the case then we attempt to form a reasonable Lewis structure with a double (or triple bond) between the 2 atoms from this list, remembering that we must not accept structures with single unpaired electrons.

Example 4: Formaldehyde, H_2CO



Lewis structure



Molecular structure

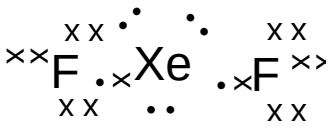
In the Lewis structure, there are single bonds between the central C atom and each of the hydrogen atoms, and a double bond to the oxygen atom. Based on three electron domains, the electronic geometry is basically *trigonal planar,* as is the molecular geometry since all regions are associated with bonding. However, due to the greater repulsion from the double bond the H-C-H angle is less than 120°.

1.4 Five or more pairs

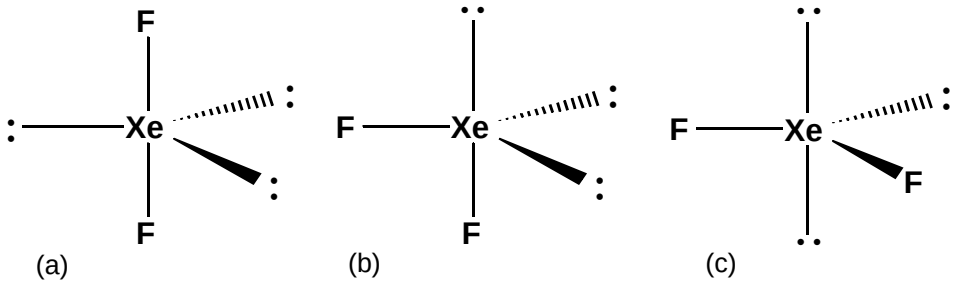
Rule #4: *Ignore interactions where the axes of the electron pairs define an angle greater than 90°.*

Example 3. XeF_2

There can be exceptions to the "Octet Rule". In a case such as XeF_2 , each F must share an electron with Xe in the Xe-F bond, so that ultimately there will be 10 electrons about the Xe atom (i.e. 8 from Xe and the two additional bonding electrons from the F atoms). Accordingly there will be two bonding pairs of electrons and three lone pairs about the central Xe atom.



Lewis structure



Possible electronic structures

The electronic geometry will be trigonal bipyramidal. There are three possible arrangements, for each arrangement (a) → (c), *the interactions of each type at ≤ 90°* are summarised below.

	(a)	**(b)**	**(c)**
lp/lp	0	2	2
lp/bp	6	3	4
bp/bp	0	1	0

Since (a) has the smallest number of lone pair-lone pair interactions, it is the predicted structure: i.e. the molecular geometry is *linear.*

1.5 Electronegativity

Rule #5: *The more electronegative the atoms bonded to the central atom, the more electron density is displaced towards the central atom. Repulsions at the central atom are intensified which rationalises:*

OH_2 (104.5°) > OF_2 (103.2°)

NH_3 (107.3°) > NF_3 (102°)

PI_3 (102°) > PBr_3 (101°) > PCl_3 (100°)

AsI_3 (101°) > $AsBr_3$ (100.5°) > $AsCl_3$ (98.4) > AsF_3 (96°)

If you have trouble with drawing the Lewis structure, there is a scheme which you may find useful, based on the formula

S = N - A

where

- S is the number of shared electrons;
- N is the number of outer valence electrons required so that each atom obeys the "Octet Rule" (i.e. 2 for H;8 for elements C-F; Group 3 either 6 or8; Group 8 10 or 12; Periods 3 & 4 8,10 or 12); and
- A is the total number of outer valence electrons actually present.

For example, for **formaldehyde HC(O)H**

A = 4 (C) + 6 (O) + 2 x 1 (each H) = 12

N = 2 x 8 (octet for C and O) + 2 x 2 (filled valence shell for H) = 20

so that S = 20 - 12 = 8 (i.e. four shared pairs of electrons)

Since there are only three atoms bonded to the central C atom, there are two single bonds (to the H atoms, which can only form single bonds) and the bond between C and O must be a double bond (i.e. two pairs of electrons).

2. QUESTIONS

Draw the approximate geometrical arrangement of the atoms in the molecules in group (i) using the VSEPR method. In your report book describe the structures in terms of the geometries of the electronic structure and the molecular structure (follow the format of Example 2). Identify the number of electronic regions in each structure. Check with your Tutor and the answers will be discussed using molecular models.

Repeat the exercise for the remaining three groups of molecules.

(i)	BF_3	NH_3 ammonia	NO_3^- nitrate ion	H_2O water
(ii)	SF_6	$POCl_3$	SO_4^{2-} sulphate ion	CO_3^{2-} carbonate ion
(iii)	SO_2 sulphur dioxide	XeF_4	$H_2C=CH_2$ Ethene (ethylene)	ClF_3

ASSIGNMENT 4
FUNCTIONAL GROUP AWARENESS - MODEL BUILDING

AIMS

The object of this assignment is to make you familiar with the important functional groups and by building models of selected examples, to give you an appreciation of the three dimensional nature of organic molecules.

1. INTRODUCTION

In organic chemistry the concept of **functional groups** is very important. It enables us to think of compounds as having an unreactive handle (the R group) and a reactive end (the functional group). Thus organic molecules can be characterised as R-Z, where Z is the functional group in question and R is the unreactive carbon skeleton. Two organic compounds with the same molecular formula but which have different structures are said to be **isomers**. In this practical only the simplest form of isomerisation, **structural isomerisation**, will be considered. In each structural isomer there is a different carbon skeleton. For molecules with functional groups this generally means that the position of the functional group in the molecule will change.

2. MODELLING

Computational modelling is a rapidly expanding field of chemistry that is used extensively in the drug design industry. In this practical you will use either one of the most commonly used modelling packages for organic chemistry called CHEM-3D (Cambridge Soft Corporation) or CPK ball and stick models to build the molecules.

3. QUESTIONS

HYDROCARBONS

Carbon forms a large number of compounds in which hydrogen is the only other atom present. These compounds are known as hydrocarbons and may be further classified as **saturated** if they contain only single bonds and **unsaturated** if they contain multiple bonds.

Alkanes: These are **saturated** hydrocarbons ie. they contain only **single** carbon-carbon bonds. They may be open-chain (often termed “aliphatic” after the Greek “aliphos”, fat, the fatty acids being the first compounds of this class to be studies), or cyclic (the cycloalkanes). Open-chain hydrocarbons form an homologous series with empirical formula C_nH_{2n+2} and the cycloalkanes a corresponding series with empirical formula C_nH_{2n}.

Alkenes: These are **unsaturated** hydrocarbons containing one or more carbon-carbon **double** bonds. Open chain alkenes with one double bond form an homologous series with empirical formula C_nH_{2n}.

Alkynes: These are **unsaturated** hydrocarbons containing a carbon-carbon **triple** bond (empirical formula C_nH_{2n-2}).
Aromatic Compounds: These are **unsaturated** cyclic hydrocarbons related to benzene (C_6H_6). NB Benzene is extremely toxic both by inhalation and by skin adsorption, its toxic effects being accumulative. When used it must be kept in a fume hood at all times.

EXERCISES

Alkanes: Make models of methane (CH_4), ethane (C_2H_6), and the isomeric alkanes (C_4H_{10}). Draw diagrams directly into your report book and give IUPAC names.

Alkenes: Make models of ethene (C_2H_4) and the isomeric C_4 alkenes (C_4H_8). Draw diagrams directly into your report book and give IUPAC names.

Alkynes: Make a model of ethyne (C_2H_2, what is its trivial name?). Draw a diagram directly into your report book and give IUPAC names.

Aromatic Compounds: Draw a three dimensional representation of benzene (C_6H_6) which clearly shows the nature of its π system in your report book.

ALCOHOLS, ETHERS AND PHENOLS

Alcohols are aliphatic compounds containing one or more hydroxyl (-OH) functional groups. The empirical formula for the homologous series is $C_nH_{2n+1}OH$ and is more generally represented as ROH, where R is any alkyl group.

Ethers may be regarded as anhydrides of alcohols, their general structure being R-O-R'. Ethers are isomeric with the alcohols, having an empirical formula $C_nH_{2n+2}O$. Diethyl ether, generally known simply as "ether", is by far the most commonly used compound of this class. It is a liquid with a boiling point of 34^{o}C at atmospheric pressure. At room temperature it gives off considerable amounts of inflammable heavy vapour, which forms explosive mixtures with air. Ether is immiscible with water and floats on it. That is why ether fires can not be extinguished with water, which simply disperses the burning ether. The danger of fire outbreaks can be reduced by using only a few mL of ether at any one time and ensuring that there are no naked flames (eg. bunsen burners) in the vicinity.

Phenols are aromatic compounds with hydroxyl groups attached to their aromatic rings. Phenol (C_6H_5OH) may be regarded as a derivative of benzene (C_6H_6). The chemical properties of phenol are, however, very different from those of the aliphatic alcohols The term "Phenol", like "alcohol", is generic as well as specific, so an hydroxyl derivative of an aromatic compound (hydrocarbon of the benzene series) is known as a phenol. Phenol itself is the simplest compound of this class.

EXERCISES

Alcohols: Make models of methanol (CH_3OH) and the isomeric propanols (C_3H_7OH). Draw diagrams directly into your report book and give IUPAC names.

Ethers: Make a model of diethyl ether, giving the alternative IUPAC name and drawing a diagram directly into your report book.

Phenols: Draw a three dimensional representation of phenol (C_6H_5OH) showing the structure of the benzene ring.

HALOALKANES

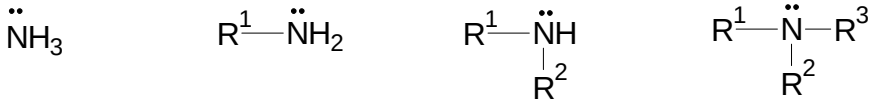
These compounds have the general form R-X (X = Br, Cl, I, F). Haloalkanes, especially bromides and iodides, are extremely useful synthetic intermediates since the halogen atom may be replaced readily with a variety of other functional groups.

EXERCISES

Make models of ethyl bromide (C_2H_5Br) and *i*-propyl bromide (C_3H_7Br) – note these compounds are here named as alkyl halides rather than haloalkanes. Draw diagrams directly into your report book and provide the IUPAC haloalkane names. You will need to be familiar with the trivial prefixes *n*- (*normal*), *i*- (*iso*) and *t*- (*tertiary*).

AMINES

Amines, the bases of organic chemistry, are formally derived from ammonia by replacing one of more of its hydrogen atoms by alkyl or aryl groups. Depending on the number of such groups, amines can be classified as **primary**, **secondary** or **tertiary**:



ammonia primary amine secondary amine tertiary amine

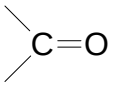
Amines can act as Lewis bases and owe their basic properties to the unshared electron pair (the "lone pair") that is on their nitrogen atom. Most simple amines have a characteristic "fishy" odour.

EXERCISES

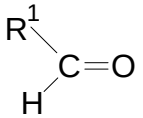
Make models of trimethylamine and methyethylamine. Draw diagrams directly into your report book and classify these amines as primary, secondary of tertiary.

ALDEHYDES AND KETONES

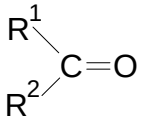
Aldehydes and ketones both have the empirical formula $C_nH_{2n}O$ and are characterised by the presence of the carbonyl functional group:



In *aldehydes* the carbonyl group is present as the aldehyde functionality:



In *ketones* the carbonyl group is present as the ketonic functionality:



R^1 and R^2 = alkyl or aryl

Both aldehydes and ketones show many of the same reactions due to the carbonyl group. However, aldehydes are much stronger reducing agents than ketones and this property is the basis of many of the chemical tests used to distinguish between them.

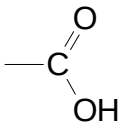
EXERCISES

Aldehydes: Make a model of ethanal. What is its common name? Draw a diagram directly into your report book.

Ketones: Make a model of propanone. What is its common name? Draw a diagram directly into your report book.

CARBOXYLIC ACIDS

Their empirical formula may be expressed by $C_nH_{2n+1}CO_2H$ ($C_nH_{2n}O_2$) or more generally by RCO_2H where the functional group is the carboxyl group:



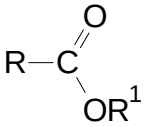
Carboxylic acids may contain more than one carboxyl group. Those of low molecular weight are readily soluble in water. The water solubility of members of any given homologous series usually diminishes as the number of carbon atoms increases.

EXERCISE

Draw the structure of ethanoic acid and indicate all the angles around the carboxylate carbon. What is its common name?

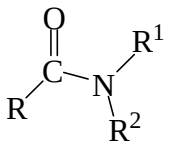
DERIVATIVES OF CARBOXYLIC ACIDS

Esters, of empirical formula $C_nH_{2n}O_2$ (isomeric with the carboxylic acids) or more generally



are compounds formed when the hydroxyl hydrogen of a carboxylic acid is replaced by an alkyl or aryl group.

Amides, of the general formula



R^1, R^2 = H or alkyl or aryl

are derived from acids by replacement of the hydroxyl group by an amine group.

EXERCISES

Draw the structures of methyl propanoate and ethanamide (acetamide) into your report book.

ASSIGNMENT 5
REDOX TITRATIONS

AIMS

To develop skills in the use of more advanced titration techniques. The experiments involve: (i) the determination of hydrogen peroxide in solution as an example of the use of a standardisation method and (ii) the use of a dichromate titration in the determination of the molecular weight of an unknown compound.

1. INTRODUCTION

The redox titrations that you will carry out in the next two experiments are used in each case to quantitatively determine the amount of a compound in solution. The first experiment involves the determination of the amount of hydrogen peroxide in an aqueous solution - a process known as the *standardisation* of a solution. Titrations are frequently used for standardisation as the concentrations of many species in solution change with time. A convenient and quick method is therefore needed to determine the concentration of such species in solution, prior to the solution being used. The second experiment illustrates the use of stoichiometry, gravimetry (weighing) and a redox titration to determine the molecular weight of an unknown iron complex.

2. EXPERIMENTAL

2.1 A Redox Reaction: Standardisation of hydrogen peroxide

Hydrogen peroxide, H_2O_2, is a substance widely used as a bleach (for hair, wood pulp, textiles, wool, straw) and as an antiseptic. In high concentration it is used as a rocket propellant because of its ability to release gaseous oxygen, O_2. However, for uses such as a bleach and an antiseptic it is sold commercially as a 3% aqueous solution. Such solutions deteriorate with time and will gradually liberate oxygen - especially if the bottles are exposed to light or heat. You may have noticed the positive pressure developed in a bottle of hydrogen peroxide which has been stored for some time. Accordingly, bottles of hydrogen peroxide in a store will have a limited "shelf life", depending on the conditions of their storage.

Hydrogen peroxide undergoes a redox reaction with potassium permanganate:

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

and the reaction may be used to determine the concentration of the hydrogen peroxide when a permanganate ion solution of known concentration is used. The permanganate ion is bright purple in colour and the other components of the reaction mixture are essentially colourless.

In the experiment, your practical group will determine the concentration of hydrogen peroxide solutions - some samples of which are taken from freshly-opened bottles and others from bottles which have been opened for some time. A standard solution of potassium permanganate is supplied - your Tutor will provide you with the concentration.

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

(**NOTE** that for opaque solutions you read the top of the meniscus!)

1. Fill the burette with the standard potassium permanganate solution, note down the concentration in your report book.

2. Accurately dilute the hydrogen peroxide by adding 10 cm^3 (using a pipette) to a 100 cm^3 volumetric flask and making it up to the mark with distilled water, as described in Section 4 of "Use of Volumetric Glassware" earlier in this practical manual. Place cap on and shake well.

3. Using a pipette, add a 10 cm^3 aliquot of the diluted hydrogen peroxide solution to a 250 cm^3 conical flask and add approximately 20 cm^3 of 2M sulphuric acid using a measuring cylinder.

3. Titrate with the potassium permanganate solution until the first permanent pale pink colouration is observed. You should be able to read to **±0.02** cm^3 by estimating between the 0.1 cm^3 divisions on the burette. For dark coloured solutions such as permanganate you read from the top of the meniscus rather than the bottom. **Your start point and your end point need to be signed in your report book by your demonstrator.**

4. Repeat the titration procedure until two titres agree within **2** cm^3 .

At the end of the session a class list will be placed on the board and each pair will enter their results. Class averages should then be taken down from this list for entry into Table 1 of your REPORT book.

CALCULATIONS AND QUESTIONS

See your REPORT book. Complete the calculations and questions in Appendix 1 and then the Results and Discussion section 3.1.

2.2 A Redox Reaction: Determination the molecular weight of an unknown compound of iron(II) using dichromate ion, $Cr_2O_7^{2-}$

Dichromate ion, $Cr_2O_7^{2-}$, is an oxidising agent and oxidises ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) in acidic solution according to the following equation:

$$14H^+_{(aq)} + 6Fe^{2+}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$$

A standard dichromate solution of known concentration will be provided. You will be provided with a solid compound of iron(II) but not provided with its formula: the aim of the experiment is to analyse the compound using the above reaction with dichromate ion and determine the molecular weight of the iron compound. You will assume that the empirical formula of the compound is FeX_n, that is there is one mole of Fe for each mole of unknown compound. In this case, an indicator (barium diphenylamine sulphonate) is used to assist in the visual determination of "end point" of the reaction.

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

1. Fill the burette with the standard $K_2Cr_2O_7$ solution.

2. You will be provided with about 10 g of the unknown compound (accurately weighed) and must quantitatively transfer the solid to a 250 cm^3 volumetric flask (the Tutor will demonstrate this technique). Add about 40 cm^3 of 6M sulphuric acid (measuring cylinder) and make the solution up to the mark with distilled water. Mix well, all the solid must dissolve.

3. Pipette 20 cm^3 of the iron solution into a clean 250mL conical flask and add approximately 20 cm^3 of 2M sulphuric acid, 5 cm^3 of concentrated phosphoric acid (both by measuring cylinder), and 3 drops of the indicator. Titrate with the dichromate solution until the development of an intense purple colouration. Record the titre at the end point.

4. Repeat until two titres agree within **± 2 cm^3**.

CALCULATIONS AND QUESTIONS
See your REPORT book. Complete the calculations and questions in Appendix 2 and then the Results and Discussion section 3.2.

ASSIGNMENT 6
ISOLATION OF CAFFEINE FROM COFFEE BEANS

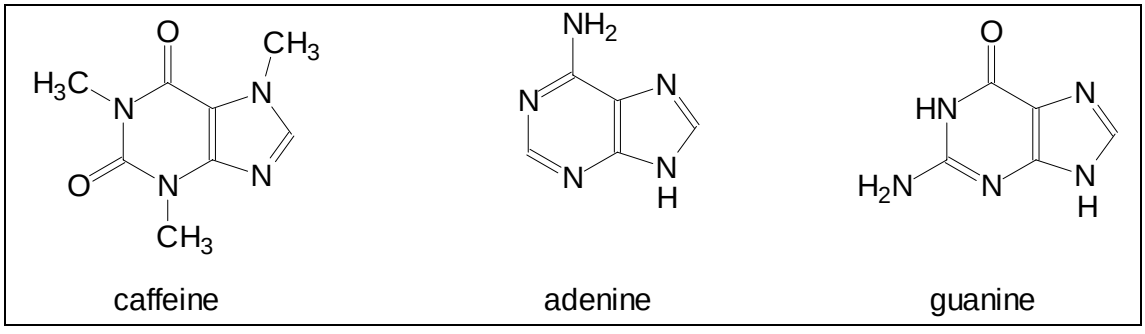
AIMS

This experiment demonstrates how the technique of extraction can be used to preferentially remove a single natural product, caffeine from a complex mixture. Thin layer chromatography will be used to confirm the identify of the extracted compound.

1. INTRODUCTION

The process of extraction works by partitioning the components of a mixture between water and an immiscible organic solvent. The more polar components are more soluble in water and thus remain in the aqueous phase, while the less polar compounds are extracted into the organic phase. Extraction is routinely used as the first stage in the purification of products of preparative reactions. Natural product chemists also use the process to obtain compounds from marine and terrestrial plants and animals. The vast majority of known therapeutic substances were first discovered in this way. The extraction of caffeine from coffee beans will be used to demonstrate the power of the technique.

Caffeine occurs naturally in coffee beans, tea leaves, cocoa seeds and cola nuts, and is included in a number of carbonated drinks. In the concentrations found in tea or coffee, it is a mild stimulant, a diuretic and is mildly addictive. In pure form it is **toxic**. It is a basic, nitrogen containing compound; its structure closely resembles those of the purine bases adenine and guanine, found in RNA and DNA.



Apart from caffeine, ground coffee beans contain a myriad of other natural products including the tannins, which are acidic. However, caffeine is the only major component that is appreciably soluble in organic solvents like dichloromethane (DCM). The rest are highly water soluble. Shaking a coffee solution (hot water extract) with a mixture of aqueous base and DCM will thus result in the extraction of the caffeine into the DCM, while the other coffee components will remain in the aqueous layer.

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

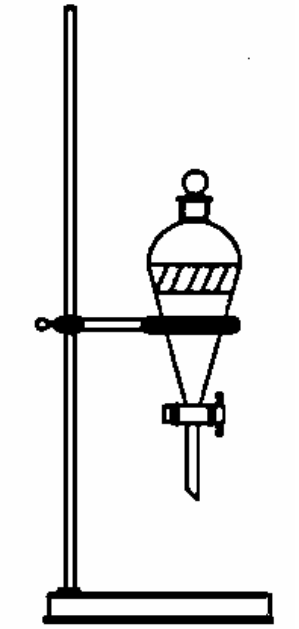
Part A: *Extraction*

Extract caffeine from coffee beans as follows:

1. Take 10g of ground coffee (note the weight which has been measured accurately) and place it into a 250 mL conical flask. Note the coffee sample name in your report book. Place 100mL of distilled water in with the coffee and heat to boiling on a hot plate for 2 minutes (Note the hot plate should be turned onto HOT before you start the prac). Remove the beaker from the heat using gloves, let the coffee solution cool slightly off boiling and then filter off the coffee grounds and wash them with 5mL of distilled water. Place the coffee solution into a 250 mL conical flask. **Carefully** add 40 mL of 5M sodium hydroxide solution and swirl until it is thoroughly mixed. **Avoid** skin contact with this caustic solution. Cool the solution in an ice bath to room temperature.

All subsequent operations will be carried out in a fumecupboard.

2. Transfer the solution to a separatory funnel that is suspended in a metal ring. Add 20 mL of DCM (**avoid** contact with skin and breathing the vapour), place the stopper on the separatory funnel, remove it from the stand, and with one hand firmly holding the stopper on, invert the funnel. Immediately open the tap to release any pressure that may have built up. **Do not** point the funnel at anyone at **any stage**. Close the tap and with the funnel still inverted, shake the mixture for 1 -2 mins, occasionally releasing the pressure by opening the tap. Return the funnel to the metal ring, remove the stopper, and allow the layers to separate.



Separatory Funnel

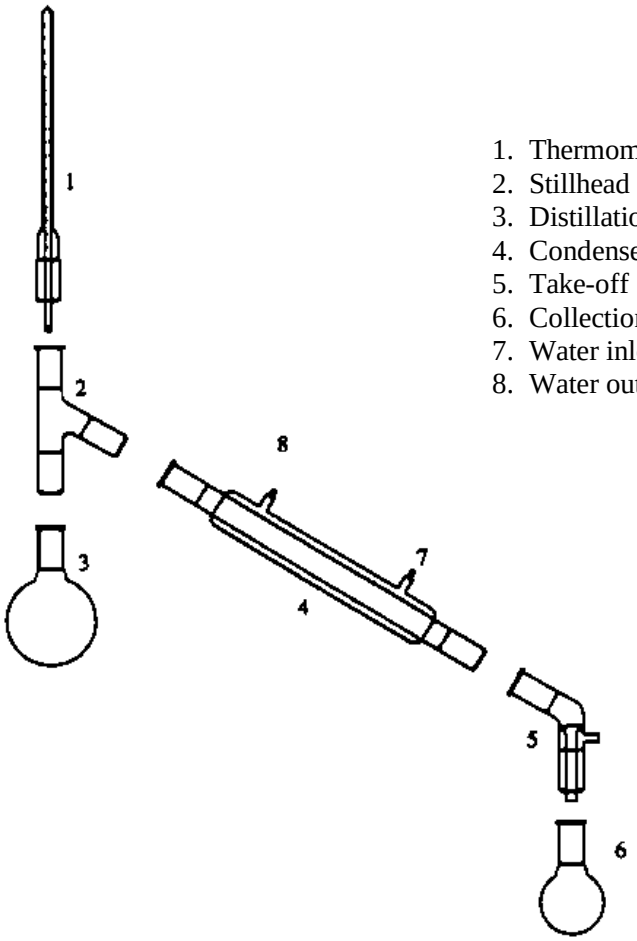
3. DCM is more dense than water (ρ 1.33 g.cm^{-3}) so the bottom layer will be the organic layer. Run the lower layer into a clean 250 mL conical flask. Try to avoid running any of the aqueous layer into the flask. It is best to leave a little organic layer in the funnel.

4. Add another 20 mL of DCM to the funnel and repeat the process. Run the second organic extract (layer) into the first. Discard the aqueous layer from the top of the funnel, so that you don't get any in the tap, and rinse the funnel with a little distilled water. Pour the combined organic extract into the funnel (check that the tap is closed!!) and wash (shake) it with 50 mL of distilled water. Allow the layers to separate and run the organic layer into a **dry** 250 mL conical flask. Once again avoid running any of the aqueous layer out with the organic layer.

5. There will still be traces of water remaining in the DCM. They can be removed with an inorganic salt that absorbs water. Put about a teaspoon of anhydrous sodium sulphate (or

magnesium sulphate) in the DCM solution and swirl it for about 2 minutes. If it is completely dry, the solution above the drying agent should appear completely clear (ie not cloudy). You may need to add more drying agent. Check with your tutor if unsure. Once dry, filter the solution through a funnel containing a fluted filter paper, into a dry flask.

6. Combine your DCM solution with another pair of student's, place in a large **pre-weighed** round bottomed flask (500mL) containing a few boiling chips, and distil off all the DCM in a distillation set-up similar to that shown below. **Make sure you lag the top part of the flask and the head of the distillation apparatus using cotton wool and aluminium foil.** Use the thermometer to record the boiling point of DCM. Pour the distillate in the "Recovered DCM" vessel so that it can be re-used.



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

7. Caffeine will be the main constituent of the material remaining in the flask. Write a description of the residue in your report book. When you are confident that the flask is completely dry inside and out, weigh it and calculate the mass of caffeine you obtained. Record the calculation in your report book. Calculate the mass % caffeine in the ground coffee beans you used in your report book. Scrape the material out of the flask and into a vial. Submit your sample with you report book, labelling the vial with both students' names, group, day and compound name (caffeine).

Part B: *TLC analysis*

Thin layer chromatography can be used to confirm the identity of the compound extracted from instant coffee. Before attempting this part of the experiment, read the "TLC analysis" section in Assignment 6.

Perform this part of the experiment individually. Dissolve two rice grain sized portions of your caffeine in approx. 1 mL of DCM. Take a TLC plate and mark it with 3 marks. Place 3 spots on the plate of varying concentration.

Take a few grains of the pure caffeine sample and make up a solution in DCM. On a new TLC plate make 3 marks and place 3 spots of increasing concentration on the plate.

Assemble the TLC tank (beaker, filter paper and Petri dish). Run (develop) your TLC plates, using acetone as the eluant. View your TLC plate under UV light and circle the spots with a pencil. Note which are the best concentrations for your sample of caffeine and for the pure sample.

Prepare a third TLC plate with only 2 marks on it. On the left hand mark place the correct number of drops of your solution and on the right hand mark the correct number of drops of the pure solution. Now develop this plate as before and note down the R_f of the compound.

Sketch your plate in your report book. Does the TLC analysis confirm that the compound you extracted is caffeine? Comment on the purity of the material you isolated.

3. QUESTIONS

1. Why is the coffee solution basified (rather than acidified) before it is extracted with DCM?

2. Describe a procedure other than TLC analysis, that could be used to confirm the identity of your product.

ASSIGNMENT 7
KINETICS

AIMS

The reaction studied in this assignment is:

$$\underset{\text{iodide}}{2I^-} + \underset{\text{persulphate}}{S_2O_8^{2-}} \rightarrow \underset{\text{iodine}}{I_2} + \underset{\text{sulphate}}{2SO_4^{2-}} \qquad (\mathbf{1})$$

The titration used to determine iodine is:

$$\underset{\text{iodine}}{I_2} + \underset{\text{thiosulphate}}{2S_2O_3^{2-}} \rightarrow S_4O_6^{2-} + 2I^- \qquad (\mathbf{2})$$

Under the conditions of the experiment the concentration of I^- is constant.

The aims of the experiment are:

(a) To determine the order of the reaction with respect to persulphate.
(b) To determine the pseudo-order rate constant and the specific rate constant of the reaction.
(c) To interpret the results in terms of a mechanism for the reaction.

You are to prepare a report following the standard format (indicated at the start of this book) as a separate document.

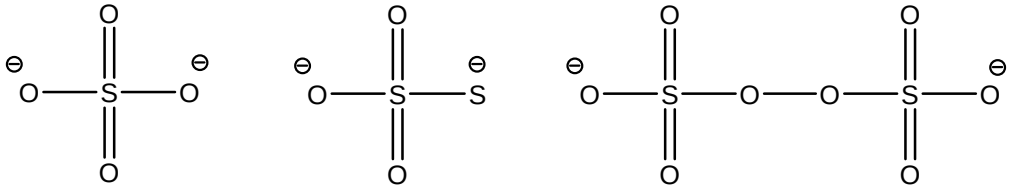
1. INTRODUCTION

Chemical kinetics is concerned with the study of the rates of chemical reactions. In general these depend on:

(i) concentration of reactants, written [reactants],
(ii) temperature, and
(iii) the presence of any catalyst.

In this assignment the dependence of the rate of reaction on reactant concentrations will be investigated at constant temperature. The **specific aims** of the assignment are stated after the theory has been explained.

The molecules involved are sulphate, thiosulphate and persulphate which have the structures shown.



1.1 Measurement of Reaction Rates

You will already know of some reactions (e.g. explosions) which are fast and others (e.g. brewing of beer) which are relatively slow. The rate of a chemical reaction is measured strictly in terms of either the decrease in a reactant concentration with time or the increase of a product concentration with time whichever is the more convenient. Experimentally this means analysing the reaction mixture for either reactant or product at various stages in the reaction. Chemical methods of analysis can be used, as in this experiment, although physical methods are usually preferred. This approach leads to graphs of the following general form.

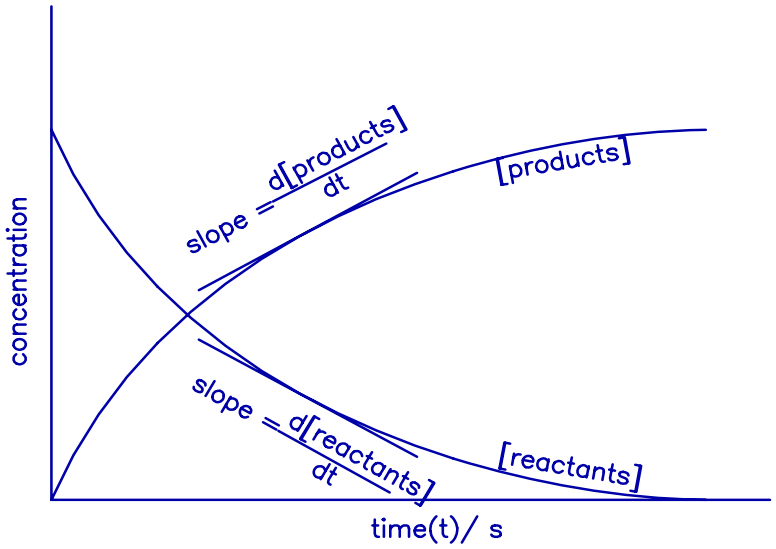


Figure 1. General form of the variation of [reactants] and [products] with time

The rate of the reaction at any particular instant is equal to the slope of the tangent to the curve at that instant. Clearly the rate varies as the reaction proceeds; usually, as shown in Figure 1, the rate decreases as the [reactants] falls. It is very useful to know the **exact** relationship between the rate and [reactants]; the best way to find this is to measure values of [reactants] and time, and analyse this data according to the mathematical equations shown below. In this way, we obtain values of two important quantities, called the **specific rate constant** (k) and the **order** of the reaction. These quantities do **not** vary with concentration, and can give us insight into the mechanism of the reaction.

1.2 Rate Equation, Specific Rate Constant and Order of a Reaction

It is generally found experimentally that the rate of reaction, as measured above, is proportional to [reactant] raised to a simple power; if there is only one reactant A (e.g. in a decomposition or isomerisation reaction), this can be written:

$$Rate = \frac{d[product]}{dt} \propto [A]^m \qquad (3)$$

If there is more than one reactant, the rate is often found to be proportional to their concentrations, **each** raised to a simple power. For instance, for the reaction:

$$aA + bB \rightarrow products \qquad (4)$$

$$Rate \propto [A]^m [B]^n \qquad (5)$$

In general, the powers m and n are not equal to each other; nor are they the same as the stoichiometric coefficients a and b in the reaction equation (**4**).

The **quantity m** is called **the order of the reaction with respect to A.**
Similarly, **n** is called the order of the reaction w.r.t. B.
The **sum m + n** is called **the overall order of the reaction.**

For many reactions, the values of m and n are simple integers, although in some cases they are fractional or zero. Equation 5 can be expressed as:

$$Rate = k[A]^m [B]^n \qquad (6)$$

The quantity k is called the **specific rate constant** of the reaction, and varies only with temperature.

{ N.B. In the experiment you are to look at reactant A = $[S_2O_8^{2-}]$, B = $[I^-]$ }

If, say, m = 1, and n = 1, the reaction is said to be **1st order w.r.t. A, 1st order w.r.t. B,** and **overall 2nd order;** k is called **the 2nd order rate constant.**

1.2.1 The determination of Order and k

The determination of the order of a reaction is based upon the fact that, for simple values of m and n, equation (**6**) can be used to predict the relationship between concentration and time. The forms of these relationships are known for various values of m and n; to determine the order, it is simply a matter of finding graphically which form the data fits. When this has been done, a simple measurement on the appropriate graph usually yields the value of k.

The data-fitting procedure that is used is as follows:
Say we are given n, and we require to determine m and k. The determination of m becomes considerably easier **if [B] is constant throughout the time of reaction**. This can be arranged by having B in large excess; then its concentration will hardly change as A is varied. Under these conditions, equation (**6**) can be rewritten as:

$$Rate = k'[A]^m \qquad (7)$$

where k' is a new constant, and equal to $k[B]^n$.
Note that under these conditions the reaction behaves as if it is of overall order m.

[In the experiment I^- is in great excess and we have **$k' = k [I^-]^1$**]

(a) if m = 1, then equation (**7**) becomes:

$$Rate = k'[A] \qquad (\mathbf{8})$$

i.e. the reaction **behaves as if it is 1st order** and is therefore called a **pseudo-1st order reaction** under these conditions. k' is called the **pseudo-1st order rate constant.** From equation (**8**) the following relationship between concentration and
time can be derived*:

$$\ln[A] = -k't + \ln[A]_o \qquad (\mathbf{9}) \qquad \text{(form } y = m\,x + c\text{)}$$

where $[A]_o$ = initial concentration of A,
and [A] = concentration of A at any time t.

Equation (**9**) predicts that (if m = 1) a plot of ln[A] vs t will be a straight line. **Moreover the gradient of the line equals -k'.**

(b) On the other hand, if m = 2, equation (**7**) becomes:

$$Rate = k'[A]^2 \qquad (\mathbf{10})$$

i.e. the reaction is pseudo-2nd order under these circumstances and k' is the pseudo-2nd order rate constant. Solution of equation (**10**) leads* to the following relationship:

$$\frac{1}{[A]} = k't + \frac{1}{[A]_o} \qquad (\mathbf{11}) \qquad \text{(form } y = m\,x + c\text{)}$$

Equation (**11**) predicts that if m = 2, a plot of 1/[A] vs t will be a straight line, of **gradient k'**.

Now values of both ln[A] and 1/[A] can be tabulated from experimental data for a reaction, and each of these functions can be plotted against time. This is exactly what you will do in this experiment. If the first plot (ln[A] vs t) is linear, it tells us m = 1 whereas if the 2nd plot (1/[A] vs t) is linear, we know that m = 2. The slope of the linear plot yields k'; if we know [B] and we are given the value of n, we can thus determine k, since $k = k'/[B]^n$.

1.3 Mechanism and Molecularity of a Reaction

It is important to determine the reaction order because it helps us to deduce the **mechanism** of a reaction. Thus, if a reaction is overall first order it **may** indicate that the rate-determining step in the reaction is **unimolecular** (i.e. **one** reacting molecule is involved). On the other hand if the reaction is overall second order the rate-determining step **may** be **bimolecular** (i.e. two reacting molecules are involved).

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* See appendix.

2. EXPERIMENTAL

You will do this experiment **In Pairs**

2.1 Measurement of the kinetics of a reaction between iodide & persulphate

(1) Pipette 25 cm^3 of saturated potassium persulphate solution into a 250 cm^3 (volumetric flask) and then dilute to the mark with distilled water. **Use only the diluted solution from now on.** Using a pipette transfer 50 cm^3 of this solution into a 150 cm^3 conical flask, labelled A. **Add 50 cm^3 of distilled water using a pipette**.

(2) Using a pipette, place 50 cm^3 of 0.4M KI solution into another 150 cm^3 conical flask, labelled B.

(3) Float flasks A and B in 600 cm^3 beakers containing tap water, and record their temperatures.

(4) Wait for 5 minutes for the solutions to obtain a steady state temperature. *Start Experiment 2.2 while waiting*.

(5) Now add the contents of flask B to flask A, put the reaction flask back in the water bath and start timing. Clamp the flask in the water bath.
Check that the total volume in Flask A is now **150mL - it must be**. As the timing is critical it is advisable to back up the timing using a second device (e.g. watch). At measured and recorded time intervals (approximately 3, 8, 15, 20, 30, 40 and 50 min) withdraw by pipette 20 cm^3 reaction mixture and "quench"[**] the sample by running it into approx. 150 cm^3 distilled water in a 250 cm^3 conical flask. For each of these samples, record the exact time (since mixing A and B) when half the pipette has emptied. [N.B. After the 15 minute sample the burette may need to be refilled].

(6) to Titrate each "quenched" sample immediately with sodium thiosulphate solution the disappearance of the yellow colour. Record your values in a rough but legible table in your report book. Note down the sodium thiosulphate concentration.

2.2 Measurement of the reference (V_∞) for the reaction between iodide & persulphate

(1) Using pipettes add 20 cm^3 distilled water, 20 cm^3 of 0.4M KI and 20 cm^3 <u>diluted potassium persulphate</u> (**2.1**) to the 100 cm^3 Quickfit flask. Stopper the flask, mix the contents and place in the 60 ^oC thermostat bath.

(2) After 30 minutes remove the Quickfit flask from the thermostat bath, and cool to room temperature before removing the stopper. Transfer 20 cm^3 to approx. 150 cm^3 distilled water, and titrate with sodium thiosulphate solution to the disappearance of the yellow colour. This gives us a $\mathbf{V_\infty}$ value as the reaction has been driven to completion.

[**] suddenly stop the chemical reaction by dilution

3. EVALUATION OF RESULTS

In this experiment, iodide ions are in great excess over persulphate ions. Therefore the concentration of iodide ions will be effectively constant over the period of the reaction. We can write a table with general expressions for the changes in concentrations (a, b, x) :

	$2I^-$	+	$S_2O_8^{2-}$	→	I_2	+	$2SO_4^{2-}$
at time = 0	b		a		0		0
at time = t	≈ b		(a-x)		x		2x
at time = ∞	≈ b		0		a		2a

From equations (**1**) and (**2**) we see that for each mole of iodine that is formed one mole of persulphate has reacted. We are titrating the liberated iodine and the stoichiometry of the titration reaction is 1 mole of iodine reacts with 2 moles of thiosulphate. From these two relationships we have the following expression:

$$\frac{nS_2O_3^{2-}}{nI_2} = \frac{nS_2O_3^{2-}}{nS_2O_8^{2-}} = \frac{2}{1} \qquad (\mathbf{12})$$

Which gives upon rearrangement:

$$nS_2O_8^{2-} = \frac{1}{2} nS_2O_3^{2-} \qquad (\mathbf{13})$$

We are interested in the change in the persulphate concentration with respect to time. Therefore we express equation (13) in terms of concentrations and volumes.

$$[S_2O_8^{2-}] = \frac{1[S_2O_3^{2-}]VS_2O_3^{2-}}{2VS_2O_8^{2-}} \qquad (\mathbf{14})$$

remember that $n S_2O_8^{2-} = [S_2O_8^{2-}] \times V\,S_2O_8^{2-}$
and $n S_2O_3^{2-} = [S_2O_3^{2-}] \times V\,S_2O_3^{2-}$

We wish to know the persulphate concentration $[S_2O_8^{2-}]$ at any time *t* which is related to the difference between the titration value for the reference at time infinity (V_∞) and the titration at time *t* (V_t) by equation (15) (consider the previous table) .

$$[S_2O_8^{2-}] = \frac{1[S_2O_3^{2-}]\{V_\infty - V_t\}}{2VS_2O_8^{2-}} \qquad (\mathbf{15})$$

You withdraw 20 cm^3 samples of the persulphate solution from flask A in the experiment ($V\,S_2O_8^{2-}$) and titrate this using thiosulphate of known concentration($[S_2O_3^{2-}]$). Therefore you have all the information needed to calculate the concentration of persulphate.

You will have to prepare a table of t(s), V_t, (V_∞ - V_t), $[S_2O_8^{2-}]$, $\ln[S_2O_8^{2-}]$ and $1/[S_2O_8^{2-}]$.
The table will need to have columns with the following entries and the appropriate units :

t	V_t	$V_\infty - V_t$	$[S_2O_8^{2-}]$ *(from (15))*	$\ln[S_2O_8^{2-}]$	$1/[S_2O_8^{2-}]$

Graphs will need to be prepared for $\ln[S_2O_8^{2-}]$ and $1/[S_2O_8^{2-}]$ versus time and from this the reaction order and the pseudo-rate constant will be obtained. **These should be completed**

during the practical and checked by your demonstrator.

CALCULATIONS AND QUESTIONS

(a) Evaluate the order of the reaction with respect to persulphate.

(b) Determine the pseudo-order rate constant k' .

(c) Given that the order of the reaction with respect to iodide is unity determine the specific rate constant. (N.B. I^- has been diluted at the start)

(d) Provide the overall rate law for the reaction.

(e) Calculate the rate at 5 minutes (use your exact value) and comment on whether this is a fast or a slow reaction.

(f) The following mechanism has been proposed for this reaction::

$$I^- + S_2O_8^{2-} \rightarrow I + SO_4^- + SO_4^{2-} \quad \text{(i)}$$
$$I^- + SO_4^- \rightarrow I + SO_4^{2-} \quad \text{(ii)}$$
$$I + I \rightarrow I_2 \quad \text{(iii)}$$
$$\mathbf{2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}} \quad \textbf{overall}$$

Which of the above steps is most likely to be **rate-determining?** (The **rate-determining step** of a sequence of chemical reactions is the reaction which is the slowest. The slowest reaction controls the overall rate characteristics of the reaction sequence).

Are the orders of reaction predicted by this mechanism in agreement with the experimental results? Remember that reactions which involve the breaking of chemical bonds will have higher activation energies than reactions which do not involve bond breakage.

APPENDIX 1.

Derivation of equations (9) and (11)

(a) **The case when m = 1**

Rate = k'[A]

Let the initial concentration of A = $[A]_o$, and at time t the concentration remaining [A]

The reaction rate is defined as the rate of decrease of the concentration of A, $\frac{-d[A];}{dt}$

Hence for equation (8) we can write:

$$\frac{-d[A]}{dt} = k'[A]$$

Rearranging, we have:

$$\frac{d[A]}{[A]} = k'dt$$

The solution of this differential equation is:

$$-\ln[A] = k't + constant$$

when t = 0, x = 0, therefore $constant = -\ln[A]_o$
Hence we have

$$-\ln[A] = k't - \ln[A]_o$$

$$or\ \ln[A] = -k't + \ln[A]_o$$

(b) **The case when m = 2**

Rate = $k'[A]^2$

Putting Rate = $\frac{-d[A]}{dt}$ we have for equation (10):

$$\frac{-d[A]}{dt} = k'[A]^2$$

Rearranging, we obtain

$$\frac{d[A]}{[A]^2} = k'dt$$

This has the solution:

$$\frac{1}{[A]} = k't + constant$$

Again, when t = 0, $[A] = [A]_o$ therefore $constant = \frac{1}{[A]_o}$

Hence we have:

$$\frac{1}{[A]} = k't + \frac{1}{[A]_o}$$

ASSIGNMENT 8
THERMOCHEMISTRY

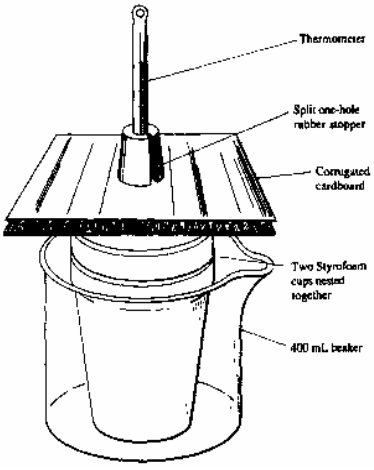
AIMS

The aim of this assignment is to measure the energy changes accompanying neutralisation reactions using a calorimeter.

1. INTRODUCTION

Every chemical change is accompanied by a change in energy, usually in the form of heat. The energy change of a reaction that occurs at constant pressure termed the *heat of reaction* or the *enthalpy change.* The symbol ΔH (the symbol Δ means "change in") is used to denote the enthalpy change. If heat is evolved, the reaction is *exothermic* ($\Delta H < 0$); and if heat is absorbed, the reaction is *endothermic* ($\Delta H > 0$). In this experiment you will measure the heat of neutralisation (or the enthalpy of neutralisation) when an acid and a base ret to form water. This quantity of heat is measured experimentally by allowing the reaction take place in a thermally insulated vessel called a *calorimeter.* The heat liberated in the neutralisation will cause an increase in the temperature of the solution and of the calorimeter. If the calorimeter were perfect, no heat would be radiated to the laboratory. The calorimeter you will use in this experiment is shown in Figure 1. Because we are concerned with the heat of the reaction and because some heat is absorbed by the calorimeter itself, we must know the amount of heat absorbed by the calorimeter. This requires that we determine the heat capacity of the calorimeter. By "heat capacity of the calorimeter" we mean the amount of heat (that is, the number of joules) required to raise its temperature 1 kelvin, which is the same as 1^0C. In this experiment, the temperature of the calorimeter and its contents is measured before and after the reaction. The change in the enthalpy, ΔH, is equal to the product of the temperature change, ΔT, times the heat capacity of the calorimeter and its contents:

Figure 1
A simple
calorimeter



$$\Delta H = \Delta T \text{ (heat capacity of calorimeter + heat capacity of contents)} \quad [1]$$

Note the *numerical difference* on the Celsius scale is the same as the *numerical difference* on the kelvin scale where ΔT is the difference between the final and initial temperatures.

The heat capacity of the calorimeter is determined by measuring the temperature change that occurs when a known amount of hot water is added to a known amount of cold water in the

calorimeter. The heat lost by the warm water is equal to the heat gained by the cold water and the calorimeter. (We assume no heat is lost to the laboratory.) For example, if T_1 equals the temperature of a calorimeter and 50 mL of cooler water, if T_2 equals the temperature of 50 mL of warmer water added to it, and if T_f equals the temperature after mixing, then the heat lost by the warmer water is

$$\text{Heat lost by warmer water} = (T_2 - T_f) \times 50\ \text{g} \times 4.18\ \text{J/K.g} \qquad [2]$$

The specific heat of water is 4.184 J/K.g, and the density of water is 1.00 g/mL.

The heat gained by the cooler water is

$$\text{Heat gained by cooler water} = (T_f - T_1) \times 50\ \text{g} \times 4.18\ \text{J/K.g} \qquad [3]$$

The heat lost to the calorimeter is the difference between heat lost by the warmer water and that gained by the cooler water:

(heat lost by warmer water) - (heat gained by cooler water) = heat lost to calorimeter

With some substitutions and use of sign conventions in heat transfer we have :

$$\text{Heat lost to calorimeter} = (T_2 - T_1) \times \text{heat capacity of calorimeter} \qquad [4]$$

Note that the heat lost to the colorimeter equals its temperature change times its heat capacity. Thus by measuring T_1, T_2, and T_f, the heat capacity of the calorimeter can be calculated from Equation [4]. This is illustrated in Example 2.1.

EXAMPLE 2.1

Given the following data, calculate the heat lost by the warmer water, the heat lost to the cooler water, the heat lost to the calorimeter, and the heat capacity of the calorimeter:

Temperature of 50 mL warmer water: 37.9^0C = T_2
Temperature of 50 mL cooler water: 20.9^0C = T_1
Temperature after mixing: 29.1^0C = T_f

Solution: The heat lost by the warmer water, where $\Delta T = 37.9^0\text{C} - 29.1^0\text{C}$, is

$$8.8\ \text{K} \times 50\text{g} \times 4.18\ \text{J/K-g} = 1840\ \text{J}$$

The heat gained by the cooler water, where $\Delta T = 29.1^0\text{C} - 20.9^0\text{C}$, is

$$8.2\ \text{K} \times 50\text{g} \times 4.18\ \text{J/K-g} = 1710\ \text{J}$$

The heat lost to the calorimeter is

$$1840\ \text{J} - 1710\ \text{J} = 130\ \text{J}$$

The heat capacity of the calorimeter is, therefore,
130K/8.2 K = 16 J/K

Once the heat capacity of the calorimeter is determined, Equation [1] can be used to determine the ΔH for the neutralisation reaction. Example 2.2 illustrates such a calculation.

EXAMPLE 2.2

Given the following data, calculate the heat gained by the solution, the heat gained by the calorimeter, and the heat of reaction:

Temperature of 50 mL of acid before mixing: 21 .0^0C
Temperature of 50 mL of base before mixing: 21 .0^0C
Temperature of 100 mL of solution after mixing: 27.5^0C

Assume that the density of these solutions is 1.00 g/mL.

Solution: The heat gained by the solution, where ΔT = 27.5^0C - 21.0^0C, is :

6.5 K x 100 g x 4.18 J/K-g = 2720 J

The heat gained by the calorimeter, where ΔT = 27 .5^0C - 21 .0^0C, is :

6.5 K x 16 J/K = 104 J

The heat of reaction is therefore : 2720 J + 104 J = 2820 J

2. EXPERIMENTAL **To be done in pairs.**

2.1. Heat Capacity of Calorimeter

Construct a calorimeter similar to the one shown in Figure 1 by using a Styrofoam cup. Use a cork borer to make a hole in the lid just big enough to admit the thermometer and slip the thermometer into a split one-hole rubber stopper to prevent the thermometer from entering too deeply into the calorimeter. The thermometer should not touch the bottom of the cup. Rest the entire apparatus in a 250-mL beaker to provide stability.

Place exactly 50 mL of water in the calorimeter cup and replace the cover and thermometer. Allow 5 to 10 minutes for the system to reach thermal equilibrium; then record the temperature to the nearest 0.1^0C.
Place exactly 50 mL of water in a 100 mL conical flask and heat the water with a hot plate until the temperature is approximately 75 ^{0}C. Do not heat to boiling, or appreciable water will be lost, leading to an erroneous result. Allow the hot water to stand for a minute or two (the temperature must be between 70 – 75 ^{o}C); quickly record its temperature to the nearest 0.1 ^{0}C and pour it as completely as possible into the calorimeter.

Replace the lid with the thermometer and carefully stir the water with the thermometer. Observe the temperature for the next 3 minutes and record the temperature every 15 seconds with continuous stirring. Plot the temperature as a function of time, as shown in Figure 2. Determine ΔT from your curve and then do the calculations indicated on the report sheet.

2.2 Heat of Neutralisation of HCl - NaOH

Dry the calorimeter and the thermometer with a towel. Carefully measure 50 mL of 3.0 *M* NaOH and add it to the calorimeter. Place the lid on the calorimeter but leave the thermometer out. Measure out exactly 50 mL of 3.0 M HCl into a dry beaker. Allow it to stand near the calorimeter for 3 to 4 min. Measure the temperature of the acid; rinse the thermometer with tap water and wipe dry. Insert the thermometer into the calorimeter and measure the temperature of the NaOH solution.

The temperatures of the NaOH and the HCl should not differ by more than 0.5^0C. If the difference is greater than 0.5^0C, adjust the temperature of the HCl by *either* warming it by holding the beaker in your hands or cooling the outside of the beaker with tap water until the temperature of the HCl is within 0.5^0C of that of the NaOH.

Record the temperature of the NaOH solution. Lift the lid and carefully add the 3.0 M HCl all at once. Be careful not to splash any on the upper sides of the cup. Stir the solution gently with the thermometer and record the temperature as a function of time every 15 s for the next 3 min. Construct a temperature-versus-time curve and determine ΔT. Calculate the heat of neutralisation per mole of water formed. You may assume that the NaCl solution has the same density and specific heat as water.

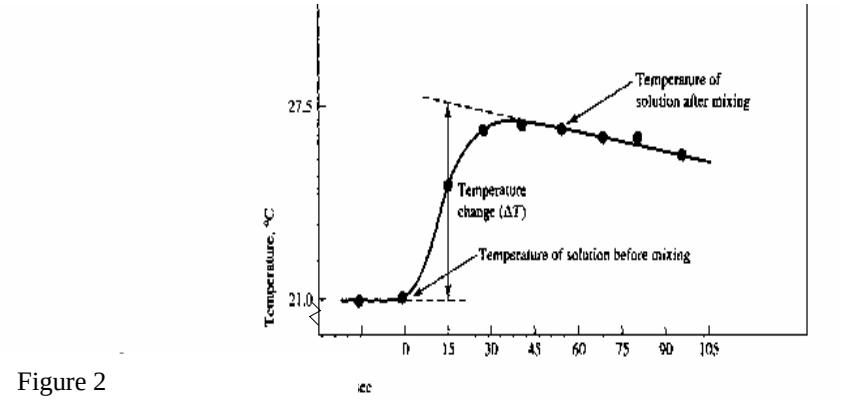


Figure 2
Temperature as a function of time – coffee cup calorimeter

2.3 Heat of Neutralisation of CH_3CO_2H - NaOH

Follow the same procedure as in Part 2.2 but use 3.0 M CH_3CO_2H instead of 3.0 M HCl. Calculate the heat of neutralisation per mole of water formed.

3. CALCULATIONS AND QUESTIONS

- Specific questions are asked at the end of the report in your report book. You should answer these questions after you have carried out the various calculations that are required as you proceeded through the experimental section.

ASSIGNMENT 9
ELECTROCHEMICAL CELLS

AIMS

The aims of this assignment are:

1) To introduce you to some simple electrochemical cells;
2) To study some oxidation-reduction reactions using electrochemical cells;
3) To study the effect of the concentration of chemical species on the behaviour of an electrochemical cell.

1. INTRODUCTION

The study of electrochemical cells is an area of physical chemistry which is interesting for many reasons. Among these are the developments and applications of cells both inside and outside the chemical laboratory (e.g. in techniques of analytical chemistry, as power sources etc.), and their use in research into branches of chemistry itself (e.g. to study the mechanisms of a variety of chemical reactions).

1.1 Oxidation and reduction

Oxidation is defined as the **loss of electrons** by a substance, which is said to be oxidised in the process.

Reduction is defined as the **gain of electrons** by a substance, which is said to be reduced in the process.

In an *oxidation-reduction* **reaction, electrons are transferred from one species to another,** and the valence states or oxidation states of elements are changed in the process. For example, consider the reaction between copper ions and zinc in aqueous solution:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \qquad (\mathbf{1})$$

The reaction goes from left to right under usual laboratory conditions. Electrons are thus transferred from Zn to Cu^{2+}. Hence Zn is oxidised to Zn^{2+} and Cu^{2+} is reduced to Cu. Zn is called the **reducing agent** (it does the reducing) and Cu^{++} is the **oxidising agent.**

There are many possible combinations of oxidising and reducing agents.

1.2 Electrochemical cells

Reaction (1) could be performed directly, but rather uncontrollably, by dipping a zinc rod into a solution of copper sulphate.

On the other hand, there is a less direct but more controlled way of carrying out the reaction, which also allows any energy changes to be used more efficiently. Consider splitting reaction (1) into two **half-reactions.**

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad (\mathbf{2})$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (\mathbf{3})$$

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

It is possible to carry out these two half-reactions in separate containers, and transfer the electrons produced in one container to the other via a conductor. We must also allow ions to travel between the containers, to maintain electrical neutrality. The arrangement

is called an electrochemical cell, and is shown schematically in Figure 1.

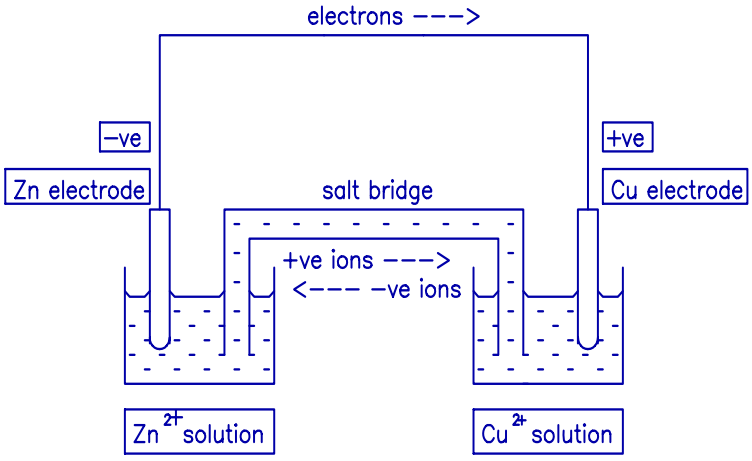


Figure 1. Schematic representation of an electrochemical cell.

The two solid metals that are connected by the external circuit are called electrodes. **By definition,** in a voltaic cell the electrode at which oxidation occurs is called the **anode;** the electrode at which reduction occurs is called the **cathode.** In this example, Zn is the anode and Cu is the cathode.

Oxidation; anode:	$Zn(s)$	$\rightarrow$	$Zn^{2+}(aq) + 2e^-$
Reductions; cathode:	$Cu^{2+}(aq) + 2e^-$	$\rightarrow$	$Cu(s)$

An electrochemical cell may be regarded as composed of two half-cells, one corresponding to the oxidation process and one corresponding to the reduction process. Electrons become available as zinc metal is oxidised at the anode. They flow through the external circuit to the cathode where they are consumed as $Cu^{2+}(aq)$ is reduced.

Care must be taken about the signs attached to the electrodes in the cell. Electrons are released at the anode, as the zinc is oxidised. Thus electrons are flowing out of the anode and into the external circuit. Because the electrons are negatively charged, a negative sign is assigned to the anode. Conversely, electrons flow into the cathode, where they are consumed in the reduction of copper. A positive sign is thus assigned to the cathode, because it appears to attract the negative electrons.

As the cell pictured in Figure 1 operates, oxidation of Zn introduces additional Zn^{2+} ions into the anode compartment. Unless a means is provided to neutralise this positive charge, no further oxidation can take place. Similarly, the reduction of Cu^{2+} at the cathode leaves an excess of negative charge (the $SO4^{2-}$ counterion) in solution at that compartment. Electrical neutrality is maintained by a migration of ions through a "salt bridge", as illustrated.

1.2.1 Measurements on cells

An electrochemical cell may be thought to possess a "driving force" or "electrical pressure" that pushes electrons through the external circuit. This driving force is called the **electromotive force** (abbreviated **emf**); emf is measured in units of volts and is also referred to as the *cell voltage* or *cell potential.*

The accurate determination of cell potential requires the use of special apparatus. The measurement must be made in such a manner that essentially no current flows between the electrodes. (If a significant current is allowed to flow, the apparent voltage of the cell is lowered as a result of the internal resistance of the cell, and because of changes in concentrations around the electrodes). This is achieved through the use of a digital voltmeter (Fig. 2).

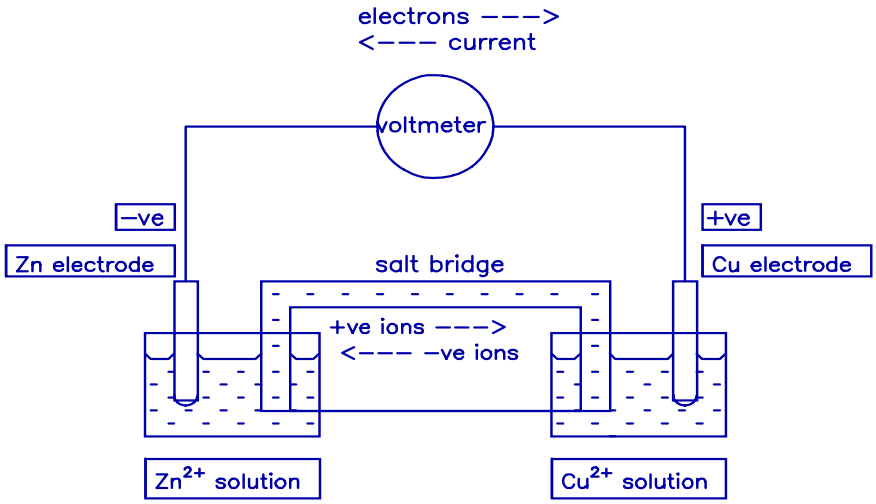


Figure 2. Measurement of cell potential with a high input impedence voltmeter.

It is of interest to know (1) how a particular combination of oxidising and reducing agents react, and (2) how much useful energy could be obtained from the reaction. If the reagents were set up in an electrochemical cell, these two pieces of information would be revealed by two measurements:

(a) the **electrical signs of the electrodes**, which effectively tell us the **spontaneous direction of the reaction**, and

(b) the **e.m.f.** which is related to the amount of work that the electrons can do in passing from one half-cell to the other This is equal to the **energy available for work from the cell reaction.**

1.2.2 Notation and convention for electrochemical cells

So far, we have represented cells by schematic drawings of their actual physical arrangements, such as that in Figure 1. This is reasonably simple to do, although it can become rather unwieldy for complex arrangements. However, more severe problems can arise with this method of representing cell information if we have to deal with manipulations of cell systems, especially when calculations are involved. The difficulties can be overcome by using the following method.

There is an international shorthand notation for cells and a convention regarding direction of cell reactions.

1) The components of the anode compartment are written to the left of the components of the cathode compartment.
2) A vertical line represents a phase boundardy.
3) A comma separates the half-cell components that are in the same phase.

4) Half-cell components appear in the same order as in the half-reaction.
5) Electrodes appear at the far left and far right of the notation.
6) A double vertical line separates the half-cells and represents the phase boundaries on either side of the salt bridge. The ions of the salt bridge are omitted.

For a half-cell consisting of a copper rod dipping into a solution of Cu^{2+} ions at unit (1M) concentration, the notation is Cu | Cu^{2+} (1 mol dm^{-3}). The zinc half-cell is written

$$Zn(s)\,|\,Zn^{2+}\,(aq,1\,M)\,||\,Cu^{2+}\,(aq,1\,M)\,|\,Cu(s)$$

similarly. When they are joined with a salt bridge, the cell is written:
This is called the **cell diagram**, and the symbols show **how the cell is constructed.**

To show the **direction of the cell reaction,** we use a convention which involves **the direction in which the cell diagram is written**, and the sign attached to the e.m.f., as follows:

If we **know** the direction of the cell reaction, the cell diagram is written with **reduction occurring on the right** and the **value of the e.m.f. is given a positive sign.** Equally well, we can use the convention to **tell us** the direction of the cell reaction. For instance if we are given a cell diagram and a positive e.m.f., we know that reduction occurs on the right in the diagram. If, for any reason, we have a cell diagram and a negative e.m.f. (for instance, as a result of a calculation) this means that reduction is occurring on the left. It would be usual then to rewrite the diagram the other way round and report the e.m.f. as positive.

1.2.3 Electrode potentials

It is desirable to be able to **predict** information for a cell, or redox reaction, rather than to have to set up the cell itself. This is possible if the potential differences across **each** of the two half-cells which constitute the cell are known. (The "electrode potentials" of the half cells.)

Unfortunately, it is impossible to measure the absolute potential differences across a half-cell in isolation. However a measurement can be made if the various half-cells are connected to a reference half cell. The e.m.f. produced from this cell is then expressed as a relative voltage. The half-cell chosen as a reference is the **standard hydrogen electrode** (or **S.H.E.**), written Pt(s) | H_2 (1 atm.) | H^+ (1 mol dm^{-3}).
The electrode potential of a half-cell X is then **defined** as the e.m.f. of the cell:

$$Pt(s)\,|\,H_2(g,1\,atm)\,|\,H^+(aq,1\,M)\,||\,X$$

Using the convention described above, the e.m.f. of any cell is given by:

$$\text{e.m.f.} = \begin{matrix}\text{electrode potential}\\ \text{of R.H.S. half-cell}\end{matrix} - \begin{matrix}\text{electrode potential}\\ \text{of L.H.S. half-cell}\end{matrix}$$

Once again, the convention described above applies to the sign of the e.m.f., the direction of the cell reaction, and the way in which the cell diagram has been written.

1.2.4 Variation of e.m.f. with concentration

The e.m.f. of any cell varies with the concentrations (or, more strictly the activities) of the species involved in the cell reaction. Consider the following cell reaction:

$$aA + bB \rightarrow cC + dD$$

The e.m.f. is given by:

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln \frac{[products]^{p}}{[reactants]^{r}}$$

$$= E^{o}_{cell} - \frac{RT}{nF} \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

where E^{o}_{cell} is the standard e.m.f.
(e.m.f. when all species are at unit concentration),
n is the number of moles of electrons transferred for the reaction as written,
F is Faraday's constant (96,500 C mol^{-1}).
T is the temperature in Kelvin
R is the gas constant (8.314 J mol^{-1} K^{-1})

This is called the Nernst equation and can be rewritten in terms of $\log_{10}$ rather than natural logarithms:

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad (4)$$

The signs attached to the values of e.m.f. in equation (4) indicate the direction of the reaction under appropriate conditions: a positive e.m.f. means that the reaction occurs in the direction written, whereas a negative value implies the opposite direction.

1.2.5 Summary of steps involved to obtain expression for e.m.f. of a cell

(i) Write equation for half-reactions in forms similar to equations (2) and (3).
(ii) Adjust the two half-equations, if necessary, so that they each involve the same number of electrons.
(iii) Combine the half-equations to give the cell reaction.
(iv) Write equation (4) for the cell e.m.f.

1.2.6 The role of electrons in oxidation and reduction processes

The transfer of electrons in a redox reaction is convincingly seen by the following types of experiment. The apparatus is simple (see Figure 2). The salt bridge is necessary to maintain the electrical neutrality. After both electrodes have been connected, a current flows and reaction takes place around the electrodes. The changes occurring are proved in various ways, and sometimes may be seen, e.g. formation of iodine from KI solution.

Not all redox processes involve only transfer of electrons however. When $KMnO_4$ in acid solution is reduced by Fe^{2+} to a salt of Mn^{2+}, Mn-O bonds must be broken, and H^{+} has a particular function, expressed clearly in the equation:

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

Thus oxidation and reduction always involve transfer of electrons, and they may also involve transfer of atoms.

Redox reactions may of course occur in the same solution, and often the results may be seen clearly, e.g. oxidation of Cl^- to chlorine by Mn^{4+}, which is reduced to Mn^{2+}.

Furthermore, the ions of elements which can exist in many valence states, such as the MnO_4^- ion, can oxidise different amounts of the same substance depending on the conditions, e.g.

ACID SOLUTION	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
NEUTRAL SOLUTION	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$
STRONGLY ALKALINE SOLUTION	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$

Potassium permanganate finds many uses as a titrant in analytical chemistry because of its strong oxidising properties, particularly in acid solution, and the fact that it reacts stoichiometrically and rapidly with a wide range of reducing agents.

2. EXPERIMENTAL

To be done in **pairs**.

The first three experiments are designed to show electron transfer in redox reactions by constructing voltaic cells and noting the half-cell reactions.
N.B. Black wire = negative –ve terminal, Red wire = +ve terminal.

For these, you are supplied with two carbon rods joined by copper wire. Two small beakers are necessary. Abrade the carbon rods before use and between changes of solution.

The second series of experiments are designed to show the quantitative behaviour of electrochemical cells.

2.1 Iron(III) chloride and tin(II) chloride

Add to one beaker 25 cm^3 iron(III) chloride solution and add 25 cm^3 of dilute (2M) hydrochloric acid. In the other beaker place 25 cm^3 of tin(II) chloride solution and half-fill with dilute hydrochloric acid. (In each case the HCl is added to assist the flow of electrons between the two solutions. Other strong electrolytes, e.g. NaCl, would be equally effective.)

Construct a salt bridge by taking a filter paper and folding it into a strip about 1 cm wide. Moisten it with dilute hydrochloric acid and, with the two beakers side by side, place the filter paper so that one end of it dips into the liquid in each beaker. Finally, rinse and dry the carbon rods, place one carbon rod in each beaker. Connect the voltmeter to the electrodes and note the reading and the **sign** of the charge on each electrode. Join the two electrodes directly (i.e. remove the voltmeter), allow to stand for 12 minutes and observe any physical changes in the beakers which indicate that the reactions are taking place. While waiting, place in two separate places on a **filter paper** a drop of potassium hexacyanoferrate (III) solution ($K_3Fe(CN)_6$). To one spot, add a

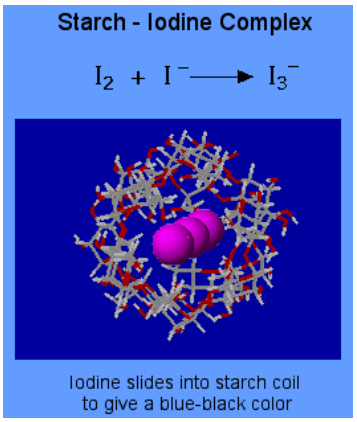
drop of iron (III) chloride and note the colour. To the other spot, add a drop of iron (II) chloride, and again note the colour. On a clean area of the labelled filter paper used previously again place a drop of $K_3Fe(CN)_6$ solution and quickly lift the carbon electrode from the beaker and add a drop of the '$FeCl_3$' solution. Note the colour and compare with the previous tests. With which oxidation state of iron does it correspond?

2.2 Potassium iodide and bromine water

CARRY OUT THIS EXPERIMENT IN YOUR FUME HOOD AND DISPOSE OF MATERIALS CORRECTLY.

Place a dilute solution of potassium iodide in one beaker and add a few drops of starch solution. (The starch is a very sensitive test reagent for free iodine: a deep blue solution is obtained).
In the other beaker place bromine water which is supplied already diluted with 2M sulphuric acid (to increase the conductivity).

The starch is a complex polysaccharide composed of two major components amylose and amylopectin. Amylose in starch is responsible for the formation of a deep blue color in the presence of iodine.
The iodine complex ion I_3^- (or I_5^-) slips inside the amylose coil to generate a coloured complex.



SAFETY NOTE: DO NOT LET BROMINE WATER TOUCH YOUR SKIN

Use a 2M sulphuric acid salt bridge and measure the cell potential and the sign of the charge on each electrode. Then join the two carbon electrodes with a wire and allow to stand for 30 minutes and observe any physical changes in the beakers which indicates that reaction is taking place.

USE WASTE BOTTLES TO DISPOSE OF BROMINE WATER

2.3 Copper sulphate and zinc sulphate

Place 15 cm^3 0.1M copper sulphate solution and the copper electrode in one beaker and 0.05M zinc sulphate solution and the zinc electrode in the other beaker. Prepare a salt bridge as before but using 2 M Na_2SO_4 solution instead of dilute hydrochloric acid.

Connect the two solutions with the salt bridge and connect the voltmeter leads to the electrodes. Immediately measure the voltage of the cell and the sign of the charge on each electrode. Join the electrodes, allow to stand for 3 minutes and observe any physical changes in the beakers which indicate that the reactions are taking place.

2.4 Silver nitrate solutions

2.4.1 0.1M silver nitrate solution and 0.01M silver nitrate

In one beaker place 0.1M silver nitrate solution and in the other 0.01M silver nitrate solution. Connect the solutions with a nitric acid salt bridge. (The salt bridge is prepared as in Experiment 2.1 except that dilute nitric acid is substituted for the dilute hydrochloric acid.) Place a silver wire electrode in each beaker, immediately measure the voltage of the cell and determine the relative sign of the charges on each electrode.

USE WASTE BOTTLES FOR SILVER SOLUTIONS

3. CALCULATIONS AND QUESTIONS

- You will fill out the cell reactions and explain what is happening in each reaction directly into your report book as you proceed through each experiment.
- For experiments 2.4 and 2.5, compare your measurements with values calculated using the method described in 1.2.4 above.
  ($E^o_{Cu^{2+}/Cu}$ = + 0.340V and $E^o_{Zn^{2+}/Zn}$ = -0.760V)

TABLE 1. STANDARD REDUCTION POTENTIALS (25°C)

Half-reaction			E^o(V)
$Li^+ + e^-$	$\rightarrow$	Li	- 3.05
$Ca^{2+} + 2e^-$	$\rightarrow$	Ca	- 2.87
$Na^+ + e^-$	$\rightarrow$	Na	- 2.74
$Mg^{2+} + 2e^-$	$\rightarrow$	Mg	- 2.37
$Al^{3+} + 3e^-$	$\rightarrow$	Al	- 1.66
$Zn^{2+} + 2e^-$	$\rightarrow$	Zn	- 0.76
$Fe^{2+} + 2e^-$	$\rightarrow$	Fe	- 0.44
$PbSO_4 + 2e^-$	$\rightarrow$	$Pb + SO_4^{2-}$	- 0.36
$Sn^{2+} + 2e^-$	$\rightarrow$	Sn	- 0.14
$Pb^{2+} + 2e^-$	$\rightarrow$	Pb	- 0.13
$2H^+ + 2e^-$	$\rightarrow$	H_2	0.00
$Sn^{4+} + 2e^-$	$\rightarrow$	Sn^{2+}	+ 0.15
$Cu^{2+} + 2e^-$	$\rightarrow$	Cu	+ 0.34
$O_2 + 2H_2O + 2e^-$	$\rightarrow$	$4OH^-$	+ 0.40
$NiO_2 + 2H_2O + 2e^-$	$\rightarrow$	$Ni(OH)_2 + 2OH^-$	+ 0.49
$Cu^+ + e^-$	$\rightarrow$	Cu	+ 0.52
$I_2 + 2e^-$	$\rightarrow$	$2I^-$	+ 0.54
$Fe^{3+} + e^-$	$\rightarrow$	Fe^{2+}	+ 0.77
$Hg^{2+} + 2e^-$	$\rightarrow$	Hg	+ 0.79
$Ag^+ + e^-$	$\rightarrow$	Ag	+ 0.80
$Br_2 + 2e^-$	$\rightarrow$	$2Br^-$	+ 1.09
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$	$\rightarrow$	$PbSO_4 + 2H_2O$	+ 1.69

ASSIGNMENT 10
CORROSION

AIMS

The aim of this assignment is to understand the causes and effects of several common examples of corrosion.

1. INTRODUCTION

Corrosion processes are chemical reactions that take place at the surface of a metal and obey well-established chemical laws. The fact that corrosion is a surface reaction means that its course may be controlled by the properties of the corrosion product. The metal compound formed may act as a barrier between the environment and the metal, and the rate of corrosion of the metal may be slowed down if the effectiveness of the barrier layer increases with time: this is frequently observed in the reaction of metals with gaseous environments. If, however, the corrosion product can be removed from the site of reaction, the corrosion rate cannot be expected to diminish with time. This is the case when soluble corrosion products are formed by the corrosion of certain metals in aqueous solutions.

All metals are prone to corrosive attack if the environment is sufficiently aggressive, eg noble metals are unaffected by most media, but they can be dissolved in *aqua regia*.

In practice, corrosion reactions are most undesirable as they effectively destroy metal or render it useless. For instance, steel girders will lose their strength and ultimately fail if rusting takes place extensively; water tanks made from steel plates will leak if only minute areas of metal are destroyed by corrosion. It will be appreciated that the economic losses resulting from corrosion are very large and the methods of combating it (such as painting structures or providing other protection) are all expensive.

In this assignment the reaction of metals with gases ('dry' corrosion) is dealt with in the first section and of metals with aqueous solutions ('wet' corrosion) in the second.

1.1 CORROSION OF METALS IN GASEOUS ENVIRONMENTS

Oxidation of Metals

The reaction of a metal with air or pure oxygen to form an oxide on the metal surface constitutes an important branch of corrosion. The oxidation of metals is a chemical reaction which can be represented by the equation:

$$xM + \frac{y}{2}O_2 \rightarrow M_xO_y$$

The oxygen atoms gain electrons to become oxygen ions and a stable oxide results, but such oxidations can only take place spontaneously if a decrease in free energy of the system occurs. Silver only forms an oxide film below 180^0C, and gold is not oxidised, but at room temperature nearly all metals exposed to the air carry an invisible film of oxide. Although oxides are more stable at low temperatures, the rates of oxidation of metals in these temperature ranges are generally low. At higher temperatures, although the free-energy decrease is smaller, the reaction is faster and rates of oxidation are considerably greater. The films are invisible when very thin, but over certain ranges of thickness of the oxide, interference colours can be produced. As the

film becomes increasingly thick, the colours disappear and a thick layer of oxide (which may flake off the metal on cooling) is obtained.

1.2 LAWS OF OXIDATION

As an oxide is formed between a metal and its gaseous environment, a barrier develops through which reactants must pass if the oxide film is to continue thickening. The rate of reaction may be may be governed by a) the transport of reactants through the oxide. or b) the rate of oxygen supply to the outer oxide surface, or c) the rate at which oxygen and metal react to give oxide. If the rate of diffusion of the reactants through the oxide film is the slow step in the oxidation and so controls the speed of reaction, the oxidation rate will decrease as the thickness of the film increases.

Let y be the thickness of an oxide film at time t, and let it increase to $y + dy$ at time $t + dt$.

The simple oxidation laws are the parabolic, logarithmic and rectilinear laws, which can be represented by the following equations:

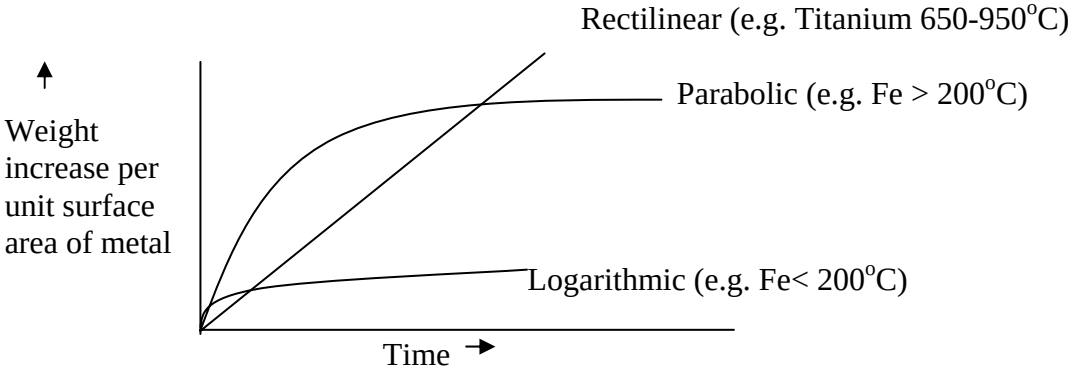
$y^2 = 2K_1t + K_2$ **parabolic law of oxidation**

$y = K_3\log(K_4t + K_5)$ **logarithmic law of oxidation**

$y = K_6t + K_7$ **rectilinear law of oxidation**

The constants (K_1 - K_6) are all temperature-dependant. The parabolic law describes the rate of growth which varies inversely as the thickness. The logarithmic law applies to metals which oxidise rapidly at first and then slowly, the film thickness becoming virtually constant. The rectilinear law shows that oxidation continues at an undiminished rate with time even though the oxide film is thickening.

The three laws are illustrated schematically in **Figure 1.**



THICKNESS OF OXIDE FILMS

Methods have been devised for stripping the oxide films from their metal base, and it has even proved possible to remove some that are too thin to show interference colours. Such a separation of oxide from metal can be simply demonstrated with aluminium if the oxide film is thickened by heating.

1.3 CORROSION OF METALS IN AQUEOUS ENVIRONMENTS

Wet corrosion processes, taking place in neutral, acid or alkaline environments, are more complex than those of dry oxidation, but again metal compounds are formed with a decrease in free energy of the system. Wet corrosion may take many forms: there may be uniform destruction of the material (as is normally encountered in oxidation); the corrosion may be highly localized, as in pitting or stress corrosion; or attack may be concentrated at areas adjacent to a second more noble metal or at points where the oxygen supply is limited.

It has been established that the mechanism of the corrosion process in aqueous solutions are electrochemical. If a metal is immersed in a conducting liquid or solution certain areas of the metal acquire a different electrode potential from the remainder of the surface, a 'positive' current flows through the electrolyte from the anodic areas to the cathodic areas, leading to the dissolution or corrosion of the anodes.

1.4 THE DANIELL CELL

If a metal **M** is immersed in a solution containing it own ions M^{n+}, the system assumes an electrode potential E_M given by

$$E_M = E_M^{o} - \frac{RT}{nF} \ell n\, [M^{n+}]$$

$$= E_M^{o} - 2.303 \frac{RT}{nF} \log_{10} [M^{n+}]$$

E_M^{0} being the standard electrode potential of the metal in the solution of ions at unit concentration, i.e. $[M^{n+}] = 1$. Here R is the gas constant, T temperature, n the number of electrons involved in the electrode reaction, and F Faraday's constant.

$$2.303 \frac{RT}{nF} \text{ has the vaue } \frac{0.059}{n} \text{ V at } 25^{o}\text{C}$$

Now, consider a simple type of Daniell cell (Fig 2). The potential of the zinc electrode at 25^{0}C is given by

$$E_{Zn} = E_{Zn}^{o} - 0.030 \log_{10} [Zn^{2+}] \qquad \text{where } E_{Zn}^{o} \text{ has the value } -0.76\text{V}.$$

Similarly, the copper electrode assumes a characteristic “half-cell” potential E_{Cu} with respect to the solution of its ions. When the zinc and copper electrodes are joined externally a current flows, the zinc becomes the anode and the copper the cathode of the cell. The zinc rod dissolves (ie corrodes) as Zn^{2}+ and releases electrons, which pass along the metallic path to the copper where they are consumed in discharging cupric ions from solution.

$$Zn \rightarrow Zn^{2+} + 2e^{-} \quad \text{(anodic reaction - oxidation)} \qquad (6)$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad \text{(cathodic reaction - reduction)} \qquad (7)$$

Naturally the rates of reaction at the anode and cathode are electrochemically equivalent, and the rate of dissolution of the anode and of deposition on the cathode are determined by Faraday's laws.

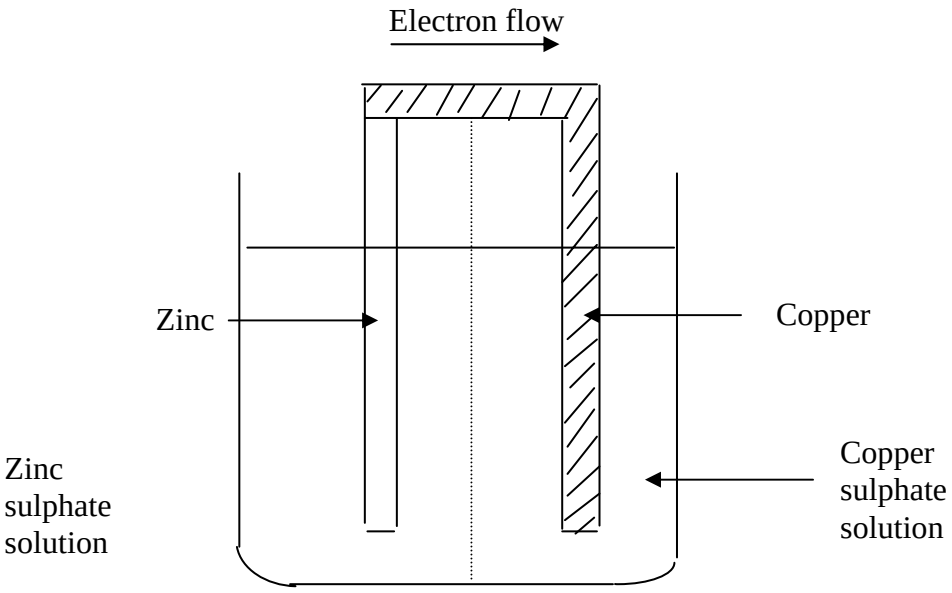


Fig 2. A simple type of Daniell cell

The copper electrode is the positive pole or cathode of the Daniell cell and it has a higher or more positive potential than the zinc anode (negative pole) of the cell. In such a current-generating cell, the direction of flow of the 'positive' current in the metallic path is from the copper to the zinc (which corresponds to the flow of electrons from the zinc to the copper); within the electrolyte, however, the 'positive' current flows from the zinc to the copper, the current being carried by the appropriate ions in solution.

1.5 A SIMPLE CORROSION CELL

If the solutions of zinc sulphate and copper sulphate in the Daniell cell are replaced by a solution of sodium chloride, a current will still flow, zinc ions again passing into solution and releasing electrons which are consumed at the copper electrode in a cathodic process. (In corrosion, it is most convenient to think of an anodic process as an electron-producing one, whereas cathodic reactions consume electrons.) The cathodic process will not, however, be the same as in the Daniell cell, for the concentration of copper ions in solution is negligible, the only cations the solution contains being sodium ions and hydrogen ions. As corrosion proceeds a third cation - zinc ions - will appear in the solution. Of the cations, the sodium ion cannot be deposited on the cathode because this would require a potential far more negative than that which even the zinc attains in this cell. The cathodic deposition of the zinc ions put into solution at the anode would imply that the cell was in equilibrium, which is certainly not the case. This means that the discharge of H may be the only possible cathodic reaction:

$$H^+ + e^- \rightarrow H \qquad \text{followed by } H + H \rightarrow H_2$$

However, there is another possible cathodic process, namely the reduction of oxygen (dissolved in the salt solution) to hydroxyl ions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^-$$

For corrosion taking place in approximately neutral, aerated solutions, this 'oxygen absorption reaction' (as it is known) is the predominant cathodic reaction. With Fe/Cu or Fe/Pt couples immersed in sodium chloride solutions, exactly similar observations may be made to those described for a Zn/Cu couple. In each case, the noble metal becomes the cathode of the cell, and, if the solution is aerated, hydroxyl ions will be formed and accumulate in the vicinity of the cathode. The base or less noble metal becomes the anode and corrodes.

1.6 CORROSION OF SINGLE METALS

It is not, however, necessary for dissimilar metals to be in contact for corrosive attack take place. Everyone is familiar with the rusting of iron or steel objects in the atmosphere or under water;

This corrosion is also an electrochemical process and so anodic and cathodic areas must be present on a single metal.

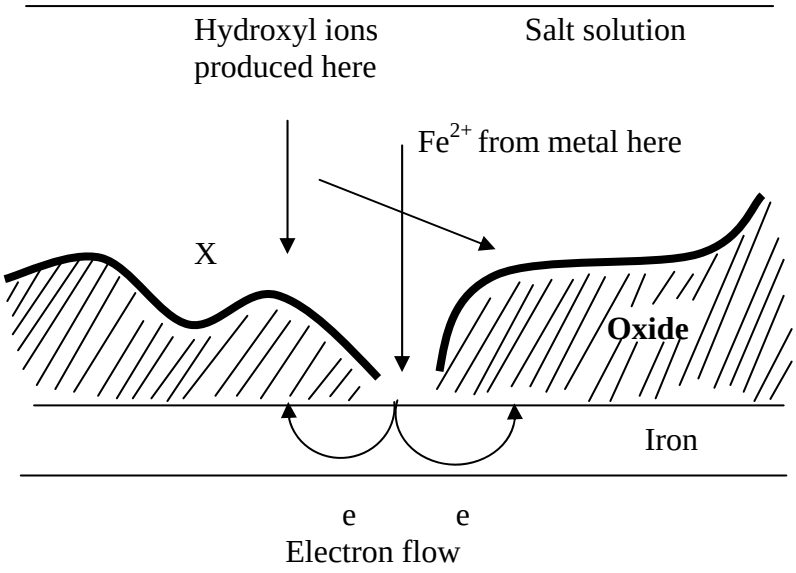
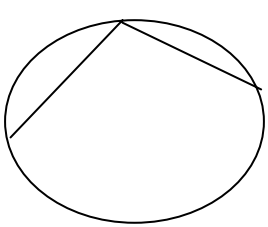


Fig 4. Corrosion of a metal at cracks in the oxide film. Ferrous ions may also pass into solution at points where the oxide has become thin, eg at X.

In the experiments, 2.5 & 2.6, the corrosion of single metals is examined. Even if the metals used had been extremely pure, corrosive attack would still be observed. The ferroxyl indicator in the case of iron in Experiment 2.5.2 demonstrates that anodic and cathodic areas can be established on the same piece of metal. The reason for this is as follows. Earlier it was noted that metals such as iron and zinc after exposure to air carry oxide films.



Abrasion lines on iron

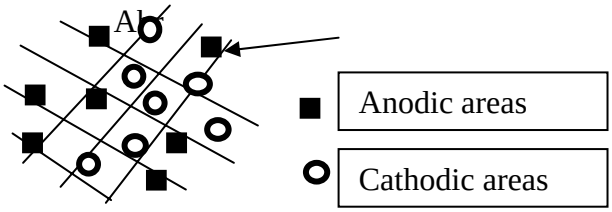


Fig 5. Primary distribution of anodic and cathodic areas on iron using ferroxyl indicator (plan)

At some points, the oxide film is possibly cracked, porous or very thin, and here it wil1 be easier for metal ions to leave the metal lattice than at places where the oxide film is more perfect. When the sheet of iron is first covered with electrolyte, anodic areas develop at the points where the film is cracked or otherwise weak, and the cathodic, electron-consuming reaction takes place at an area nearby where the oxide is thicker (Fig 4).

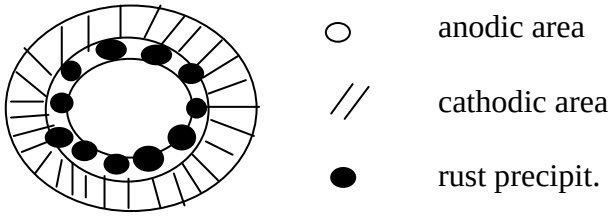


Fig 6. Secondary distribution of anodic and cathodic areas on iron (plan)

The initial or primary distribution of anodic and cathodic areas is often random, but sometimes the anodic sites are distributed in the directions of abrasion on the iron (Fig 5). After a time, a secondary distribution of the anodic and cathodic areas develops (Fig 6). At first, the oxygen dissolved in the drop is uniformly distributed but it will be slowly consumed by the cathodic reaction. Replenishment of oxygen in solution from the air is most rapid at the edges where the drop is thinnest and much slower in the centre where the drop is thick. Consequently the cathodic reaction will become predominant in the periphery of the drop, and if any anodic spots develop in this area the high OH^- precipitates the ferrous ions as fast as they pass into solution and any anodic areas will be sealed. In the centre of the drop, lower oxygen concentration will ensure that the amount of hydroxyl ion produced will small and the anodic reaction will predominate. So, after a few hours, the centre of the drop becomes blue and the outer rim pink, and at the junction of the two zones a membrane of rust is formed. If the salt solution is first saturated with oxygen, the initial distribution persists for some time. If, however, the solution is de-aerated by bubbling nitrogen through it before the experiment, the secondary distribution is observed from the start.

In experiment 2.5.2 a rather similar state of affairs exists. In a vertical specimen, the part nearest the water-line of the liquid will be well aerated, and the cathodic reaction will take place most readily at this area. Lower down the specimen, the rate of oxygen replenishment is low and so such areas will become anodic and pass into solution. At a point between the anodic and cathodic zones, membrane like precipitates of white zinc hydroxide or rust form. At the 'water-line' specimens of each metal may develop interference tints owing to the presence of a film.

If the specimens in Experiments 2.5 and 2.6 are allowed to corrode for a day and are then washed, dried and examined, it would be found that (Experiment 2.5.2) the lower portion of the iron nail is roughened owing to the removal of metal, whereas the cathodic area near the water-

line is not attacked. For longer times of corrosion, the anodic area is usually found to move slowly upwards until the whole specimen is corroding, with the most intense attack occurring at the water-line. The cathode is now the area immediately above the water-line over which alkali formed in the solution will have crept. On the horizontal specimen (Experiment 2.6) only that part of the metal under the central portion of the drop will have suffered corrosion - the metal under the outer rim of the drop will not be corroded.

1.7 DIFFERENTIAL AERATION PRINCIPLE

It can be concluded that the parts of a metal surface that are in contact with liquid of the highest oxygen concentration will become cathodic and be protected from corrosion, and the areas where oxygen concentration is low will be corroded. This is known as the ‘differential aeration' principle and is of importance in explaining many corrosion phenomena. The fact that currents flow between a well-aerated electrode and a less aerated one can readily be demonstrated.

1.8 CONTROL OF CORROSION RATE BY CATHODIC OR ANODIC PROCESSES

As stressed earlier the anodic and cathodic reactions must go in step with one another but the overall rate of electrochemical corrosion may be principally governed by either the anodic or the cathodic reaction rate. For many base metals, such as iron and zinc in aqueous solutions, the rate of the cathodic reaction is the rate-determining step in corrosion of the metal, that is, the reaction is under cathodic control. If the supply of oxygen to the cathode is increased, the rate of the cathodic reaction is raised and the anodic reaction correspondingly speeds up. A similar effect is obtained if the area of the cathode is increased, the anodic area remaining constant. If the cathodic area is constant and that of the anode is increased, the total amount of corrosion would be approximately the same but the amount of dissolution per unit area of the larger anodic area would be decreased and the effects of corrosion diminished.

It is always dangerous to have large cathodic areas associated with small anodic areas, for attack on the anodes will be intense. Riveting brass or copper plates together with iron bolts will lead to rapid failure. Steel rolled at high temperatures (ca 1100^0C) is covered with a 'mill scale' of iron oxide. The scale cracks easily, revealing bare metal; if the material is used in this condition rapid rusting occurs in many environments because the dangerous combination of large cathode (oxide scale) and small anodes (gaps in the scale) exists.

2. EXPERIMENTAL

You will work in pairs.

N.B. Before proceeding with Experiment 2.1 start Experiment 2.5 which is a slow experiment.

Experiment 2.1

2.1.1 Take a thin piece of iron sheet about 3" long and 2" wide and having abraded it with a fine emery paper, degrease with acetone and cotton wool. Hold the metal strip horizontally and heat one end in a bunsen flame so that a steep temperature gradient is imposed along the length of the specimen. After a short time, a series of interference colours develops at the hot end of the specimen and the colours move towards the cooler end. Several orders of interference may be observed, the distinction between the colours within each order becoming progressively less with the higher orders.

Write a balanced equation for the reaction – the product is Fe_2O_3.

2.1.2 Repeat the experiment, using a strip of copper.

These tints are the result of interference of the light reflected at the upper and lower surfaces of the film. If the metal strip is heated for a long time, a flaky oxide film is formed which may detach itself from the metal base during the oxidation or, more probably, when the specimen cools down. Films of other metal compounds on metals (eg sulphides and iodide) also exhibit similar sequences of interference tints.
Write a balanced equation for the reaction – the product is Cu_2O.

Experiment 2.2

MERCURY IS A VERY TOXIC SUBSTANCE. CARRY OUT THIS EXPERIMENT IN YOUR FUME HOOD AND DISPOSE OF MATERIALS CORRECTLY.

Take a small sheet of aluminium and place it on a petri dish. Using a pasteur pipette apply a small drop of saturated mercuric chloride solution to the strip (5-7mm diameter). Holding the aluminium firmly, scratch the surface at the side of the drop with a nail (3 to 4 small scratches). Leave for about 1 minute and then wash the mercuric chloride solution off with distilled water. Quickly "pat" dry the strip with a tissue or cotton wool (DO NOT RUB) and place it on a second petri dish. Cover with a large beaker and watch as a white powdery growth of aluminium oxide appears (5-10 minutes).

At the cuts in the oxide film, mercury forms an amalgam with the aluminium and eats into metal along the metal/oxide interface and soon severs the oxide from its base. When the solution is washed off and the strip dried, an aluminium/mercury amalgam covers the surface and the aluminium oxidizes rapidly as it is in a finely divided state.

Please dispose of used $HgCl_2$ solution and aluminium strip in the residue containers as instructed by your demonstrator.

A WASTE CONTAINER IS PROVIDED FOR ALL MERCURY WASTES INCLUDING PETRI DISHES.

In 2.3 and 2.4 use the electrodes from your kit, they are small enough to fit in 100mL beakers.

Experiment 2.3

2.3.1 Join a strip of copper to one of iron (nail, abraded) using a wire with alligator clips at either end and immerse the couple in a beaker containing 'ferroxyl' indicator (which is supplied) as shown (Fig 3). The solution will detect both ferrous and hydroxyl ions. Leave the beaker and its contents undisturbed and observe what happens. Report your observations.

2.3.2 An iron nail (abraded) is first coated with copper by dipping it into a solution of copper sulphate for 3 minutes. Follow this by washing with distilled water followed by complete immersion of the metal in a shallow layer of ferroxyl indicator. Report your observations.
In these experiments, the solution adjacent to the copper cathode becomes pink (i.e. OH^- is produced) and the solution near the iron anode turns blue (Fe^{2+} ions in solution producing a blue colour with ferricyanide). Both the anodic and cathodic reaction products are soluble but the ferrous and hydroxyl ions move towards one another and form a precipitate of ferrous

hydroxide somewhere between the anode and cathode of the cell. As the corrosion product is not formed in contact with either electrode, there is no tendency for either the anodic or cathodic process to be stifled and corrosion continues: this is in contrast with dry oxidation in which the corrosion product frequently slows down the reaction rate.

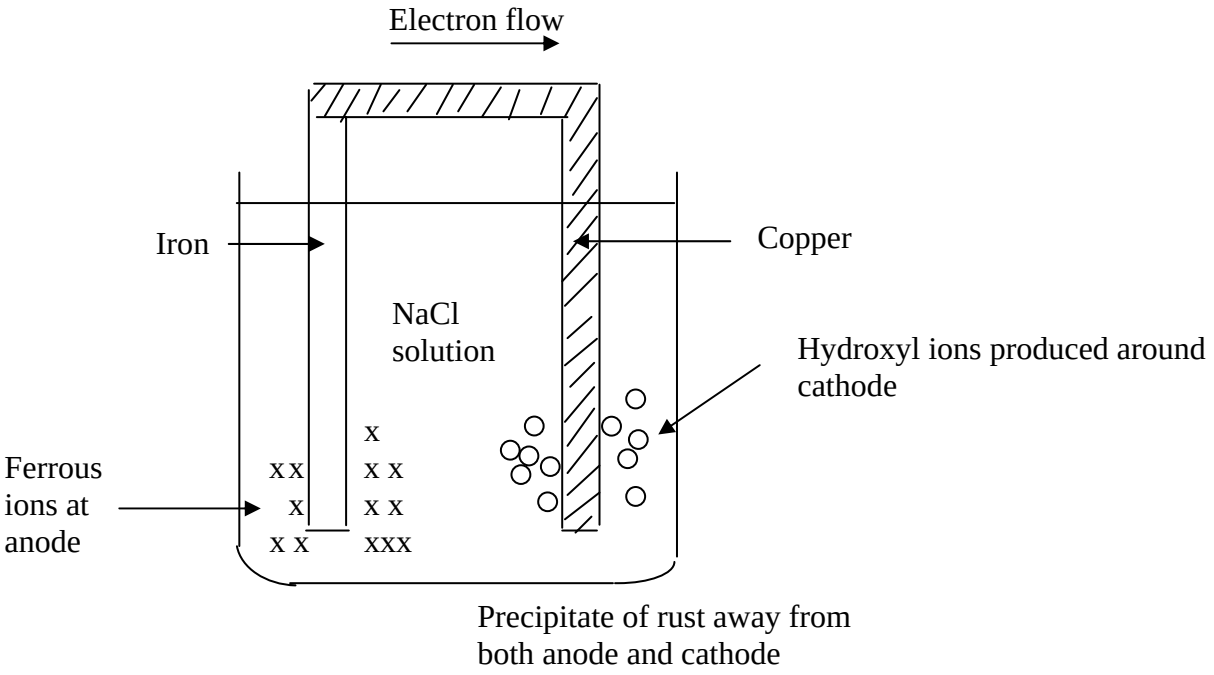


Fig 3. A simple corrosion cell

Experiment 2.4

2.4.1 Take an iron nail and a sheet of zinc, abrade and degrease in the usual way, connect with a wire (Experiment 2.1) and stand the sheets vertically in a beaker containing 3 per cent salt solution so that only the lower half of the metal is immersed. Add 'ferroxyl' indicator to give a yellow colour in solution and leave for 5 minutes. Observe any changes in solution and note them in your report book.

2.4.2 Repeat 2.4.1 with no zinc. Observe the nature and position of the corrosion product.

Experiment 2.5

Take a thin sheet of clean, abraded iron and place a drop (about 2.5cm in diameter) of 'ferroxyl' solution on the centre of the sheet. Observe the initial distribution of anodic areas at the start. Keep the specimen undisturbed for 2 hours and prevent undue evaporation of the drop by covering the specimen with a large watch glass or beaker, the edges of which rest on a ring of cotton wool soaked in water. Watch how the distribution of anodic and cathodic areas changes with time.

Experiment 2.6

Place two iron nails (abraded) into the compartments of a divided cell, the cell being most easily prepared by placing a porous sintered glass crucible ($80) in a beaker. Fill the crucible and the beaker with 3 per cent salt solution, add some ferroxyl indicator (a few mL) and join the two electrodes with a voltmeter. As the two pieces of iron have the same composition and are in

contact with equally aerated solutions, no current should flow. On bubbling air over one of the electrodes inside the crucible, the one inside the crucible becomes the cathode of the cell; it will have a more positive potential than the non-aerated electrode and a potential will be observed.

This experiment proves that the areas of a metal immersed in solution to which access of oxygen is limited or denied are those most liable to corrosive attack. For this reason, any accumulations of debris or inert matter in metal containers for liquids should be avoided. Insoluble corrosion products (such as rust) formed in a system can shield any areas on the metal with which they come in contact and so promote further attack.

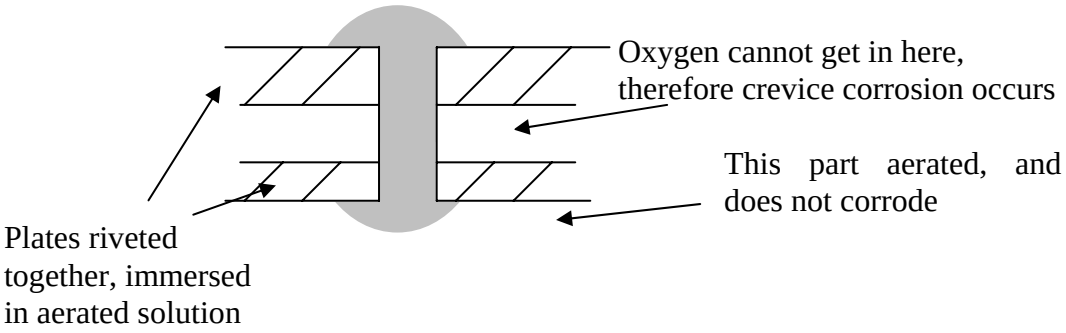


Fig 7. Crevice corrosion taking place between riveted plates.

Crevices in structures (eg where two plates have been riveted together) which are in contact with liquids are also areas where oxygen replenishment is difficult and corrosion may be expected (Fig 7). In wet corrosion, corrosion products are frequently voluminous and, if attack does take place between plates in close contact, the rust or other corrosion product is capable of forcing the plates apart and causing further trouble. Better design for such objects can eliminate many of these features and is often the best method of avoiding this kind of corrosion.

3. QUESTIONS

You are asked to provide observations and explanations for the corrosion chemistry. Where possible you should provide equations to support your answer.

ASSIGNMENT 11
WATER QUALITY STUDIES

AIMS

The aim of this assignment is to become familiar with several of the water quality parameters used in assessing a water body for the effects of pollution. The parameters investigated include Chemical Oxygen Demand (COD), pH and chloride content.

1. INTRODUCTION

Water is one of the basic essentials to all forms of life, including man. Natural water in lakes and rivers contains a certain amount of dissolved gases (eg. oxygen, nitrogen and carbon dioxide), inorganic salts and sediments. The nature of the inorganic content in the natural waters depends on the geological surroundings. The ability of natural water to support animal and plant life is obviously dependent on the level of dissolved oxygen in it.

Unfortunately, these water expanses have been used as convenient sinks for all types of waste, mainly from industrial and domestic effluents. Excessive and uncontrolled dumping have resulted in some degree of fatality to aquatic plants and animals, as well as human life. Consequently, the control of water pollution has evolved into an area of major scientific research.

In this experiment the properties of water samples obtained from various sources will be examined. The following tests will be performed.

(a) chemical oxygen demand
(b) degree of acidity (pH)
(c) estimation of total chloride content

While these tests are not exhaustive, they form the basis for determining the suitability of water for human consumption. For a rigorous study of water pollution, many other tests (eg. trace metal levels, pesticide concentration, phosphate analysis as a nutrient indicator, etc) would need to be performed; however these tests are beyond the scope of this course.
Table 1 lists some of the more important allowable levels for public drinking water supplies. Note that the data in this table are not the only criteria necessary for classifying water as suitable for drinking. The 1998 water contamination problem in Sydney was a problem with significant microbial populations in the water supply and so there are range of microbiology tests that are also applied. Alkalinity and total suspended solids are also investigated by government authorities, along with specific tests for toxic compounds.

Table 1 Typical standards for a drinking water supply.

Parameter	Permissible levels	Desirable levels
Total dissolved solids	1000 mg dm^{-3}	<200 mg dm^{-3}
Dissolved O_2 applicable to free flowing streams (not lakes)	4 ppm (monthly mean) 3 ppm (individual sample)	near saturation (8-10 ppm)
pH (range)	6 - 8.5	7.4 - 7.8
Chloride (mg dm^{-3})	300	< 25
BOD (mg dm^{-3})	< 20	as low as possible

1.1 Chemical Oxygen Demand (COD)

Organic pollutants can lead to a lowering of the dissolved oxygen content of water. Much of the organic material is oxidised by bacteria in the water and the oxygen required by the bacteria for this process is abstracted from the water. Unless the water is re-aerated, a lowering of the dissolved oxygen content will occur.

The amount of organic material may be estimated in two ways.

1. B.O.D. (Biological Oxygen Demand), which is defined as the amount of oxygen (in mg) taken up during a five day period by one litre of water sample. This is essentially a measure of the amount of organic material oxidised by bacteria in the water in the five-day period. This test is the best method for estimating organic pollution levels but obviously requires considerable time.

2. C. O.D. (Chemical Oxygen Demand**)** is a more rapid test which gives a measure of chemically oxidisable material in the water sample. The oxidisable material in the water is oxidised with hot potassium dichromate solution. This method suffers from some obvious disadvantages. Firstly, some material oxidised by the dichromate may not be oxidisable by the water bacteria (or vice versa), and secondly some inorganic materials will interfere. However, the test gives a reasonably rapid indication of the amount of organic material present. The idealised oxidation reaction is as follows.

$$C_6H_{12}O_6(s) + 4Cr_2O_7^{2-} + 32H^+ \rightarrow 6CO_2\uparrow + 8Cr^{3+} + 22H_2O$$

The glucose ($C_6H_{12}O_6$) comes from sugars, fats, carbohydrates etc. A similar reaction, involving oxygen, is possible with the aid of bacteria.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Hence 4 moles of $Cr_2O_7^{2-}$ are as effective as 6 moles of oxygen in oxidising 1 mole of glucose. Accordingly, 1 mole of $Cr_2O_7^{2-}$ used in the oxidation procedure is equivalent to 1.5 moles of oxygen.

1.2 Acidity (pH)

Water is an *amphiprotic solvent* which means that it behaves both as an acid and as a base. This is easily understood from the dissociation of the O-H bond in water according to the following equilibrium.

$$H_2O \leftrightarrows H^+ + OH^-$$

In aqueous solution this is best represented as the self-ionisation of water.

$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$$

The equilibrium constant for this reaction $K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$. The concentration of *hydronium ions* H_3O^+ (or protons as they are often called) in neutral water is 10^{-7} M. This is an inconvenient number to work with and so the scale used is a logarithmic one called the *pH scale* which runs from 0 - 14.

$$pH = -\log_{10}[H_3O^+]$$

If we have an acidic water then the pH value will be low eg. 2 - 3, while a basic water will have a higher pH eg. 11 - 12, neutral water is in the middle at a pH of 7. When we refer to an acidic solution then we are referring to a solution with a high hydronium ion concentration which will have a low pH.

To determine the pH of a water two methods are in common use. The first is a semi-quantitative test that makes use of a Universal Indicator which generates colour changes in response to the H^+ concentration that can be related to the numeric value of the pH. These Universal Indicator (either solution or test strips) use a set of organic dyes that respond to changes in the pH environment to give these colour changes.

The second method is to use a pH meter. This is simply a device for measuring quickly and accurately the cell potential or e.m.f. (**E**lectro**M**otive **F**orce) of an electrochemical cell formed by placing two electrodes in the solution. The e.m.f. is determined by the individual electrode potentials of the two electrodes, one of which (the indicator electrode) is sensitive to pH while the other (the reference electrode) is not. The e.m.f.. is thus dependent on the pH of the solution. Probably the most widely used indicator electrode is the **glass electrode**. This is a relatively fragile electrode and we will use a more robust and modern pH **semiconductor electrode**.

1.3 Estimation of Total Chloride Content

Chloride is one of the anions which exists in appreciable concentrations in sea water, sewage effluent and natural lakes. While chloride is an essential anion, too high a chloride concentration can be harmful to (freshwater) plants and animals. Thus, the control of chloride is of major concern to the environmental engineer. A useful technique for the estimation of chloride is **Volhard's method**. An excess of standard silver nitrate solution is added to the water sample, thus precipitating all the chloride as silver chloride.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}\downarrow$$

The excess silver nitrate (i.e. that left after precipitating chloride) is then **back-titrated** using standard ammonium thiocyanate ($NH_4^+SCN^-$). The indicator used for the titration is ferric ion (Fe^{3+}).

$$Ag^+ + SCN^- \rightarrow AgSCN_{(s)}\downarrow$$
$$Fe^{3+} + SCN^- \rightarrow \underset{\text{red}}{Fe(SCN)^{2+}}$$

The ferric ion reacts with the thiocyanate ions to form a red complex, this will only occur after all the Ag^+ has been precipitated as AgSCN and free SCN- starts to appear in solution.

The following side reaction can occur

$$AgCl + SCN^- \rightarrow AgSCN_{(s)}\downarrow + Cl^-$$

Since Ksp(AgCl) > Ksp (AgSCN), where Ksp is the **solubility product**. This reaction is slow and may be prevented by coating the precipitated silver chloride with bromobenzene.

2. EXPERIMENTAL

You will work in pairs. Each pair should bring to the practical class a 1- 2 litre bottle filled with a water sample of their choice. N.B. do not collect samples from secondary sewerage treatment outlets as this is a hazardous occupation.

NOTE: The Chemical Oxygen Demand Experiment should be commenced at the start of the practical session. Duplicate determinations are required. Other experiments can be completed during the two hours the samples are boiling for the COD measurements.

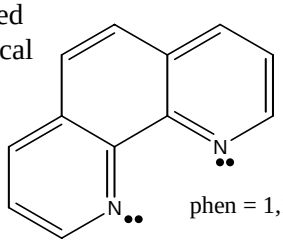
2.1 Chemical Oxygen Demand

In this experiment, an excess of standard $K_2Cr_2O_7$ is added to the polluted water and the unreacted dichromate is titrated against ferrous ammonium sulphate using ferroin as an indicator.

This procedure of reacting the unknown against a known excess of a reagent A and then titrating using reagent B to determine how much A has been used up is referred to as a **back-titration** and is a commonly used procedure in analytical chemistry.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$



phen = 1,10-phenanthroline

The indicator ferroin turns an intense red colour due to the co-ordination of three molecules of 1,10-phenanthroline to the Fe(II) ion. In the presence of strong oxidising agents, the solution turns blue due to the formation of the $[Fe(phen)_3]^{3+}$ complex.

> [*The technician does the following so that you can get the prac finished on time:*
> *To 25 cm^3 (pipette) of water sample in a 250 cm^3 conical flask, add 25 cm^3 of standard (0.01 M) potassium dichromate solution (pipette), followed by 60 cm^3 (measuring cylinder) of 6 M H_2SO_4.*
> *Boil the contents of the flask for 2 hours, and then cool to room temperature.*]
>
> Add 5 drops of ferroin indicator and then titrate the unreacted dichromate using standard (0.10 M) ferrous ammonium sulphate. The end point is taken when the colour of the solution changes suddenly from blue green to reddish brown.

- Note your titre result and the exact concentrations of dichromate and ferrous ammonium sulphate in your report book.

2.2 Degree of Acidity

The pH of your water sample should be checked using Universal test strips and using a pH meter.

Before performing these experiments fully acquaint yourself with the operation of the pH meter (see instruction card supplied with the instrument). You must not place water above the white mark on the electrode and when in use the electrode plate should only just be covered. Before using your pH meter you should calibrate it using buffer solutions at the set pH values of pH 4.0 and pH 7.5.

- Record the values obtained from the using the Universal Indicator Test strips and the pH meter in your report book.

2.3 Estimation of Total Chloride Content

2.3.1 Standardisation of the Ammonium Thiocyanate

Pipette exactly 10 cm^3 of standard (0.01 M) silver nitrate into a conical flask.
Add 3 cm^3 of 6 M nitric acid (measuring cylinder) and 1 cm^3 of ferric nitrate solution.

N.B. CAUTION Concentrated Acid handle with care.

Titrate, with vigorous shaking, with the ammonium thiocyanate solution until a faint red colour appears. Note the ammonium thiocyanate solution concentration in your report book.
Repeat the titration until concordant (within 0.1 cm^3) results are obtained.

- Record the titre results in your report book.

2.3.2 Determination of Total Chloride Content of a Water Sample

Carry out ALL the following manipulations in the FUMEHOOD.

Pipette 100 cm^3 of your water sample into a 250 cm^3 conical flask. Add 3 cm^3 6 M HNO_3.

N.B. CAUTION Concentrated Acid handle with care.

Pipette exactly 10 cm^3 of standard 0.01 M silver nitrate into the water sample. Add 3 cm^3 of A.R. bromobenzene* (measuring cylinder) and 1 cm^3 40% ferric nitrate (plastic disposable pipette).

*** HANDLE WITH CARE : avoid contact with skin.**

Thoroughly mix the contents of the flask.

Titrate with the previously standardised ammonium thiocyanate.

- Record the titre result in your report book and the exact concentration of silver nitrate used.

3. CALCULATIONS AND QUESTIONS

3.1 Chemical Oxygen Demand

Calculate the C.O.D. of your water sample according to the method shown below.
Express your answer as mg dm^{-3} of O_2 in the water sample.

Method of calculation of C.O.D.

moles of dichromate added = $[K_2Cr_2O_7]$ x Vol $(K_2Cr_2O_7)$
(mol dm^{-3}) (dm^3)

moles of ferrous ammonium (FAS) = [FAS] x Vol (FAS) used in titration
(mol dm^{-3}) (dm^3)

Now 1 mole of $Cr_2O_7^{2-}$ reacts with 6 moles of Fe^{2+} (see equation above):

$\therefore$ moles of dichromate reacting with FAS = [FAS] x Vol (FAS) x 1/6
(mole dm^{-3}) (dm^3)

Therefore, the number of moles of dichromate used by water sample (which we shall call ***A***)

$$\boldsymbol{A} = \{[K_2Cr_2O_7] \times Vol(K_2Cr_2O_7)\} - (\{[FAS] \times Vol(FAS)\} \times 1/6)$$

(mol dm^{-3}) (dm^3) — added standard; (mol dm^{-3}) (dm^3) — titration

Now 4 moles of $Cr_2O_7^{2}$ are equivalent to 6 moles of O_2 (see the equations above),

$\therefore$ moles of oxygen = ***A*** x 6/4

$\therefore$ $[O_2]$ (mol dm^{-3}) = ***A*** x 6/4 x 1/ Vol of water sample (dm^{-3}) (recall n = c V)

$\therefore$ C.O.D. (mg dm^{-3}) = *A* x 6/4 x 32 x 1000 x 1/ Vol of water sample (dm^{-3})

where (i) the factor of 32 is the molecular weight of O_2
(ii) the factor of 1000 represents the conversion of g to mg

3.2 Degree of Acidity

- Is your water sample within the permissible limits for a drinking water supply? (consult Table 1).

3.3 Estimation of Total Chloride Content

3.3.1 Standardisation of the Ammonium Thiocyanate

- Calculate the concentration of the ammonium thiocyanate solution.

3.3.2 Determination of Total Chloride Content of a Water Sample

- Calculate the chloride concentration of your water sample as mg dm^{-3} of Cl.
  This is a back-titration and so the same type of working as used in part 3.1 will be required.

- Comment on your result in terms of the source of the water that you have chosen.

ASSIGNMENT 12
WATER HARDNESS

AIMS

The aim of this assignment is to become familiar the concept of water hardness and in doing so learn about the use of complexiometric titrations, use of micropipettes, serial dilutions, calibration curves and spectrophotometry.

1. INTRODUCTION

Water hardness is one of the standard parameters measured in water quality studies. The hardness of water refers to the presence of Ca^{2+}, Mg^{2+} (and to a lesser extent Fe^{3+}) in a water sample. Water hardness typically results from the presence of dissolved inorganic salts, especially those containing calcium and magnesium. The degree of hardness due to calcium and magnesium (ie. "Total Hardness") is usually expressed in terms of the concentration, in mg L^{-1}, of calcium carbonate equivalent to the total calcium and magnesium concentration (ie. on a mol $CaCO_3$ = mol (Ca^{2+} +Mg^{2+}) basis).

Table 1 Typical standards for a drinking water supply.

Parameter	Permissible levels	Desirable levels
Hardness (mg $CaCO_3dm^{-3}$)	60 - 150	< 60

1.1 Hardness – Complexiometric method

The total Ca^{2+} and Mg^{2+} ion concentration may be determined volumetrically by titration with the complexing agent ethylenediaminetetraacetic acid (EDTA), using Erichrome Black T, a blue dye, as an indicator – this is referred to as a complexiometric titration as a metal complex is formed between the alkaline earth cation and the ligand which binds to it EDTA.

The blue dye, Erichrome Black T, is added to a sample of water buffered to pH 10.
The buffering is necessary for three reasons:

- the dye is an acid base indicator and is red in acid solution as a result of a reaction with H^+.
- at this pH the desired $Mg(dye)_2$ complex is formed. The resultant solution is red owing to the formation of a complex between Mg^{2+} and the dye.
- The reaction between Ca^{2+} and EDTA is incomplete at low pH.

$$Mg^{2+} + 2\ \text{Erichrome Black T} \leftrightarrows Mg(dye)_2$$
$$\text{(Blue)} \qquad\qquad \text{(Red)}$$

When the titrant EDTA is added to the buffered solution containing free Ca^{2+}, Mg^{2+} and $Mg(dye)_2$, it will react initially with the free Ca^{2+} and Mg^{2+} before displacing the dye from the $Mg(dye)_2$ complex.

$$\{Ca^{2+} + Mg^{2+}\} + 2EDTA \leftrightarrows \{Ca(EDTA) + Mg(EDTA)\} + \text{protons}$$
$$\text{colourless complexes}$$

During the titration the colour of the solution gradually changes from red to purple. At the end point when all the Ca^{2+} and Mg^{2+} ions have been complexed with EDTA, the solution becomes blue. The blue colour is characteristic of the un-complexed dye provided the pH has been maintained at pH = 10.

$$\underset{\text{red}}{Mg(dye)_2} + EDTA\text{-}H_2^{2-} \leftrightarrows \underset{\text{blue}}{MgEDTA\text{-}H_2} + 2dye$$

1.1 Hardness – Spectrophotometric method

An alternative approach may be used for determining the hardness which eliminates the difficulty of visually identifying the end point – which often is the main error in the measurement. In the spectrophotometric method we make use of the fact that Ca^{2+} and Mg^{2+} metal complexes formed with the ligand Calmagite® are colourless and have no absorption at 650nm. The Calmagite® ligand alone forms a blue solution (at pH 10) and has a strong absorption at 650nm.

In the analytical method we prepare a calibration curve using a series of $CaCO_3$ plus Calmagite® standards and run these through a spectrometer operating at 650nm. we are able to relate the intensity of the absorption at 650nm to the amount of calcium that is present in each of the standards. The results are plotted and the linear plot is then is used to determine the concentration of Ca^{2+} (and Mg^{2+}) that is present in any unknown water sample that is reacted with Calmagite® in the same fashion as the standards and then placed into the spectrometer.

2. EXPERIMENTAL

You will work in pairs. Each pair should bring to the practical class a 1- 2 litre bottle filled with a water sample of their choice – must not be seawater. N.B. do not collect samples from secondary sewerage treatment outlets as this is a hazardous occupation.

NOTE: One half of the class will be assigned to the complexiometric titration and the other half of the class to the spectrophotometric determination at the start. Once you have completed the experiment you have been assigned at the start you will then commence on the other experiment.

2.1 Hardness – Complexiometric Method

Because the hardness of water varies over wide limits it is necessary to first carry out a rough titration, using a fairly concentrated EDTA solution, to determine a suitable EDTA concentration to give an accurate analysis.

To 50 cm^3 (pipette) of your water sample in a 150 cm^3 conical flask, add approximately 5 cm^3 of ammonia buffer **WARNING: strong smell of ammonia perform in fumecupboard**.
All subsequent operations in 2.1 are to be carried out in the fumecupboard.
Check, with wide range indicator paper, that the pH of the solution is 10. Add one drop of Erichrome Black T solution.
Titrate the solution with standard 0.1M EDTA solution very roughly using a small measuring cylinder. Add EDTA in small amounts to the solution, mixing well after each addition. Check the pH of the solution after every few additions - if the pH falls below 10 add more buffer. The colour at the end point is **blue**.

If the titre for this rough titration is less than 2 cm^3, change to 0.01 M EDTA and do another rough titration. If the 0.01M EDTA rough titre is less than 2 cm^3 then you will need to perform your accurate titrations using 0.001 M EDTA. A titre of greater than 5 cm^3 for 0.1 M EDTA indicates extremely hard water and subsequent accurate titrations need to be performed using the 0.1 M EDTA. A rough titre of > 2 cm^3 with 0.01M EDTA and < 2cm^3 with 0.1M EDTA

means you will use 0.01 M EDTA for your accurate titres.

Note you will have to make your own dilutions for the EDTA solutions from the 0.1 M EDTA solution using volumetric flasks, pipettes and the dilution equation $c_1V_1 = c_2V_2$.
If it is necessary to change EDTA concentrations you **MUST WASH OUT THE BURETTE THOROUGHLY** with the new EDTA solution. (Do not return any unused EDTA to the stock bottles). You will use a 25mL pipette and 250mL volumetric flasks to carry out the necessary 10 fold or 100 fold dilutions.

Repeat the titration with the new (or original 0.1 M if it is applicable) EDTA solution until concordant titres are obtained (agreement of two titres to within 2 cm^3).

- Note the titre values and the exact concentration of EDTA that you have used for the titration.

2.2 Hardness – Spectrophotometric Method

2.2.1 Using micropipettes.

A set of two micropipettes is available to you in a set of shared equipment. The caps of the micropipettes indicate the volume ranges over which they can be used: 10-100µL, and 100-1000 µL .

Set the desired volume by holding the micropipette body in one hand and turning the adjustment knob until the correct volume shows on the digital indicator. Like all machines there is some 'play' in the volume adjustment knob. To overcome this problem it is recommended that you always approach the desired volume by dialing downward (at least one-third revolution) from a larger volume setting – that is you will always finish a setting with a **clockwise motion**.

Attach a new disposable tip to the shaft of the pipette. Press on firmly with a slight twisting motion to ensure a good seal. Depress the plunger to the **FIRST POSITIVE STOP**. This part of the stroke is the calibrated volume displayed on the digital dial. Note **you must not fully depress the button** as this is the second stop and doubles the volume transferred.

Holding the micropipette vertically, immerse the disposable tip into the sample liquid to a depth of about 1.5 mm (do not exceed 3mm). Release the pushbutton slowly, allowing the solution to gently rise in the pipette tip.

To DISPENSE THE SAMPLE, place the tip end against the side wall of the receiving vessel and depress the plunger slowly to the **FIRST STOP**. Wait about 1 second for the solution to drain. Keeping the tip in the solution take your finger off the plunger this loads the tip with the mixture. Now push the plunger of the pipette to the first stop again (releases the mixture and cleans out the tip) and take the tip out of the solution. Whilst you are holding the pipette just above the surface of solution depress the plunger to the **SECOND STOP**, expelling any residual liquid in the tip

Withdraw the micropipette from the vessel and **then** let the plunger return to the UP POSITION.

Remove the tip before placing the micropipette on the bench or in it's holder.

A fresh tip should be fitted for each sample to prevent carryover between samples.

2.2.2 Preparation of the $CaCO_3$ standards.

You are provided with a 1000ppm standard of calcium carbonate, Ca Std. The ppm unit is part-per-million which in this case means mg / L. (1000ppm = 1000 mg $CaCO_3$ /L.) Load 10 pipette tips into your tray.

You will be preparing 5 standards of different concentrations in volumetric flasks.

1. Add x μL of Ca Std using a 10 -100 μL pipette into a 10mL volumetric flask.
2. To the x μL Ca Std in the volumetric flask, add 250 μL of 0.1% Calmagite indicator and 400 μL of 1% KOH buffer using the 100 -1000 μL pipette.
3. Make up to the mark with distilled (RO) water.
4. Cap the volumetric flask and invert carefully 3 times to ensure good mixing.
5. Label each volumetric flask as appropriate with the concentration.

Each time you use a different solution you **must change the pipette tip**.

x (μL) :	0	10	20	30	40
Concentration (ppm):	0 ‘Control’	1	2	3	4

You will now have 5 volumetric flasks containing the different concentrations of Ca^{2+}. Pour each sample into a cuvette (¾ fill the cuvette), cap with Parafilm® and wipe the sides of the cuvette with a tissue to remove any liquid and fingerprints. Hold the cuvettes using the grooved side and place into the spectrometer under guidance of your demonstrator. They will explain the operation of the spectrometer and how you should Measure the absorption at 650nm for each sample using the 40μL (pink) sample as the blank (keep this you will need it later in2.2.3). Check that your results are OK with a demonstrator and then clean out your volumetric flasks – this is important as you will need them again and so will other students as there are limited number (70) of them. Enter your data in your report book and the plot the graph which is the calibration curve.

2.2.3 Serial Dilution of the water sample

At the outset you will not know the concentration (hardness) of your water sample and so it is useful to carry out a **serial dilution** of the sample to obtain an absorbance that can be measured using your calibration curve.

In the serial dilution an aliquot (10 mL portion) of the original sample is pipetted (glass pipette) into a volumetric flask (100 mL) and diluted to the mark using distilled (RO) water. The volumetric flask is inverted and shaken three times to mix it. A 10 mL aliquot is pipetted out of this volumetric flask (1) and transferred to a second 100 mL volumetric flask (2) which is then diluted to the mark using distilled water and mixed. A 10 mL aliquot is taken from this second volumetric flask may be transferred to a third volumetric flask which is diluted to the mark and so on... In this experiment you should prepare the first and second volumetric flasks initially, if the water is very hard you may

need to prepare the third volumetric flask. Label each volumetric flask with the appropriate dilution.
As you can see this makes a series of concentrations where the first member is undiluted, the first volumetric flask is a **x10 dilution**, the second volumetric flask a **x100 dilution**, etc. (You can easily verify this using $c_1V_1 = c_2V_2$)

You will carry out the following procedure with your undiluted water sample and the 2 serial dilutions in volumetric flask 1 and volumetric flask 2.

Take a small sample of water around 5 mL (either undiluted or from one of the volumetric flasks) and place it in a clean, dry sample vial (this is so that you can get you micropipette tip into the sample). Then carry out steps 1 – 4. This operation is repeated then 3 times for you undiluted, x10 diluted and x100 diluted.

1. Using a 10 -100 μL pipette 20 μL of water from the sample vial into a 10mL volumetric flask.
2. To the sample in the volumetric flask, add 250 μL of 0.1% Calmagite indicator and 400 μL of 1% KOH buffer using the 100 -1000 μL pipette.
3. Make up to the mark with distilled (RO) water.
4. Cap the volumetric flask and invert carefully 3 times to ensure good mixing.
5. Label each volumetric flask with the appropriate dilution.

At this stage you should have 3 x 10 mL volumetric flasks containing the various dilutions for running on the spectrometer. If both of the serial dilutions are blue then you will need to repeat the dilutions. Proceed in exactly the same fashion as 2.2.2 placing the samples in cuvettes, capping with Parafilm® and running absorbance of the samples at 650nm. Record your results in your report book. Only absorptions that lie in the range spanned by the calibration standards (0 – 4ppm) can be used. Using the appropriate dilution factor (either x1, x10 or x100) calculate the original undiluted hardness of the water in ppm $CaCO_3$ (mg / L).

3. CALCULATIONS AND QUESTIONS

3.1 Hardness – Complexiometric method

- Calculate the 'total hardness" of your water as mg dm^{-3} of $CaCO_3$, given that one mole of EDTA reacts analytically with one mole of Ca^{2+} or Mg^{2+} ions.
  Refer to Table 2 and quote the hardness rating of your water.

Table 2. Water hardness

Hardness range (mg dm^{-3} $CaCO_3$)	Description
0 - 60	soft
61 - 120	moderately hard
121 - 180	hard
> 180	very hard

3.2 Hardness – Spectrophotometric method

- Calculate the 'total hardness" of your water as mg dm^{-3} of $CaCO_3$.
- Compare your value with the value obtained in the complexiometric method and comment

on the errors involved in both methods and how improvements could be made.

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.