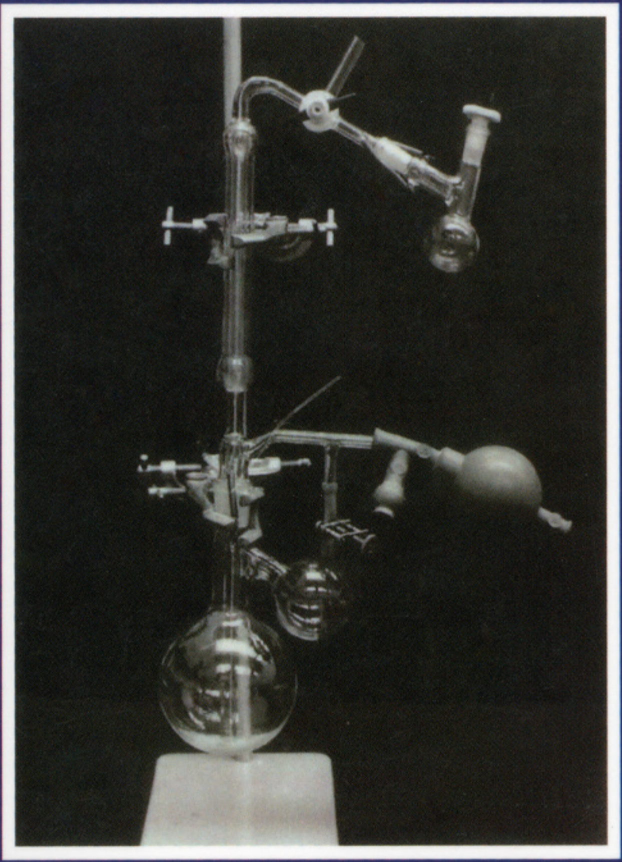
EXPERIMENTAL INORGANIC/PHYSICAL CHEMISTRY

An Investigative, Integrated Approach to Practical Project Work



Mounir A. Malati

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"Talking of education, people have now a-days" (said he) "got a strange opinion that every thing should be taught by lectures. Now, I cannot see that lectures can do so much good as reading the books from which the lectures are taken. I know nothing that can be best taught by lectures, except where experiments are to be shewn. You may teach chymestry by lectures – You might teach making of shoes by lectures!"

James Boswell: *Life of Samuel Johnson, 1766* (1709-1784)

"Every aspect of the world today – even politics and international relations – is affected by chemistry"

Linus Pauling, Nobel Prize winner for Chemistry, 1954, and
Nobel Peace Prize, 1962

MOUNIR A. MALATI

Mounir Malati obtained his BSc degree in the Department of Chemistry in Cairo University's Faculty of Science in 1943, and then was appointed Demonstrator in the Department of Chemistry, Alexandria University, and next in Cairo University until 1946. He afterwards became Science Master in a Cairo independent high school until 1953. He went to England for graduate research in the Physical Chemistry Department of Leeds University, where he was awarded his PhD in 1957 for research on photochemical electron transfer reactions.

Returning to Egypt, he spent a few months as Chemistry Lecturer at the Women's Teacher Training College, Cairo before joining the National Research Centre in Giza to take charge of a research unit, where he was promoted to become Research Associate Professor, supervising a number of graduates working for higher degrees. In December 1962 he again came to the United Kingdom, researching for a year at Imperial College, London, and then took a job as Senior Research Officer with the Paint Research Association.

In 1965 he joined Medway College of Technology (now Mid-Kent College) to teach inorganic, physical and radiochemistry for BSc, Grad.R.S.C., and Higher National Certificate courses. At the same time he also supervised projects for undergraduates and graduates, where five former students from Egypt obtained PhD degrees under his supervision. He also supervised five Mid-Kent College students who were awarded PhD degrees, at the same time collaborating with four post-doctoral fellows.

He has presented research papers at international conferences in the UK, USA, Canada and mainland Europe, some dealing with experiments presented in the book. His present interests include photocatalysis for greenhouse gas control and the removal of water pollution. He is also interested in photochemistry and reactions of complex compounds and adsorption of ions by oxides of Si, Fe, Mn and Ti. He has over 150 publications.

Experimental Inorganic/Physical Chemistry

An Investigative, Integrated Approach to Practical Project Work

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Chatham

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To my wife Margaret
and my daughters
Mervat and Suzy

Preface

Practical Chemistry courses have changed considerably over the past three decades. Practical examinations have been replaced by project work, complemented by assessed experiments lasting for two-three practical sessions. Even at H.N.D./H.N.C. level, assignments have replaced practical examination. In project work, not only accurate measurements and analytical results are assessed but also the student's ability to organise and plan the practical work and to report and discuss the results intelligently. In project work, an integrated approach is necessary where the artificial division of Chemistry into Inorganic, Physical or Analytical is unnecessary. The title and sub-title of the book emphasise these aspects and reflect my experience and interests. My research for my Ph.D. degree was in the Physical Chemistry Department and my work at the National Research Centre was mainly on the upgrading of inorganic minerals using physico-chemical methods. Over thirty two years I taught Inorganic, Physical and Radiochemistry and I have developed numerous projects based on an integrated approach with emphasis on investigation. Most of the experiments described in the book have been tried and tested or developed in our laboratory. Many of the results have been published. To widen the scope of the book, I have also included experiments based on published papers or taken from the references given at the end of Chapters 2 and 18.

To correlate the practical work to the theory, Chapters 3-17 start with a theoretical introduction to the chemistry of the group or element dealt with in the chapter. Generally a short theoretical background precedes experimental instructions.

Most of the experiments described in the book can be carried out using readily available inexpensive chemicals and do not require expensive specialised instruments. Safety precautions are given in Chapter 1 and are taken into account throughout the book.

The Appendices are an integral part of the book. Appendices 3-18 contain the results of the experiments described in the respective chapters or references where the results are found. The necessary calculations are also given in the Appendices, including treatment of kinetic data. References to other experiments are included in the Appendices. Most of the references are given without the Authors names or the title of the paper to save space. However, when quoting a reference from a journal not readily accessible to English-speaking chemists, the names of the Authors are given. Each section of an appendix is numbered (preceded by A) to correspond to the respective section in the main chapter.

Although it is assumed that students using the book have done a course in Chemistry, including practicals, at A level or equivalent, Chapter 1 deals with good laboratory practice and simple operations. The theoretical background to the various techniques is briefly explained in Chapter 2 together with references to more detailed treatments.

I acknowledge the help and encouragement I received from the late Lord Dainton during my study in Leeds and throughout my work in the U.K. I also acknowledge the help and encouragement I received from the late Professor A. Riad Tourky during my study and work in Egypt.

I am grateful to Ever Ready (Central Laboratory), the Royal Society of Chemistry and the Society of Chemical Industry for financial assistance. Thanks are due to Dr. John Burgess for help and advice. I thank Mrs. Pamela Elsegood for the word-processing of the text, Mr. John-Paul Phillips for producing the figures and Mrs. Rosmary Harris for preparing the camera-ready text.

This book would not have materialised without the enthusiasm and hard work of most of my students, my research students (both in Chatham and in Egypt) and my post-doctoral collaborators.

I hope this book will encourage students to appreciate the thrill of carrying out investigative projects.

Mounir A. Malati
Mid-Kent College of Higher and Further Education

LIST OF ABBREVIATIONS

a(or act.)	activation
acac	acetylacetonate
(aq)	aqueous
bipy	bipyridine
Bq	disintegrations s^{-1}
conc.	concentrated
cm	centimeter
c.p.m.	counts $minute^{-1}$
C.T.	charge transfer
c.p.s.	counts s^{-1}
dm	decimeter
DMF	dimethylformamide
DMG (or HDMG)	dimethylglyoxinato
DMSO	dimethylsulphoxide
DTA	differential thermal analysis
E_a	activation energy
EDTA	ethylenediaminetetraacetic acid
en	diaminoethane
emf	electromotive force
ESR	electron spin resonance
Et	ethyl
E^o	standard redox potential
F	Faraday constant
(g)	gas
g	gram
h	Planck's constant
i.r.	infrared
i.s.	initial state
J	joule
k	kilo
k or k_r	rate constant
K	degree Kelvin
L	ligand
LF	ligand field
L.F.S.E.	ligand field stabilisation energy
LMCT	ligand to metal C.T.
L or N_A	Avogadro constant
M	metal
m	metre
max	maximum
MLCT	metal to ligand C.T.
nm	nanometre
NMR	nuclear magnetic resonance
o	(superscript) standard
Ox	oxalate
Oxine	8-hydroxyquinoline
phen	1,10-phenanthroline
pn	diaminopropane
PZC	point of zero change
PZZ	point of zero zeta potential
R	gas constant
s	second
(s)	solid
TGA	thermogravimetric analysis
tr	transition
t.s.	transition state
OG	free energy change
OH	enthalpy change
OS	entropy change
OV	volume change
⌛	wavelength
⌨$_e$	effective magnetic moment
⌨$_B$	Bohr's magneton
🗀	molar extinction coefficient
🖰	frequency or neutrino
✌	magnetic susceptibility
et al	and others
ibid	in the same place (or journal)
O_h	octahedral
T_d	tetrahedral

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1

Good Safe Laboratory Practice

1.1 INTRODUCTION

Safe and efficient work in the laboratory requires that the bench should be tidy and clean. Only the required labware should be intelligently arranged and left on the bench. A student should have a cloth for dealing with spillages and a glass cloth for drying the outside of glassware. When set aside for further work, this glassware should be covered with watch glass, rubber bung or parafilm and suitably labelled. Practical results (volumes of solutions or liquids, masses of solids or precipitates, physical or kinetic results) should be recorded as soon as they are obtained in a notebook, together with the theoretical basis, special observations, procedure, calculations and the date. Spectra should be labelled with the compound and conditions used as well as the date and operator's initials. Adhering to these rules is essential in project work which may extend over weeks or even months. Determinations or experimental runs should be carried out at least in duplicate, and the results analysed statistically.

1.2 USE AND CARE OF GLASSWARE

Ordinary glassware, such as beakers, flasks (conicals round-or flat-bottom) or stoppered bottles and Winchesters (2.5dm^3) should be cleaned after use, dried from the outside with a cloth and stored in a cupboard on tissue paper upside down. Otherwise, borosilicate glassware may be dried at 110°C in an oven before storage. Alternative drying is by rinsing with pure acetone and blowing air to dry. A useful cleaning procedure is to add a few drops of acetone to a few drops of conc. hydrochloric acid and apply with a brush to stained glassware before rinsing thoroughly with tap and then distilled water. A warm 10% detergent solution may clean glassware in 15 minutes especially on brushing. This is to be followed by conc.HCl and rinsing. A test of cleanliness is to fill with distilled water when a continuous film of water is formed on draining.

All polythene wash bottles have a screw on cap and hand pressure forces liquid from the bottle's jet. Water is usually used in wash bottles but sometimes hot water, acetone-filled or alcohol-filled bottles are used and should be clearly labelled. The bottle's jet is used to wash and transfer precipitates, with the help of glass rods.

Desiccators contain the desiccant in the base which is covered by a perforated metal gauze or plate. They have closely fitting covers with polished perimeters lightly greased so they can be slid on or off the rim of the desiccator's body. A commonly used desiccant is self-indicating silica gel. When it turns pink, it has to be heated to produce the blue dried form. Sodium hydroxide pellets, concentrated sulphuric acid or phosphorus V oxide are sometimes used as desiccants. For efficient desiccation, a vacuum desiccator is required. The cover of such a desiccator has a greased glass joint carrying a stop-cock used for evacuation. For safety, the desiccator is kept in a wooden box with a lid.

Graduated glassware may be used for rough or accurate volume measurements. Graduated cylinders or separating funnels are suitable for rough work whereas pipettes and burettes are used for accurate work, especially when they are grade A or had been calibrated. To calibrate a burette, fill to the mark with distilled water. Allow a certain volume, say 5 cm^3 at a time, to be delivered into a previously weighed bottle with a stopper. Weigh and find the weight of the water delivered. Repeat until the burette bottom reading is reached. Calculate, using the density or water at the laboratory temperature, the actual volume of the aliquot of water collected. Plot the corrected volume against the burette's nominal volume reading. When small titres are expected, microburettes should be used. They are calibrated in a similar way. Small volume micropipettes may have two marks, with the nominal volume between the marks etched on the glass. Micropipettes are emptied by pressing a teat attached to the top stem. Other glassware is commonly used for preparations and includes crystallisation and Petri dishes, condensers and beads or helices to stop bumping when liquids are boiling or in distillations.

Ordinary glassware can be rinsed with distilled water after cleaning and then used unless they have to be dried. Graduated cylinders and funnels can be rinsed with the liquid to be measured. Two or three small volumes of the solution must be used for rinsing pipettes or burettes before filling. Rinsing the item can be done by rotating in a horizontal position so that the rinsing solution wets all the surface. No graduated glassware should be dried by heating. After use and washing thoroughly with distilled water, they are best stored upside down, covering the top end with suitable loose caps.

Special care has to be taken when inserting a glass tube or a funnel through a rubber bung to avoid broken glass and injury. A little lubricant is used to ease the slow movement of the glass through the bung which is kept close to the glass. However, if any glass is broken, the large pieces should be carefully removed to a special labelled box and the small pieces transferred to it by a brush and pan. When glassware supplied with standard ground joints, their use is recommended. The joints should be very lightly greased: as should glass stopcocks. When regreasing is needed, the old grease is removed using a suitable solvent.

When hot distilled water or other hot liquids are needed e.g. for washing a precipitate, the neck of the bottle should be covered by an insulating material to permit safe handling.

Sintered glass crucibles, funnels and filter sticks are widely used for filtration, the latter two are necessary for much preparative work.

1.3 USE OF OTHER LABWARE

Porcelain labware is suitable for heating to temperatures much higher than the softening temperature of borosilicate glass. Porcelain crucibles are used for heating solids, igniting precipitates but are attacked by alkalis, sodium carbonate, pyrophosphates and hydrofluoric acid HF. Porcelain basins or boats are useful for evaporating liquids and melting solids. Sintered porcelain crucibles, in different porosites, are available and are suitable for gravimetric analysis but should be heated gradually. Mortars and pestles are usually made of porcelain. Except for some very inert residues, porcelain equipment can be usually cleaned by a hot 0.1M solution of tetrasodium EDTA (ethylenediaminetetra-acetic acid). Crucibles and basins made of silica may replace porcelain ones for most purposes, but borosilicate glassware cannot be safety heated above 200°C especially sintered glass crucibles. Filter papers supported on ordinary or Buchner funnels are cheaper than sintered glassware and have a wide range of porosities which determines the rate of filtration and physical strength. Ashless filter paper is suitable for gravimetric analysis. Glass fibre papers and micro-filtering sticks are useful to replace paper e.g. when iodine is liberated or with strong acids.

Some metals, in the form of crucibles or basins, find uses in the laboratory. Nickel crucibles and dishes are suitable for fusions with alkalis or sodium peroxide. For the latter fusion, iron crucibles may be employed although they are less durable. Spatulas and scoops are usually made of nickel, whereas tongs and holders may be made of either nickel or steel. Silverware can replace nickelware for fusions. The more expensive platinum crucibles and dishes are also suitable for fusions e.g. with sodium carbonate or borax or for evaporating HF or concentrated sulphuric acid. Cleaning platinum ware is by fusing some sodium carbonate and dissolving the residue followed by digestion with conc.HCl. Pt-clad stainless steel is cheaper and more durable than platinum. Zirconium crucibles have been available in recent years.

1.4 WEIGHING

Modern single pan balances have greatly simplified weighing especially with the taring facility. Rough balances may have the pan exposed to air but analytical balances have the pan enclosed in a glass case. In both cases, the weight is directly displayed. It is advisable even for accurate weighing to start using a rough balance. The solid is added to a tared weighing bottle with its stopper using a metal or plastic scoop. When the approximate amount is weighed, the bottle is weighed in the analytical balance to the nearest fourth decimal of a gram and then reweighed after emptying the contents into a suitable glass container. This is known as **weighing by difference.** For preparative work when the purest chemicals are not usually used, rough weighing to the nearest centigram is adequate. In no circumstance should a hot object be placed on a balance pan. Hygroscopic materials should not be weighed on the analytical balance, although its case usually contains a silica gel container.

1.5 HEATING

Bunsen burners are used for many heating operations. The blue flame of the burner should be usually maintained by adjusting the hole at its base. Only when a reducing atmosphere is required for qualitative analysis is the yellow flame used and is formed by nearly blocking the hole. Rounded glassware can be heated in the direct flame but even then continuous shaking of the container is necessary to avoid accidents. Wooden holders or metal tongs should hold the glassware. For other glassware or silica or porcelain containers, a metal gauze over the flame ensures a safe rate of heating. Electric hot plates or heating mantles are necessary when flammable liquids are heated or distilled. Only the latter heaters are safe for highly flammable liquids such as ether. Electric drying ovens are suitable for heating to a medium temperature say 250°C.

Heating in a muffle furnace can be adjusted to about 1200°C. Gradual heating is recommended for sintered porcelain crucibles.

1.6 INTRODUCTION TO SAFETY

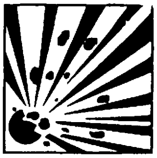
To avoid or minimise accidents in the chemical laboratory, such as fires and explosions, and to ensure that students and staff are not exposed to other health hazards, they should be aware of the risks involved in handling chemicals and in carrying out reactions. In addition, they should know the measures required to deal with hazardous situations. They should be familiar with the use and situation of fire extinguishers, protective blankets, eye wash facility, first aid box, as well as evacuation procedure in case of fire or explosion. Chemicals manufacturers are obliged by law to label all hazardous chemicals with a warning sign to indicate the type of hazard. When chemicals are dispensed in containers other than those supplied by manufacturers, these containers should be also clearly labelled for the possible hazards.

1.7 WARNING SYMBOLS

Tests or experiments marked with an asterisk (*) are meant for demonstration only.

The European Union Directives specify the warning symbols used which refer to the following hazards:

1.7.1 Explosive



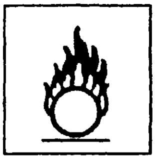
Some substances which may explode by impact when dry or in contact with combustible substances are labelled explosive and are supplied wet with water or a suitable solvent. These explosive chemicals should be stored away from combustible chemicals in safe storage metal cabinets and should never be allowed to become dry. Picric acid is an example. Its aqueous solution is sometimes used for treating burns. It is dangerous to allow students to experiment with explosive substances.

1.7.2 Highly or extremely flammable

The symbol does not distinguish between the two groups. However, when a liquid has a flash point below 0°C and boiling at or below 35°C, it is classified as extremely flammable. Such chemicals should be stored in labelled steel cabinets surrounded by a container to allow for spillage. No flames should be allowed in the laboratory when they are used. Ether is an example of an extremely flammable liquid, which is used for recrystallisation of some complexes and for washing many preparations. In addition to its flammability, its vapour is harmful. Ethanol is highly flammable, and is usually on the shelves of the normal chemical laboratory. It should be only heated on a water bath.

1.7.3 Oxidising

Substances which are rich in oxygen may react exothermally with other chemicals producing fires and/or explosions. This is more likely when the oxidising chemical reacts with or even comes in contact with

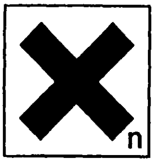


a flammable substance. Oxygen cylinders and flammable gas cylinders such as hydrogen or acetylene should be kept in separate strong metal cages outside laboratories. Oxidising solids or liquids should be used carefully, preferably in small quantities. If heating is required, electric mantles should be used. Peroxy compounds contain a weak O-O single bond and may react explosively with flammable liquids. Perchlorate salts of transition metal complexes containing organic ligands are potential explosives.

1.7.4 Toxic or very toxic

These are substances which may cause serious or very serious acute or chronic effects when inhaled or accidentally contact the eyes, the mouth or the skin. Cyanides which are soluble in water are poisons and produce the very toxic HCN. In exceptional cases, mature well-trained students may be allowed to use small quantities of KCN under close supervision. The safe handling of toxic chemicals is to wear protective laboratory coats, eye goggles and rubber or synthetic polymer gloves.

1.7.5 Harmful

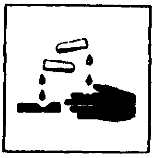


If the chemical has a limited effect on health when it reaches a person by any of the above-mentioned routes, it is described as harmful. This term does not imply that careful safe handling of these chemicals should be relaxed.

Carcinogens

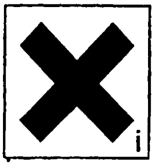
A large number of organic chemicals have been tested on animals to assess the possible risks of causing cancer. However, a limited number of organics are used in the book and carcinogens are avoided.

1.7.6 Corrosive



Substances which destroy living tissues are described as corrosive and should never be handled without protective gloves and goggles. Concentrated sulphuric and nitric acids are known examples. The effect increases if the substance is hot. Safety pipetting is always essential especially in this case as well as other precautions when dealing with toxic, harmful materials.

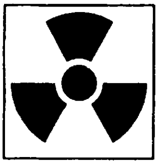
1.7.7 Irritant



This term applies to chemicals which produce inflammation of the skin or the mucous membrane in the nose or mouth. This may happen immediately or by repeated or prolonged contact. Besides the usual protections, the use of hand creams may be beneficial

1.7.8 Radioactive

The radioactive chemicals occasionally used in the laboratory are U or Th compounds. They are not considered to be as dangerous as those of medium or high activity. They should be kept in metal containers.



Besides the usual precautions for hazardous chemicals, in dealing with radioisotopes radiation hazards should be considered. The time spent near a β or a γ source should be minimised. In working with open sources, disposable gloves are worn and safely removed and disposed of in a labelled pedal bin. A tray lined with tissue paper is used when solutions or liquids are used. The paper should be safely removed and placed in the "radioactive" bin. The tray should be checked by a monitor for any contamination after removal of the lining. Any spillages are mopped with decon solution using tissue paper to be disposed of as above. All glassware containing active liquids should be surrounded by another glass container to capture any spillage and prevent spreading of activity in case of breakage. Handling solid powders or heating or boiling liquids should be in the fume cupboard behind a safety screen. Samples to be counted should be in a form not likely to contaminate surroundings and are transferred to the counting room with an outer container. Background readings are taken before and after counting to ensure that the counter was not contaminated. After practical work is finished, all disposables are safely removed, the hands should be carefully washed and preferably monitored with a hand monitor. Writing up should be in the counting room not in the laboratory.

1.8 RISK AND SAFETY PHRASES

The letter R refers to risk phrases and S denotes safety phrases. A list of the relevant phrases are found in Manufacturers catalogues. A combination of risk and safety phrases is also included. It is therefore necessary for students to be familiar with these phrases. Some prepared complexes whose potential risk has not been ascertained should be handled with extra care. Hence all precautions taken with the other harmful chemicals should be adhered to and any harmful effects reported to the staff supervising the work.

1.9 EXPLOSIONS AND FIRES

Although individual chemicals may not be considered explosive or flammable, contact between two such chemicals, especially on heating, may cause explosion and/or fire. Potassium metal is banned from laboratories. When concentrated sulphuric acid is added to a small crystal of potassium chlorate, $KClO_3$, a small explosion is heard due to the formation of the explosive chlorine dioxide. Flammable gases like hydrogen and acetylene, when mixed, within certain limits, with oxygen or air could explode when ignited.

1.10 FIRE EXTINGUISHERS

Coded symbols for recommended fire extinguishers are listed in Appendix A1.1.

1.11 SPILLAGE TREATMENT

Another set of coded letters are used for recommended spillage treatment. These are given in Appendix A1.2. The treatment is recommended for small spillages after ascertaining the chemical spilt and being equipped with the required items.

1.12 WASTE DISPOSABLE

Coded numbers are used by Fisher Scientific UK for recommended procedures. Toxic metals from experiments should be collected in labelled Winchesters before disposal or before recovery.

1.13 CAREFUL USE OF CONCENTRATED ACIDS AND ALKALIS

Glacial acetic (ethanoic) acid is flammable and its vapours irritate the respiratory system, the skin and the eyes. It reacts explosively with oxidants such as permanganate and sodium peroxide. Although hydrochloric acid is safer than other mineral acids, the HCl fumes from conc.HCl irritate the eyes and the skin. On the other hand, perchloric acid can cause explosions with traces of organic compounds. It is advisable to dilute it by adding the concentrated acid slowly to a large volume of water in a thoroughly cleaned container. The same dilution process is recommended for nitric and sulphuric acid. For the latter, the water should be cooled while the conc. acid is slowly added while stirring. Explosions are also known when the acid reacts with oxidants such as permanganate and perchlorate. The acid is a very powerful oxidant and can burn the skin and damage the eyes. A mixture of concentrated sulphuric and nitric acid is also sometimes used for cleaning glassware and is equally hazardous. Concentrated nitric acid can cause burns and produce fires with combustible materials e.g. explosive reactions of the acid with acetic acid, alcohols, acetone, ammonia, hydrogen peroxide and iodide. When it reacts with metals, the toxic oxides of nitrogen are usually formed. A mixture of conc. HCl and conc. nitric acid (3:1 by volume) known as aqua regia is often used for cleaning crucibles and produces chlorine and NOCl, the latter is intensely irritating and toxic.

Concentrated ammonia is an irritant and the vapour affects the eyes, the skin and respiratory system. In hot weather, if the cap of its vessel is not carefully released, copious vapour rushes from the container. Solid hydroxides of sodium and potassium should not be used to dry tetrahydrofuran. Peroxides and peroxo-compounds should be carefully used.

1.14 HANDLING ORGANIC SOLVENTS

No solvents should be poured down the sink. Special precautions have been mentioned for dealing with flammable solvents. Although solvent waste may be mixed in dirty labelled solvent Winchesters, chlorinated solvents should be kept apart. Facilities may be also available for recovering some solvents and these should be stored separately.

1.15 SOME SIMPLE TESTS AND OPERATIONS

1.15.1 The flame test

The alkali metal salts and those of the Ca triad and Cu impart a colour to the non luminous Bunsen flame. A Pt wire is cleaned first by dipping its tip in conc. HCl and placing it at the lower outer edge of the flame, repeating this until no colour can be observed. A little of the salt to be tested is placed at the edge of a watch glass containing a little conc. HCl. After contacting the salt and then the acid, the wire is exposed to the flame again and the colour noted with and without a blue filter. If a hand spectroscope is available, it can be used to observe the visible line spectrum of the metal. A demonstration is described in *J.Chem.Educ.*, 73 (1996) 80.

1.15.2 Melting point determination

Organic solids are usually characterised by their melting points and so are some metal complexes with organic ligands or organometallics. The finely ground and dried solid is heaped on a flat surface and introduced to the open end of a capillary melting point tube using a small spatula. Tapping the upright tube forces the powder to the sealed end. The tube is then placed in an electrically-heated oil bath or metal block adjacent to the thermometer of the melting point apparatus. Fast initial heating using a booster should change to slow heating near the expected melting point. The solid is viewed through a magnifying lens and the temperature noted as the first drop of liquid appears until all solid particles disappear.

1.15.3 Handling air-sensitive reagents

Suppliers of air-sensitive reagents usually dispatch them securely sealed under nitrogen. They also supply equipment and literature for handling not only air-sensitive chemicals but also hazardous chemicals. All these chemicals should be handled by experienced technicians or third year undergraduates, following the instructions sent with the equipment.

References

1 *Student Safety Sheets*, 2nd ed.,Cleapass School Services at Brunel University, 1997.
2 L. Bretherick, Ed., *Hazards in the Chemical Laboratory*, 4th ed., The Royal Society of Chemistry, London, 1991.
3 F. R. Spellman, *Safe Work Practices for the Environmental Laboratory.* Technomic Publishing, Basel, 1997.
4 A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd ed.,, Longmans, London, 1961.
5 *Vogel's Textbook of Quantitative Inorganic Analysis* by J. Bassett e*t al.* Longmans, London, 1979.
6 *The Sigma Aldrich Library. Chemical Safety Data,* Ed., R. E. Leuges, Vols. 1 and 2, 1988.
7 *B.D.H. Hazard Data Sheets.*

References 4 and 5 are especially useful for Chapter 2.

2

Techniques

2.1 CHARACTERISATION OF SOLIDS

Most of the solids to be used in the experiments described in the book are powders prepared in the laboratory or supplied or purchased by suppliers of chemicals. Most of these powders have to be characterised, especially when used in physicochemical experiments. Some powders may be standard materials, whose characteristics are available, although further characterisation may be desirable. The more usual techniques required are described below. Some of these may require specialised equipment and/or training. This may be available in some institutions but it may be carried out on a commercial basis.

2.1.1 X-ray methods (*Anal.Chem.*53(1981)349A)

Bragg's law

When monochromatic X-rays of wavelength λ fall on a plane of a crystal, the planes of atoms or ions act as a diffraction grating. At integral values of λ, the intensity of the diffracted rays is a maximum. Under these conditions, the angle of incidence θ is related to the distance d between successive planes by the relations:

$$n\lambda=2d \sin \theta \qquad (2.1),$$

Where n is referred to as the order of the diffracted radiation. The number 2 arises because the reflected radiation passes twice between the adjacent layers of nuclei. This was first derived by Bragg.

X-ray diffraction (XRD)

In an X-ray tube, a heated filament produces thermal electrons in the tube which is maintained at low pressure or in an inert He atmosphere. The electrons are accelerated by a large electric potential and when they strike the target metal, inner electrons are expelled, the vacancy being filled with the accompanying emission of the characteristic X-rays of the target. **Moseley** observed the relation between the frequency ν of the K_α line and the **atomic number** Z:

$$\nu = \text{constant}\,(Z-1)^2 \qquad (2.2),$$

The finely ground powder to be examined is packed into a glass cylindrical container which is placed at the centre of a goniometer (rotatable table). The X-rays from the tube passes through a filter to produce monochromatic rays and these are passed through a collimator or mounted on the goniometer. An ionisation, scintillation or semiconductor detector is mounted together with an exit collimator on a second goniometer and is slowly rotated round the sample. The intensity of the diffracted X-rays is recorded as a function of angle. Since there is a very large number of crystals in the powder, there will be enough of them with a crystal face exposed to the incident X-ray beam and at angles, calculated from Bragg's law, intensity peaks can be recorded. From these, the characteristic distances of the crystal can be calculated and compared with those of crystals whose structures have been fully determined. In this respect, XRD is used for qualitative identification of crystalline solids. X-ray fluorescence is fully discussed in *Anal.Chem.*, **56**(1982)1095A..

2.1.2 Mass spectrometry (MS)

In MS, a mixture of gaseous ions are separated according to the radio mass/charge or m/e. A plot of the relative concentrations of gaseous ions as a function of m/e is a mass spectrum. The main components of a mass spectrometer are: an inlet system, an ion source, a mass analyser and a detector, all enclosed in a high vacuum enclosure. The signals from the detector are processed and a readout or display of the spectrum is obtained. In most cases, positive ions are studied. If the sample is a solid or liquid, especially inorganic complexes, the sample is first vaporised in a heated inlet and part of the vapour or part of a gaseous sample reaches the ionising part where ionisation is induced by any of various methods: electron bombardment, thermally or by using electric arcs or sparks. When ionisation is induced by collusions in a gaseous reaction, this is termed **chemical ionisation,** which is a gentler method. Other methods are also used. Since the majority of the ions produced have e=1, their (m/e) = m. A molecular or parent ion has the same mass as the molecule from which it is derived. However, ionisation may break the molecule into fragments. An ion with the highest concentration is the base ion. A magnetic field is usually applied in the analyser to separate ions of different m/e ratios. In double focussing spectrometers, an electric analyser is combined with the magnetic analyser. Since the time required for ions to travel a certain distance depends on their mass, time of flight MS can be also used. Electron multipliers amplify the signal 5-7 fold. This is displayed in strip chart recorders or processed by computer devices. The main uses for inorganic compounds is molecular mass determination and qualitative analysis by comparison with spectra of standard compounds.

2.1.3 Magnetic measurement

Paramagnetic Substances

Practically all substances, when placed in a magnetic field, an opposing field is induced and hence they are repelled by the applied field and are said to be diamagnetic. However, ions, molecules or atoms with unpaired electrons, are attracted by a magnetic field since they have permanent magnetic moments. This property is termed paramagnetism which is much stronger than diamagnetism. Transition metal species with d^n configuration (n=1-9) are usually paramagnetic. Determination of their magnetic moments has a number of chemical implications.

When a substance is placed in a magnetic field of intensity H, the emerging flux density, B, is given by:

$$B = \mu_o(H+M) \qquad (2.3),$$

where μ_o is a constant, the permeability of vacuum and M is the magnetic moment per unit volume. Alternatively expressed:

$$B/\mu_oH = 1+(M/H) \text{ or } \mu_r = 1+X_v \qquad (2.4),$$

where μ_r is termed the relative permeability of the substance and X_v is its volume susceptibility. When X_v is divided by the density ρ, the mass susceptibility, X_M, is obtained and when the latter is multiplied by the relative molar mass, the molar susceptibility, X_M, results. This is negative for diamagnetic species but is positive for paramagnetic species. X_M is usually corrected for the small diamagnetic susceptibility. Then X^1_M is used to denote the correct susceptibility. It varies inversely with the thermodynamic temperature.

The Gouy balance

The most common method for measuring magnetic susceptibilities is by the use of the Gouy balance. The sample, in the form of a cylinder (in a non-magnetic tube) of cross-sectional area A is suspended from one pan of an analytical balance so that its lower end may be subjected to a strong magnetic field of intensity H whereas its upper end is in a much weaker field of intensity H_0. Usually an electromagnet is used to supply H. On applying the field, a force F acts on the specimen and it can be shown *(J.Chem.Educ.* **48** (1971) 180) that:

$$F = \tfrac{1}{2}\mu_oA(X_v-X_o)(H^2-H_o^2) = \Delta m \text{ x } g \qquad (2.5),$$

where X_0 is the volume susceptibility of air displaced by the sample (whose oxygen is paramagnetic), Δm is the change in mass on applying the field and g is the gravity acceleration. If the same tube is used under given experimental conditions, then:

$$X_m=(VX_o+Cm_2)/m_1 \qquad (2.6),$$

where V is the volume of the sample, m_1 is its mass, m_2 is the apparent change in mass on applying the field and C is a constant.

The effective magnetic moment, μ_e and Bohr's magneton, μ_B.

The unit of magnetic moments, the Bohr's magneton is defined by:

$$\mu_B = eh/4\pi m_e \qquad (2.7),$$

where e is the charge on the electron, m_e is its rest mass and h is Planck's constant. The effective magnetic moment, μ_e, is related to X^1_M by the relation:

$$X^1_M=(N_a\mu_o\mu_e^2\mu_B^2)/3kT \qquad (2.8),$$

where k is Boltzmann's constant and N_A is the Avogadro constant. Collecting the constant terms together as D, then:

$$\mu_e=D(X^1_MT)^{1/2} \qquad (2.9),$$

Although the orbital movement of the unpaired electrons may contribute to μ_e, in many cases this contribution is quenched and the main contribution is due to the spin of the unpaired electrons. The magnetic moment is then referred to as the "spin only" moment, μ_{so}, which is related to the number of unpaired electrons, n, by:

$$\mu_{so} = (n(n+2))^{1/2}\mu_B \qquad (2.10),$$

Measurement of the susceptibility by the Gouy balance

Weigh the tube empty. Fill it with boiled out water to the mark and reweigh it. Note the temperature on the thermometer near the tube. Use the density of water at this temperature to calculate the volume of the water. Dry the tube and reweigh it in absence of a magnetic field and when you apply a current to the elctromagnet to produce a field. Repeat using two more magnetic fields by adjusting the current applied. Because of the diamagnetism of the tube, the weight is slightly smaller in presence of the field. Work out the weight loss in presence of the field.

Grind a pure sample of a susceptibility standard e.g. $Hg[Co(NCS)_4]$ (Sec.14.3.2). Add a little to the tube, tap it several times to pack the solid well, repeat until the tube is filled to the mark. Weigh the filled tube without the magnetic field and then with the field on (note the current). Repeat the filling of the tube and the weighings. Take an average of the increases in weight observed. Note the temperature near the tube.

Repeat the procedure at other magnetic fields (at least 3) by adjusting the current supplied to the electromagnet. Note in each case the current and the temperature.

From the known value of X^1_M for the standard at the given temperature, calculate the constant C in equation (2.6). (*Educ.Chem.*, **8** (1971) 222).

Fill the tube with a prepared sample, using a high magnetic field chosen from the ones used for the standard sample. Repeat the filling of the tube as detailed above, noting the mass of your sample and the increase in mass on applying the field, taking an average of measurements. Use equation (2.6) to calculate X_m, taking X_o as $4\pi x 0.029 x 10^{-6}$. The units of magnetochemistry are fully discussed in *J.Chem.Educ.* 49(1972)114; 49(1972)505.

Evans modification of the Gouy method

In this method the force which a sample exerts on a suspended permanent magnet is measured. The sample is stationary and the magnets are moving. When a sample is introduced the equilibrium in the system of permanent and electromagnets is displaced. The force required to restore the equilibrium is measured as a voltage drop.

Determination of the magnetic susceptibility by the Evans method

Turn the RANGE knob to X1 and allow 10 minutes. Adjust the zero knob to give 000 reading. Weigh the sample tube, place it in the tube guide and take a reading R_o. Pack the tube with a standard as above, reweigh and take another reading R. Note the temperature. Calculate the calibration constant, C, from the relation:

$$X_m = Cl(R-R_o/10^9m \qquad (2.11),$$

where m is the mass of the sample in g, *l* is its length in cm and X_m is the mass susceptibility in c.g.s. units which is available in the literature. Use one of your prepared complexes instead of the standard and repeat the operation and find X_m for your sample. Repeat the packing in each case and calculate an average value of R for both standard and sample. Multiply X_m by $4\pi x 10^{-3}$ and X^1_M by $4\pi x 10^{-6}$. Then calculate μ_e, taking D as 800.

If the reading is off the scale, change to range x10. A negative reading indicates adiamagnetic substance. For correction of the diamagnetism of the ligands, a list of the so-called Pascal constants is found in *Modern Coordination Chemistry*, Eds. J.Lewis, R.G.Wilkins, Interscience, 1966).

2.1.4 The point of zero charge (PZC) and the point of zero zeta potential (PZZ) of powders *(Chem.Rev.* 65(1965)177; *Ind.Engng.Chem.*57(1965)32)

PZC

The surface of the particles of many metal oxides, suspended in aqueous solution, is hydroxylated. Depending on the pH, the surface hydroxyl groups dissociate and give a positively charged surface at low pH's but a negatively charged surface at high pH's. The equilibria involved may be represented by:

$$\text{-M}_H\text{OH}^+\text{(surf)} \rightleftarrows \text{-M(OH)(surf)+H}^+ \rightleftarrows \text{-MO}^-\text{(surf)+2H}^+ \qquad (2.12),$$

Assuming that in the process represented by the overall backward reaction (2.12), the free energy change depends on the elctrostatic attraction between an oxide ion and $2H^+(aq)$. Then it can be shown that:

$$\text{PZC}=18.6+11.5[(Z/R)+0.0029(\text{CFSE})] \qquad (2.13),$$

where Z is the formal charge of the metal ion, R is the sum of its radius + twice the radius of an oxide ion and CFSE is the ligand field stabilisation energy. The numerical constants in (2.13) were calculated using the non-SI units usually adopted in the literature in the past. The latter term between brackets can be regarded as CFSE correction to Z/R. A large number of oxides, hydrous oxides and hydroxides were found to comply with (2.13).

Measurement of PZC of an oxide powder

Suspend 4.0g of the powdered oxide in 200cm^3 of 0.01M KNO_3 solution in a double-walled beaker shown in Figure 2.1 replacing the sintered glass stick by a combined glass electrode. Insert a microburette and a thermometer suspended from the rubber bung of the beaker. The suspension is magnetically stirred throughout while passing oxygen-freed and CO_2- freed nitrogen from a gas cylinder. Measure the pH accurately. Add small measured volumes of 0.1M HNO_3 or 0.1M KOH. After each addition, monitor the pH until a steady value is reached. Calculate the amount of H^+ or OH^- abstracted or released by the solid from a comparison with a blank run in which no solid was used. Calculate the resultant adsorption density (Γ_H - Γ_{OH})at each pH and plot it against pH. The PZC is the pH at which the resultant = 0.

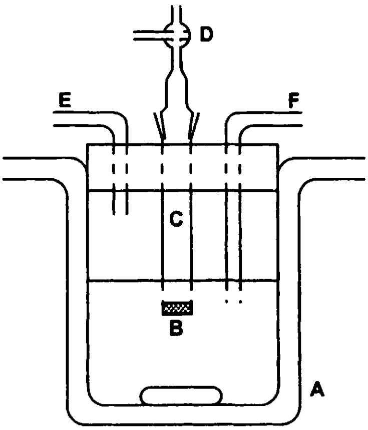


Figure 2.1 Apparatus for studying kinetics of a reaction between a solid and a solution or for the determination of PZC.

PZZ

There is a subtle small difference between PZC and the point of zero zeta potential, PZZ. In the case of oxide particles, the latter is defined as the pH at which the zeta or electrokinetic potential = 0. When a suspension of the particles in an inert electrolyte solution at a given pH is subjected to a potential gradient, the particles move towards one or the other electrode, depending on their charge, which in turn depends on the pH . When the thermostatted suspension in a cylindrical or rectangular cell is microscopically observed, the rate of movement of individual particles can be measured. However, the charged internal surface of the cell causes an electroosmotic flow of the liquid near the surfaces. In a closed cell, there will be a return flow of the liquid at the centre of the cell. It is therefore necessary to measure the particle mobility, μ, at either of the two "stationary levels" where the two flows balance. The stationary levels are at 0.146 of the diameter of the cylindrical cell from the floor or the ceiling. The levels are at 0.21 or 0.79 of the depth of the rectangular cell. The usual units of the mobility are μm s^{-1}/V cm^{-1}. This requires knowledge of the potential gradient, X, across the cell's electrodes, which is given by:

$$X = I/kA \tag{2.14}$$,

where I is the current, A is the cross-sectional area of the cell and k is the specific conductivity of the dispersion. To measure k, the cell is filled with 0.01M KCl and the conductivity is measured using a conductivity bridge.

To cover the cell's Pt electrodes with Pt black, fill the cell after cleaning it thoroughly, with a solution of 3.0g chloroplatinic acid and 0.025g of $Pb(CH_3CO_2)_2$ in 100 cm^3. Connect the electrodes to a D.C. supply (e.g. 2 accumulators) via a reversing key and a rheostat. Adjust the current so that hydrogen evolution is moderate and reverse the current every half minute. Continue for a few minutes until each electrode is covered with a black Pt deposit. Then connect the 2 electrodes together, using a spare Pt wire electrode as anode and fill the cell with dilute sulphuric acid and electrolyse for 15 minutes. Wash thoroughly with distilled water and then with 0.01 M KCl a few times and then fill with the latter solution. Measure the conductivity of the elctrolyte, C, using a conductivity bridge. From the known specific conductivity of the KCl solution at the temperature of the experiment, calculate the interelectrode distance, d, from the relation:

$$d = kA/C \tag{2.15}$$,

where A is the cross-sectional area of the cell. Calculate the latter from the dimensions of the cell, measured with a travelling microscope.

Sonicate a suspension of 10 mg of an oxide in 1 dm^3 of 0.01 M KCl solution for 2 hours. Decant portions of the suspension in a beaker, adjust the pH to a suitable value by using 0.01 M KOH or 0.01 M nitric acid. Sonicate for 1 hour and measure the pH using a pH meter. Introduce the suspension in the cell, thermostat it by circulating water from a thermostat around the cell. Apply a potential difference of say 50 V across the cell and time the movement of a particle through a distance (say 13.0×10^{-3} cm (the distance of 2 divisions on the calibrated divisions of the graticule in the eye piece). Make at least ten measurements at each stationary level, noting to which electrode the particles move. Reverse the polarity of the D.C. supply and make 10 measurements. Take the average of the velocity readings and calculate the mobility from the velocity and the potential gradient, i.e. applied voltage/cross-sectional area. Repeat using similar suspensions with pH values in the range of 2-10. Plot the mobility including its sign against pH and estimate the PZZ, where the curve crosses the zero mobility line.

2.1.5 Gas adsorption and surface areas *(Characterisation of powder surfaces, Eds.* G.D. Parfitt and K.S.W. Sing, Academic Press, London, 1976).

The most common method for the determination of surface areas of powders is by the adsorption of an inert gas e.g. nitrogen or krypton. Adsorption is carried out in a high vacuum system and at low temperature. The BET isotherm, which is based on multi-layer physical adsorption, can be expressed in the form:

$$P/[V(P_o-P)]=[1/(V_m.C)]+(C-1)P)]/[P_o(V_m.C)] \tag{2.16}$$

where V is the volume of gas adsorbed at pressure P, V_m is the volume corresponding to a monolayer, P_o is the saturated vapour pressure of the liquid form of the gas at the temperature of measurement and C is a constant. For $P_o/P=0.05-0.30$, the plot of $P/[V(P_o-P)]$ against P/P_o is expected to be linear. Hence V_m and C can be calculated from the slope and intercept. From the known area of the molecule of nitrogen or the krypton atom, the surface area of the solid powder is calculated. Measurements are usually carried out by trained surface scientists or on a commercial basis. Other characteristics of powders e.g. porosity are also possible.

2.1.6 Adsorption of Ions by Oxide Powders (*J.Photo.Sci.*, **13**(1965)152).

The surface of powders of metal oxides and of silica, suspended in aqueous solution are known to be hydroxylated. Infrared spectra of many of the solids indicate the presence of surface hydroxyl groups. Assuming that the equilibria (2.12) take place in an aqueous suspension of an insoluble oxide, the positively charged particles at pH's <PZC would adsorb anions whereas cations are likely to be adsorbed at pH's >PZC when the particles are negatively charged. However, the pH also affects the speciation of metal ions in solution. The position of the adsorbed ions in the solid/solution electric double layer may vary with the surface field strength. Solids such as silica or manganese dioxide seem to have a weak field strength whereas titania has a strong field surface. (W. Stumm et al *Croat.Chem.Acta,* **42**(1970)223).

The structure of the electric double layer at a solid/solution interface (S.F. Estefan, M.A. Malati, *Tenside Detergents,* **11**(1974)205).

It may be assumed that Figure 2.2 represents the structure of the electric double layer at an oxide/aqueous solution interface. The potential determining ions i.e. hydrogen and hydroxyl ions are next to the surface. This is followed by what is sometimes termed the Stern layer in which hydrated mobile ions are located. The outermost layer is the diffuse or Gouy layer. The shear plane C^1 is in the Gouy layer. The inner Helmholtz plane is thought to coincide with the centres of dehydrated immobile ions, described as being specifically adsorbed. Hydrated immobile ions may be assumed to have their centres coincident with what is termed the Outer Helmholtz plane, located in the Stern layer. This tentative picture is useful in emphasising the state of hydration of adsorbed ions.

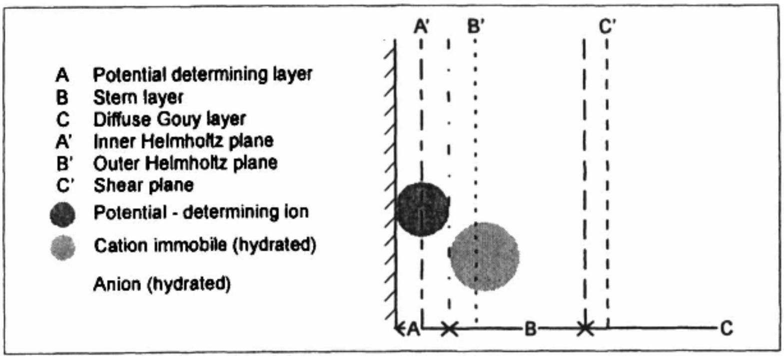


Figure 2.2 A sketch of a proposed structure of the electric double layer at a solid-electrolyte interface.

The Langmuir adsorption Isotherm (W.A. Adamson, *Physical Chemistry of Surfaces*, 3rd edn., Interscience, New York, 1976)
Adsorption equilibrium is reached when the amount of adsorbate taken up by the solid adsorbent does not change with time. The amount adsorbed g^{-1} of solute, X, is calculated from the difference between the initial and equilibrium concentration C. By varying the initial concentration and determining X, Langmuir assumed that X reaches a limiting value, X_m, presumably when a monomolecular layer is formed on the surface. The variation of X with C, known as the **Langmuir adsorption isotherm** can be represented in a linear form by:

$$C/X=(C/X_m)+1/(bX_m) \qquad (2.17),$$

where the parameter b is related to the heat of adsorption; Q. The latter can be estimated from the variation of b with the thermodynamic temperature T:

$$\ln b=\ln b^1+(Q/RT) \qquad (2.18)$$

where b^1 is a constant and R is the ideal gas constant. This isotherm is often applied to the adsorption of ions by oxide powders.

2.1.7 Elemental analysis

In many industrial laboratories and in numerous institutions, analysis of solids, to determine the percentages of C, H, N etc., is carried out routinely by trained technicians. These analyses are also valuable for complex compounds with organic ligands or organometallics. Such analyses, though not carried out by students, will help them to characterise their prepared products.

2.2 TITRIMETRY USING INDICATORS

A **primary standard** is a readily available chemical supplied in a very pure form, labelled differently by different manufacturers, together with information of % purity and maximum limits of impurities. It should not change in air and hence during storage or weighing. It should be readily soluble in water and will generally react stoichiometically and rapidly with chemicals to be analysed. Preferably, its RMM/n (n depending on the reaction) should be fairly high. A **standard solution** is either prepared from a primary standard solid or standardised after preparation. In common titrimetric (volumetric) analysis, the solution whose concentration is required, termed **titrand** or

titrate, is placed in a clean (not necessarily dry) conical flask and the standard solution of the **titrrant** is placed in a burette, previously rinsed with the same solution. This is gradually added to the flask, while swirling, until a visible change in colour or turbidity indicates the **end point**. This should be as close as possible to the true **equivalence point** based on the stoichiometry of the reaction. This change is usually due to the change in colour of an **indicator,** originally added to the flask, at the end-point. In some cases, no indicator is required when the colour of a reactant or product signals the end-point.

2.2.1 Acid base titrimetry

The hydrogen ion exponent, pH, is defined by:

$$pH=-\log[H^+] \qquad (2.19),$$

where $[H^+]$ is the hydronium ion (hydrated H^+) activity ≈ its concentration in dilute solution. The dissociation constant, K_a, of an acid, HA, is expressed as:

$$K_a=[H^+][A^-]/[HA] \qquad (2.20),$$

and its exponent, pK_a, is given by:

$$pK_a=-\log K_a \qquad (2.21),$$

A strong acid is practically completely by dissociated in dilute solution. Corresponding to pH, pOH is defined as:

$$pOH=-\log[OH^-] \qquad (2.22),$$

and the dissociation constant of a base, BOH, K_b is defined as :

$$K_b=[B^+][OH^-]/[BOH] \qquad (2.23),$$

and $$pK_b=-\log K_b \qquad (2.24),$$

A strong base is one which is practically completely dissociated to OH^- in dilute solution. The neutralisation of an acid by a base is represented by:

$$HA+BOH \rightarrow AB+H_2O \qquad (2.25),$$

where AB is the salt formed. If both acid and alkali are strong, AB will be also completely dissociated in dilute solution. When a strong acid is titrated with a strong base (in the burette), the variation of pH as the titration proceeds is depicted in Fig.2.3. As the alkali is gradually added, the pH increases first gradually and then sharply until it reaches 7.0. Since the **autoprotolysis constant** of water, K_w , is given by:

$$K_w=[H^+][OH^-]=10^{-14} \text{ at } 298K \qquad (2.26),$$

$$\therefore \quad \text{At pH7.0, } [H^+]=[OH^-]=10^{-7} \qquad (2.27).$$

Thus a solution of a salt of a strong acid (S.A.)and a strong base (S.B.) will be neutral and have a pH=7. Using a more dilute strong acid will simply shift the left hand section of Figure 2.3 upwards whereas using a more dilute strong base will displace the right hand section downwards.

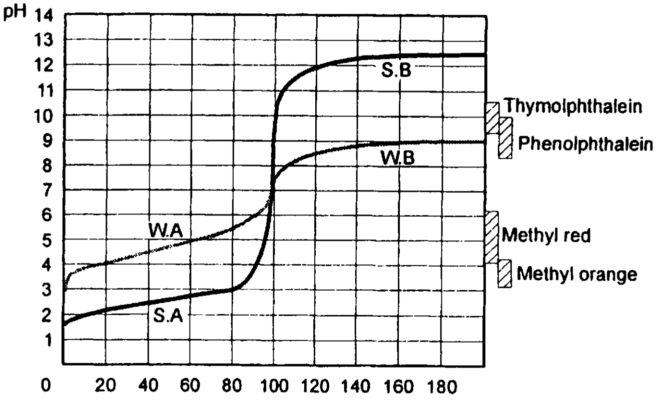


Figure 2.3 Acid/ base titration curves and the range of four indicators.

However, when a weak acid (W.A.) is titrated, the left hand curve will not only shift upwards but it will also increase more gradually than in the case of a strong acid of the same concentration and hence the steep part will be shorter. Similarly when a weak alkali (W.B.) is used, the steep part will be shorter. When both acid and base are weak, there will be no steep section of the titration curve. Thus salts of a weak acid and a strong base will give solutions of pH>7 whereas those of a strong acid and a weak alkali will have solutions of a pH<7. This means that these salts are hydrolysed in solution. Disregarding the activity, the titration curve can be represented by:

$$pH=pK_a+\log[salt]/[acid] \qquad (2.28),$$

In the case of di-or tri-basic acids, which have 2 or 3 pK_a's, the titration curves will have 2 or 3 inflection points.

Acid/base indicators are very weak organic acids or bases which have a different colour in the acidic form In_a from the basic form In_b. When the ratio of the concentration of the two forms is >10, the colour of the predominant form will be visible. This ratio of the two forms is related to pH by the relation:

$$pH=pK_{In}+\log[In_b]/[In_a] \qquad (2.29),$$

where K_{In} is the dissociation constant of the indicator. Hence the pH range of the indicator i.e. over which it changes colour is given by:

$$pH=pK_{In}\pm 1 \qquad (2.30).$$

Figure 2.3 also contains titration curves of a weak acid with a strong base and of a strong acid with a weak base as well as the ranges of some acid/base indicators. When a sharp colour change is required over a narrower pH range than indicated by (2.30), a mixture of two indicators may be used if their pK's are close together and their overlapping colours are complementary.

2.2.2 Redox titrations

When a bright platinum plate is immersed in a solution containing the oxidised and the reduced forms of a system, of equal unit activity (concentration) eg Fe^{3+} and Fe^{2+} in aqueous solution, the potential of the Pt electrode can be measured by coupling it with a standard hydrogen electrode, whose potential is taken as O by convention. The e.m.f. of the cell is the standard redox potential (eg of the Fe^{3+}/Fe^{2+} couple), $E^{\varnothing}$. Generally the potential, E, is given by:

$$E=E^{o}+[RT/nF]\ln([Ox]/[Red]) \qquad (2.31),$$

where Ox is the oxidised form, Red is the reduced form, R is the gas constant, F is the Faraday constant, T is the thermodynamic temperature and n is the number of electrons involved in the redox change e.g. n=1 for the Fe^{3+}/Fe^{2+} system. The more negative $E^{\varnothing}$ is, the more reducing is the system and the more positive $E^{\varnothing}$ is, the more oxidising is the system.

For a general redox reaction:

$$a\,Ox_1+b\,Red_2 \leftrightarrows b\,Ox_2+a\,Red_1 \qquad (2.32),$$

where 1 and 2 refer to two different redox couples and a and b refer to the number of species involved in the reaction, the equilibrium constant K is given by:

$$\log K=(n/0.059)(E_1^{o}-E_2^{o})=\log([Ox_2]^b.[Red_1]^a)/([Red_2]^b[Ox_1]^a) \qquad (2.33),$$

where n is the number of electrons involved and the numerical constant applies to standard temperature and includes the other constants in (2.31). Hence, provided $(E_1^{o}-E_2^{o})$ is sufficiently large, K will be large and the reaction is thermodynamically favoured, although kinetic considerations will decide its speed and hence the feasibility of a titration. The speed may be affected by the presence of catalysts. If H^+ ions are required in (2.32), the reaction will be pH-dependent.

Although a reagent e.g. permanganate may act as a **self indicator** because of its intense colour and the very faint colour of its reduced form: Mn^{2+} in acid solution, generally **a redox indicator** is necessary to find the end-point visually. A redox indicator is usually an organic molecule which has different colours in the oxidised and reduced forms i.e. In_{ox} and In_{red}. The ratio of their concentration is given by:

$$E=E_{In}^{o}+(RT/nF)\ln([In_{ox}]/[In_{red}] \qquad (2.34),$$

In some cases, an external indicator is used i.e. drops of the solution are withdrawn near the end-point and are used as spot tests for a product. The redox titration curve is similar to that of acid/base titration curves since the logarithmic function of (2.33) is similar to that of (2.28). It is worth noting here that E^o values of redox couples are greatly altered in presence of complexing agents. Only in a few acid/base titrations does pK_a change in presence of other compounds e.g. the addition of polyhydroxyl organics increases K_a of boric acid markedly.

2.2.3 Precipitation titrations

In most precipitation titrations, silver nitrate solution is used and a silver salt, AgA, precipitates from solutions of an anion A^-. At the end-point, $[Ag^+]=[A^-]$ and the solubility product S of AgA is given by:

$$S=[Ag^+][A^-] \qquad (2.35)$$

or using exponents of concentration (at the end-point)

$$pAg^+=pA^-=(S_{AgA})^{1/2}=\tfrac{1}{2}pS_{AgA} \qquad (2.36),$$

since at the end point $[Ag^+]=[A^-]=(S)^{½}$. For the titration of a salt of A^- ions against the volumes of silver nitrate solution used as a titrant will be of a similar shape to Figure 2.3 with the vertical part becoming smaller as the solubility product becomes larger. The end-point can be detected by the addition of a salt of another anion which forms a coloured precipitate with silver ions beyond the end-point e.g.K_2CrO_4 in neutral solutions. In this case, there will be a small titration error (the drop of silver nitrate to give a visible coloured precipitate). When thiocyanate solution is used as a titrant for silver nitrate in acid solution, an Fe(III) salt solution is used as an indicator. This forms initially a red precipitate with silver ions but the extra drop of thiocyanate at the end-point produces a red colour of an iron (III) complex. Alternatively, an adsorption indicator is used. A unique class of indicators used in precipitation titrations are the adsorption indicators. These are organic acidic or basic dyes. When the precipitated particles are colloidal and carry a charge, at the end-point, the indicator's ion is preferentially adsorbed on the particles, producing a visible colour change. Even in absence of such indicators, under certain conditions, turbidity observed during the titration disappears at the end-point.

2.2.4 Complexometric titration (mainly using E.D.T.A.) (*Anal.Chem.*26(1954)741); E.D.T.A. (Figure 2.4) or ethylenediaminetetraacetic acid, is the usual reagent used. E.D.T.A. behaves as a dicarboxylic acid with two strongly acidic groups. There are 2 ammonium protons: the first ionises at ~ pH6.3 and the second at ~ pH11.5. The disodium salt may be represented for simplicity as Na_2H_2Y. With metal ions, 1:1 complexes are usually formed:

$$M^{2+}+YH_2^{2-}\leftrightarrows MY^{2-}+2H^+ \text{ or } M^{3+}+H_2Y^{2-}\leftrightarrows MY^-+2H^+ \qquad (2.37),$$

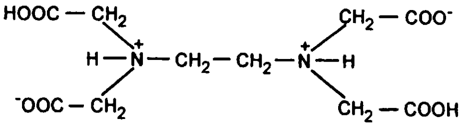


Figure 2.4 The structure of EDTA.

A decrease in pH will reduce the concentration of the complexing species. Hence the formation of E.D.T.A. complexes with metal ions is best carried out in alkaline solutions.

When pM(= $-\log[M^{n+}]$, is plotted against volume of E.D.T.A. used for titration, a sharp rise indicates the end-point. Changes in pM can be detected by using indicators which form complexes with specific metal ions. The complexes differ in colour from the free indicator and there is a sudden colour change at the end-point, when the E.D.T.A. has completely complexed (preferentially) the metal ions, thus liberating the free indicator.

Types of Titration:

(1) In direct titration, a solution is buffered to ~pH10 and then titrated with E.D.T.A. solution. Auxiliary complexing agents may be added to prevent the precipitation of the metal hydroxide.

(2) Back titration: When no suitable indicator is available for direct titration, an excess of standard E.D.T.A. is added and the excess is titrated against standard Zn^{2+} or Mg^{2+} ion solution.

(3) Replacement titration: When a particular metal ion does not form a sufficiently stable complex with E.D.T.A., magnesium EDTA complex is added and the Mg^{2+} ions set free are titrated with E.D.T.A.:

$$M^{n+}+MgY^{2}\rightleftarrows(MY)^{(n-4)+}+Mg^{2+}\text{. The latter is equivalent to }M^{n+}\text{.} \tag{2.38}$$

(4) The $2H^{+}$(aq.) ions set free may be titrated with standard alkali using acid-base indicators or a pH meter and a glass electrode.

Complexone or E.D.T.A. acts as a hexadentate ligand towards many metals M e.g. Co(III), (Fig.2.5), as a quinquedentate ligand towards Ni(II) and as a tetradentate ligand towards Pd(II).

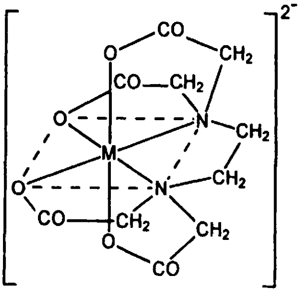


Figure 2.5 Structure of a metal (M) EDTA octahedral complex.

Ampoules

Certain chemicals e.g. mineral acids and alkalis require time consuming standardisation after careful purification. Commercially available ampoules contain the required amount of solution which produces a given volume of standard solution when quantitatively transferred and diluted in a volumetric flask. The narrower part between the main body and the sealed top is scratched all round with the metal file provided. By applying careful pressure on either side of the scratch, the glass is neatly broken separating the two parts of the ampoule. The contents are emptied through a funnel into a volumetric flask and together with the rinsings of the insides of the ampoule's parts and funnel, the volume is made up to the mark.

2.3 GRAVIMETRY

In gravimetric analysis, a weight of a substance or a volume of its solution is transformed into a pure form of an element or compound suitable for direct weighing. The analysis usually involves precipitation of a pure chemical which can be easily filtered, dried and weighed.

2.3.1 Precipitation from solution

The initial velocity of precipitation is proportional to (Q-S)/S where Q is the concentration of the substance precipitated and S is the equilibrium solubility. It was found that the particle size of a precipitate decreases with increasing concentration of reactants. To obtain a filterable pure precipitate, (Q-S)/S should be as small as possible. Increasing S would be also desirable either by using a reagent which slightly increases S or by warming or heating during precipitation. Heating also enhances crystal formation. Scratching the glass container may help crystallisation. However, as the precipitated particles grow they may entrain impurities found in the solution. Adsorbed surface impurities may contaminate a precipitate especially if it is gelatinous. Such precipitates are also slow to filter.

When a precipitating species can be slowly generated in solution by a chemical reaction, the precipitate produced will have larger particles than in the direct precipitation described above. Hence it is easy to filter the precipitate quickly. The procedure is known as **precipitation from homogeneous solution.**

2.3.2 Washing, drying and weighing precipitates

The most generally used filtering media in gravimetry are sintered (borosilicate) glass crucibles with a porosity code of 1-4, the average diameter of the pores of the fused fritted plate of a No.4 crucible is 5-10μm, suitable for the finest precipitates. Larger pores are found for the other crucibles. All these crucibles can be safely heated in an oven at 105-150°C. Special care is needed if temperatures up to 200°C are required. Other similar filtering crucibles made of either silica or porcelain are available; the former can be heated up to 1000°C. Porcelain filtering crucibles can be heated to high temperatures up to red heat. Any precipitate on any of these crucibles is removed after use by mechanically dislodging it from the sintered disc followed by dissolving the remainder in a suitable solvent. Cleaning mixtures (Sec.1.2) are used if required. Aqua regia (conc .HCl:conc. nitric acid in 3:1 by volume) is also suitable for cleaning.

In gravimetry, precipitates should be washed well to remove excess of the precipitating solution, and other constituents. A minimum amount of washing solution is used, subject to qualitative confirmation of the absence of impurities in the filtrate. Although water is usually a suitable washing medium, it is avoided when there is a possibility of peptising the precipitate, causing some losses. If this is likely or if the precipitate has some solubility in water, a dilute electrolyte solution, especially ammonium nitrate would be useful since the residual salt decomposes to volatile products during heating to constant weight. A wash with ethanol followed by ether is used for barium sulphate for quick drying by suction under vacuum.

After precipitation, the beaker is usually set aside for some time, may be in the dark and covered with a watch glass. This allows the precipitate to settle at the bottom, leaving a clear supernatant liquid. This is then carefully directed into the crucible or filter paper with a glass rod kept against the beaker's lip, allowing ample space below the rim of the crucible or filter. A time-saving method is **washing by decantation.** A suitable volume of the washing liquid is added to the precipitate, and after stirring and perhaps heating, the suspension is allowed to settle and the supernatant liquid is filtered as before. This can be repeated a few times. Eventually the well stirred suspension is filtered so that most of the washed precipitate is transferred to the crucible or filter paper. Any particles adhering to the beaker's walls are dislodged with the rubber-covered end of a glass rod (policeman) aided by a stream of liquid from a wash bottle. The crucible containing the washed precipitate is then dried in an oven at the recommended temperature for a specified time. These conditions are based on results of thermogravimetric analysis (Sec.2.6.2) and depend on the identity of the precipitate, its particle size and porosity. Then it is carefully transferred to a desiccator, keeping its lid slightly opened until the heat of the crucible is dissipated when the lid is slid to cover the desiccator. The desiccant or other chemical used depends on the nature of the precipitate. It is advisable to use a vacuum desiccator, when its air is evacuated through the stopcock on the lid, the stopcock is then closed. After cooling, the crucible is weighed and then redried for a shorter period, say 20-30 minutes, repeating the procedure to check that a constant weight is attained. Silica or porcelain crucibles can be heated to higher temperatures in which case an electric muffle furnace is used, where temperature is indicated by a pyrometer.

When an ashless filter paper is used, this is well drained and carefully folded (after removal from the funnel) and placed point down in a weighed cleaned silica or porcelain crucible previously heated to constant weight at the temperature to be used for the precipitate. The crucible, supported on a clay or silica triangle, is slowly heated with a very small flame at a distance below the crucible, keeping the lid away. Gradually increase the flame so that the paper is dried and slowly chars without burning. After complete carbonation, the crucible is strongly heated, with its lid, to red heat, preferably using a Meker burner, which allows more air into the flame. After heating for ½ hour, the crucible is allowed to cool and weighed as usual, reweighing it after 15 minutes heating at red heat.

2.3.3 Electrogravimetry

This is based on **Ohm's law** and **Faraday's laws of electrolysis.** In an electrolytic cell, a d.c. current, I, is applied between two electrodes dipping in one or more solutions. However, Ohm's law is modified to allow for the back galvanic emf, E_b, which opposes the applied emf, E_a, so that:

$$I = (E_a - E_b) \div R \qquad (2.39),$$

where R is the resistance. When the current is plotted against the applied potential, after an initial small increase, the current increases sharply, the corresponding voltage at this point is the **decomposition potential,** E_d. The electrode potentials, E_{ca} and E_{an} are the cathode and anode potentials respectively. These are related to E_d by the relation:

$$E_d = E_{ca} + E_{o.c} - (E_{an} + E_{o.an}) + IR \qquad (2.40),$$

where the overpotentials of the cathode and anode are $E_{o.c}$ and $E_{o.an}$. These are due to their **polarisation** or departure from their reversible values. These are dealt with in Physical Chemistry or Electrochemistry textbooks.

In an electrogravimetric determination, usually 2 gauze electrodes (Pt, Pt/Ir or Pt on Ti) dip in a solution of a salt of the metal to be determined, with the inner electrode rotating and the outer one fixed. The cell is connected to a d.c. supply via a fixed resistance and an ammeter. A small variable resistance and voltmeter in parallel with the cell are included in the circuit. In practice usually, the solution is that of a complex of the metal whose concentration and temperature are adjusted to ensure the separation of the metal as an adherent and smooth form which can be readily washed to remove the adhering electrolyte before drying and weighing. The technique can be adapted to separate two metals, provided their E_d's are sufficiently different.

2.4 SPECTROSCOPIC METHODS

Classification of these methods depends on the part of the **electromagnetic spectrum** to which they apply and also on the type of spectrum studied. In all cases, **Planck's equation**:

$$E = h\nu = hc/\lambda \qquad (2.41),$$

applies. In (2.41) E is the energy of the transition responsible for emission or absorption of radiation whose frequency is ν and whose wavelength is λ, c is the speed of light and h is **Planck's constant**. When multiplied by the **Avogado constant** N_A, the energy is per mol.

2.4.1 U.v./visible spectrophotometry. *(Anal.Chem.*57(1985)276A; 339A; 27(1955)26.

The Beer-Lambert law

When radiation of a given wavelength and of intensity I_0 passes through a layer of thickness l of a solution whose molar concentration is c, the intensity of I of the transmitted emerging radiation can be expressed as:

$$\log(I_0/I)=\varepsilon.c.l \qquad (2.42),$$

where ε is the **molar extinction coefficient**, a constant depending on the wavelength and on the nature of the solute/solvent system. The dimensionless log (I_0/I) is referred to as the **absorbance,** A, the relation is the Beer-Lambert law, also expressed as:

$$A=\varepsilon.c.l. \qquad (2.43).$$

The absorbance is usually read on the scale of a spectrophotometer. The absorbed intensity, I_a, can be calculated from the relation:

$$I_0=I_a+I \qquad (2.44),$$

Another scale on a spectrophotometer is the **transmission** as $(I \times 100)/I_0$. A test for the applicability of Beer's law is the plot A against c giving a linear plot provided I and l are kept constant for a given wavelength. This is usually chosen at a maximum absorption. When there is more than one absorbing species at the wavelength used, the measured absorbance is:

$$A=l(\Sigma\varepsilon.c) \qquad (2.45),$$

where the expression between brackets is the sum of the product (ε.c) for all the absorbing species. This relation applies unless the absorbing species interact or are involved in a chemical reaction.

Electronic absorption spectra of transition metal complexes

(A.B.P.Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, 1984)

The most important spectra are those of transition metal ions or complexes of d^n(n=1-9) configuration which usually absorb in the visible/u.v. regions of the electromagnetic spectrum (rarely in the near i.r. region). The electronic transitions responsible for the absorption may be classified into:

(a) **d-d transitions** i.e. between the split levels of the d orbitals;
(b) **charge transfer (C.T.) transitions** i.e. between orbitals mainly of ligand character to levels mainly of metal character or vice versa;
(c) **C.T.T.S.:** charge transfer from a metal level to a solvent;
(d) **intraligand transitions:** between levels mainly of ligand character.

The number of bands, their position in the electromagnetic spectrum, their intensity and shape depend on the d configuration of the metal, the ligands, their geometry and field strength as well as any covalence in the metal-ligand interaction. At this stage, it is useful to note that the energy of these transitions are usually within the range of the energy of light quanta in the visible/u.v. region.

Visible/u.v. spectrophotometers

In a single beam instrument, light from a lamp is focused on a slit and passes through a **monochromator.** The narrow beam of light thus produced passes through a cell containing the solution under test. The intensity of the transmitted light is detected by a suitable detector and measured and usually displayed as a **spectrum** by scanning the desired wavelength range. The spectrum shows the variation of absorbance with wavelength. In the manual instruments, the wavelength chosen is set and measurement is repeated at wavelength intervals. A double beam instrument has the same components plus a chopper at the monochromator exit which splits the light into a beam to the cell containing the sample solution and the other to the cell usually containing the solvent. The relative intensity of the transmitted beams is detected and recorded. In a recording instrument, the wavelength range is set and the instrument automatically records the spectrum. In the visual and simpler instruments filters are used instead of monochromators. In the former, matching colour intensities is done visually with no electronic detectors. The **tungsten filament lamp** emits radiation in the visible region (380-780nm), whereas the **deuterium discharge lamp** emits radiation in the u.v. region (190-380nm), shorter wavelengths are absorbed by air. In some instruments, the range is extended to 1000nm or further in the near i.r. Lasers which emit stronger radiation are used in some instruments. Phototubes, generally a red-sensitive and a blue-sensitive tubes are used for detection in single beam instruments but **photomultipliers** are commonly used for double beam instruments. Modern instruments are computer-based with derivative spectral plots and with facility for 2 or 3 wavelengths and possible combination of absorption, reflection, transmission and fluorescence. In all instruments, a shutter is located before radiation reaches the detector. The usual procedure is to start with the shutter closed and set the dark current control to give 0% transmission. The shutter is then opened to allow radiation from the lamp to pass through the blank cell and the slit width control is adjusted to give 100% transmission and the shutter is then closed. By moving the cell containing the test solution in the light path, the shutter is opened and a reading is taken of either absorbance, % transmission or even the concentration (in computer-based instruments).

The ideal measured absorbance is in the range 0.4-0.8. When measuring highly absorbing solutions, a narrow (2 or 5 mm) cell should be used. Alternatively, a standard solution of known lower concentration than the test solution is used in the blank cell and 100% transmission set as above. Then the measured absorbance of the test solution is corrected by adding the calculated absorbance of the standard. On the other hand, for low absorbing solutions, wider (4-10 cm) cells should be used. An alternative method is to use the test solution in the blank cell and set 100% transmission and then measure the absorbance of a standard of a higher known concentration, of the same species. This is corrected by subtracting the calculated absorbance of the standard. A combination of the two procedures is also possible. The details of these expanded scale, differential or precision spectrophotometry are found in *Anal.Chem.***27**(1955)716, **26**(1954)1740.

In modern instruments, radiation of 2 or 3 wavelengths is passed through the solution before reaching the detector. This reduces interferences (*Anal.Chem.***44**(1972) 93A).

Some instruments display derivative spectra, have variable band pass, multi-component analysis and concentration curve fitting etc.

Spectrophotometric titrations

When an analyte, a, or titrant, t, or the product, p, of their reaction absorbs in the visible (or u.v.) region of a spectrophotometer range, the end-point of titration can be located by measuring the absorbance at a suitable wavelength as the titration proceeds, provided that a, t and/or p obey Beer's law in the concentration range of the titration system and provided ε_a, ε_t and/or ε_p are sufficiently different. When the absorbance is plotted against the titrant volume v, the end-point is the intersection of two straight lines. The measured absorbance A should be corrected for the change in volume during titration by multiplying A by (V+v)/V, when V is the original volume of solution. The shape of the plot depends on the relative magnitudes of ε_a, ε_t and ε_p. The choice of wavelength(s) for measurements depends on these magnitudes. A spectrophotometer can be adapted for measurement by inserting a titration vessel in the light path provided it fits in the gap in a reproducible position and that it has optical glass on either side of the light path. Certain spectrophotometer suppliers provide suitable titration vessels. A quick method is to set the instrument reading to zero, use a probe-type cell and after inserting the analyte solution, I is adjusted (or the sensitivity adjusted) to give a convenient absorbance reading (say around 1). The volume of the titrant at which there is a sudden change in absorbance represents the end-point.

Light from the lamp of a commercial instrument is transmitted to a dip-type probe cell via an optical fibre. Light transmitted from the test solution is reflected to the instrument's detector by a mirror at the base of the cell via another glass fibre.

Fluorimetry and phosphorimetry

(Anal.Chem.,**53**(1981)332A; **55**(1983)669A; *J.Chem.Educ.***53**(1976)191; **54**(1977)183).

Some organic compounds and a few inorganics emit radiation when exposed to radiation which excites an electron to a higher energy level. On returning to the ground level, characteristic radiation is emitted. If there is a time lag between excitation and emission, the emitted radiation is termed phosphorescence and is measured by phosphorimetry,. Otherwise, the emitted radiation is called fluorescence and is recorded by fluorimetry. These techniques have only a limited application in inorganic chemistry. The instruments used are similar to absorption spectrophotometers but the light source is usually a mercury or a Xe lamp and the emitted radiation, at right angles to the exciting radiation, is passed through a second monochromator before being detected and recorded as in absorption spectrophotometry.

Reflectance spectrophotometry

Some solids interact with solvents. In this case, the absorption spectrum of the solution will be different from that of the solid. For these solids and for insoluble solids, reflectance spectrophotometry would be a suitable technique for characterising the solids. More expensive spectrophotometers are provided with an integrating sphere, which allows for diffuse reflectance measurements. Less satisfactory results are obtained by preparing a nujol mull of a small amount of the solid. Impregnate a rectangular strip of filter paper with the mull and press it against the wall of a spectrophotometer cell, using an identical strip impregnated with neat nujol in the reference cell and record the absorption spectrum (J.R.Wasson, *Chem.Anal.***56**(1967)36).

2.4.2 Infrared (ir) and Raman spectroscopy

Transitions between vibrational and rotational levels of a molecule correspond to energy in the ir region of the spectrum. An ir-active vibration should produce a periodic change in the dipole moment. Hence highly symmetric molecules are ir-transparent. The near ir region lies at 14000-3600 cm^{-1} and the mid ir region at 3600-200 cm^{-1}. The **wave numbers** ν ie the reciprocal of the wavelength in cm, is the usual unit used which characterises an absorption band. The vibration frequently ν of a covalent bond between atoms A and B is given by:

$$\nu = (1/2\pi c)(f/\mu) \qquad (2.46),$$

where c is the speed of light, f is the **force constant** and μ is the **reduced mass:**

$$\mu=(m_A.m_B)/(m_A+m_B) \qquad (2.47),$$

where the m's are the masses of A and B. The force constant and the frequency (and hence ν) are characteristic of the band or organic functional group. Such ranges of ν are given in tables and there are atlases of ir spectra of organic and organometallic molecules and of complexes with organic ligands. Very few inorganic ligands exhibit ir bands. In a double beam spectrophotometer, radiation from the source (SiC Globar, a Nernst (ZrO_2+V_2O_3) glower, a Ni/Cr wire or a laser) is reflected separately to both the sample holder and the reference. The beam emerging from the latter is combined with that from the former at a motor-driven chopper. The beam then passes through a monochromator before detection and display on a chart or a screen. The detector may be a thermocouple, a bolometer, a Golay pneumatic cell or a pyroelectric cell.

Either NaCl or KCl are transparent over most of the ir region and are used for the optical parts of ir spectrophotometers and for cells or windows. Generally inorganic solids are examined for qualitative characterisation and identification and for the presence of impurities. In the mull technique, the finely ground solid is mixed with ten times its bulk with **Nujol** or mineral oil. The mixture is ground preferably in a vortex mixer and a few drops of the **mull** are spread on a NaCl plate and covered with another plate and the two plates gently pressed in a demountable cell. Since Nujol or other oils have absorption bands typical of CH vibrations, perfluorocarbon oils are suitable alternatives. The alternative method for spectra of solids is to grind about 1mg of the finely ground solid with about 0.1 - 0,.2g of dried pure **KBr** in an agate mortar or in a vibratory mill. The mixture is subjected to pressure in a hydraulic press under vacuum to produce a nearly transparent **disc** which is placed in its holder in the sample position.

*Fourier transform (F.T.ir) spectroscopy) (J.Chem.Educ.***63**(1986)A5)

The advantages of this type is high resolution, combined with wavelength precision and accuracy in addition to speed. In most instruments, a Michelson interferometer is used to change the frequency of radiation to a proportionately slower frequency and the superimposed signals are fed into a computer to provide an enhanced spectrum.

*Ramam spectroscopy (Anal.Chem.,***62**(1990)140R; **59**(1987)881A

The details of this technique are beyond the scope of this volume. It is, however, worth noting, that, the region of 100-700cm^{-1}, which characterises metal-ligand bands is difficult to study by i.r. spectroscopy but can be studied by Raman spectroscopy, which is also compatible with aqueous solutions.

Visible/near i.r. (n.i.r.) spectroscopy

Modern instruments cover the range 400-2500nm and include a reflectance module. Samples can be measured non destructively with no pretreatment. Samples can be **even** scanned in their containers.

2.4.3 Atomic absorption spectroscopy *(J.Chem.Educ.*,**51**, 1974 ,687; 752 *Anal.Chem.*, 1982, **54**, 1515, **56**(1984), 933A; 875A)

In atomic absorption spectrophotometry, a **hollow cathode lamp** is used which emits the characteristic line spectrum of the cathode metal. The light from the lamp passes through an atomised mist of the gaseous element and a line of the emitted spectrum (the resonance line) is absorbed. A monochromator then allows this line alone to reach the detector and the narrow absorption band is recorded and/or displayed. Because atoms have no rotational or vibrational levels, transitions from one electronic level to another produces narrow absorption or emission lines. Doppler and pressure broadening vary from 0.01-0.001nm.

The cathode of the lamp which is filled with Ar or Ne at low pressure, sputters when a H.V. is applied to the electrodes. Collision of the noble gas and metal atoms excite the latter then they emit radiation in the visible/u.v. region of the spectrum. The metal compound in the sample to be analysed, dissolved in a suitable solvent, has to be transformed to a mist of gaseous atoms. This is generally achieved by aspirating the solution into a **nebuliser** where a mist is sprayed in a flame of a flammable gas with an oxidising gas. The gas mixture may pass through the nebuliser first or it may burn directly. Alternatively, **furnace atomisers** are used, when smaller volumes of test solutions can be handled. The solution is placed in a horizontal graphite tube or a carbon rod which are heated in an electric furnace.

Some lamps can be used for several elements. A low pressure mercury lamp can be used for the determination of mercury. However, because of some instability of the lamp output, a double beam spectrophotometer gives more reliable results than single beam instruments. In the former, a rotating sector mirror chopper splits the beam from the lamp into a reference beam and a sample beam, which passes through the burner or atomiser. A mirror combines the two beams which pass through the monochromator. Then the ratio of the intensity of the two pulses is electronically measured, thus elminating any fluctuation of the lamp output. Instruments display absorbance and/or u.v. transmission.

Atomic absorption spectrophotometry depends on the application of Beer's law (Sec. 2.4.1). It is therefore necessary to construct a calibration plot by preparing a series of standard solutions, the most concentrated of which should give a reading ~0.8.

By plotting the absorbance against concentration, the linear plot is used to determine the concentration of a test solution by interpolation. Alternatively, increasing known amounts of the element are added to a constant volume of the test solution and the absorbance of these solutions is measured under identical conditions. The plot of absorbance *vs* added concentration is extrapolated to give the concentration of the unknown. The results of atomic absorption depend, besides the concentration of the test solution, on the type of compound tested and solvent used as well as the type and temperature of the flame. Suppliers of instruments usually recommend not only the flammable and oxidising gas but also their rate of flow, the burner height and slit width.

Some instruments have been developed for both atomic absorption and atomic fluorescence. However, a powerful source e.g. a laser is required for the latter spectrometry. In principle, when a gaseous metal atom is excited by absorption of radiation, it emits fluorescence radiation when it reverts to the ground state. This can be recorded in a monochromator/detector set up, not unlike atomic absorption. (*J.Chem. Educ.*, **59**, 1982, 909; 895; *Anal.Chem.*, **53**, 1981, 332A' 1448A; **54**, 1082, 553, 1006A).

2.4.4 Emission spectroscopy

Flame photometry

In this simple technique, the metal to be determined, in the form of a solution of a suitable compound, is sprayed into a flame. As in atomic absorption, when the solvent evaporates in the flame, the solid obtained is atomised and a gaseous metal ion is excited to a higher electronic level. When this drops to a lower level, a line spectrum is emitted and its intensity is measured. Flame photometers rely on the use of filters to isolate the line emitted, which is detected by a photocell and its output is measured by a calibrated galvanometer. The method is applicable to 16 metals. Reliable results are only obtainable by careful control of the experimental conditions. These depend on temperature (i.e. the type and rate of flow of the flammable gas and the oxidant which is usually air), the rate of flow of the solution to the flame as well as the compound tested and solvent used. A method used to minimise the effects of these variables is to add a known constant amount of an **internal standard** of a compound of a metal other than the metal to be determined but with similar excitation characteristics. The ratio of the intensities of the standard and the test sample is determined. A calibration plot of the logarithm of the intensity ratio and the logarithm of the concentration of the test element is drawn. The concentration of an unknown is found by interpolation of the calibration plot. Alternatively, the standard additions method as in Sec.2.4.3 is used. In all cases, allowance should be made for any dilution effects.

Plasma, arc or spark emission spectroscopy

In these techniques, the excited atom source is not a flame but a plasma e.g. Ar plasma, a d.c. or a.c. arc or a spark. Since higher temperatures are achieved in plasmas, excited ions may be also formed as well as excited atoms. In any case, the lines are more numerous than in other techniques. The lines to be detected are selected by narrow band pass monochromator and are detected by sensitive photomultipliers. The functions of the instrument are controlled by a micro-processor and are displayed on a photographic plate, a cathode ray tube, a recorder or a printer. Qualitatively, the lines obtained from a sample are compared with tables compiled for various elements as atoms or ions. The latter are more intense when plasmas are used. The presence of 3 major lines of an element is taken as positive identification. Most elements can be identified by these methods. Solid samples can be embedded in an electrode of the source. Quantitative analysis is possible for instruments giving an intensity reading. By assigning a channel for each element, the measured intensity depends on the amount of element present.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

This is a recent rapid technique particularly suitable for the determination of a number of elements simultaneously (*Anal.Chem.*63(1991)12A). A demonstration of inductively coupled plasma is described in *J.Chem.Educ.*75(1998)316, which contains literature references.

2.4.5 N.M.R. Spectroscopy *(Anal. Chem.,* 67(1995)559A)

If a nucleus has a spin quantum number of 1 or ½ or their multiples, and is placed in a strong magnetic field, H, it may align with the field or against it, the latter being less stable. For a nucleus of quantum number I, there are (2I+1) orientations in a magnetic field. Nuclei with I=½ which have a high magnetic moment and high isotopic abundance e.g. ^1H, ^{19}F and ^{31}P exhibit nuclear magnetic resonance (N.M/R.) spectra. If an energy=difference between the two levels is applied to a sample, these magnetic nuclei will align opposite to the field. The frequency ν of the energy absorbed is given by:

$$\nu = \gamma H/2\pi \qquad (2.48),$$

where γ is a constant. For a proton in a field =14100 gauss, the resonance absorption is at 60 MHz. This is in the radiowave frequency range. The samples studied by N.M.R. are liquids or solutions. When the isotopic abundance is not high e.g. ^{13}C, ^{15}N, stronger magnetic fields are required. The field H in (2.48) is that at the nucleus but since nuclei are shielded by electrons, H is slightly different from the applied field. This shielding depends on the bonding of the nucleus to other atoms in a molecule investigated. The separation of the resonance frequency from that of a standard (generally TMS or tetramethylsilane) is called the chemical shift δ (in units of ppm). In another convention, 10 is assigned to TMS and the shift $\tau = 10 - \delta$.

In proton MR spectra, a narrow range of chemical shifts characterises various functional groups in organometallic and especially in organic compounds. These spectra are useful for identification and characterisation of these compounds.

Spin-spin coupling

When two neighbouring magnetic nuclei A and B interact, one nucleus can alter the electron shielding of the other by polarisation. Hence the field effecting B depends on whether A is in the upper or lower spin level and as a result two peaks (a doublet) appear in the spectrum, assuming A and B have I=½. In general, the coupling pattern and hence the **multiplicity** of a signal depend on the number and spin of nuclei coupled. It can be shown that the multiplicity of a signal $=2nI+1$, where n is the number of nuclei of B coupled with a nucleus of A and I is the quantum number of A. Multiplicity patterns are also useful for identification and characterisation.

Basically an NMR spectrometer consists of the following parts: (a) a strong magnet to give a stable homogeneous field; (b) a radiofrequency transmitter to supply the irradiating energy at right angles to the field; (c) a magnetic field sweep to sweep the magnetic field over the resonance region; (d) a radiofrequency receiver coil around the sample holder; (e) a detector to process the signal, and (f) a recorder to display the spectrum. The spectrum can be obtained by keeping the frequency constant and varying the field, or by varying the frequency and keeping the field constant. The latter method is used in instruments for highly accurate chemical shifts. Only solutions can be normally tested. The solvent chosen should ideally have no peaks in the region expected for the solute examined. For proton spectra, solvents which contain no H are preferred e.g. tetrachloromethane.

Electron Spin Resonance Spectrometery (E.S.R) iseyond the scope of this volume. (*J.Chem.Educ.*, **53**(1976)394).
However, briefly the technique applies to species with unpaired electrons. When these are placed in a magnetic field, the interaction between this field and that produced by the unpaired electrons lifts the spin degeneracy. As a result, a frequency of maximum absorption is observed in the microwave spectral region. Oxidation states of some metal complexes can be established by their esr spectra.

2.5 ELECTROCHEMICAL METHODS *(Anal.Chem.*,59(1987)2450).

Different electrochemical techniques depend on whether they are bulk methods as in conductometry or interfacial methods. The latter may be static as in potentiometry or dynamic. Dynamic methods are classified on the basis of the current used. Conductometry uses a constant current but controlled current methods include voltametry, amperometry and coulometry.

2.5.1 Potentiometry

When a metal M dips in an aqueous solution of its ions, M^{n+} , whose activity is a (in dilute solution, a can be replaced by $[M^{n+}]$), a potential E is set up related to a by the **Nernst equation:**

$$E=E^{o}+[RT/nF]\ln a \qquad (2.49),$$

where R and F are the gas and Faraday constants respectively and T is the thermodynamic temperature. When a=1, $E=E^{o}$, the standard reduction potential of the couple M^{n+}/M. E cannot be measured unless this **half cell** is coupled with another electrode .E_{h}^{o} for the **standard hydrogen electrode** is taken as 0 by convention. This electrode contains a platinised platinum plate connected to a metal contact. The platinum is immersed in HCl solution whose a $[H^{+}]=1$ and through which hydrogen gas is bubbled (at 1 atmosphere and 25°C). Hence when the metal electrode in the M^{n+}/M half cell is coupled with the standard hydrogen electrode, the measured e.m.f. of the cell=the reduction potential E in (2.49). However when the two half cells are brought in contact, a **junction potential** is established. This can be practically eliminated by using a **salt bridge.** This can be simply made from a U tube filled with potassium chloride (or ammonium nitrate) solution and with porous plugs at the two ends which dip in the solutions of the two electrodes. In practice it is more convenient to use another standard electrode. One of these is the **calomel electrode** which can be made from a tube in which a metal wire dips in a pool of mercury. This is covered by a paste of calomel (Hg(I)chloride) and a KCl solution is added. Commercially available electrodes can dip directly in the test solution. Another so-called reference electrode is the silver-silver chloride electrode. This consists of a silver wire, electrolytically coated by AgCl immersed in KCl solution (usually 0.1M KCl).

Indicator electrodes

The potential of such electrodes depends on the activity of a specific ion. The most widely used is **the glass electrode.** This consists of a tube ending in a special glass bulb filled with a 0.1M HCl in which a Ag/AgCl electrode is inserted. The special glass is sensitive to H^{+} ions and is specific for pH measurements. A **combined glass electrode** is often used in which a calomel electrode is coupled with the glass electrode. The combined electrode, dipped in a solution, can be used for measuring its pH directly using a **pH meter.** The latter measures the e.m.f. of cells including a glass electrode. A digital microvoltmeter is included in the electric circuit and its scale shows pH's as well as mV readings, the latter with positive and negative scales. When used for measuring pH values, it has to be calibrated by immersing the electrode in a buffer solution of accurately known pH value and adjusting the scale to this value by coarse and fine controls. It is advisable to use two buffer solutions, whose pH values cover the unknown pH to be measured.

pH titrations

In acid/base titrations, when the solutions are coloured or when the titration curve does not exhibit a clear inflexion point, colour indicators cannot be used and the glass electrode is used with a pH meter. From the plot of pH *vs* volume of titrant, the end-point can be located. This method is necessary when no suitable indicator for the pH range near the end-point is available.

Ion selective electrodes (J.Chem.Educ., 74(1997),159; 167, 53(1976)328.

Special glasses were formulated to be sensitive to univalant ions other than H^+ such as sodium, silver, potassium and lithium. These electrodes can be used to determine these ions in the same way as the glass electrode is used for pH determination. However, errors are encountered when any of these electrodes is used in presence of high concentrations of other univalent ions. Hence it is advisable when using them to have buffered calibration and test solutions. **Liquid membrane electrodes** contain a macrocyclic compound which selectively complexes with a given cation, a cation exchanger or an anion exchanger. These materials are dissolved in an organic water immiscible solvent. The anion sensitive electrodes can be used for the determination of nitrate, sulphate, perchlorate and tetrafluoroborate. The cation sensitive electrodes are specific for potassium, calcium or the latter together with magnesium (used for water hardness). These membranes can be transformed to solid discs which are cemented to a PVC tube and act as **heterogeneous membrane electrodes. Neutral carrier membranes** have been developed for the determination of Sr, Ba, ammonium etc. A solid state membrane may be a single crystal, a sparingly soluble salt or the latter embedded in an inactive matrix. The electrode is sealed at the end of a tube filled with a reference solution in which a reference electrode is immersed. Single crystal LaF_3 is selective for fluoride ions. Sparingly soluble salts pressed into a membrane may have ionic conductivity. Silver sulphide membrane is selective for silver and sulphide ions. When mixed with other silver salts, the electrodes are selective to the anion such as halide or pseudohalide electrodes. When mixed with metal sulphides, the electrodes are selective to the cation of the sulphide. Electrodes sensitive to divalent metal ions like copper, cadmium and mercury have been also developed. When a wire electrode is coated with an ion-selective membrane, very small electrodes are obtained which can be used to detect ions in other applications. **Ion selective field transistors** have the selective membrane coated on the gate of the transistor. The activity of the ion to be analysed is dependent on the drain current. **Ion-selective meters**, though have a more complex electric circuit, are basically similar to pH meters with scales for activities of cations and anions as well as H^+. A **gas-sensing electrode** consists of a gas permeable membrane enclosing an ion-selective electrode e.g. the glass electrode, with an electrolyte between the two membranes and a reference electrode enclosed in the permeable membrane. The gases determined are involved in pH-dependent equilibria. A modification of this is the **air-gap electrode,** in which the test solution is separated from the glass electrode by an air gap. These can be used for the determination of bicarbonate, bisulphite or ammonium ions. The gas is generated by the addition of an acid or alkali.

Potentiometric redox titrations

When an inert metal electrode, usually Pt, is immersed in a solution containing the oxidised and reduced forms of a metal ion or of an element, the electrode potential is given by:

$$E=E^{o}+(RT/nF)\ln([Ox]/[Red]) \qquad (2.50),$$

where the symbols have their usual significance. When the ratio of the two forms are equal, $E=E^{o}$. If measurements are carried out at 25°C and the constants are given their numerical values, the relation becomes:

$$E=E^{o}+(0.0591/n)\log([Ox]/[Red]) \qquad (2.51).$$

The variation of E with the ratio [Ox]/[Red] is represented graphically in Fig.2.6. As discussed in Sec.2.2.3, a titration of an oxidant against a reductant is possible if their E values are sufficiently different and if a suitable redox indicator is available. However, if the latter is not available or if the colour of the solutions prohibit the use of an indicator, potentiometric redox titration can be carried out by connecting the metal electrode and a reference electrode (dipping in the titration vessel through its salt bridge) to a pH meter. The plot of E against the volume of titrant will show an inflection point which indicates the end-point where the equivalence point of reductant and oxidant is reached.

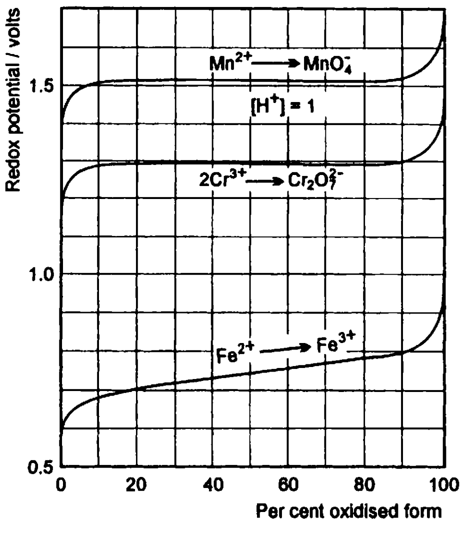


Figure 2.6 The variation of the redox potential with the reductant/oxidant ratio.

Location of end-points in potentiometric titration

When the titration curve shows a sharp rise in potential, the inflection point can be easily located. But a more accurate determination is by plotting the differential: dE/dV, where V is the volume of titrant. The end-point will be at the maximum of the plot. Alternatively, a plot of the second differential is obtained. The end-point corresponds to zero (change from positive to negative). Various other methods, using plastic sheets with parallel lines or circles of various diameters or by geometric treatment of the titration curve have been applied for end-point determination.

Depending on the availability of a suitable electrode, a potentiometric method may be used for acid/base, precipitation or complexometric titrations. A glass electrode together with a reference electrode can be used for acid/base titrations especially when the test solution is coloured or when no suitable indicator is available. When an electrode is selective to one of the ions to be precipitated, the end-point of a precipitation titration is located potentiometrically.

Automatic titrations

Automatic burettes, whose delivery is controlled by a motor, have been developed. When a mains-operated potentiometer, connected to a chart recorder, is used for titration, the delivery from the burette can be linked to the recorder and the titration is carried out automatically with the titration curve recorded on the chart. A **pH-stat** modification enables delivery from the burette to be recorded so as to maintain a constant pH in the reaction vessel.

2.5.2 Conductometry

Ohm's law can be expressed as:

$$I=E/R=Ea/pl \qquad (2.52),$$

where E and I are the potential difference and current respectively, R is the resistance of a conducting solution whose length is l and cross-sectional area is a. The resistivity ρ is the reciprocal of the conductivity k whose common unit is S cm^{-1}, but its SI unit is Sm^{-1}. k is dependent only on the nature and concentration of the ions in an electrolyte solution. The molar conductivity Λ is related to the concentration C of the solution or its dilution V by the relation:

$$\Lambda = 1000k/C=1000kV \qquad (2.53),$$

where C and V have the units: Mol dm^{-3} and dm^{3} containing 1 mol (the factor 1000 is used when non SI k is used). At high dilution, Λ is the sum of values from the ions in solution. Values of various ions at 25°C have been known from accurate measurements.

For conductivity measurement, or conductometric titrations, a glass cell or a glass titration vessel is used. At either end, two platinum plates of the same dimensions are sealed. These are covered with Pt black (as in Sec.2.1.4) and filled with distilled water when not in use. The electrodes are connected to one arm of a Wheatstone-type bridge (Fig.2.7). The power supply is usually an a.c. source e.g. mains-operated oscillator of frequency 100-300Hz. The opposite arm of the bridge contains variable known resistances. The other two arms may be a wire along which a slider is moved to locate zero current indicated by headphones or other detectors. Rather than measuring the dimensions of the cell, it is filled with a standard KCl solution (0.1 - 0.001M) whose k is accurately known over a temperature range. The cell is placed in a thermostat, preferably at 25°C and its resistance measured by the conductivity bridge. Its cell constant (=*l*/a) is calculated from the measured resistance and the known *k*. Actual measurements of *k* and hence Λ are only required when the number of ions formed by one "molecule" of electrolyte is to be determined. In the acid/base conductometric titrations, the highly conducting H^+ or OH^- ions are neutralised. Generally, when the number of ions in solution decreases during titration and reaches a minimum at the end-point, titrations can be done conductometrically. A plot of conductivity against volume of titrant would exhibit a minimum at the intersection of two linear parts, although one line may be much less steep than the other e.g. when a weak acid or base is titrated. Conductometric titrations may be acid/base or complexometric titrations and can be carried out using more dilute solutions than normal indicator-based titrations. Although in a precipitation titrations, mobile ions are removed from solution as the reaction proceeds, the technique is not very suitable since the precipitate may adhere to the electrodes and it may not be easy to clean them. Commercial instruments are now available which combine pH- and ion-meter with a conductivity meter which have automatic cell constant determination as well as printer/personal computer parts.

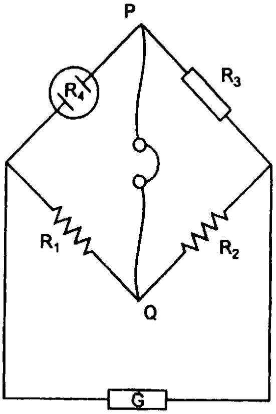


Figure 2.7 The Wheatstone bridge for measuring the conductivity of a solution in the cell R_4, showing the resistances R_1, R_2 and R_3, the A.C. generator G and the detector between P and Q.

High frequency titrations

When an electrolyte solution is placed in a high frequency electric circuit, chemical changes in solution may produce a change in the resistance and/or the capictance of the oscillator's circuit. As a result, the oscillator characteristics will change. If any of these changes is measured, a change in the solution's conductance or dielectric constant will be reflected by a change in the measured electric property. Since the electrodes of the oscillator circuit can be outside the vessel in which the reaction is taking place, precipitation or electrode polarisation, which interfere with usual conductometric titrations, will not affect the result of the high frequency titrations. This titrimetric method is suitable for acid/base, precipitation or EDTA titrations.

The optimum frequency for practical use is proportional to the low frequency conductivity of the solution and inversely proportional to its dielectric constant. A cell usually used for titration is a glass tube with two metal bands fitted around the tube, which are connected to the oscillator circuit. The level of liquid in the cell should be above the upper metal band and the liquid is stirred during the titration mechanically or magnetically. When an inductive cell is used, the electric circuit only responds to changes in the conductance of the cell's contents. The method is successful over a limited concentration range but it is less sensitive than normal conductometric titration.

2.5.3 Coulometry

This is based on Faraday's first law i.e. the extent of an electrochemical process is proportional to the quantity of electricity (= current x time). In **primary analysis,** the species to be analysed undergoes the reaction whereas in **secondary analysis,** a species generated at the electrode reacts with the species to be analysed. The mass W of the species produced or ions consumed when Q coulombs are passed through the solution are given by:

$$W = MQ/nF \qquad (2.54),$$

where M is the RAM or RMM of the species, n and F have the usual significance. Analysis may be carried out at a controlled potential or at a constant current. In the former, the current decreases exponentially with time and hence it is convenient to use a current-time integrator. A coulometer e.g. the silver coulometer, consists of a noble metal basin e.g. Pt, acting as cathode containing a 10% silver nitrate solution in which a pure Ag rod (the anode) dips. The electrodes are connected to a d.c. source. From the mass of silver deposited, Q is calculated.

In coulometric titrations, a titrant is generated, at a controlled current, in the titration vessel. A high concentration of the electroactive species which generates the titrant ensures a 100% generation efficiency. The end-point of the titration is detected potentiometrically or by a suitable alternative.

2.5.4 Voltammetry *(Anal.Chem.*57(1985)101A; 46(1974)257A; *J.Chem.Educ.,*50 (1973)A131)

In voltammetry, a potential is imposed on an electrode (**the working or indicator electrode**) of an electrochemical cell and the current is measured and plotted as a function of the applied potential. The plot is referred to as a **polarogram** or **voltammogram.** When the potential is sufficient to cause reduction or oxidation of a species near or at the working electrode surface, a current flows through the electrode. Since this current depends on the nature and concentration of such species, the technique is suitable for qualitative and/or quantitative analysis. However, the method only applies to species which can be either oxidised or reduced: **electroactive species.** In presence of an appreciable concentration of an indifferent electrolyte such as O.1M KCl, the current due to the migration of ions can be disregarded and the measured current is essentially the current due to the diffusion of the electroactive ions: the **diffusion current,** I_d. The plot of the variation of the potential at the working electrode with time is termed the **excitation waveform.** Depending on this and on the type of electrode used, variants of voltammetry can be distinguished. In general, the instrument which applies the potential is called a **potentiostat** and together with the current monitoring equipment, they constitute a **voltammetric analyser.**

Polarography (*Anal.Chem.*54(1982)698A; *J.Chem.Educ.*60(1983)296; 47(1970)A81). When the **dropping mercury electrode,** DME, is used as the working electrode, the technique is referred to as polarography. The instrument used is called the **polarograph** which displays or records a polarogram. The anode of the cell is a pool of mercury whose surface area is much larger than the mercury drop protruding from a capillary tube of DME. Hence the anode can be considered as non-polarised and its potential taken as constant in presence of anions such as chloride or sulphate which form insoluble mercury salts. The cell's behaviour, therefore, depends on the reactions at the cathode (the DME). Due to the interference of oxygen in redox reactions, it has to be excluded by purging the cell with nitrogen, freed from traces of oxygen by bubbling through acidified chromium(II) solution. A potential is gradually applied to the cell. A plot of the variation of the current against the applied voltage is depicted in Fig.2.8 when the cell contains a reducible ion e.g. M^{n+} .

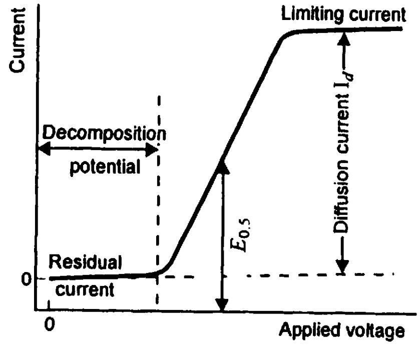


Figure 2.8 Variation of the current with the applied voltage in polarography.

The DME acquires an increasingly negative potential but as the potential rises, initially very little current passes; from a to b. This small current is termed the **residual current.** At b the emf of the cell is sufficient to induce the reaction:

$$M^{n+} + ne + Hg \rightarrow M/Hg \qquad (2.55).$$

The potential is referred to as the **decomposition potential** of the cation. The rapid linear increase in current from b to c results from the depolarisation of the DME as the metal ions are discharged as M/Hg. The system obeys Ohm's law from b to c. The general electrode reaction is:

$$Ox + ne \rightarrow Red \qquad (2.56),$$

where Ox and Red refer to the oxidant and reductant respectively. The oscillations observed in the polarogram beyond c are due to the constantly changing size of the mercury drop. If a device (drop knocker) is included in the set-up, it allows the current measurement to be done just before the drop falls and the oscillations will not appear. In presence of other reducible species, the polarogram will exhibit a repetition of the polarographic wave. **The half-wave potential,** E½ is the potential when the current $=\frac{1}{2}I_d$. A plot of E against $\log[I/(I_d-I)]$ for a reduction intercepts the potential axis at E½. Qualitative polarographic analysis is done by comparing the value of the halfwave potential of the oxidant or reductant tested with known values of electroactive species. For meaningful conclusions, differences in E values of different species should not be <0.1V. In some polarographs, **derivative polarograms** can be obtained. In these d*I*/dE plots, a maximum is exhibited at E½. It is then possible to identify species with close values of E½.

Oscillographic polarography

Common polargraphy uses d.c. but **a.c. polarography** was later developed. A.c. polarographs incorporating a **cathode ray oscilloscope** may be operated by a controlled potential or a controlled current. In the latter, the complete voltage sweep is applied at the last third of the lifetime of the mercury drop and maximum voltage occurs immediately before the drop falls. This is displayed on the screen of the oscilloscope. It was found that the peak current is proportional to the concentration of the electroactive species. In another development, **differential polarography** two cells are used with near identical DME's. One cell contains the test solution and the other contains only the indifferent electrolyte and the difference between the currents flowing through the two cells is measured. Alternatively, one cell contains the test solution and the other contains a known concentration of the electroactive species. This method is referred to as **comparative polarography.**

*Cyclic voltametry (J.Chem.Educ.*60(1983)285; 290; 702; 772).

In this technique, the potential imposed on the indicator electrode dipped in an unstirred solution is cycled and the current is measured and plotted against the potential of the indicator electrode *vs* a saturated calomel electrode. The potential is a linear potential with a triangular wave form, which sweeps between two set values: the **switching potentials.** When a negative switching potential is applied to a platinum indicator electrode, the negative scan causes reaction (2.56) to take place. The cathodic current increases until [Ox] at the cathode surface approaches zero, when the current is at a peak. This is followed by a decay in the current as the bulk solution is depleted of the oxidant. The scan potential is then switched to positive when the electrode causes the reaction:

$$\mathrm{Red} \rightarrow \mathrm{Ox} + ne \qquad (2.57).$$

Thus the reductant adjacent the electrode is oxidised. The anodic current increases until [Red] at the electrode surface approaches zero. The current then decays and the cycle is completed when the potential reaches the initial switching potential. During the forward scan, a new oxidation state is rapidly formed and its fate is indicated by the reverse scan. This reversibility is an advantage of this technique.

2.5.5 Amperometry (*Anal.Chem.*54(1980)IR.

Since the limiting current is independent of the voltage applied to DME, the diffusion current, which is the difference between the limiting and residual currents, is proportional to the concentration of the species which is involved in the electrode reaction; provided enough supporting electrolyte is present in the cell. When the electroactive species is removed from the cell, the diffusion current decreases until the end-point is reached. A plot of the diffusion current against the volume of titrant will show an intersection of two straight-lines. This is the basis of **amperometric titrations.** The diffusion current may be proportional to the concentration of the species to be tested, to the excess of the added reagent or to one of the products of reaction. Occasionally two or three species may be electroactive. Variants of the method have been used by replacing DME by a **rotating platinum electrode** or by replacing both cathode and anode by two platinum discs. The first variant is useful when the applied potential is equal to or <1.0V. The working electrode in this case is a platinum wire protruding from a standard mercury seal and is rotated at a constant speed, and the electrical connections are made by Cu/Hg wires. Solutions can be titrated when the [electroactive] is about 10^{-4}M. When two platinum plates dip in the test solution and are connected to a potentiometer with a microammeter in the circuit, the method is referred to as **dead stop titrations.** If a reactant is involved in a reversible redox reaction, both electrodes are depolarised until the oxidised or reduced form is removed by a titrating agent. When the electroactive species is thus removed, only one electrode remains depolarised after the end-point. The current =0 at or just after the end-point. The titration curve in this case does not exhibit the intersection of two lines but it still displays zero current at the end-point. Modern instruments combine various voltamemtry/ polarography techniques with coulometry and amperometry, using Windows PC with multiple curve plotting.

2.6 THERMAL METHODS (*Educ.Chem.*,8(1971)97)

2.6.1 Thermometric titrations

Chemical reactions take place spontaneously if accompanied by negative ΔG^{o} but, depending on the sign of ΔS^{o}, the reaction may be exothermic i.e. accompanied by negative ΔH^{o} or endothermic. In this case ΔH^{o} is positive, since

$$\Delta G^{o}=\Delta H^{o}-T\Delta S^{o} \qquad (2.58).$$

In thermometric titrations, the solution to be titrated is kept thermally insulated and the titrant is added usually from an automatic burette. The change in temperature is plotted as a function of the volume added, when a marked increase or decrease in temperature is observed. Before the addition and after the end-point, only small temperature changes are observed. At these stages, temperature is usually plotted as a function of time. The end-point is where the titration curve intersects with the post end-point section. Occasionally, one stage of a reaction is exothermic e.g. the titration of sodium malonate ($CH_2(COONa)_2$) with perchloric acid when one Na is replaced by H. This is followed by the endothermic replacement of the second Na. Normal titration curves may be less satisfactory than derivative or second derivative curves where $\Delta T/\Delta V$ or its differential is used (T is temperature or related reading and V is volume of titrant). Although commercial equipment is available, it is possible to use an insulated Dewar vessel as a titration vessel. Immersed in the solution is a thermistor which acts as a temperature sensor and forms an arm of a Wheatstone bridge. The imbalance potential from the bridge is recorded as a function of titrant volume (or time when a constant rate of delivery from an auto-burette is used). It is advisable to use a much higher concentration of the titrant than that of titrand to minimise enthalpy dilution effects. **Enthalpimetry** is a method of quantitative analysis in which the change in enthalpy resulting from the addition of an excess of a reagent to a known volume of solution, is determined. The heat capacity of the reaction vessel should be accurately known.

2.6.2 Thermogravimetric analysis *(TGA) (Anal.Chem.* 56(1984)1471A)

In thermogravimetry, the mass of a sample, or the change in its mass is monitored as a function of temperature or time and displayed in a **thermogram.** Either the temperature is varied in a controlled manner and a mass/temperature thermogram is obtained, or in isothermal studies, the temperature is kept constant and the mass/time plot is displayed. The loss of mass results from the loss of volatile or gaseous products whereas a mass increase may be due to a reaction with the prevailing atmosphere. In some cases, the mass, w, is expressed in RMM units or a differential thermogram is obtained i.e.dw/dT plotted against T, when the inflection points are replaced by maxima at certain temperatures. The results of TGA depend on a number of factors. The mass of solid used should be as small as to be compatible with precise weight measurements. Instrumental factors include: rate of heating, furnace atmosphere control, crucible geometry and sample characteristics. Modern thermobalances allow for the use of a range of sample masses. A mass is placed in a sample holder in the furnace, whose temperature ranges from ambient to 1500°C. There is a range of heating or cooling rates. Usually Ar or nitrogen are used to purge the furnace atmosphere, although oxygen or even air is used at some stage. The rest of the thermo-balance is thermally isolated from the furnace. When the mass of a sample changes, the balance beam is deflected. This interposes a light shutter located between a lamp and one of two photodiodes. The imbalance in the photodiode current is fed into a coil located between the poles of a magnet. The magnetic field created by the current restores the position of the beam. This current is transformed by a data acquisition system to mass change. In modern instruments, the voltage output of the thermocouple, which is placed near but not in contact with the sample, is translated to temperature of the sample through a microcomputer.

The main processes which can be studied are: loss of water of crystallisation, thermal decomposition, oxidation and desorption. Qualitatively, the identity of a sample can be confirmed by comparing its thermogram with that of a standard sample. In some decomposition reactions, an intermediate can be established from an inflection in the thermogram e.g. $2CuO.SO_3$ in the thermogram of $CuSO_4.5H_2O$. Limited quantitative analyses have been done e.g. a mixture of the oxalates of Ca, Sr and Ba which decompose at different temperatures.

2.6.3 Differential thermal analysis (DTA) *(J.Chem.Educ.,*54(1977)582)

In DTA, the difference in temperature between a sample and an inert standard (e.g. α alumina or SiC) is measured and plotted as a function of temperature, while both sample and standard undergo a programmed heating, usually in a linear rate. The plot obtained, the **differential thermogram** shows exothermic peaks; where ΔT (the temperature difference) is a positive maximum, or endothermic peaks where ΔT is a minimum. These minima usually accompany physical changes whilst chemical changes usually produce exothermic peaks. However, the size and shape of the peaks indicate changes e.g. in crystallinity. Phase transitions are shown in the differential thermograms but not in TGA. DTA is useful in characterising clay minerals and complex materials like cements. In **differential scanning calorimetry,** the difference in energy required to keep the sample and standard at the same temperature is measured and plotted against temperature. The technique may be used to measure activation energy and rate constants for a given transition.

2.7 SOLVENT EXTRACTION AND ION EXCHANGE

Solvent extraction is a useful separation technique especially for transition metal compounds. Ion exchange resins are similarly useful for separating cations or anions.

2.7.1 Solvent extraction *(J.Chem.Soc.,* (1949)1841).

The partition law

When a solute is in equilibrium with two immiscible liquids, the ratio of its concentration in the two liquids is constant at constant temperature, provided the solutions are considered ideal. This ratio is the **partition coefficient** p.

When an organic reagent, HR, reacts with a metal ion, M^{n+}, the following equilibria are established in aqueous solution;

$$HR \leftrightarrows H^{+}+R^{-} \qquad (2.59),$$

$$M^{n+}+nR^{-} \leftrightarrows MR_n \qquad (2.60).$$

In a mixture of water and an immiscible liquid, the species HR and MR_n are partitioned between water, w, and the organic solvent, o. The partition coefficients are:

$$p_r=[HR]_w/[HR]_o \qquad (2.61)$$

and

$$p_c=[MR_n]_w/[MR_n]_o \qquad (2.62)$$

where the subscripts r and c refer to the reagent and the complex (or compound) respectively. Since ionic species are likely to be more soluble in water whereas MR_n and HR are likely to be more soluble in the organic phase, metal ions M^{n+} can be extracted from aqueous into organic solvents in the form MR_n. The distribution ratio, D, is given by:

$$D=[MR_n]_o/([MR_n]_w+[M^{n+}]_w) \qquad (2.63),$$

This apparently depends on pH. Applying the law of mass action, it can be shown that;

$$D=K[HR]_o^{\,n}/[H^{+}]_w^{\,n} \qquad (2.64),$$

$$\text{where } K=[K_rp_r]^n/K_cp_c \qquad (2.65),$$

where the equilibrium constants: K_r and K_c refer to (2.59) and (2.60) respectively. Replacing K by $\mathcal{K}$, where

$$\mathcal{K}=K[HR]_o^{\,n} \qquad (2.66),$$

it can be shown that

$$D=\mathcal{K}/[H^{+}]_w^{\,n} \qquad (2.67).$$

The percentage of extraction, E, is related to $\mathcal{K}$ by the relations:

$$\begin{aligned}\log E-\log(100-E) &= \log D\\ &= \log\mathcal{K}+n\mathrm{pH} \qquad (2.68)\end{aligned}$$

This emphasises the role of pH in the process. It has been suggested that the pH corresponding to 50% extraction, $pH_{½}$, is a useful indicator of the effect of pH since:

$$pH_{½}=-(1/n)\log\mathcal{K} \qquad (2.69),$$

Thus extracting a given metal ion from a mixture with other ions may be achieved at a given pH value.

2.7.2 Ion exchange resins

An ion exchanger can exchange ions with the surrounding solution without changing its structure. Ion exchange resins may contain acidic groups which are strongly acidic (-

SO_3H) or weakly acidic (-COOH). These resins exchange with cations in solution. Anion exchange resins contain quaternary ammonium groups with replaceable OH groups. Cations replace H from acidic resins e.g.

$$RSO_3H+NaCl\quad RSO_3Na+HCl \qquad (2.70),$$

Anions replace OH's from an anion exchange resin e.g.

$$RNMe_3OH+NaCl\quad RNMe_3Cl+NaOH \qquad (2.71),$$

Resins have different affinities to different ions and hence can be used not only for separating cations from anions but also for separating different cations or different anions. Electrostatic considerations explain the greater affinity of a resin for ions of higher charge. For cations of the same charge, the affinity follows the **lyotropic series.** Thus the affinity increases from Mg ions down the alkaline-earth group. This is the order of decreasing size of the hydrated ions. Ion exchange equilibria generally obey the law of mass action and hence thermodynamic functions can be calculated.

Preparation of the resin

Slurry about 20g of a cation exchange resin (sodium form, or hydrogen form of a mesh giving about 0.5mm diameter) with 100cm^3 of 2M hydrochloric acid in a beaker. Decant off the liquid. If a sodium form of the resin is used repeat with one further 100 cm^3 of 2M hydrochloric acid. Wash the resin well with boiled-out distilled water several times. The supernatent liquid should be clear.

Preparation of the column

A 50 cm^3 burette, without its tap and closed instead by a screw clip-on plastic tubing, is a suitable container. Place a plug of glass wool in the neck of the burette, fill the column with water and then run in the resin as a slurry (swirled well) added in portions, tapping after each addition. 'Backwash' the column. This consists of reversing the direction of flow (normally downwards) and may be carried out by attaching a reservoir (e.g. a separating funnel) to the lower end of the column by sufficient tubing to allow a head to be raised above the water level in the column. First fill the tubing with water, making sure to remove air-bubbles. The rate of back-flow can be carefully controlled by varying the height of the reservoir and should be such that the beads of resin are in a gentle fluid motion throughout the whole column. When no air bubbles remain and when the column has an even amber colour, the 'backwashing' is complete. Allow the resin to settle down slowly. The water level must never fall below the top of the resin in the column at this or any subsequent stage.

Run through the column about 20 cm^{3}of boiled-out distilled water and check that this is chloride-free, and acid-free. Run through the column 80 cm^3 of water as above and titrate this with 0.05M sodium carbonate using methyl red as indicator. This blank titre suitably adjusted for volumes, must be used in correcting subsequent titres.

2.8 CHROMATOGRAPHY

2.8.1 Gas chromatography (GC) (*J.Chem.Educ.*59(1982)614).

In gas chromatography, an inert gas (**the carrier gas**) is the mobile phase whereas the **stationary phase** is a liquid adsorbed on a solid or organic species loaded on a solid or a solid. The two former cases are used on **partition GC.**, which has more applications.

Although this is most useful to separate and quantify components of organic mixtures, it can be applied to relatively volatile inorganic completes or organometallics.

A **gas chromatograph** consists of a column (a U or coiled tube) packed with the stationary phase, into which the material to be analysed is injected by a syringe through a rubber septum. Depending on the adsorbability of the sample components onto the solid, they are separated. This is expressed as **retention time**. When a stream of the gas passes through the column, different species are eluted and are detected. The results are displayed as recorder reading against time or a **chromatogram**. The different components give different peaks on the chromatogram, whose areas depend on the amounts of the components. The carrier gas (He, Ar or nitrogen) passes from a cylinder to the column via a two stage pressure regulator, a flow controller and a **rotometer** into a flow splitter. This divides the gas stream into a part which sweeps the column and another part into the detector. Various detectors are used in different instruments such as thermal conductivity, flame ionisation, flame photometric or electron capture detectors. The column and injection part are electrically heated. The output from the detector, through a data system, is recorded. Most parameters of modern instruments are computer-controlled. **Head space GC** is used when a volatile component is analysed in presence of non volatile species. In the headspace above the column, only the gaseous components are injected.

2.8.2 Liquid chromatography (LC)

The mobile phase in this technique is a liquid whereas the stationary phase may be one of the three mentioned above, an ion exchange resin or a liquid in the interstices of a solid polymer. Because the mobile liquid moves down a column of the stationary phase by gravity, separations of components of a mixture are slow. In a later development, **high performance liquid chromatography (HPLC)** was developed *(J.Chem.Educ.* 74(1997)45). The liquid, to which a small amount of analyte mixture has been injected, is pumped at a uniform rate at high pressure into a column. Separation of the components of the mixture depends on their retention time on the column (=time between injection and detection). For a specified column and experimental conditions i.e. flow rate and temperature, the retention time is characteristic of a given compound. The area under a peak in the chromatogram is proportional to the concentration of the compound responsible for the peak. Most applications of HPLC are in the field of organic and biological compounds.

2.8.3 Paper and thin layer chromatography (TLC) (*J.Chem.Educ.*,75(1998)640).

In these microscale techniques, a strip of filter paper or a glass or plastic plate act as the stationary phase. The plate is coated with a thin layer of silica gel or similar material. The paper or plate, suspended in a glass tank containing a solution of the analyte mixture in a suitable solvent, is adequate. The components of the mixture and the solvent ascend the paper or the coating of the plate by capillary action. Their separation depends on their R_f values defined by:

$$R_f = (\text{distance to the zone centre/distance to solvent front}) \qquad (2.72),$$

these distances are measured from the marked starting line. Qualitatively, a component is identified by comparing its R_f with a pure standard. Quantitatively, the area of a spot and its photodensity have to be measured and compared with a known concentration of a standard. Various methods are used for a zone detection.

2.8.4 Ion chromatography *(Anal.Chem.,47(1975)180).*

In this technique, the mobile phase is pumped into an injector where the sample containing the ions to be analysed is added and the solution is injected to an appropriate ion-exchange column (the **separating column**) where the ions under test are separated. The conducting ions of the mobile phase are then removed in a second ion-exchange column (the **suppressor column**). The eluate from the system will only contain the sample ions which are detected by a conductivity detector and displayed as an **ion chromatogram**. As an example, if the mobile phase is HCl acid to which a mixture of cations have been added, a cation-exchange column (in the H^+ form) separates the cations. The suppressor column would be an anion exchange column in the hydroxide form where the hydroxide ions are exchanged by the chloride ions from the acid. The H^+ ions from the acid solution are neutralised by the hydroxide ions and the eluate will only contain the cations whose conductivity is detected. In a similar way, for the analysis of anions, an anion-exchange separating column is used with a cation-exchange suppressor column. In modern instruments, the stripping column continuously regenerates the reactant ions. Other detectors have been also used in modern instruments e.g. electrochemical methods, spectrophotometry. The instruments are PC-based. In **single column chromatography**, the conductivity of the mobile phase ions is electronically suppressed without the use of a suppressor column.

2.9 CONTROLLED ATMOSPHERE TECHNIQUES

Some chemicals interact with atmospheric gases: oxygen, water vapour or carbon dioxide. Some reactions require high pressures. In these cases, special facilities and equipment are required.

2.9.1 The glove box

For the preparation, manipulation and/or analysis of air-sensitive chemicals, the use of a glove box may be necessary. When purged with an inert gas eg nitrogen, the inert atmosphere in the glove box will allow handling air-sensitive substances.

A sketch of the glove box is depicted in Fig.2.9. The pressure in the box should be maintained at a positive pressure of nitrogen. About 1.5-2 cm of oil on a manometer tube represents a satisfactory pressure and will cause the gloves to become inflated outside the box. The mercury lute acts as a safety valve and will prevent the build up of pressures greater than 1 cm of mercury in the box.

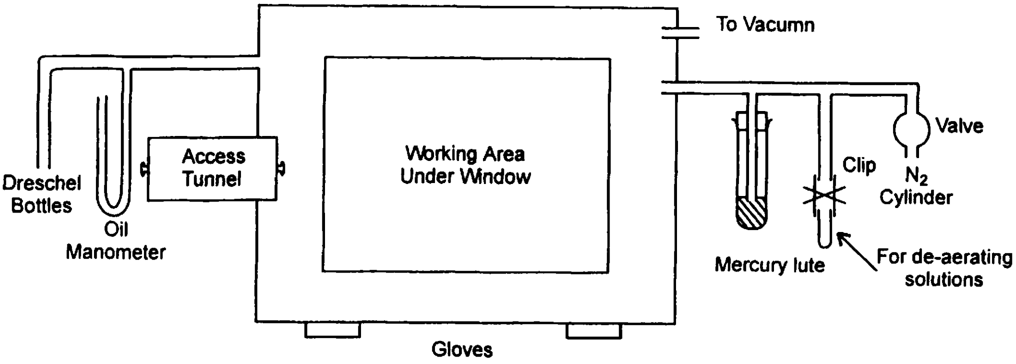


Figure 2.9 A sketch of the glove box.

For filling the box with nitrogen, a large plastic bag is connected at the point **a** inside the box on the nitrogen inlet tube. The bag is allowed to inflate thus displacing air from the box space. When the bag is full, it is disconnected from **a** so that the nitrogen will fill the box space. It is advisable to repeat this process twice more.

A steady flow of nitrogen (about 1 bubble every 2 seconds) should be maintained during the operations and the flow should be increased during the filtration stages to maintain the positive pressure. A continuous check on the manometer level should be made during the use of the box. The hands should be fitted into the gloves (talc is used to help fitting the gloves) slowly and hands should be withdrawn from the gloves slowly. Rapid movements cause rapid changes of pressure in the glove box space.

It is advisable to deaerate liquids and solutions to be used in the box by passing a stream of nitrogen for 5 minutes. Boiled-out water should be used for solutions.

The glove box can be also used for handling moisture-sensitive materials which may not be affected by oxygen. In such cases, an efficient desiccant e.g. phosphorus V oxide is placed in large area containers and the box filled with moisture-free gas, keeping a desiccant container in the box's tunnel. For chemicals sensitive to carbon dioxide, soda lime is used instead of a desiccant.

2.9.2 The vacuum line (D.F.Shriver; M.A.Drezdzon, *The Manipulation of Air-sensitive Compounds,* Wiley, 1986).

Ordinary laboratory vacuum is obtained by rotary vacuum pumps and is adequate for operations such as filtration under a reduced pressure of the order of 10^{-2}-5×10^{-3} mm mercury. The exhaust of the pump should be directed to a fume cupboard. However, lower pressures are required for some operations and preparations. In a traditional vacuum line, the low pressure side of the rotary pump is connected to a trap to be cooled in a solid carbon dioxide in acetone to trap any condensible material from the rotary pump. The trap and the rest of the vacuum system are made of borosilicate glass and held in position by a fixed frame of metal rods, clamps and bosses. The high vacuum side of the trap is connected to a mercury or an oil diffusion pump. Either of these will evacuate the system of glass manifold to 10^{-5}-10^{-6} mm mercury. The outlet from the diffusion pump is connected to a trap, to be cooled in liquid nitrogen, and is sealed to the manifold whose parts are joined by standard joints (which may be sealed with a low melting wax). A McLeod gauge, which measures the pressure, is usually inserted in the line between the cold trap and the rest of the line. The parts of the line are isolated by vacuum stopcocks. These and the joints should be lightly greased with vacuum grease. The system is evacuated by running the rotary pump before heating the liquid in the diffusion pump. Following outgassing for > an hour, the pressure is checked on the gauge. Otherwise the gauge is isolated from the system. By heating a part of the system while cooling an adjoining tube (or part) in a suitable refrigerant, volatile chemicals can be transferred from the hot section to the cold finger. Samples which are to be separated from the system are sealed via a thickened narrow tube which can be sealed off under vacuum. If a gas is to be isolated e.g. for examination by mass spectrometry, a break seal is used.

2.9.3 Other reduced pressure apparatus

A simple apparatus assembled from ordinary laboratory parts (Fig.2.10) is suitable for operation at ordinary laboratory vacuum. It can be used for preparative and for analytical purposes. A is a graduated separating funnel fitted with a rubber bung B carrying a bunsen valve C (slit rubber tube with one end closed by a piece of glass rod). The stopcock of A fits into a rubber bung covering a sintered glass crucible D, which delivers liquid to Buchner flask E. A reactant placed in A is quickly mixed with a liquid reactant and the Bunsen valve is quickly used with bung B so that if any gas is evolved, it escapes through C without allowing air into the system. When the reaction is "complete", the solution produced, freed from any solids by the sinter, is delivered into the evacuated Buchner E, where it may react with a reagent or may be titrated using a burette, whose bent tip fits into the rubber bung E.

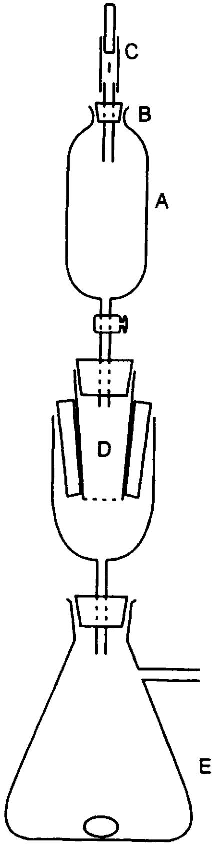


Figure 2.10 A sketch of an apparatus for preparations under reduced pressure.

A more elaborate system can be evacuated before mixing the reactants and is essentially similar to the above apparatus. Details appear in M.A. Malati, _Lab.Prac._ (1982) 1172.

2.9.4 High pressure work

Reactions requiring high pressure can be carried out in autoclaves or a small bomb. A recent paper describes a reactor for either vacuum or pressure work _(J.Chem.Educ._ 71(1994)807).

2.10 PHOTOCHEMICAL METHODS

2.10.1 Lamps and accessories

The mercury or xenon lamps are usually used as light sources in ordinary photochemical laboratory experiments. Mercury lamps may be low, medium or high pressure, depending on the pressure around the mercury arc. The latter two types emit several lines of the mercury spectrum in the visible and uv regions whereas the predominant line emitted by the low pressure lamp is at 254nm. Hence this type of lamp is most suitable for quantum yield determinations. Filters have to be used to remove any lines or radiation not required. The xenon lamp gives a continuous spectrum in both the visible and u.v. regions. The short wavelength radiation especially from the mercury lamps converts oxygen to ozone and hence they are operated under a nitrogen atmosphere. In less powerful lamps, a filter is used to absorb the undesired radiation. All the lamps produce a lot of heat and they have to be cooled generally by a water jacket (thimble). Unless the u.v. radiation is not wanted, quartz thimbles should be used. Generally xenon lamps are cooled by a fan. Lamps may be either of the dip type, where their thimbles may be immersed in a liquid or solution. Other lamps in the form of coils or U tubes may be positioned above or alongside a reaction vessel usually made of quartz. In some photoreactors, the reaction vessel is at the centre of an equidistant array of lamps. Lenses required to direct light towards a reaction vessel should be made of quartz unless u.v. light is meant to be excluded. When the effect of intensity of radiation on the quantum yield is studied, the simplest method is to place a copper gauze between the lamp and the reaction vessel. If the latter is made of quartz and is thermostatted, the thermostat should have a quartz window.

2.10.2 Quantum yields and actinometry (V.Balzani, V.Carrassiti, *Photochemistry of Co-ordination Compounds,* Academic Press, 1970, London, pp8-12)

The rate of a photochemical reaction depends on the wavelength of radiation and the rate of light absorption and it is generally little affected by temperature. The rate is expressed as quantum yield, Φ, defined as:

Φ = number of species reacting or produced s^{-1}/number of quanta absorbed s^{-1} (2.73),

Ordinary or instrumental analytical methods are used to determine the rate of disappearance of and/or rate of formation of species involved in the reaction. The number of quanta absorbed depends on the nature and concentration of the absorbing species as well as the intensity of radiation absorbed i.e. the output of the lamp. Although physical methods can be used for this purpose (Sec.2.4.1), a more convenient and simpler method is to use a chemical actinometer. The term refers to a chemical system whose Φ is accurately known at various wavelengths.

Uranyl oxalate actinometry (*idem*.pp.291-293)

A mixture of a uranyl salt e.g. nitrate and an excess of oxalic acid (giving mainly uranyl oxalate) is one of the earliest and better studied systems for actinometry. The rate of disappearance of oxalic acid on irradiation is easily determined by titrating an aliquot of the solution and repeating the titration after exposing an identical aliquot to the same light source used for the photo-reaction and under identical conditions, to those used in the reaction under study.

The % of light absorbed by the layer of the actinometric solution irradiated should be determined spectrophotometrically (Sec.2.4.1) at the wavelength of radiation used. A similar determination for the solution investigated is also required. The situation is complicated when polychromatic radiation is used.

2.10.3 Photocatalysed reactions

A sketch of a **semiconducting particle** is depicted in Fig.2.11, where the filled **valence band VB** is separated from the vacant **conduction band CB** by a **band gap** E_g, whose value depends on the nature of the semiconductor as well as surface deposits or impurities etc. When a suspension of such particles is irradiated with a light source whose energy exceeds E_g, electrons are promoted from VB to CB, creating positive holes in VB. On migrating to the surface, electrons reduce any suitable species available. On the other hand, holes migrate to the hydroxylated surface reacting with it producing OH radicals which would oxidise any available suitable species in solution. The efficiency of the process is greatly reduced by electron/hole recombination. On the other hand, the presence of efficient hole and/or electron scavengers increases efficiency.

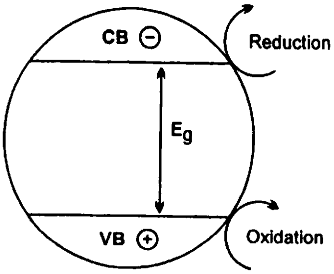


Figure 2.11 A sketch of a semiconductor particle and photocatalysed reaction.

2.11 STUDY OF KINETICS OF REACTIONS

(F.Wilkinson, *Chemical Kinetics and Reaction Mechanisms*, Van Nostrand Reinhold, 1980)

2.11.1 Homogeneous reactions

For the study of fast reactions, special equipment and techniques are needed but they are beyond the scope of this book. For reactions which take place at a rate which can be easily measured, the apparatus in Fig.2.12 is suitable, convenient and easy to use. A solution of one reactant is pipetted into flask A and a solution of the other reactant is carefully pipetted into flask B. The apparatus is then assembled, with coolant water in the jacket around D, blocking the tube f and opening the 3-way tap e to air. When a reaction is studied in absence of oxygen, O_2-free N_2 flows from f to e. The assembled apparatus is kept in a thermostat to maintain the temperature of the reacting solutions constant. After thermal equilibration, the two solutions are mixed thoroughly in flask A by careful tilting, while a stopwatch is started. At intervals, aliquots of the reaction mixture are transferred to the flask C by applying pressure at g and opening the stopcock e to allow the flow of the solution from A to C, which is cooled in salt/ice mixture to quench the reaction. A quenching reagent may be used instead. The concentration of a reactant and/or product is determined in the collected aliquots by a suitable method as quickly as practicable. If spectrophotometry is used, a spectrophotometer cell is filled with a reaction mixture, slightly warmed to stop condensation on the cell walls and the spectra quickly recorded at the suitable wavelength(s). If a thermostatted cell is available, the separate reactant solutions are thermally equilibrated at the desired temperature before quickly being mixed in the cell which is maintained at this temperature. Fast scan spectrophotometers would be very useful and only the spectra in the range of interest are recorded at intervals (on the same paper).

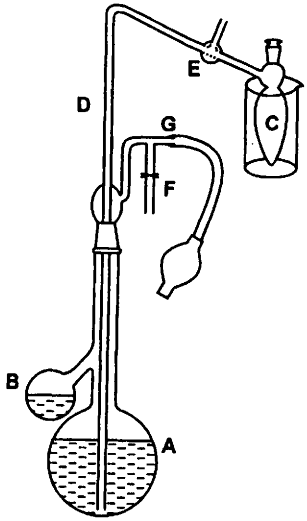


Figure 2.12 Apparatus for kinetic studies of homogeneous reactions in solution (the front cover is an actual picture)

2.11.2 Reactions accompanied by gas evolution

When a homogeneous or heterogeneous reaction produces a gaseous product, the reaction can be followed by measuring or recording the volume of gas as a function of time.

When the rate of gas formation is not very fast, an apparatus depicted in Fig.2.13 can be used. One reactant solution is pipetted into the thermostatted funnel A and the other reactant is placed in flask B. When both are thermally equilibrated by water pumped from a thermostat into their jackets, by opening the funnel's stopcock, the solution in A is mixed with the contents of B while magnetically stirring throughout the run. The gas evolved is collected in the gas burette C and its volume measured at timed intervals after adjusting the level of liquid in the tube D with that in C and simultaneously noting the temperature of the thermometer attached between C and D and the atmospheric pressure on a barometer in the laboratory. For precise data, the atmospheric pressure is corrected for the water vapour pressure at the same temperature as C and D. In this case, the volumes measured are adjusted to give values at the same temperature and pressure.

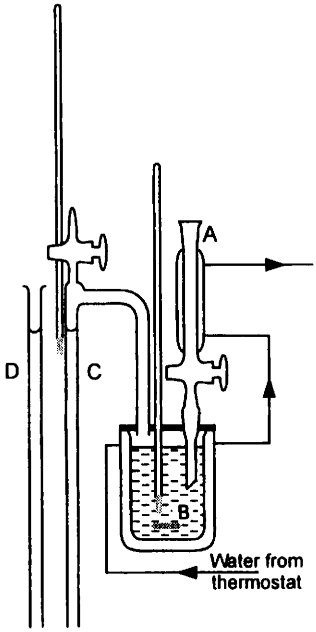


Figure 2.13 Apparatus for studying a reaction accompanied by gas evolution.

When a physicochemical process is accompanied by fast evolution of a gas, a simple apparatus (Fig.2.14) can be used to follow the kinetics. One reactant is placed in flask E whereas the other component is pipetted into flask F. Flask E has a magnetic follower and both flasks can be thermostatted by surrounding them with a large beaker with water at a given constant temperature. F has a side tube connected to the tip of a syringe G whose plunger is initially pushed fully inwards. The plunger's head is in contact with a slide wire potentiometer H. The signal generated by the movement of the plunger drives a chart recorder J, whose chart speed is adjustable. The reaction is started by rotating the ground joint of E by 180° so that its contents are mixed with the contents of F. Another apparatus is described in *J.Chem.Soc.Faraday Trans.-A*81(1985)1113.

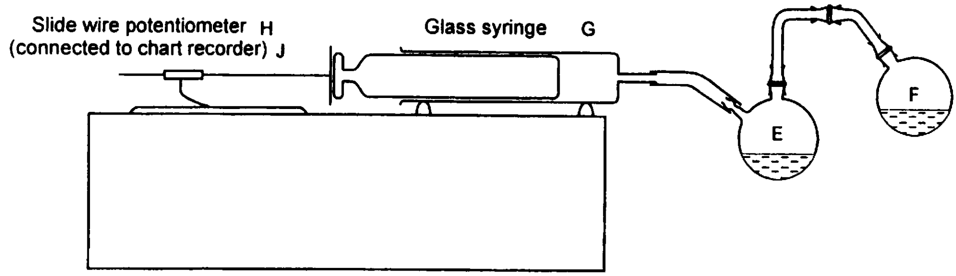


Figure 2.14 A sketch of an apparatus for studying reactions accompanied by fast evolution of gas.

2.11.3 Reaction between a solid and a solution

Fig.2.1 can be used for studying such reactions. The weighed solid is introduced in the double-walled beaker, preferably covered with a measured volume of water. The suspension is magnetically stirred while running water from a thermostat in the space between the two beakers. A known volume of a solution of the other reactant thermostatted at the same temperature is pipetted (and if necessary nitrogen is passed through the suspension), while continuously stirring. At suitable intervals, small amounts of solution are sucked through the sintered glass stick and a suitable volume is pipetted for measurement of the concentration of a reactant and/or product by a suitable technique. If a probe which is unaffected by the solid but responds to either reactant and/or product is available, this can be used instead of the filter stick and its readings give the concentration at suitable intervals.

2.11.4 Order and energetics of reactions *(J.Espenson, Chemical kinetics and reaction mechanisms, McGraw Hill, New York, 1981)*

To understand the mechanism of a reaction, it is essential to establish not only its stoichiometry but also its order. This may be 0,1,2 or rarely 3. In addition, the energetics of the reaction are helpful diagnostic indicators of the mechanism. Especially the free energy, enthalpy and entropy of activation have to be determined from kinetic results at different temperatures.

When the rate of the disappearance of a reactant is represented by:

$$-dc/dt=kc^n \qquad (2.74),$$

where c is the concentration at time t, k is the rate constant, n is the order of the reaction. To test for a first order reaction with respect to a reactant whose concentration is c, it is usually convenient to plot log c against t, when a linear plot indicates a first-order reaction i.e.

$$kt=\ln(c_o/c_t)$$

where the subscripts refer to initial time (t=o) and time t. Another test is to determine the time at which half the reactant has disappeared, $t_{0.5}$, using different initial concentrations since:

$$t_{0.5}=\ln 2/k \qquad (2.75)$$

(see also, *J.Chem.Educ.***62**(1985)802; **63**(1986)888; **67**(1990)459).

For second or third order kinetics, it is usually possible to keep the concentration of one reactant ~10 times that of a second reactant and follow the concentration of the second, in which case, a linear plot of log c against time indicates first order for that reactant. Otherwise, when using equal concentrations of both reactants, determine the concentration at various times. A linear plot of 1/c against t indicates a **second order reaction.** Using $t_{0.5}$ method, the order n is related to $t_{0.5}$ by:

$$t_{0.5} \text{ is proportional to } 1/ka^{n-1} \qquad (2.76)$$

A time to complete a certain fraction of reaction, τ, may be used and then (2.76) becomes:

$$\tau \text{ is proportional to } 1/a^{n-1}$$

Third order and fractional order reactions are less common. Reversible and consecutive reactions are dealt with in textbooks of chemical kinetics. It can be shown from the **theory of absolute reaction rates** that the rate constant is related to the **free energy of activation** ΔG_a, by the relation:

$$k = (kT/h)e^{-Ga/RT}$$

where k nd h are Boltzmann and Planck's constants and R and T have their usual significance. Since ΔG_a is related to the activation parameters ΔH_a and ΔS_a, the latter can be determined from the relation:

$$\ln(kh/kT) = \Delta S_a/R - \Delta H_a/RT \qquad (2.77)$$

A linear plot of ln(kh/kT) against 1/T will have a slope of $-\Delta H_a/R$ and the intercept $=\Delta S_a/R$. These activation parameters especially the sign of ΔS_a may be helpful in elucidating reaction mechanisms.

2.12 NUCLEAR AND RADIOCHEMICAL TECHNIQUES

(*Anal.Chem.*56(1984)199R; R.A. Faires; G.G.J. Boswell, *Radioisotope Laboratory Techniques*, 4th ed., Butterworths, London, 1981).

2.12.1 Measurement of radiation

A sensitive photographic strip is worn by regular users of isotopes to monitor the radiation dose to which they have been exposed, when the strip is developed. Generally counting α- or **β-particles** or γ **rays** depends on their energy and the physical state of the source. Either gas ionisation, scintillation or semiconductor counters are used.

When a positive central wire is placed in a negatively charged cylinder containing an inert gas, ionising radiation reaching the gas will produce positive inert gas ions and electrons which are collected by the wire. Depending on the voltage applied and cylinder design, the counter is classified as an **ionisation chamber**, a **proportional** or a **Geiger-Muller, G-M, counter.** At low voltages, the output pulse from an α source will be > that of a β sample. The ionisation chamber is suitable for counting of an α **emitter** or energetic β sources. At higher applied voltages, the energetic ejected electrons cause further ionisation but the pulse sizes are proportional to the primary ionisation and the counter is a **proportional counter** still with α/β discrimination. The proportionality becomes limited at higher voltages until the tertiary or even quaternary ionisation fills the gas space in the G-M region where no α/β discrimination is possible. A common G-M counter has an **end window** through which the particles enter. The material and thickness of the window depend on the type and energy of the particles to be counted. To stop self-perpetuating ionisation, either external or internal (chemical) quenching is used. The suitable voltage to be applied to a G-M counter is at the mid-point of its **plateau** which is the region where the count rate does not change rapidly on increasing the voltage. γ rays are not usually counted by ionisation counters because of their poor ionising power. Instead, they are counted in **solid scintillator counters.** A NaI/Tl(doped) crystal scintillator is usually enclosed in a sealed Al case. When γ rays penetrate it, light pulses are produced which are linearly related to the γ energy. Scintillation photons falling on a photocathode produce photoelectrons collected in a multiplier. However, the high potential in the multiplier produces thermionic emission even in the absence of radiation. This **thermal noise,** which can be reduced by cooling, has to be taken into account together with the **background counting** (common to all counters). In a γ spectrometer, either integral or differential counting can be carried out. In the former, all pulses whose height exceeds a set limit are counted, but in the latter, a **pulse height analyser**, allows pulses of height between 2 set limits to be registered. Solid scintillators are also available for β counting (pure organic compounds) or for α counting (doped ZnS). For very weak β emitters, **liquid scintillation counting** is necessary. The liquid scintillator, generally with a suitable solvent, is mixed with the active sample, preferably dissolved, and the light pulses produced are sensed by 2 photomultipliers. Only pulses reaching both are counted, thus minimising background pulses.

2.12.2 Neutron activation analysis (M.W. Rophael; M.A. Malati, *Chem.Labor Betrieb.* 34 (1983)51)

An intimate mixture of an α emitter and Be will produce neutrons with a range of energies. When these are moderated i.e. slowed to thermal energy, they can induce an **(n,γ) reaction** in some nuclei. This can be represented by:

$$^{A}X+{}^{1}n\rightarrow{}^{A+1}X+\gamma \qquad (2.78)$$

The isotopic product, being richer in neutrons, is likely to be a β^- emitter and its activity can be measured without prior separation from the target. High energy neutrons induce other nuclear processes. Although the activity of ^{A+1}X builds up as neutron irradiation continues, it will simultaneously decay usually by the process:

$$^{A+1}X\rightarrow{}^{A+1}Y+\beta^-+\nu \qquad (2.79),$$

where ν is an **antineutrino,** which escapes detection. It can be shown that after irradiation for 7 half lives, the activity attains a practically constant value; the **saturation activity.** This can be calculated from a knowledge of the **neutron flux** i.e. number $s^{-1}m^{-2}$ and the neutron **activation cross section** of ^{A}X (in m^2) as well as its mass and RAM. However, it is usually easier to activate a standard with known mass of X and count its activity under identical conditions of activation and counting, as the sample. Then:

$$A_1/A_2=W_1/W_2 \qquad (2.80).$$

where A refers to activity and W refers to mass and 1 and 2 stand for sample and standard respectively.

References

1 *Analytical Instrumentation Handbook,* 2nd ed., Ed.G.W.Ewing, Marcel Dekker New York, 1997.

2 D.A.Skogg; J.J.Leary, *Principles of Instrumental Analysis*, 4th ed. Saunders College Publishing, Fort Worth, 1992.

3 R.D.Braun, *Introduction to Instrumental Analysis*, McGraw Hill, New York, 1987

4 D.T.Sawyer; W.R.Heineman; J.M.Beebe, *Chemistry Experiments for Instrumental Analysis*, John Wiley, New York, 1984.

5 G.Pass; H.Sutcliffe, *Practical Inorganic Chemistry*, 2nd ed., Chapman and Hall, London, 1974.

6 D.M.Adams; J.B.Raynor, *Advanced Practical Inorganic Chemistry*, John Wiley, London, 1965.

7 R.J.Angelici, *Synthesis and Technique in Inorganic Chemistry,* 2nd ed., Saunders, Philadelphia, 1977.

Also References 4 and 5 from Chapter 1. Some parts are useful in: *Experimental Organic Chemistry* L.M.Harwood, C.J.Moody, Blackwell, Oxford, 1984.

3

The *s* Block Metals

3.1 INTRODUCTION

The *s* block comprises metals in group 1 : the alkali metals, and metals in group 2 : the alkaline-earth metals. By losing their outer s electrons, the alkali metals form M^+ ions and the alkaline-earth metals form M^{2+} ions. These are preferentially formed by the latter metals in spite of the higher ionization energy because this is more than compensated by the lattice energy of the solid M(II) compounds or the hydration energy of the M^{2+} ions in solution. The M^{2+} ions are smaller than the preceding M^+ ions and in both cases, the ionic radius increases down the groups. In the solid alkali metals, the lattice is not close packed unlike most of group 2 metals. The conduction band of the latter has 2 electrons contributing to the metallic band compared to one electron in the alkali metals where the metallic bonding in the solid is weaker. Accordingly the alkali metals are lighter and have lower melting points than their neighbours in group 2. Hence the alkali metals are more reactive than the neighbouring alkaline-earth metals, reactivity increases down each group. Although most of the *s* block metal compounds are ionic, as the polarising power of the cation increases, departure from ionic character is encountered especially in compounds with large and more negatively charged anions. The ionic potential Φ, which is equal to the cation charge/its radius, may be taken as a measure of polarising power. Φ decreases down each group but it is higher for group 2 than their alkali metal neighbours. Thus Be compounds show the greater departure from ionic character. Parallel to this is the tendency to form complex and covalent compounds. Accordingly, group 2 metals form more numerous and more stable complexes than the alkali metals... Because of the higher lattice energy of group 2 salts, they form more insoluble salts than those of group 1. However, solubility depends on the free energy of solution. This represents a difference between two large and opposing energy terms : the lattice energy, which is endothermic in the relevant Born Haber cycle, and the free energy of hydration which is exothermic. Generally the two terms vary with the charge and size of the ions in a similar trend. As a result, solubility of a series of salts may increase or decrease down a group. On the other hand, the basic character of the hydroxides, though higher for MOH than $M(OH)_2$, it increases down the group. Cations having a high Φ generally give less thermally stable compounds than those of the preceding alkali metal salts. Thus the oxosalts of group 2 metals are thermally less stable than those of group 1. This is related to the difference in the lattice energy between the reactant and the solid product.

3.2 QUALITATIVE TESTS

3.2.1 Tests on the metals

The metals Li, Na, Ca and Ba are kept under oil to avoid contact with atmospheric moisture and oxygen. Use small pieces (about 2mm in diameter), dry between filter paper and carry out the following tests.

(a) Cut the metal piece with a knife, note its hardness and the appearance of the freshly cut surface. Compare the trend down the group and the difference between the two groups.

(b) Place a piece of metal (or 1 cm of Mg ribbon) in a clean dry crucible. Heat gently at first and then more strongly if necessary. When the reaction subsides, cool the crucible and divide the product into two parts. Add to a part:

  (i) some water, note the solubility and test with a red litmus paper;

  (ii) some NaOH solution (except in the case of Na), heat and expose to any gases a Hg(I) nitrate paper.

(c) Place about 20 cm^3 of water in a basin, fill a test tube with water and, with your thumb on its mouth, invert it and dip it in the water (the atmospheric pressure keeps it filled). Carefully (by using tweezers) place a piece of Li or Na under the mouth of the tube. If a gas collects in it, test with a small flame.* When the reaction subsides, test the solution with red litmus paper and add some solution to copper (II) sulphate solution.

(d) Add 10 cm^3 water to a boiling tube, add a piece of Ca or Ba in the water, quickly insert a glass wool plug near the mouth of the tube and expose a small flame. If the reaction is sluggish in the case of Ca, warm gently. Test the product of reaction with red litmus paper.

(e) Repeat test (c) using ethanol instead of water.

(f) To a piece of Ca or 1 cm Mg ribbon, add 2 cm^3 dil. HCl. Compare the difference in the vigour of reaction. For Mg use 2 cm^3 of water and note any effect with warming.

3.2.2 Tests on oxides and hydroxides

Use the solids: Li_2O, Na_2O_2, LiOH, NaOH, KOH, MgO, $Ba(OH)_2$ and freshly prepared CaO, obtained by strongly heating the carbonate.

(a) Leave a pellet of the alkali metal hydroxides on a watch glass exposed to air for an hour:

(b) Test the solubility of each solid in water (about 0.1 g in 3 cm^3 water), heat if necessary and test the solution or suspension with a pH stick.

(c) Prepare a solution of the hydroxides in water and add to separate portions:

  (i) iron(III) chloride solution;

  (ii) solid ammonium chloride, heat and expose a wet mercury (I) nitrate paper;

(d) Add ice cold water to sodium peroxide, shake and slowly add an ice cold very dilute acidified permanganate solution:

(e) Repeat using warm water in a tube with glasswool plug at the top, heat and expose a glowing splint:

(f) Repeat using water, add Cr(III) chloride solution, heat until the colour changes.

(g) Saturate a few cm^3 of water with CaO, note any change of temperature and shake to saturate. Filter and pass carbon dioxide through the clear filtrate. Note the effect of more carbon dioxide.

3.2.3 The effect of heat on the oxosalts

Use the carbonates or nitrates of Li, Na, K, Mg, Ca and Ba.

(a) Heat each carbonate and pass any evolved gas through clear lime water. Alternatively, suck the gas above the solid in a Pasteur pipette and transfer the gas to a little lime water.

(b) Repeat using sodium bicarbonate or its solution.

(c) Heat each nitrate in a tube provided with a glass wool plug near its mouth, test any gas(es) with a glowing splint and a moist blue litmus paper. Cool the residue, add water and test the solution or suspension with pH stick.

(d) Repeat for Na or K nitrates but cool the residue, shake with water and then add iron(II) sulphate solution acidified with dilute acid.

3.2.4 Solubility of the salts of the *s* block metals

The alkali metals have few insoluble salts with sodium having the smallest number. Whereas Li ions are precipitated by some anions, the heaviest alkali metals are precipitated by other usually large anions.

1. Prepare a solution of LiCl in water. Add to separate portions:
   - (a) potassium hydrogen phosphate after adding a little alkali, boil if no precipitate appears;
   - (b) sodium fluoride solution;
   - (c) ammoniacal ammonium carbonate solution.
1. Prepare a concentrated solution of sodium chloride and add to it a solution of magnesium or zinc uranyl acetate.
2. Prepare a solution of potassium chloride and add to separate portions:
   - (a) a solution of sodium hexanitrocobaltate(III);
   - (b) a concentrated solution of sodium perchlorate;
   - (c) a solution of hexachloroplatinic acid.

Rubidium and caesium salts behave similar to potassium salts. The **flame test** distinguishes each metal from the others especially if the coloured flame is viewed through a small spectroscope.

4. Subject the chlorides to a flame test.
5. To separate portions of magnesium sulphate solution add:
   - (a) sodium or barium hydroxide solution;
   - (b) sodium carbonate solution;
   - (c) disodium hydrogen phosphate solution;
   - (d) repeat (b) but in ammonia/ammonium chloride solution;
   - (e) 8-hydroxyquinoline in ammoniacal solution in presence of ammonium chloride, boil if no precipitate appears.
6. Prepare a solution of each of Ca, Sr or Ba chlorides or nitrates and add separately to portions of each solution:
   - (a) sodium carbonate solution;
   - (b) sodium oxalate solution;
   - (c) dilute sulphuric acid;
   - (d) saturated calcium sulphate solution;
   - (e) potassium chromate solution.

Note in each case trends in the ease of precipitation reflecting solubility trends.

3.2.5 Other Tests

- (a) Carefully add water to a small quantity of NaH and expose to any gas a small flame. When the reaction subsides test the solution with red litmus paper,
- (b) Repeat using CaH_2 instead of NaH,
- (c) Use total hardness test strips to test samples of tap and mineral water.

3.3 ANALYTICAL CHEMISTRY OF THE ALKALI METALS

Since these metals form few stable complexes or insoluble compounds, there are very few titrimetric or gravimetric analytical methods. Some instrumental methods are suitable.

Determination of alkali metal ions by ion-selective electrodes (Sec.2.5.1)

Use 0.01M stock solutions of the chlorides of Li, Na or K in deionised water. Prepare a series of solutions, by successive dilution, in the range 10^{-3}-10^{-5}M, dip the available ion-selective electrode, with a combined reference electrode, into each solution and use a pH meter or ion meter to read the mV or concentration reading. Plot the reading against [M^+] and use the standardisation plot to determine the concentration in an unknown solution.

Atomic absorption is also useful for the alkali metals, data are given with the data for group 2 metals in the next section. Although flame photometry is also suitable for the alkali metal, the difficulty of obtaining reproducible results makes the technique less reliable for quantitative work.

3.4 ANALYTICAL CHEMISTRY OF GROUP 2 METALS

Because these metals form more insoluble compounds and more stable complexes, titrimetric, gravimetric and instrumental methods are available for their determination.

3.4.1 Complexometric titrations

The stability of the alkaline-earth EDTA complexes decreases down the group as expected from the increased ionic radius. However, Ca^{2+} ions are exceptional in forming the most stable EDTA complex. For this reason, calcium cannot be titrated using the Erio T indicator, since no colour change to steel blue is observed. However, when a suspension of magnesium complexone is added, the calcium replaces magnesium in the complexone releasing Mg^{2+} ions which can be titrated. This replacement titration may be used to standardise EDTA solution.

Eriochrome black T (or solochrome black) is a satisfactory indicator in EDTA titrations. Between pH 7 and 11, the indicator is blue due to the predominance of the anion (HD^{2-}). Over this pH range, Mg^{2+}, Zn^{2+}, Mn^{2+} or M^{3+} (M=lanthanide) give red complexes. On titrating these metal ion solutions, the solution is red until the end point is reached, when it assumes the blue colour of HD^{2-}.

With the exception of Be, the four alkaline-earth salts in solution can be determined by direct titration with standard EDTA solution at pH 12 using bromothymol blue indicator.

3.4.1.1 Complexometric determination of barium

Prepare 0.01 M solution of purest barium chloride or nitrate. Pipette 25.0 cm^3 into a conical flask, add ~75 cm^3 water and a few cm^3 of M NaOH to give a pH 12 ±0.5 (use a pH meter to check) and dissolve in the solution 50 mg methylthymol blue/potassium nitrate mixture (containing 1% w/w indicator). Titrate with standardised 0.1 M EDTA solution until the colour changes from blue to grey. Similarly, Mg^{2+}, Ca^{2+} or Sr^{2+} can be titrated.

3.4.1.2 Standardisation of EDTA solution

Pipette 25.00 cm^3 of standard 0.10 M calcium salt solution into a 250 cm^3 conical flask. Dilute to about 100 cm^3 and add 2 cm^3 of the magnesium complexonate suspension (shake before use), 5 cm^3 of the buffer solution (pH = 10) and 2-3 drops of Erochrome Black T indicator. Titrate with the approximately 0.1 M EDTA solution to a steel blue end point. Repeat to obtain concordant results. Calculate, from the average titre, the concentration of EDTA as mol dm^{-3}. Alternatively use accurately weighed ~ 0.2 g purest calcium carbonate dried at 105°C, add water and dil. HCl to dissolve. Boil to expel carbon dioxide dilute to 100 cm^3 and continue as above.

3.4.2 Gravimetric analysis

Each of the alkaline-earth metals can be determined gravimetrically by at least one method but a specific precipitant is used for each. In the three examples described below, the conditions required in each case are described.

3.4.2.1 Gravimetric determination of magnesium

Magnesium ions in its salt solutions can be precipitated as ammonium magnesium phosphate hexahydrate by an excess of a solution of diammonium hydrogen phosphate. The small solubility of the precipitate in water is overcome in presence of ammonia. The precipitate can be washed with ethanol and ether and dried in air or it can be converted to magnesium pyrophosphate by heating in a muffle furnace.

Prepare a solution of 6 g purest magnesium sulphate in 250 cm^3 water. Pipette a 25.0 cm^3 aliquot into a 400 cm^3 beaker. Add 5 cm^3 conc. HCl, 125 cm^3 water and a few drops of methyl red indicator. Dissolve 25 g of the purest $(NH_4)_2HPO_4$ in 100 cm^3 of water and add to the beaker 10 cm^3 of the freshly prepared solution, slowly and with stirring, until the colour changes to yellow and then add ammonia solution dropwise, with stirring, to keep the colour yellow and then add 5 cm^3 conc. ammonia. Cover the beaker with a watch glass and allow it to stand at a temperature <25°C for >4 hours. Filter through a prepared sintered glass crucible and wash with small volumes of 0.8 M ammonia until the filtrate does not give turbidity with acidified silver nitrate. Then wash with small volumes of ethanol and then with small volumes of dried ether. Continue suction for 10 minutes and allow to stand in a desiccator before weighing.

Repeat using a prepared sintered porcelain crucible for filtration. Proceed as above until the filtrate is chloride free. Then dry the crucible in an oven at 150°C for an hour and then gradually heat in a muffle furnace to 1100°C to constant weight. Calculate from each experiment the concentration of magnesium in mol dm^{-3}.

3.4.2.2 Gravimetric determination of calcium

When a hot solution of a calcium salt in HCl is treated with ammonium oxalate, calcium oxalate monohydrate is precipitated. The small solubility of the precipitate in water is reduced in ammonium oxalate solutions (common ion effect). The precipitated calcium oxalate is washed, dried and weighed. However, because of its hygroscopic nature and the possibility of coprecipitation, it is preferable to convert it to the carbonate in a muffle furnace.

Prepare a solution of 5 g purest calcium carbonate in dilute HCl. Heat to dissolve the powder and then boil to expel carbon dioxide, cool and make up to 250 cm^3. Pipette 25.0 cm^3 of the solution into a 400 cm^3 beaker, add 175 cm^3 water and a couple of drops of methyl red indicator. Heat so that the solution boils gently and then add slowly a warm solution of 2 g purest ammonium oxalate in 50 cm^3 solution. Ensure that the temperature of the suspension is ~80°C and then add, dropwise and with constant stirring, a filtered 1:1 ammonia solution until the colour changes to yellow. Allow to cool, after covering with a watch glass and stand for an hour. When the precipitate settles, check for complete precipitation with a little oxalate solution. Filter through a prepared sintered glass crucible. Dry at 105°C to constant mass.

Repeat using a sintered porcelain crucible instead of the glass crucible. Follow the procedure as above until the precipitate settles after standing for an hour. Decant the supernatant into the crucible. Transfer the precipitate with a jet of water and with the aid of a "policeman" to the crucible. Wash with small volumes of 0.1% ammonium oxalate until the filtrate is chloride-free. Dry at 120°C for an hour and then heat gradually in a muffle furnace at 500° ± 25°C to constant weight. Calculate from each experiment the concentration of calcium in mol dm^{-3}.

3.4.2.3 Precipitation followed by titrimetric determination of calcium

When the precipitated calcium oxalate is dissolved in hot dilute sulphuric acid, the oxalic acid liberated can be titrated against standardised permanganate.

Precipitate calcium oxalate as described above, filtering through GF paper. After washing the precipitate on the filter, transfer it carefully and quantitatively into a conical flask, add dilute sulphuric acid and heat to dissolve making sure of the presence of excess acid. Heat to 80°C and titrate against standardised permanganate to the first faint pink colour, ensuring that the temperature is maintained at 70°-80°C. Repeat and calculate from the average titre the concentration of calcium in mol dm^{-3}.

3.4.2.4 Gravimetric determination of Ba as $BaCrO_4$

Ba^{2+} ions in solution, which is buffered by CH_3COOH/CH_3COONH_4, are precipitated by the addition of $(NH_4)_2CrO_4$ solution, prepared by adding NH_3 to $(NH_4)_2Cr_2O_7$ solution.

Pipette 25.0 cm^3 of 10^{-3} M Ba^{2+} solution (or weigh out accurately about 0.3 g of purest $BaCl_22H_2O$ and dissolve in H_2O and dilute to ~190 cm^3. Ensure that the solution is neutral and then add 10 cm^3 of 0.6 M CH_3COOH solution and 10 cm^3 of neutral CH_3COONH_4 solution. Heat the solution to boiling and add the hot $(NH_4)_2CrO_4$ solution (prepared by the method given below), dropwise with constant stirring, until present in slight excess. Stand the solution on a hot water bath until the precipitate settles and test for complete precipitation. Allow to cool and filter through a No.4 sintered glass crucible, previously dried to constant weight. Wash the precipitate with hot H_2O until 1 cm^3 of the washings gives scarcely any colour with neutral $AgNO_3$ solution. Then dry to constant weight at 120°C and weigh as $BaCrO_4$. Duplicates are required. Calculate the average barium concentration in mol dm^{-3} in the solution.

Preparation of $(NH_4)_2CrO_4$ solution.

Dissolve 10 g purest $(NH_4)_2Cr_2O_7$ in 100 cm^3 H_2O and add filtered dilute NH_3 solution until the solution is clearly yellow and distinctly alkaline (~40 cm^3 will be required). When this solution is heated, it should be maintained clearly yellow and distinctly alkaline (if necessary) by further addition of dilute NH_3 solution.

3.4.3 Instrumental methods

The most general method for both groups is atomic absorption (Sec.2.4.3). Follow the recommendations of the manufacturers of the instruments in preparing the solutions, the appropriate gas mixture, gas flow rates etc. The main wavelengths, λ, of measuring are given below.

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
λ/nm	670.8	589.0	766.5	780.0	852.1	234.9	285.2	422.7	460.7	553.6

High frequency titration

In theory when two electrolyte solutions react and produce a sparingly soluble product, high frequency titration can be used for the determination of either constituent of the precipitate. An example of this is the titration of calcium ions by a solution of a soluble oxalate. A different basis of high frequency titration depends on the titration of a highly conducting solution against another highly conducting solution when a product of low conductivity is produced. An example of this is the titration of a beryllium salt solution with NaOH solution.

3.4.3.1 Titration of calcium ion solution against oxalate solution

Prepare a 0.001 M solution of purest calcium chloride or nitrate and a 0.01 M solution of purest alkali metal or ammonium oxalate. Pipette a suitable volume of the calcium salt solution into the high frequency titration vessel and add the oxalate solution from a burette while magnetically stirring. Record the readings at suitable added volume intervals and plot reading against volume of titrant. Resolve the plot into two straight lines and locate the point of intersection and compare it with the theoretical equivalence point.

Determination of calcium using an ion-selective electrode

Calcium-selective electrodes are available commercially. The electrode is coupled with a reference electrode and the e.m.f. of the cell is measured using a millivolt meter or an ion meter.

Prepare a stock solution of 10^{-2}M calcium chloride or nitrate. By successive dilutions, prepare a series of solutions in the range 10^{-3}-10^{-5}M. Use an aliquot of each solution in a beaker in which the two electrodes are immersed and measure the mV reading when it settles. Plot the readings against $[Ca^{2+}]$ and use the standard curve to find the concentration in an unknown solution.

3.5 SURFACE CHEMICAL STUDY OF THE *s* BLOCK

3.5.1 The adsorption of the *s* block ions by precipitated silica

The adsorption of the alkali metal and alkaline-earth metal ions by adsorbents e.g. precipitated silica, is interesting since it reveals the effects of the size and charge of the ions on the energetics of adsorption. Precipitated silica has a high adsorptive capacity and is a suitable candidate for the study.

3.5.2 The adsorption of Na^+ and of Cs^+ ions on precipitated silica

The choice of these two ions represents a sufficient difference in their size to be reflected in the energetics of adsorption.

Weigh out 1.0 g portions of precipitated silica into round bottom polypropylene centrifuge tubes. Prepare a stock solution of 0.01 M solution of purest sodium or caesium nitrate in deionised bidistilled water. Prepare by successive dilution a series of solutions in the range 10^{-3}-10^{-5} M. Pipette a 20.0 cm^3 aliquot of the most concentrated solution into the tube containing the silica. Shake in a shaking thermostat or preferably an orbital incubator at a constant rate and at 25°C for 1, 1.5, 2, 2.5 and 3 hours using a different suspension for each. At the end of shaking, centrifuge and withdraw an aliquot of the supernatant for the determination of $[Na^+]$ or $[Cs^+]$ by a suitable instrumental method. Repeat using the most dilute solution. Once the time to reach adsorption equilibrium is established, carry out the series of tests using 1.0 g of silica and 20.0 cm^3 of each of the sodium or caesium solutions shaken for the determined time at 25°C. At the end of the shaking period, centrifuge and determine the equilibrium concentration as above. Hence calculate the amount adsorbed and plot it against the equilibrium concentration. Repeat the series for the solutions of the other ion and check the applicability of Langmuir's adsorption isotherm. Repeat the runs using two or three other temperatures in the range 5°- 60°C.

3.5.3 The adsorption of Ca^{2+}, Sr^{2+} or Ba^{2+} ions on precipitated silica

These three ions represent a gradual change in size and they are usually involved in ionic reactions. It is also useful here to convert the silica surface to the K^+ form by prior equilibration with 0.01 M potassium nitrate solution. Such a solution is used to prepare solutions of the nitrates of the three metals so that the ionic strength is nearly constant in the runs.

Weigh out 1.0 g of precipitated silica as above. Prepare a stock of 0.01 M potassium nitrate and pipette 25.0 cm^3 of the solution into each centrifuge tube. Shake as above for 3 hours, centrifuge and withdraw 20.0 cm^3 of the supernatant solution and replace it by an alkaline-earth nitrate solution. Prepare a stock 0.01 M solution of each nitrate in 0.01 M KNO_3 and using the latter solution for dilution. Prepare a series of solutions in the range 10^{-3}-10^{-5} M. Determine the time required to attain adsorption equilibrium at 25°C as described above. Use this determined time and shake the silica/$M(NO_3)_2$ suspension at 25°C before centrifuging and withdrawing an aliquot of the supernatant for the determination of the cation by a suitable method. Repeat at two or more temperatures in the range 10°-45°C. Treat the data as above. If the Langmuir adsorption isotherm is found to apply, calculate the heat of adsorption. Compare the results with those obtained for Na^+ and Cs^+.

3.5.4 The isoelectric point of precipitated barium sulphate

Although barium and sulphate ions are evidently potential-determining for barium sulphate, the ξ potential (or electrokinetic mobility) may vary with pH in electrolyte solutions. The pH at which the particles do not move under a d.c. field is the isoelectric point (Sec.2.1.4).

Grind a little of purest precipitated barium sulphate to a very fine powder. Suspend a little of the powder in a large volume of 10^{-3} M NaCl or KNO_3 and disperse by sonication. Discard any settling particles and fill an electrophoretic mobility cell with the dilute suspension avoiding any air bubbles in the cell. Ensure that the electrodes have been covered with platinum black, and that the cell is at a constant temperature. Measure the pH of the suspension before filling the cell. Apply a d.c. current of say 50 V between the electrodes and measure the distance a particle travels in a short measured timed interval. Make the measurement at the predetermined stationary levels. Repeat the measurement 10 times and repeat the same procedure after reversing the polarity. Take the average of the 20 mobility measurements. Adjust the pH of another suspension and repeat. Using suspensions of pH values covering the range 3-10, plot the average mobility against pH taking into account the sign of the particles. Repeat using 10^{-3} M electrolyte solution. The two plots should cross at the pH where the mobility is zero, which is the isoelectric point.

4

Boron and Aluminium

4.1 INTRODUCTION

B and Al are the first two elements in group 13. Like other p block groups, the top element deviates from the general behaviour of the heavier elements. Thus B is not a metal unlike the typical metals: Al, Ga, In and Tl. Al resembles Be whereas B resembles Si: these are examples of diagonal similarity. However, it is convenient to consider B and Al in this chapter to highlight the differences in the ionic/covalent character of their compounds. These represent the +3 oxidation state which is dominant in the case of B and Al. Al(I) is unstable under ordinary conditions but the +1 oxidation state becomes more stable down the group and is more stable for Tl than the +3 state. Elemental B is not a reactive element especially when pure. Al, on the other hand, is a strongly electropositive metal and once the protective oxide layer on its surface is removed, it becomes readily attacked by acids or alkalis. The two normal oxides of boron are acidic but the two acids are very weak. The acid strength increases when B is complexed with organic compounds with two adjacent C-OH groups. Boric acids give an extensive range of borates. Al oxides, on the other hand, and the hydroxide are amphoteric and are attacked by both acids and alkalis. In fact Al metal dissolves in alkali solutions. There is a limited number of aluminates. The contrast between the covalent boron halides and Al halides is significant. Whereas AlF_3 has an ionic lattice, the chloride has a layer structure and a low melting point but the dimeric bromide and iodide have molecular lattices. This gradual change reflects the increased polarisability of the halide as its size increases. Al^{3+} is more polarising than the alkaline-earth ions M^{2+}. Hence Al compounds depart more from ionic character than the M^{2+} compounds. Parallel to this is the tendency of Al to form more numerous and more stable complex compounds, with a preference for chelating ligands containing coordinating O atoms. However Al^{3+} like Mg^{2+} has a[Ne] configuration. Hence aluminium compounds and complexes are diamagnetic and generally colourless. Boron, like other p block elements forms peroxosalts which liberate hydrogen peroxide on hydrolysis. Boron also forms tetrafluoroborates containing the tetrahedral anion derived from HBF_4. The salts hydrolyse in aqueous solution.

4.2 QUALITATIVE TESTS

4.2.3 Tests on boron compounds and borates

(a) Test the solubility of orthoboric acid in water, dip a pH stick in the solution.
(b) Test the solubility of the acid in ethanol.
(c) Heat the acid in a dry test tube, expose a blue cobalt paper to any condensing vapours.

(d) Add water to $NaBH_4$, repeat with orthophosphoric acid exposing a small flame to the mouth of the tube. Dip a pH stick in the residue.

(e) Prepare a solution of borax in water and add separately to small portions of the solution:
   (i) conc. sulphuric then carefully heat*;
   (ii) conc. HCl;
   (iii) a little conc. sulphuric acid and 5 times its volume of methanol in a small basin and ignite the alcohol (to be done in a fume cupboard);
   (iv) dil. HCl, dip a piece of turmeric paper and then dry it at 100°C;
   (v) silver nitrate solution;
   (vi) barium chloride solution;

(f) *The borax bead test.* Make a loop in a platinum wire. Dip the red-hot loop into powdered borax quickly. Heat in the flame until a colourless glass-like bead is formed on cooling. Moisten the bead and then dip it into a finely powdered salt of the following metals: Cr, Mn, Fe, Co, Ni or Cu. In each case, heat the bead in the lowest part of the reducing (luminous) bunsen flame. Note the colour when it cools then place it in the lower oxidising flame and note the colour when it cools. After each salt has been tested, heat the loop strongly to fuse the bead and remove it from the wire by jerking it, allowing the fused borax into some water.

(g) Add cold water to a little sodium peroxoborate, shake and decant some solution and add to it dropwise very dilute acidified permanganate. Heat the remainder after adding a glass wool plug near the top of the tube and test with a glowing splint.

4.2.2 Tests on aluminium and its compounds

4.2.2.1 Aluminium and its alloy (Devarda's alloy, mainly Al and Cu)

(a) Add to a little Al foil the following:
   (i) dil. HCl, if no effect, scratch the surface with a knife and expose a small flame near the mouth of the tube,
   (ii) mercury(II) chloride solution, shake for a few minutes, decant the liquid and repeat (i). Compare the results of (i) and (ii),

(b) To a little Devarda's alloy, add the following:
   (i) dil. NaOH, warm and expose a small flame,
   (ii) sodium nitrate solution and dil. NaOH; expose near the mouth of the tube a moist red litmus paper and a drop of conc. HCl,
   (iii) repeat (ii) using sodium nitrite solution.

4.2.2.2 Anhydrous Al_2Cl_6 and hydrated aluminium chloride

(a) Heat a little of the anhydrous chloride in a dry test tube and expose a moist blue litmus paper near the mouth of the tube.
(b) Repeat (a) with the hydrated salt, expose a blue cobalt paper.
(c) Add water to the anhydrous chloride, note any temperature change and test with a pH paper.
(d) Dissolve the hydrated chloride in water and test with pH paper.

4.2.2.3 Tests on aluminium salts and compounds

(a) Prepare a solution of the sulphate or chloride and add to separate portions:
   (i) NaOH solution dropwise, shake and continue adding;
   (ii) ammonia solution, shake and add more;
   (iii) disodium hydrogen phosphate solution, test the solubility of any precipitate in dil. HCl and separately in NaOH solution;
   (iv) sodium carbonate solution dropwise and then in excess.

(b) Mix a solid salt with sodium carbonate, heat on a charcoal block. When the residue is cool, add a drop of cobalt nitrate solution.

(c) Add a little water to a little $LiAlH_4$ and expose to any gas(es) a small flame. Test the residue with a pH stick. If a solid residue is left add NaOH gradually and shake.

4.3 ANALYTICAL CHEMISTRY OF BORON

Low concentrations of boron can be determined in water (0.4-0.6 mg dm^{-3}) by atomic absorption spectroscopy using nitrous oxide/acetylene flame (fuel rich) and measuring absorbance at 249.8 nm.

Titrimetric determination of boric acid

The acid is so weak that it cannot be titrated against strong alkalis but in presence of organic compounds with 2 or more adjacent -COH groups, which form a complex with boric acid, the latter can be titrated with strong alkali.

Weigh out accurately about 0.8 g of the purest acid and make up to 250 cm^3 with water in a volumetric flask. Pipette 25.0 cm^3 of the solution into a conical flask, dilute to 50 cm^3 with water, add a few drops of phenolphthalein and 3.0 g mannitol. Titrate with standard 0.1 M NaOH until the first pale red colour is detected. Repeat to obtain concordant results and calculate from the average titre the concentration of the acid in mol $dm^{-3.}$

4.4 PREPARATION AND CHARACTERISATION OF BORON COMPLEXES

The tetrafluoroborates are the more important complexes. Ammonium fluoride is usually the source of fluorine when these complexes are prepared.

4.4.1 Preparation of ammonium tetrafluoroborate

When boric acid is dissolved in sulphuric acid solution and the solution heated with ammonium fluoride, the ammonium tetrafluoroborate is formed.

Add carefully and slowly 15 cm^3 conc. sulphuric acid to 25 cm^3 of water stirred in a beaker cooled by iced water. Remove the coolant and add to the acid solution 6 g powdered boric acid and heat to dissolve it. Transfer to the fume cupboard and place on a hot plate/magnetic stirrer (Teflon-covered magnet). Add to the hot liquid, while stirring 15 g ammonium fluoride in small amounts (to avoid any loss of HF), continue heating below 100°C for half an hour. Allow to cool and then place in an ice/water bath to complete precipitation. When crystallisation seems complete, filter under suction. Dry by continued suction while pressing between filter paper. Transfer the crystalline product into a beaker containing 15 cm^3 acetone. Shake well and refilter and finally weigh your product to the nearest cg and calculate the % yield based on ammonium fluoride.

Recrystallise by dissolving the crude into a small volume of hot water to which 1 cm^3 of conc. ammonia has been added. Boil to precipitate any silica impurity. Decant the clear liquid or filter into a porcelain basin. Concentrate on a hot water bath and allow to crystallise by cooling. Collect the final product by filtration as above.

4.4.2 Preparation of thalium tetrafluoroborate *(J.Chem.Educ.*74(1997)1332).

The heavier metals in group 13 resemble Al but the tendency to form +1 compounds becomes increasingly significant down the group, so that Tl(I) compounds are generally more stable than Tl(III) compounds. Tl(I) behaves similar to other M^+ salts. $Tl[BF_4]$ is more useful to use than the ammonium complex in nonaqueous media.

The preparation described in the reference is based on the reaction between the metal and HBF_4 in presence of hydrogen peroxide. The two former reactants are not usually available.

4.5 ANALYTICAL CHEMISTRY OF ALUMINIUM

Aluminium can be determined by atomic absorption, the conditions being similar to those used for B except that the wavelength of measurement is 309.3 nm and that the optimum concentration is 0.1 - 0.3 of the range used for B.

4.5.1 Complexometric determination of aluminium

A known excess of EDTA solution is added to an aliquot of the aluminium salt solution, the excess is then titrated against standard zinc sulphate solution.

Prepare a 0.01 M solution of purest potassium or ammonium aluminium sulphate in a 250 cm^3 volumetric flask. Pipette 25.0 cm^3 of the solution into a conical flask, run from a burette 40.0 cm^3 of standard 0.01 M EDTA solution, add ammonia solution, dropwise with stirring, to bring the pH to 7-8 (use a pH stick to check the pH). Boil for a few minutes, cool and adjust the pH again as before. Add 50 mg of Solochrome black/potassium nitrate mixture and titrate quickly with standard 0.01 M zinc sulphate solution until a wine red end point is reached. Repeat to obtain concordant results. Calculate from the average titre the [Al(III)] in mol dm^{-3}.

4.5.2 Gravimetric determination of aluminium

8-Hydroxyquinoline is a chelating ligand (referred to as oxine) which forms insoluble complexes with a number of di- and trivalent metals. The oxinates of these metals contain 2 or 3 oxinate groups per metal ion. In the case of aluminium the complex has 3 chelating ligands. Complete precipitation takes place at pH values of 5-10.

Prepare a solution of 1.3 g purest ammonium aluminium sulphate, dissolve in water, slightly acidified with dilute sulphuric acid to prevent hydrolysis and make up to 250 cm^3 in a volumetric flask. Pipette 75.0 cm^3 of the prepared solution, add 1 cm^3 conc. HCl and dilute to about 100 cm^3. Prepare a 2% w/v solution of purest 8-hydroxyquinoline in 2 M acetic acid. Heat the aluminium solution to 70°-80°C and add, slowly with stirring, 25 cm^3 of the oxine solution. If a precipitate has not formed, slowly add 2 M ammonium acetate solution until a precipitate just appears. Heat to boiling and then add 25 cm^3 of the acetate solution, dropwise and with constant stirring. Check for complete precipitation by the appearance of a yellow supernatant (the colour of excess oxine). When cold, filter through a prepared weighed G4 sintered crucible. Wash the precipitate on the filter with cold water until the filtrate is colourless. Dry the crucible in an oven at 110°C to constant weight. Duplicate determinations are needed. Calculate from the average weight the [Al(III)] in mol dm^{-3}.

Semiquantitative determination of aluminium

Strips for the approximate determination of low concentrations of aluminium are available commercially. The colour produced by a reagent in the strip, when immersed in an $[Al^{3+}]$:10-250 ppm, is a semiquantitative test for the ion.

4.5.2.1 Fluorescence of 8-hydroxyquinoline (oxine) and its complex with Al

When a solution of oxine in ethanol is irradiated with a medium pressure mercury lamp, it emits fluorescence with a broad maximum at 429 nm. When the solution is made acidic or alkaline, the maxima shift to longer wavelengths. A shift to longer wavelengths also results from complexation with metal ions. Quantum yields of fluorescence have been reported at 80 K and were the same for the neutral or anionic ligand but slightly higher for Al oxinate *(Spectrochim.Acta* 22(1965)1803).

Prepare a concentrated solution of oxine in ethanol. Expose it to a medium pressure mercury lamp and observe the fluorescence. If a spectrofluorometer is available, measure the intensity of the emission at ~430 nm. Saturate ethanol with the precipitate obtained in the gravimetric method and carry out the same procedure on the solution. If possible measure at 490 nm.

4.6 COMPLEX COMPOUNDS OF ALUMINIUM

Al^{3+} ions, like other metal ions with noble gas configuration, form preferentially complexes with oxygen-coordinating ligands. Unlike boron, which forms tetrahedral complexes, the larger aluminium ion forms octahedral complexes with the chelating ligands which stabilise the complexes by the chelate effect. Aluminium oxinate, already mentioned for the determination of aluminium, is an example of an octahedral complex where the O and N of the ligand are coordinated to the aluminium in a six coordinate neutral complex. Even the aluminate ion is best represented as $[Al(H_2O)_2(OH)_4]^-$. The major exception is $[AlH_4]^-$ ions, which are tetrahedral.

4.6.1 Preparation and analysis of potassium trisoxalatoaluminate (III) trihydrate

Like trivalent 3d transition metal ions, Al^{3+} readily forms the oxalato-complex where the two oxygens of the ligand are coordinated to the metal. The complex can be readily prepared by reacting potassium aluminate (formed by dissolving the metal in KOH) with oxalic acid. Adding ethanol leads to the precipitation of the complex.

The percentage oxalate can be readily determined by titration against permanganate after heating with sulphuric acid.

Weigh 1 g of aluminium shavings into a 200 cm^3 beaker. Add 10 cm^3 water and 30 cm^3 KOH (20% w/v) solution, added slowly. After the evolution of gas subsides, heat to boiling until all the metal has dissolved. If necessary filter from any residual impurity through GF paper. Add 10 cm^3 water to the filtrate, heat to boiling and then add 14 g of powdered oxalic acid dihydrate in portions until the precipitate first formed just disappears on continued boiling. Filter under suction, cool the filtrate and then add 50 cm^3 ethanol, cool in ice/water when crystallisation starts. Shake vigorously to induce crystallisation. When this seems to be complete, filter under suction, wash the crystals on the filter by an equivolume ethanol/water mixture. Dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on Al.

Weigh out accurately about 0.2 g of your preparation into a weighed Pyrex container. Place in an oven at 105°C and heat to constant weight. Calculate the % water of crystallisation.

Weigh out accurately about 0.2 g of your preparation into a 200 cm^3 beaker, add 50 cm^3 dilute sulphuric acid. Heat to boiling and titrate with standardised 0.02 M permanganate solution to the first very faint pink end point. At the end point, the temperature should be about 80°C. Repeat and calculate from the average result the % oxalate and hence the % purity of your preparation.

The solution in sulphuric acid, after appropriate dilution, can be used to determine the % K and % Al by atomic absorption.

4.6.2 Preparation and characterisation of $[Al(C_5H_7O_2)_3]$

Aluminium nitrate reacts with pentane 2,4-dione (acac) in alkaline media to form the six coordinate neutral complex Fig.4.1. This can be characterised by elemental analysis and ir spectra.

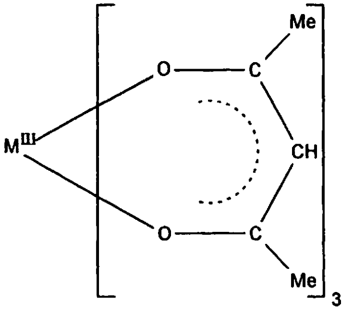


Figure 4.1

Weigh out 8 g aluminium nitrate nonahydrate into a beaker, add 50 cm^3 water to dissolve the solid. Stir the solution well, add 2.5 cm^3 of the dione and then add dropwise 2 M ammonia solution until the solution is alkaline. Cool in ice until crystallisation seems complete. Filter under suction while pressing between filter paper and then dry at 70°C. Weigh your product to the nearest cg and calculate the % yield based on Al.

Obtain elemental analysis of your product. Determine its m.p. Check its solubility separately in water and in organic solvents. Compare the solubility of this complex with the one prepared in Sec.4.6.1 above and comment on your observations.

4.6.3 I.r. spectra of the complexes

Grind each of the two prepared complexes to a fine powder. Prepare a KBr disc of each and run an ir spectrum. Assign the bands and compare them with the bands of the ligands.

5

The Carbon Group

5.1 INTRODUCTION

Among the groups of the p block, the greatest difference between the top and bottom elements is found in this group. The top element carbon is a typical non-metal while the heaviest member of the group: lead is a typical metal. The elements Si, Ge and grey Sn are semiconductors with decreasing band gap energy down the group. Their structure is like that of diamond the insulator. The formation of tetrahedrally arranged σ bonds is the preferred mode of bonding in carbon compounds. Carbon compounds are dealt with in organic chemistry. Because of the ability of carbon to form π bonds with other carbon atoms or with N or O, carbon compounds are different from Si compounds; CO_2 is a gas whereas SiO_2 is a giant molecule. The oxidation state of +4 is the prevailing state in silicon compounds. Silicon, like carbon, prefers tetrahedral coordination. Silicon is surrounded by four oxygens in silicates, sharing of O between tetrahedra leads to the large number of silicate structures. Silicon differs from carbon in its ability to expand its valence shell beyond 8. Hence six coordination is encountered in $[SiF_6]^{2-}$. Silicon has available d orbitals and this explains some differences between C and Si compounds. The oxidation state of +2 starts to appear in Ge and becomes more stable down the group. Thus Sn(II) compounds are reductants, reverting to the more stable Sn(IV), whereas Pb(IV) oxide and compounds are oxidants. By contrast, Pb(II) salts are stable. This is sometimes referred to as the **inert pair effect.** Pb(II) salts are mainly ionic because the large Pb^{2+} ion is not very polarising. Most lead salts are sparingly soluble and, in this respect, resemble barium salts.

5.2 QUALITATIVE TESTS ON C, Si AND THEIR COMPOUNDS

(a) Connect a piece of charcoal or graphite, using crocodile clips, to a 6 V battery and a 6 V bulb in series and note any change.

(b) Repeat using a piece of silicon.

(c) Add 1 cm^3 conc. sulphuric acid to a little charcoal in a boiling tube, put a glass wool plug near the mouth of the tube and test with an acidified dichromate paper.*

(d) Add a little water to 1 cm^3 of tetrachloromethane, shake well and note any temperature change or pH change.

(e) Repeat using $SiCl_4$ adding the water gradually and feeling the tube.

(f) To a little alkali metal formate (methanoate) in a boiling tube, add 1 cm^3 of syrupy phosphoric acid. Heat in the fume cupboard, expose a filter paper strip dipped in $PdCl_2$ solution. Place a glass wool plug at the mouth of the tube, heat and then remove the plug and expose a small flame.

(g) Prepare a solution of sodium bicarbonate, heat gently, use a pasteur pipette to suck any gas and then deliver the contents to a little lime water.

(h) Bubble CO_2 (from Kipp's apparatus or cylinder) slowly through 2 cm^3 of clear lime water, continue bubbling for a while.

(i) Prepare a solution of sodium carbonate and add separately to portions of the solution:
   (i) barium chloride solution, then add dil. HCl;
   (ii) calcium chloride solution and then dil. HCl;
   (iii) magnesium chloride solution and then dil. HCl;
   (iv) silver nitrate solution and test the solubility of any precipitate in: dilute nitric acid or dilute ammonia;
   (v) hot silver nitrate solution and then boil gently;
   (vi) mercury(II) chloride solution;

(j) To separate portions of sodium bicarbonate solution, add:
   (i) magnesium sulphate solution, then boil;
   (ii) mercury(II) chloride solution;
   (iii) a few drops of universal indicator;

(k) Add to solid potassium cyanate (KOCN) dilute sulphuric, suck any gas with a pipette and deliver the contents to lime water. When the effervescence subsides, add NaOH solution, heat and expose at the mouth of the tube a mercury(I) nitrate paper.

(l) To separate portions of KOCN solution add:
   (i) silver nitrate solution, test the solubility of any precipitate in dilute nitric acid and in dilute ammonia;
   (ii) cobalt acetate solution to a concentrated solution, then add alcohol;
   (iii) copper(II) sulphate solution to which a few drops of pyridine have been added, then shake with a little $CHCl_3$.

(m) Add 2.5 M sulphuric acid to a little KSCN, heat carefully to boiling exposing an acidified dichromate paper to the mouth of the tube.*

(n) To separate portions of a solution of KSCN add:
   (i) silver nitrate solution, check the solubility of any precipitate in excess reagent and in ammonia solution;
   (ii) copper sulphate solution in excess, allow to stand;
   (iii) mercury(II) nitrate solution and then excess reagent;
   (iv) iron(III) chloride solution, then shake with a little ether away from flames;
   (v) cobalt nitrate solution, then add a little acetone;
   (vi) zinc and dil. HCl, shake and expose a lead acetate paper;
   (vii) ammonia and then hydrogen peroxide, allow to stand and acidify with dil. HCl and suck any gas and deliver into a little lime water. To the remaining solution add barium chloride.

(o) Prepare a dilute solution of sodium silicate and add to separate portions:
   (i) dil. HCl and then heat to boiling;
   (ii) ammonium chloride solution;
   (iii) silver nitrate solution, test the solubility of any precipitate in dilute ammonia or dilute nitric acid;
   (iv) barium chloride solution, then add dilute nitric acid;
   (v) ammonium molybdate solution.

(p) Mix a little silica with powdered calcium fluoride in a small porcelain crucible, add a few drops of concentrated sulphuric acid. Warm and expose a drop of water in a capillary tube.

5.3 ANALYTICAL CHEMISTRY OF CARBON COMPOUNDS

Carbon dioxide obtained by oxidation of carbon compounds can be determined by absorption in a known excess of standard NaOH, when a mixture of carbonate and hydroxide are formed, which can be titrimetrically analysed.

Carbonates of metals, if thermally unstable, can be analysed by heating to the appropriate temperature and the loss in weight gives the % carbon dioxide.

Acidimetric titrations of carbonates and their mixture with either hydroxide or bicarbonate are simple to carry out with acid-base indicators or potentiometrically using a glass electrode and a pH meter.

Thiocyanates can be determined gravimetrically as the copper(I) thiocyanate or titrimetrically using silver nitrate or mercury(II) nitrate.

5.3.1 Gravimetric determination of carbon dioxide in calcium carbonate

Weigh out accurately about 0.3-0.4 g of the carbonate into a weighed silica crucible. Heat in an oven at 105°C to constant weight and find the weight of any water lost. Then place in a muffle furnace and heat to constant weight at 1200°C. Repeat and calculate the % carbonate in the sample.

When the residue is cooled to room temperature, use a weighed portion for the determination of calcium by dissolving in HCl using any suitable method (Sec.3.4.3). Compare the results of calcium and carbon. To a small portion of the residue add water dropwise and note any changes.

5.3.2 Titration of sodium carbonate solution against HCl

When a solution of sodium carbonate is titrated against standard HCl, the titration curve shows two inflection points: one at pH~8.5 when the carbonate is transformed to bicarbonate; the other at pH~4 when the bicarbonate is neutralised to give NaCl and carbon dioxide.

Prepare 0.1 M sodium carbonate using the purest anhydrous salt. Pipette 25.0 cm^3 in a conical flask, add a few drops of thymol blue indicator. Cool to ~0°C and stir magnetically as you titrate with standardised 0.2 M HCl until the colour changes from yellow to blue. Repeat and calculate the average titre. Repeat two titrations using bromophenol blue as indicator when the colour changes at the end-point from blue to yellow. Compare the two titres with the different indicators.

If an autotitrator is available, pipette the carbonate solution into the titration vessel, in which a combined glass electrode is placed and fill the autoburette with the acid. Choose a suitable rate of delivery from the burette and connect the pH meter to the chart recorder. Compare the results with the results using indicators.

5.3.3 Titration of sodium bicarbonate against HCl

Use 0.1 M purest bicarbonate and 0.1 M HCl and use bromophenol blue indicator and continue as above. Calculate from the average of duplicates the concentration of bicarbonate in the original solution.

5.3.4 Titration of a mixture of carbonate and bicarbonate

Prepare a solution which is 0.1 M in sodium carbonate and 0.05 M in sodium bicarbonate. Pipette 25.0 cm^3 of the solution, add a few drops of thymol blue indicator and titrate with 0.2 M HCl as in Sec.5.3.2. Repeat to obtain concordant results. Repeat using bromophenol blue indicator and record the average volume of acid used. The first titre corresponds to ½ the carbonate and the second titre corresponds to both carbonate and bicarbonate.

5.3.5 Titration of sodium carbonate in presence of hydroxide

When the mixture is titrated with standardised HCl using bromophenol blue indicator, the titre gives the total (carbonate + hydroxide) content. In another aliquot the carbonate is precipitated as barium carbonate and the hydroxide is determined by titration with the acid using thymol blue indicator (without need to filter barium carbonate). The second titre gives the hydroxide content of the solution.

Prepare a solution which is 0.1 M in NaOH and 0.05 M in sodium carbonate. Titrate 25.0 cm^3 aliquot against standardised 0.2 M HCl using bromophenol blue indicator. Repeat and calculate the average volume. Use another aliquot of the mixed solution, warm to 70°C, add 1% barium chloride solution gradually until all the carbonate has been precipitated. Cool, add a few drops phenolphthalein indicator and titrate with the acid until a drop removes the pink colour. The titre gives the hydroxide neutralised. Repeat and work out the average titre. From the difference between the titres in the two cases, calculate the [carbonate] in mol dm^{-3}. Calculate from the second titre [hydroxide] in mol dm^{-3}.

5.3.6 Titration of potassium thiocyanate solution

Because potassium or ammonium thiocyanates are deliquescent, their solutions are usually standardised by titration against standard silver nitrate solution. The latter is usually pipetted into the titration vessel and the thiocyanate solution added from the burette. Iron(III) sulphate solution is used as indicator since it forms an intensely red complex with thiocyanate at the end-point.

Weigh out accurately about 10.5 g purest KSCN, dissolve in water, transfer to a 1 dm^3 volumetric flask and make up to the mark.

Pipette 25.0 cm^3 of standard 0.1 M silver nitrate solution into a 250 cm^3 flask and add 1 cm^3 of 40% w/v solution of purest ammonium iron(III) sulphate acidified with nitric acid. Titrate with the thiocyanate solution until the appearance of a faint brown colour in the flocculated suspension of white silver thiocyanate. Repeat and calculate from the average titre [SCN^-] in mol dm^{-3}.

5.3.7 Gravimetric determination of thiocyanate

In SO_2 saturated solution, Cu(II) is reduced to Cu(I) which is precipitated by thiocyanate as CuSCN.

Weigh out accurately about 6.7 g purest KSCN, dissolve in water and make up to 1000 cm^3 in a volumetric flask. Pipette 25.0 cm^3 of the solution into a 400 cm^3 beaker, add water to a volume of 100 cm^3 then add 50 cm^3 freshly prepared solution saturated with sulphur dioxide. Then add, slowly, with stirring, 0.1 M copper(II) sulphate solution until no more precipitate is formed. Add 10 cm^3 of the sulphur dioxide solution, check for complete precipitation, allow to stand for 3-4 hours and filter through a prepared G4 sintered glass crucible. Wash with cold water containing drops of the sulphur dioxide solution, until the filtrate does not give a colour with hexacyanoferrate(II) solution. Dry to constant weight at 120°C and calculate from the average weight [SCN] in mol dm^{-3}.

5.4 PHOTOCATALYSED REDUCTION OF CARBONATE

When metallised anatase (a form of TiO_2) is suspended in aqueous solution of sodium carbonate and the suspension is irradiated, the photopromoted electrons reach the surface of the particles and are likely to reduce carbonate to one or more of the potential reduction products. Methanol is such a reduction product and is technically useful. Oxygen, which competes with carbonate for the electrons, should be excluded e.g. by bubbling nitrogen throughout an experiment. If sulphite is also present in the irradiated solution, the photoproduced holes are likely to oxidise sulphite to sulphate, when they reach the surface of the anatase particles.

Prepare silverised anatase as described in Sec.16.8. Prepare a solution which is 0.5 M in sodium carbonate and 0.05 M in sodium sulphite. Weigh out silverised anatase into a photochemical reaction vessel and pipette a volume of the carbonate/sulphite solution so that a 0.5% w/v suspension is obtained and sonicate the suspension to ensure good dispersion. Insert the vessel to surrounded the quartz thimble of a medium pressure mercury lamp so that its level is above the lamp's arc. Purge the suspension with a slow stream of nitrogen, using a trap cooled with ice/salt mixture at the gas exit. Stir the suspension magnetically as you switch on the lamp and irradiate for 2-3 hours while cooling the mercury arc as recommended by the manufacturers, while the coolant and nitrogen stream are maintained in the stirred suspension. At the end, switch off, centrifuge the suspension if necessary, filter through G4 sintered porcelain crucible. Combine the filtrate and condensate and determine [MeOH]. Calculate the yield of MeOH per kW hour.

Spectrophotometric determination of MeOH (Analyst, **80**(1955)704)

When MeOH solution is mixed with a solution of ammonium hexanitrocerate(IV), the spectrum of the coloured solution shifts due to the replacement of a nitro group by OMe. The absorbance at the wavelength of maximum absorption (against a reagent blank) is linearly related to [MeOH].

Prepare a 1.0 M purest ammonium hexanitrocerate(IV) solution in 4 M nitric acid and store the solution overnight. Prepare a series of MeOH aqueous solutions in the concentration range 0.01- 0.09% w/w or v/v. Pipette 5.0 cm^3 of the 0.09% methanol solution and 2.0 cm^3 of the cerium complex solution, make up to 10.0 cm^3 in a volumetric flask with 4 M nitric acid. Shake well and record the spectrum in a 10 mm cell over the range 400-700 nm and locate the wavelength of maximum absorption. Repeat and measure the absorbance at this wavelength as soon as possible after starting a stop watch when the solutions were mixed. In all cases use a blank solution made up of 2.0 cm^3 of the cerium solution made up to 10.0 cm^3 with nitric acid. Check that the absorbance is steady for the first 5 minutes of mixing. Use this time and this procedure to measure the absorbance for the different MeOH solutions prepared. Plot the absorbance against [MeOH] to obtain a calibration plot. Use this plot to find out [MeOH] in the above-mentioned experiment.

Determination of [sulphate] in the product of the photocatalysed run

Pipette an aliquot of the combined filtrate/condensate in a beaker, add dil. HCl to decompose the unreacted carbonate and sulphite, warm to expel carbon dioxide and sulphur dioxide, then add gradually and with stirring a 0.2 M warm barium chloride solution. Check for complete precipitation. Cover the beaker and place it on a hot water bath for an hour. Then filter through a prepared G4 sintered glass crucible. Wash the precipitate with water until the filtrate is chloride-free. Wash with small volumes of EtOH and then ether. Dry by suction and keep in a vacuum desiccator before weighing. Calculate from the average of duplicates $[SO_4]$ in mol dm^{-3} $(kW\ hr)^{-1}$.

Alternative methanol determination by head space chromatography

If the facility is available, prepare a series of MeOH solutions in the range 5×10^{-5}-10^{-3} M. Set the head space oven temperature at 60°C. Use a 20 m Carbowax capillary column (at 40°C), with nitrogen gas carrier at a pressure of 8 psi. It is best to have automatic head space sampling from 2 cm^3 vials. Plot the relative peak height against [MeOH] and use the calibration plot to determine unknown [MeOH]. (J.T.S.Irvine, *Ph.D.Thesis, University of Ulster,* 1986, p.123).

5.5 ANALYTICAL CHEMISTRY OF SILICATES

Naturally-found silicates are complex mixtures of minerals which are best characterised by XRD, TGA and DTA. Special methods of chemical analysis are available and are used in special laboratories. However, cement, which is an industrial silicate product, can be analysed more readily than natural silicates. The composition of cement is usually expressed as oxides of Si, Ca, Al, S, Fe(III) and Mg besides the alkali metals Na and K.

Chemical analysis of ordinary Portland cement

Determination of Si, Al, Fe(III), Mg, Mn and Ti

When cement is fused with NaOH and the product dissolved in HCl, the chlorides are determined by atomic absorption.

Weigh out accurately about 0.4 g of the cement (previously dried to constant weight at 105°C) into a zirconium crucible. Add 2.5 g of purest NaOH. Carefully heat until the alkali pellets melt. Then heat strongly until the flux is completely fluid and glows red. After cooling, immerse the crucible in a beaker containing 200 cm^3 of 15% HCl and stir magnetically to dissolve the solid. Then transfer quantitatively into a 250 cm^3 volumetric flask and make up to the mark after dissolving 0.5 g purest KCl. Use an atomic absorption spectrophotometer and follow the Manufacturer recommendation to find the concentration of Al, Si, Fe, Mg, Mn and Ti. Calibrate the instrument using matrix matched standards (*Analyst,* **95**(1970)124). Use inductively coupled plasma emission system if available.

Determination of Na and K

Weigh out accurately 0.7 g of dried cement into a 250 cm^3 beaker. Disperse in water, add 10 cm^3 conc. HCl and 150 cm^3 hot water. Bring to the boil and keep hot for 5 minutes. Cool and transfer quantitatively to a 250 cm^3 volumetric flask and make up to the mark. Dissolve in a 100 cm^3 aliquot 0.191 g purest KCl and in another 100 cm^3 aliquot 0.254 g purest NaCl. These chlorides are added as ionisation suppressors. Use the atomic spectrophotometer in the emission mode and measure the readings for the two solutions, using the manufacturer's recommended operating conditions. Use calibration standards to find [K] and [Na]. Calculate from the results of spectrophotometry the percentages of oxides of the elements determined.

Determination of sulphur

Weigh out accurately 1.0 g of the cement, add 25 cm^3 cold water and 5 cm^3 conc. HCl and stir well. Heat to dissolve and make up to 50 cm^3 and heat nearly to boiling in a water bath for 15 minutes. Filter if necessary, washing any residue with hot water. Combine the filtrate and washings, dilute to 250 cm^3 and heat to boil and slowly add a hot 10% w/v of purest barium chloride solution. Keep on the hot water bath for 3 hours, maintaining a volume not <230 cm^3. Filter the precipitate and treat as in Sec.5.4. Calculate the % by weight of S expressed as SO_3.

Determination of Ca

Weigh out accurately about 0.2 g of dried cement and treat as above for the determination of the alkalis. Pipette 25.0 cm^3 of the solution into a conical flask and use the same procedure as in Sec.3.4.1 for the complexometric determination of calcium. Calculate from an average of two concordant titres, the concentration of calcium in the solution and hence the % Ca in the dried cement expressed as CaO%.

5.6 SURFACE CHEMICAL STUDY OF PRECIPITATED SILICA

Precipitated silica is a useful adsorbent which is commercially available but its surface area or levels of impurity are not specified by the suppliers.

5.6.1 Characterisation of precipitated silica

As an adsorbent, the surface area of precipitated silica is required. This can be measured by gas adsorption (Sec.2.1.5). Since the commercial samples also contain impurities, chemical analysis is useful for characterisation.

Chemical analysis of precipitated silica

The main impurities in precipitated silica are the alkali metals: Na and to a smaller extent K. Besides, the chloride content is relevant if the powder is to be used for studying the adsorption of cations. The water content can be simply determined by the loss of mass at 120°C.

Weigh out accurately about 12 g of the powder and disperse in water, stir well and filter through a G4 sinter. Wash with water on the filter. Combine the filtrate and washings and make up to 100 cm^3 in a volumetric flask. Add 1.0 cm^3 of 5% potassium chromate indicator and titrate against standard 0.03 M silver nitrate. Repeat and calculate from the average titre the % Cl in your sample. Use a similar volume of the solution to determine the concentration of Na and K by atomic absorption or flame photometry and express your results kg^{-1} of silica.

Determination of PZC of precipitated silica

Use a 1 dm^3 beaker in the set up in Fig.2.1 and insert a combined glass electrode, a thermometer, the tip of a microburette, an inlet and an outlet for circulating nitrogen. Weigh out 3.0 g of the silica into the inner beaker, add 150 cm^3 of 0.01 M potassium nitrate. Pass a steady stream of nitrogen through the suspension which is magnetically stirred and circulate water at 298 K from a thermostat. Allow to stand preferably overnight before adding from the burette small volumes of 0.1 M nitric acid. When the pH is practically constant, note the change in pH. Continue to cover the acidic range. Repeat using 0.1 M KOH and cover the alkaline range. Calculate the adsorption density i.e. $\Gamma(H^+)$-$\Gamma(OH^-)$ and plot against pH. Determine PZC from the intersection of the curve with zero adsorption density.

5.6.2 The adsorption isotherms of the divalent ions of Co, Ni, Cu and Zn

The sequence of the adsorption of these four ions, which are adjacent in the periodic table, is expected to assist in elucidating the adsorption mechanism. The silica powder is shaken with 0.1 M potassium nitrate solution before equilibrating with the transition metal nitrate solution. The filtrate after adsorption, is analysed for the metal ion concentration by atomic absorption and/or polarography.

Prepare stock solutions which are 0.1 M in the metal nitrate and in potassium nitrate. Using the latter solution for dilution, prepare a set of solutions which are in the concentration range of 0.01- 0.0001 M of M^{2+}. Check the time required to attain adsorption equilibrium by shaking 1.0 g portions of the silica with 25.0 cm^3 of 0.1 M potassium nitrate in a shaking thermostat at 298 K for a few hours before adding 50.0 cm^3 of the most concentrated transition metal nitrate solution and adjusting the pH to 6.0, using 0.1 M KOH or 0.1 M nitric acid. At intervals withdraw, through a filtering stick, a small volume and analyse for the transition metal concentration. When this concentration becomes practically constant, adsorption equilibrium will have been reached. Using a thermostatting temperature of 50°C, repeat the operation but shake the suspension for the determined equilibration time before centrifuging and measuring the metal ion concentration at equilibrium. Calculate the amount adsorbed g^{-1} powder. Repeat using solutions of the other concentrations of metal ions and plot the adsorption isotherm i.e. amount adsorbed g^{-1} against equilibrium concentration. Carry out similar runs for the other metal nitrates. If the isotherms have a Langmuir shape, find the limiting amount adsorbed, X_m (equation 2.17) and plot against the metal's atomic number. Compare the trend with the trend of the logarithms of the stability constants of the hydroxo-complexes of the four metals (cf. *J.Chem.Soc.*(1951)3192). The latter plot is an example of what is usually termed the **Irving-Williams sequence.**

5.7 QUALITATIVE TESTS ON TIN AND ITS COMPOUNDS

5.7.1 Tin

(a) Examine a piece of white tin and notice its hardness and malleability.
(b) Add a little conc. HCl to a few pieces of Sn, warm and apply a flame near the top of the tube. Decant the clear solution into another tube and add dropwise acidified permanganate.
(c) Repeat using dilute nitric acid. Add to a portion of the decanted solution NaOH solution to neutralise and then an excess of NaOH. Heat and expose a mercury(I) nitrate paper at the mouth of the tube.
(d) Repeat using NaOH solution, test near the top of the tube with a small flame.

5.7.2 Tin(II) compounds

Prepare a solution of tin(II) chloride in HCl freshly and add to portions separately:

(i) NaOH solution gradually and then in excess;
(ii) dilute ammonia gradually and then in excess;
(iii) H_2S solution after adjusting the pH to 0.6; test the solubility of any precipitate separately in conc. HCl or yellow ammonium sulphide;
(iv) mercury(II) chloride added slowly and shaking after each addition;
(v) a piece of zinc;
(vi) iron(III) chloride in HCl;
(vii) silver nitrate solution;
(viii) acidified permanganate added dropwise.

5.7.3 Tin(IV) compounds

Prepare a solution of tin(IV) chloride in dil. HCl and add separately to portions of the solution:

(i) NaOH solution gradually and then in excess;
(ii) dilute ammonia gradually and then in excess;
(iii) H_2S solution after adjusting the pH to 0.6; test the solubility of any precipitate separately in conc. HCl or yellow ammonium sulphide;
(iv) iron metal, test the supernatant after shaking with mercury(II) nitrate;
(v) zinc, shake and add more tin solution.

5.8 ANALYTICAL CHEMISTRY OF TIN

Although tin can be precipitated by various complexing agents e.g. dithizone and then transformed to the dioxide which is weighed, the process is lengthy and other metal impurities interfere. The volumetric determination with iodate is adequate but it is simpler and quicker to determine Sn(II) by titration with standard iodine solution.

5.8.1 Volumetric determination of tin(II) chloride

In this direct titration, iodine oxidises Sn(II) to Sn(IV) and the extra drop of iodine is detected by starch indicator.

Weigh out accurately about 2.0 g of purest tin(II) chloride into a beaker, add 150 cm^3 conc. HCl and shake to dissolve. Transfer quantitatively to a 250 cm^3 volumetric flask and make up to the mark using boiled-out distilled water. Pipette 25.0 cm^3 of the solution to a 250 cm^3 Buchner flask, add ~75 cm^3 boiled-out water and 2 cm^3 freshly prepared starch solution. Insert the tip of a burette containing 0.05 M iodine solution into the bung of the flask. Apply gentle suction and titrate with the iodine solution to the first appearance of a blue colour. Repeat to obtain concordant results and calculate from the average titre the concentration of Sn(II) in mol dm^{-3}.

5.9 PREPARATION AND ANALYSIS OF TIN IODIDES

(*J.Chem.Educ.*74(1977)573)

Both tin(II) and tin(IV) iodides can be prepared from the elements under different conditions. Since the former is sensitive to air, the preparation has to be carried out under a nitrogen atmosphere. Both iodides can be assayed gravimetrically by oxidation with nitric acid to give tin(IV) oxide. They can be characterised, depending on the availability of instruments, by XRD and ^{119}Sn NMR spectroscopy.

5.9.1 Preparation of SnI_2

Weigh out 0.5 g tin (purest 20 mesh) and 1.2 g purest iodine into a 3 neck 100 cm^3 flask fitted with a reflux condenser and gas inlet and outlet (with an oil bubbler). Flush with nitrogen for 15 minutes before adding 10 cm^3 of 2 M HCl. Reflux gently for an hour until the solution is pale yellow. Filter while hot (using fluted filter paper) into another 3 neck flask which is kept hot while purged with nitrogen as before. Then cool in an ice bath while nitrogen is flushing the flask. When crystallisation seems complete, filter under suction, wash on the filter with 10 cm^3 cold water and dry by continued suction and eventually in a vacuum desiccator. Weigh your product and calculate % yield based on Sn.

5.9.2 Preparation and analysis of SnI_4

Place 25 cm^3 of glacial acetic acid and 25 cm^3 of acetic anhydride in a quickfit round bottom flask. Add 0.5 g of tin foil, cut into small pieces and then add 2.0 g of powdered I_2. Reflux on a sand bath (or a hot plate) until a rather vigorous reaction begins. If necessary, add a crystal of KI to start the reaction. When the initial reaction has subsided, boil the reaction mixture until the violet vapour of iodine is no longer visible. If any unreacted tin remains, add about 0.2 g of iodine and reboil for a while to complete the reaction of tin and iodine. Cool the reaction flask and filter off the orange crystals of tin(IV) iodide through a Buchner funnel and immediately recrystallise your product from chloroform. Dry the crystals in a vacuum desiccator and calculate the % yield based on Sn. Determine the melting point of your product, then test a small sample with water and investigate the products so obtained.

Weigh out accurately about 0.5 g of your preparation into a prepared weighed porcelain crucible, add 1 cm^3 3 M nitric acid, cover the crucible and leave overnight. Add another 1 cm^3 3 M nitric acid and leave for several hours before heating gently on a hot plate for several hours and then heat with a low flame to remove any volatile compounds. Then heat strongly for half an hour, cool in a desiccator and weigh the crucible. Reheat and reweigh to attain constant weight. Calculate the % purity of your preparation.

Alternatively weigh out accurately about 0.25 g of your product into a stoppered bottle and then add 30 cm^3 of conc. hydrochloric acid and 3 cm^3 of chloroform.

Titrate with standard 0.025 M potassium iodate solution, vigorously shaking after each addition of the solution, until the violet colour of the organic phase is just discharged. The aqueous layer will be pale yellow in colour at the end-point.

Repeat and calculate the % purity of your preparation.

5.10 COMPLEX COMPOUNDS OF TIN

Sn(II) or Sn(IV) in the form of chloro-complexes can be precipitated with large cations e.g. *trans*-$[Co(en)_2Cl_2]^+$ (Sec.14.8.1).

5.10.1 Preparation of $[Co(en)_2Cl_2][SnCl_3]$

(G. Spacu; P. Spacu, *Bull.Soc.Sci.Cluj,*5(1931)473)

Weigh our 2.25 g tin(II) chloride dihydrate, add enough ammonium chloride to dissolve the solid in water. Heat to the boiling point and add, slowly and with stirring, a concentrated solution of the cobalt(III) complex until precipitation seems complete. Filter under suction and wash on the filter with ethanol and continue suction while pressing between filter paper. Weigh your product and calculate the % yield based on Sn.

The complex can be analysed for chloride by dissolving in dilute nitric acid and titrating chloride with silver nitrate.

5.10.2 Preparation of $[Co(en)_2Cl_2]_2[SnCl_6]$ *(Bull.Soc.Sci.Cluj,*5(1931)473).

Dissolve 2.6 g tin(IV) chloride and 2 g ammonium chloride in hot ethanol and add to it a concentrated solution of 1.5 g of the Cobalt complex with stirring. Cool in an ice bath until precipitation seems complete. Then filter under suction and dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on Sn.

5.11 QUALITATIVE TESTS ON LEAD AND ITS COMPOUNDS

5.11.1 Lead and its oxides

(a) Rub a piece of lead sheet with fine sanding paper until a shiny surface appears. Rinse with water and dry with tissue paper and then dip in dilute nitric acid. Test the hardness and malleability of lead. Then add 2 cm^3 of dilute nitric acid to a portion, heat until some dissolves. Decant the clear liquid and add to it dil. HCl.

(b) Add to another portion of the cleaned lead NaOH solution. Heat in a boiling tube and expose a flame near the top.

(c) Weigh out about 0.2 g PbO in a small porcelain basin. Heat on a Bunsen burner until the powder changes colour. Cool the residue, weigh it and add to it conc. HCl (in the fume cupboard) and expose a moist blue litmus paper.

(d) Add 2 cm^3 dilute nitric acid to a little PbO and heat until it dissolves then add a little dil. HCl.

(e) Test the solubility of PbO_2 in dilute nitric acid. Heat for a few minutes, decant the supernatant and add dil. HCl.

(f) Add a little conc. HCl to PbO_2 in the fume cupboard, heat and expose a moist blue litmus paper.

(g) Add to 2 g Pb_3O_4 5 cm^3 4 M nitric acid and heat with stirring. After cooling, filter through GF paper by suction and dry by suction. Test the residue as in (e) and (f). Test the filtrate as in (d).

(h) Using Pb_3O_4 repeat test (f).

(i) Add glacial acetic acid and acetic anhydride to Pb_3O_4 and heat gently. After cooling add water to a portion and shake. Add to another portion acetone and shake.

5.11.2 Lead(II) salts

With the exception of a few soluble lead salts, notably the nitrate and acetate, the salts are sparingly soluble and generally white. Prepare a solution of lead nitrate and add to separate portions:

(i) dil. HCl, discard the supernatant and test the solubility of separate portions of the precipitate in conc. HCl and in excess boiling water. Cool the latter and add water to the former;

(ii) KI solution, test the solubility of any precipitate in excess of the reagent; and in boiling water then add water in the former case and cool in the latter case;

(iii) dil. sulphuric acid, test the solubility of any precipitate in a hot concentrated ammonium acetate, or in NaOH solution;

(iv) NaOH solution, test the solubility of any precipitate in excess;

(v) KBr solution, discard the supernatant and test the solubility of the precipitate in excess boiling water, then cool;

(vi) NaF solution;

(vii) potassium chromate solution; test the solubility of any precipitate separately in NaOH solution or dilute nitric acid;

(viii) slightly acidify before adding sodium sulphite solution;

(ix) oxalic acid; after slightly acidifying with acetic acid

(x) iodic acid solution;

(xi) sodium periodate solution;

(xii) ammonium sulphide, then add hydrogen peroxide.

5.12 ANALYTICAL CHEMISTRY OF LEAD

Lead(II) ions in aqueous solution can be titrated with EDTA solution using xylenol orange indicator and hexamine to control the pH. They can be precipitated as chromate which may be weighed or it may be dissolved in dil. HCl, adding excess KI and titrating the liberated iodine with standard thiosulphate. Among the suitable instrumental methods, amperomatic titration is an example.

5.12.1 Complexometric titration of lead(II)

Lead forms a stable complex with EDTA. Titrations are carried out at pH6 when the colour of xylenol orange changes to yellow.

Weigh out accurately about 4.16 g of the purest lead nitrate, dissolve it in water, add a few drops of dil. HNO_3 and make up to 250 cm^3 in a volumetric flask.

Pipette 25.0 cm^3 of the solution into a 250 cm^3 conical flask, add 25 cm^3 distilled water and 3 drops of xylenol orange indicator. If necessary, add cautiously drops of HNO_3 (very dilute) until the colour changes to yellow. Then add powdered hexamine until the colour changes and the pH is ~6 (use narrow range indicator stick or paper). Titrate with 0.05 M EDTA solution until the colour changes to yellow. If the addition of hexamine at this stage reverts the colour, continue titration after adding more hexamine until the colour changes to yellow. Repeat to get concordant results and calculate, from the average titre, the percentage of lead in the salt.

5.12.2 Gravimetric determination

An accurate method for the gravimetric determination of Pb^{2+} ions in solution is to precipitate the sparingly soluble $PbCrO_4$. K_2CrC_4 solution is a suitable precipitating solution. A coarse and filtrable precipitate is obtained by the slow addition of 4% K_2CrO_4 solution to a boiling acidified Pb^{2+} solution. The limitation of the determination is due to the general insolubility of other metal chromates.

Weigh out accurately about 0.3 g of the purest lead nitrate and dissolve it in excess 1:4 acetic acid, add 2 g of sodium acetate and dilute to 150 cm^3. Heat the solution to boiling and slowly add from a pipette 10 cm^3 of hot 4% K_2CrO_4 solution. Boil gently for 10 minutes, filter $PbCrO_4$ through a prepared G4 sintered glass crucible, previously heated to constant weight at 120°C. Wash thoroughly with a hot dilute solution of CH_3COONa or with hot water. Dry at 120°C to constant weight and weigh as $PbCrO_4$. Duplicates are required. Calculate the average % lead in the salt and compare the result with the result from the complexometric titration.

5.12.3 Precipitation of lead as chromate followed by titration

Following the precipitation of lead chromate, dil. HCl dissolves the precipitate and the dichromate formed oxidises iodide to iodine which can be titrated against thiosulphate.

Repeat the above precipitation of lead chromate. No need to use a weighed dried crucible. After filtration and washing the precipitate, place it in a 250 cm^3 beaker, add 1:1 HNO_3 to dissolve the chromate followed by 20 cm^3 of 10% KI solution, stir to liberate iodine, add water and titrate with standardised 0.05 M thiosulphate solution until the colour of iodine fades. Then add 2 cm^3 of freshly prepared starch solution until the dark iodine/starch adsorption complex disappears, leaving a green Cr(III) solution. Alternatively, filter through a GF filter paper, transfer it quantitatively and carefully, after washing, to a conical flask and continue as above.

5.12.4 Complexometric titration of tin and lead in solder

When solder (an alloy of tin and lead) is dissolved in HCl/nitric acid mixture, Sn(IV) and Pb(II) are formed in solution. On adding a known excess of EDTA, both ions are complexed and the excess EDTA can be titrated against standard lead nitrate, as in the above procedure (Sec.5.12.1). Hence the total content of Sn+Pb is calculated. If NaF is then added, F^- will preferentially complex with Sn, liberating EDTA already combined with it. On titrating this with the same lead nitrate solution, the titre is equivalent to Sn alone. Hence Pb can be calculated from the difference between the total (Sn+Pb) and the Sn.

Prepare 0.2 M EDTA solution and 0.01 M lead nitrate solution. Weigh out accurately about 0.4 g of the solder, add 10 cm^3 conc. HCl and 2 cm^3 conc. nitric acid. Warm in the fume cupboard to dissolve the solid and then boil gently to expel the nitrogen oxides and chlorine (in about 5 minutes). Check with a moist blue litmus paper. Cool slightly and add from a pipette 25.0 cm^3 of the EDTA solution and boil for a couple of minutes to dissolve any precipitated lead chloride. Add 100 cm^3 water, cool and make up to 250 cm^3 in a volumetric flask. Pipette two 25.0 cm^3 aliquots into two 250 cm^3 conical flasks. To each flask, add a few drops of xylenol orange and 15 cm^3 of 30% solution of hexamine. Ensure that the pH is ~6 and then titrate with the standard lead solution until the colour changes from yellow to red. Add 2.0 g of purest NaF to one flask shake to dissolve the solid, when the colour turns to yellow. Then titrate with the lead solution until a stable red colour is formed. A temporary pink colour changing to yellow on shaking indicates that you are near the end-point. Continue titration dropwise until the colour changes to red. Prepare a 0.02 M EDTA solution by 10 fold dilution from 0.2 M EDTA. Pipette 25.0 cm^3 of the diluted EDTA solution into a 250 cm^3 conical flask, add 1 cm^3 conc. HCl and a few drops of the indicator and the hexamine solution as above and titrate with the standard lead nitrate solution. This is a check on the molarity of the two solutions. Calculate from your results the % Sn and % Pb in the sample of solder.

5.12.5 Amperometric titration of lead (Sec.2.5.5)

Prepare a stock 0.01 M lead nitrate solution and then dilute a given volume 10 fold. Prepare 0.05 M potassium dichromate from the purest solid and 0.01 M potassium nitrate (supporting electrolyte). Use any available instrument provided with a dropping mercury electrode. Pipette 25.0 cm^3 of the diluted lead solution into the titration vessel and add 25.0 cm^3 of the potassium nitrate solution. Ensure that the parts of the cell assembly are properly connected. Bubble oxygen-free nitrogen through the cell for 20 minutes. Apply a potential of -1.0 V *vs* the standard calomel electrode. Add from a burette the dichromate solution slowly with continuous stirring, bubbling the gas after each addition. Measure the current and note that it will decrease from a high value. Plot the current against volume of titrant. The end-point is indicated when the current reaches a minimum before increasing. Repeat to obtain concordant results and calculate from the average the concentration of lead in mol dm^{-3}.

5.13 COMPLEX COMPOUNDS OF LEAD

5.13.1 Lead(II) complexes (*J.Chem.Educ.* 74(1997)291)

The first complex formed when KI solution is added to the sparingly soluble yellow PbI_2, is the white $KPbI_3$.

To a small crystal of KI add a drop of 0.1 M lead nitrate solution and note its appearance, preferably by looking through a low power microscope. Repeat using larger and larger crystals and compare their appearance on adding a drop of lead solution in each case.

5.13.2 Lead(IV) complexes

When PbO_2 is dissolved in cold conc. HCl, H_2PbCl_6 is formed in solution and its ammonium salt can be precipitated by adding ammonium chloride. Conc. sulphuric acid reacts with the complex precipitated, forming the covalent lead tetrachloride.

To some PbO_2 in a boiling tube, cooled in ice/salt mixture, add conc. HCl with shaking until the solid dissolves. Prepare a concentrated ammonium chloride solution, cool it in an ice bath and add the solution slowly to the acid solution until enough is added to precipitate the complex compound.

Carefully add conc. sulphuric acid to the complex and note the formation of an oil-like compound. Divide the separated oil into two portions: add water to a portion note the changes occurring and test with a pH stick. Add tetrachloromethane to the second portion and shake. Draw your conclusions.

*Preparation of pyridinum hexachloroplumbate(IV) (Inorg.Synth.*22(1983)149)

Like other elements in this group (except C), Pb(IV) forms octahedral hexahalo-complexes $[EX_6]^{2-}$ which are precipitated with large cations. When lead(II) chloride, suspended in HCl is saturated with chlorine, the unstable $H_2[PbCl_6]$ is formed. This is stabilised by precipitating the anion by large cations with low polarising power.

Grind purest lead(II) chloride to a fine powder. Weigh out 4.0 g of the powder and suspend in 80 cm^3 conc. HCl in an all glass washing bottle whose inlet tube terminates in G4 glass cylinder placed in the fume cupboard. Cool the set up in an ice bath and stir the suspension vigorously by magnetic stirring while bubbling chlorine through it at a rate of 3 bubbles s^{-1} until the solid dissolves. Replace chlorine by bubbling air to remove unused chlorine. Cool the pale lemon yellow solution to 0°C, add 2 cm^3 of purified pyridine dropwise with stirring to precipitate the complex. Filter through a G4 funnel, wash with small volumes of ice-cold ethanol. Dry by continued suction and then in an oven at 50°C. Weigh your product and calculate the % yield based on lead.

Weigh out about 0.2 g of your preparation into a beaker, add water with continuous stirring until the solid is transformed to the dark lead(IV) oxide. Filter through a G4 crucible, wash with water and dry at 105°C to constant weight. Calculate from duplicate results, the % purity of your preparation.

5.14 THE PHOTOCATALYSED REMOVAL OF LEAD IONS FROM SOLUTION

When the photocatalyst anatase is suspended in lead(II) acetate solution and the suspension is irradiated by a u.v. source, it is expected that the photoexcited electrons in the conduction band of the catalyst would reduce lead ions in solution, whereas the holes generated in the valence band would react at the surface forming OH radicals. These are likely to oxidise the acetate ions to CO_2.

Heat a sample of anatase pigment at 500°C to activate it and then silverise it as in Sec.16.8. Prepare a 0.05 M solution using purest lead acetate. Irradiate 0.7% w/v suspension of the anatase in the lead solution. Purge with nitrogen before and during irradiation. Connect at the gas exit two bubblers containing standard 0.5 M NaOH and a third containing $Ba(OH)_2$ solution. Ensure that the latter does not become turbid. After irradiation for 2-3 hours, filter the anatase through a G4 sinter and titrate an aliquot of the filtrate with 0.05 M EDTA solution as in Sec.5.12.1. From this titre and the titre of the original lead solution, calculate the amount of lead lost as a result of the reaction. To determine the amount of CO_2 generated by the oxidation of acetate, combine the contents of the two bubblers containing NaOH and quantitatively make up in a volumetric flask. Titrate an aliquot with 0.5 M HCl as in Sec.5.3.5 and calculate the concentrations of carbonate and hydroxide and hence the amount of CO_2 produced. To determine the lead ions adsorbed by the catalyst during irradiation, suspend the same mass of catalyst in the same volume of lead solution and agitate in the dark for the same time as the time of irradiation. Filter the anatase and titrate an aliquot of filtrate with EDTA as above and calculate the amount of lead adsorbed by the catalyst. Alternatively after irradiation, wash the catalyst on the filter and suck dry. Stir a mass of the catalyst with 0.05 M sodium acetate for the same period as that used in irradiation. Filter and titrate an aliquot of the filtrate with EDTA as above. Suck the residue dry and weigh a portion into a boiling tube, add dilute nitric acid, warm until the solid turns clearly white. The filtrate contains lead and silver nitrates. The lead can be determined by titrating an aliquot of the filtrate. When the residue is washed thoroughly and weighed, the loss in weight due to the acid treatment can be calculated. This is the combined weight of silver and lead. The weight of silver is determined in the original catalyst in a similar way as above.

To follow the progress of the photocatalysed reaction, withdraw samples of the suspension at intervals, centrifuge and filter. Titrate an aliquot of the filtrate with EDTA and hence calculate the concentration of lead not lost. Plot this against the time of withdrawal of the aliquot.

6

The Nitrogen Group

6.1 INTRODUCTION

Fig.6.1 depicts the Ebsworth diagram of N and P in acidic solution as well as N in basic solution. The top two elements in this group: N and P are typical non-metals. The metallic character, which appears in the heavier elements, increases down the group, although the conductivity of solid Bi is not high. The typical oxidation numbers of all the members of the group are +3 and +5 but the stability of the +3 state in Bi is greater than the +5 state (inert pair effect). The chemistry of N and P is dominated by covalent bond formation. On the other hand, ionic compounds of Bi(III) are the common bismuth compounds. The oxides of N and P are acidic in nature (except the neutral N_2O and NO), the amphoteric nature becomes apparent in the oxides of the heavier elements.

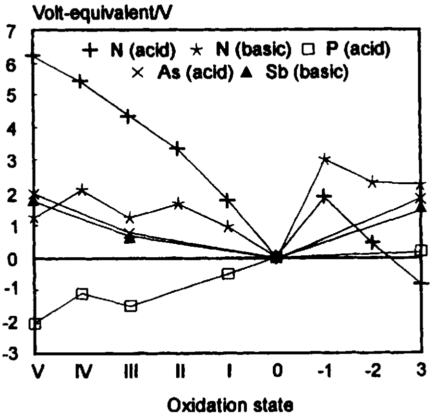


Figure 6.1 Volt-equivalent versus oxidation number diagram for group 15 elements.

Phosphates show various structures, reminiscent of the structures of the silicates. Although N and P show many similarities in their compounds, nitrogen and its oxides are gases whereas phosphorus and its oxides are solids. The gaseous nature arises from the ability of N to form π bonds to itself and to oxygen. N and P form similar hydrides but the basic nature of the hydrides of N is hardly observed in PH_3 or P_2H_4. The hydrides of the heavier elements become increasingly unstable down the group. With the exception of NF_3, nitrogen halides are unstable unlike the halides of the other elements in the group. Nitrogen is also unique in its inability to form pentahalides due to its inability to expand its valence shell beyond 8 and this limits the maximum coordination number to 4. On the other hand, the remaining elements exhibit coordination numbers of 6.

Athough nitric acid and nitrates are oxidants, nitrous acid can act either as an oxidant or a reductant depending on the conditions. On the other hand, the phosphoric acids have no oxidising properties whereas the lower acids and salts are reductants, due to the presence of weak P-H bonds. This weakness is related to the similarity of the electronegativities of P and H. The higher oxosalts of the heavier elements are oxidants, unlike phosphoric acid. Because of the high toxicity of arsenic and its compounds, they are excluded from this Chapter. The extensive chemistry of nitrogen, which exhibits the largest number of oxidation states will be adequately covered, together with phosphorus compounds. Less attention will be given to the less common Sb and Bi. It is worth noting here the trends in chemistry of the triad: As, Sb and Bi. The gradual increase in basic character of the oxides especially in the +3 state, is common to other p block groups. Thus arsenic(III) oxide is acidic whereas Sb(III) oxide is amphoteric but Bi_2O_3 is only basic. As expected, the pentoxides are less basic and less ionic. Neither As or Sb form a lower acid, the compounds are rather considered as hydrated trioxides. However a well characterised H_3AsO_4 is known but the higher oxide of Sb is only known in solution and it is a stronger oxidant than H_3AsO_4. The latter's salts resemble the phosphates but Sb(v) oxosalts contain octahedral SbO_6 units. $Bi(OH)_3$ is a basic compound.

6.2 QUALITATIVE TESTS ON NITROGEN COMPOUNDS

6.2.1 Tests on ammonia and its salts

(a) Add to a little magnesium nitride NaOH solution, warm and expose to any gas a moist mercury(I) nitrate paper.
(b) Heat in a long dry test tube a little ammonium chloride and note the appearance near the cold top.
(c) Repeat (b) placing a glass wool plug near the top of a shorter tube, exposing to any gas a moist red litmus paper.
(d) Repeat (c) placing a moist blue litmus paper below the glass wool plug.
(e) Repeat (c) and (d) using ammonium carbonate instead of chloride.
(f) Repeat (c) using ammonium sulphate instead of chloride.
(g) Repeat (d) using ammonium sulphate and placing an acidified dichromate paper below the plug.
(h) Heat a little solid ammonium salt with NaOH solution and expose to any gas: (i) moist red litmus paper; (ii) a drop of conc. HCl on a glass rod; (iii) a moist mercury(I) nitrate paper; (iv) a paper dipped in Nessler's solution; (v) a universal indicator paper.
(i) Prepare a solution of ammonium chloride or nitrate and add to separate portions:
    (i) a solution of $Na_3[Co(NO_2)_6]$;
    (ii) a solution of $H_2[PtCl_6]$;
    (iii) a little of Nessler's solution (Sec.6.3.1.2).

6.2.2 Tests on hydroxylamine and its salts

Add to separate aliquots of a solution of the hydrochloride:

(a) copper sulphate solution;
(b) iron(III) chloride solution;
(c) mercury(II) nitrate solution;

(d) silver nitrate solution;
(e) iron(II) solution made alkaline with NaOH, expose a blue litmus paper to the mouth of the tube;
(f) zinc and dil. HCl, then add NaOH, warm and test as in (e);
(g) Nessler's reagent.

6.2.3 Tests on hydrazine and its salts

(a) Add a little manganese(IV) oxide to some drops of hydrazine hydrate, shake and warm.
(b) Prepare a solution of a hydrazinium salt and add to separate portions:
  (i) ammoniacal copper(II) sulphate solution;
  (ii) acidified permanganate solution;
  (iii) ammonium molybdate solution;
  (iv) silver nitrate solution;
  (v) dilute iodine solution in KI or in ethanol;
  (vi) iron(III) chloride solution, shake, add NaOH warm and test with a moist mercury(I) nitrate paper at the mouth of the tube;
  (vii) zinc in dil. HCl shake for a few minutes, decant the clear supernatant into another tube, add NaOH solution, heat and test as in (vi).

6.2.4 Tests on nitrites

(a) Add dil. HCl to a solid nitrite in the cold, shake and expose to the mouth of the tube a moist blue litmus paper.
(b) Prepare a solution of sodium nitrite and add portions separately to:
  (i) iron(II) sulphate solution acidified with acetic acid, shake and then warm the mixture;
  (ii) silver nitrate solution;
  (iii) KI solution, acidify with acetic acid, test with a starch paper;
  (iv) acidified permanganate solution;
  (v) urea and dil. HCl, suck any gas with a Pasteur pipette and squeeze into a little lime water;
  (vi) solid ammonium chloride, boil for a few minutes, then test with pH paper;
  (vii) zinc or Devarda's alloy then NaOH, shake and expose at mouth of the tube mercury(I) nitrate paper;
  (viii) cobalt(II) sulphate solution containing KCl and NaCl.

6.2.5 Tests on nitrates

(a) Add conc. sulphuric acid carefully to a solid nitrate, warm and test any vapour with a moist blue litmus paper.*
(b) Repeat adding copper turnings.
(c) Add a solution of nitrate to a freshly prepared iron(II) sulphate solution, then add conc. sulphuric acid slowly down the side of the tube so that it forms a heavier layer below the mixed solution, note the junction between the two layers, then gently mix the two layers.
(d) To separate portions of a solution of a nitrate, add:
  (i) H_2S solution, test for any gas with moist blue litmus paper;
  (ii) Zn in acetic acid or Devarda's alloy in NaOH solution, test as in Sec.6.2.4 b(vii).

6.3 ANALYTICAL CHEMISTRY OF NITROGEN COMPOUNDS

6.3.1 Ammonia and ammonium salts

6.3.1.1 Volumetric determination of an ammonium salt

Ammonium salts in solution can be determined by adding a known excess of a standard alkali. After boiling the solution until all the ammonia has been lost, the excess alkali is titrated with a standard strong acid solution e.g. HCl. This is an example of a back titration. If both the acid and alkali titrated are strong, most acid-base indicators can be used.

Pipette 25.0 cm^3 of 0.1 M NH_4Cl solution into a 250 cm^{3}conical flask, add 50 cm^3 of the standardised ~0.1 M solution of NaOH (use a pipette for the addition) and place a small funnel in the neck of the flask. Boil the solution carefully until a $Hg_2(NO_3)_2$ paper is no longer turned black, indicating that no more NH_3 evolved. (The black colour is due to finely divided mercury formed by the reaction between Hg_2^{2+} ions in solution and NH_3). Cool the flask, add a few drops of methyl orange indicator and a little distilled water down the sides of the flask. Titrate with standard 0.1 M HCl in the burette to the first sudden change of colour. Duplicate determinations are required. Calculate the concentration of NH_4Cl in g dm^{-3} of the solution.

6.3.1.2 Colorimetric determination of ammonium salts

Nessler's solution or reagent contains potassium tetraiodomercurate(II) and is available commercially although it can be prepared in the laboratory easily. When the reagent is added to a dilute ammonium salt solution, the liberated ammonia reacts forming an orange brown colloid:

$$2K_2[HgI_4]+2NH_3 \rightarrow NH_2Hg_2I_3+4KI+NH_4I \qquad (6.1)$$

In dilute solution, the absorbance of the coloured compound can be measured in a spectrophotometer.

Using purest ammonium chloride and ammonia-free distilled water, passed through a mixed cation/anion exchange resin, prepare a 0.1 M solution. By successive dilution, prepare a series of solutions in the range 10^{-7}-3×10^{-6} M. Pipette 10.0 cm^3 of each solution into a 50 cm^3 volumetric flask, dilute to ~45 cm^3 using the same water and add 2.0 cm^3 Nessler's reagent before making up to the mark. After 10 minutes, measure the absorbance at 410 nm in a 4 cm cell. Plot absorbance against concentration to check the applicability of Beer's law. Use the calibration plot to find the ammonium ion concentration in unknown solutions.

6.3.1.3 Potentiometric determination using ammonia selective electrode

If an ammonia selective electrode is available, it can be used for measuring [ammonium] using a pH meter.

Prepare a stock 0.1 M ammonium chloride solution using the purest salt and ammonia-free water (see above). Diluting with this water, prepare a series of solutions in the range 10^{-2}-10^{-5} M. Pipette 50 cm^3 of each solution into a beaker, pipette 0.5 cm^3 of 10 M NaOH solution and stir magnetically after placing the electrode in the vessel and connecting the circuit to the pH meter. Note the mV reading and record its value when it is stable (in 2-5 minutes). Repeat using the other solutions and plot the mV reading against NH_4^+ ion concentration. Use this calibration plot to determine the concentration in an unknown solution.

Although ammonium can be determined gravimetrically either as the hexachloplatinate or tetraphenyl borate, either of the above methods is suitable for quick and accurate measurements.

6.3.2 Hydrazine and its salts

Hydrazine and its salts can be titrated in solution using manganese(III) solutions. Salts of hydrazine generally act as reductants and they can be titrated by suitable redox titrations. Under Andrews' titration conditions, iodate is reduced to ICl (I_2 is initially liberated). Hydrazine salts can be titrated against standard KIO_3 solution.

Investigation of the Reaction between $N_2H_5HSO_4$ and KIO_3

Weigh out accurately about 0.7 g of $N_2H_5HSO_4$ and make up to 250 cm^3 in a volumetric flask. To a 25.00 cm^3 aliquot of the hydrazinium ion solution contained in a 250 cm^3 reagent bottle, add 30 cm^3 conc. HCl and 5 cm^3 CCl_4. Add slowly standard M/60. KIO_3 solution from a burette, shaking the stoppered bottle carefully between additions, until the purple colour disappears from the organic layer. Near the end-point, the additions should be made dropwise. Duplicate determinations are required. From the average titre, deduce the molar ratio of IO_3^- to $N_2H_5^+$ and hence an equation representing the reaction. Safety goggles must be worn during the titration.

6.3.3 Hydroxylamine and its salts

Hydroxylamine and its salts generally act as reductants and hence can be titrated with suitable redox titrations. Iodine oxidises hydroxylamine or its salts, being reduced to iodide. Starch is used as an indicator in this titration.

Investigating the reaction between hydroxylammonium chloride and iodine

Weigh out accurately about 0.86 g of purest $HO.NH_3.Cl$ and make up to 250 cm^3in a volumetric flask. Pipette 25.0 cm^3 aliquot of the solution into a conical flask and dilute to about 150 cm^3. Warm the solution on a hot plate, fitted with a magnetic stirrer. Add 0.15 g purest MgO (used to avoid acidity of the solution) and add slowly (standardised) 0.05 M iodine solution from a burette keeping the suspension warm. When the colour of iodine fades slowly, add 2 cm^3 of freshly prepared starch solution to the conical flask and continue the titration slowly until the blue colour of the starch/iodine adsorption complex persists for 30 seconds. From the average of two concordant titres, deduce the molar ratio I_2 to $(HO.NH_3)^+$ and hence an equation representing the reaction, based on changes in oxidation numbers.

6.3.4 Nitrites

6.3.4.1 Titrimetric determination of nitrites

Nitrites are oxidised in acid solutions by permanganate which is reduced to Mn(II), the permanganate acts as a self indicator. Due to the volatility of HNO_2 (formed in acidified solutions of nitrite) and their oxidation in air, nitrite cannot be directly titrated against permanganate. It is more appropriate to add an aliquot of the nitrite solution beneath the surface to a known excess of permanganate, back titrating the excess with a standard reductant e.g. iron(II) solution.

Weigh out accurately ~1 g purest potassium nitrite, dissolve in boiled-out water and make up to 250 cm^3 in a volumetric flask. Deliver from a burette 30.0 cm^3 of standardised 0.02 M permanganate solution into a 600 cm^3 beaker. Add 30 cm^3 of 1 : 5 v/v of sulphuric acid solution and dilute to about 300 cm^3. Heat the beaker to 40°C and add slowly, while stirring magnetically, 25.0 cm^3 of the freshly prepared nitrite solution, which is placed in a burette. Ensure that the tip of the burette is below the surface of the liquid in the beaker. Rinse the jet of the tip of the burette with water, collecting the rinsing in the beaker. Cool the beaker and add from a burette a standardised 0.1 M iron(II) solution until a drop decolorises the solution. Add a few cm^3 in excess noting the total volume used and titrate the excess against the permanganate solution. Repeat and calculate from average results [nitrite] in mol dm^{-3}.

6.3.4.2 Spectrophotometric determination of nitrites

Nitrites diazotise sulphanilic acid in acid solution. When the diazo compound is coupled with 1-naphthylamine-7-sulphonic acid, a purplish-pink azo dye is formed which has an absorption maximum at 525 nm. Prepare a stock solution of potassium nitrite by weighing out accurately ~0.5 g and making up to 1 dm^3 in a volumetric flask using boiled-out water. Using this water, prepare by successive dilution a series of solutions in the concentration range of $0.25\text{-}1.50 \times 10^{-6}$ M. Pipette 80 cm^3 of each solution into a 100 cm^3 volumetric flask, add 4.0 cm^3 of 3.33% w/v of sulphanilic acid in 20% v/v glacial acetic acid:water. Mix the solution well and allow to stand for 20 minutes. Then pipette 10.0 cm^3 of 1-naphthylamine-7-sulphonic acid reagent (12 cm^3 glacial acetic acid added slowly with stirring to 0.2 g of reagent followed by 120 cm^3 water, warming to dissolve before making up to 150 cm^3 and storing in the dark). Mix well, make up to 100 cm^3, shake again and allow to stand for 20 minutes. Measure the absorbance at 525 nm in a 1 cm cell using water as a blank. Repeat for the other solutions. Plot absorbance against [nitrite] and check the applicability of Beer's law. Use the calibration plot to determine the concentration in unknown solutions (provided they are colourless).

6.3.5 Nitrates

Since practically all nitrates are soluble, no gravimetric method is suitable with the exception of precipitation with an organic base:nitron. The usual volumetric method is to reduce nitrate to ammonia, which is distilled into a known excess of standard acid, back titrating the excess with standard alkali (compare Sec.14.6.1).

However, the easiest instrumental method which is suitable in presence of nitrite is by ion chromatography (Sec.2.8.3). The ion chromatogram has separate peaks for the two ions. The concentration in an unknown is found by comparing the peak area with a calibration curve.

Prepare a stock solution which is 0.01 M in potassium nitrate and 0.01 M in potassium nitrite as well as separate solutions with the same concentration in either anion. By appropriate dilution prepare a series of solutions with a range of nitrite concentrations from 5 to 100 mg dm^{-3}. Prepare a similar range of concentrations of the nitrate and of the mixture of the two anions. Follow the instructions of the Manufacturer of the ion chromatograph and determine the peak area of each solution (or the peak height counts) and plot against anion concentration. Use the calibration plots to determine concentrations of unknown solutions. Determine the concentration of the two anions in a sample of acid rain (Dionex Application Note 31).

6.3.6 Nitrogen(II) oxide and nitrogen(IV) oxide

A semiquantitative method for determination of the two gases in a gaseous stream is based on a colour reaction between NO_2 and N,N-diphenylbenzidene. A commercially available tube is inserted in a gas stream flowing at a given rate. The approximate concentration of the gas is found from the calibrated scale on the tube. NO does not react but in similar tubes containing Cr(VI) oxide, NO is oxidised to NO_2 and the same colour is developed and can be read from the calibrated scale. When the two gases are present together, the reading in the second tube corresponds to the gas mixture and the difference between results from the two tubes gives the concentration of NO.

6.4 THE U.V.-ENHANCED DECOMPOSITION OF AMMONIUM NITRITE

A solution of ammonium nitrite is usually obtained by mixing equimolar solutions of ammonium chloride and sodium nitrite since the solid is not thermally stable. On heating the mixed solution, it decomposes to water and nitrogen. The kinetics of the thermal decomposition can be readily followed by measuring at intervals the volume of nitrogen evolved from a thermostatted solution. Since a solution of ammonium nitrite exhibits absorption peaks in the u.v., it is likely that u.v. irradiation may increase the rate of gas evolution i.e. the rate of decomposition.

The absorption spectrum of ammonium nitrite solution

Prepare a stock solution which is 0.4 M in ammonium and 0.4 M in nitrite ions. Fill a 2 mm spectrophotometer cell and record the spectrum over the range 250-390 nm. Dilute an aliquot 10-fold and record the spectrum over the range 230-250 nm. Dilute an aliquot of the latter solution 10-fold and record the spectrum over the range 200-230 nm. Measure accurately the absorbance at 254 nm and calculate the molar extinction coefficient, preferably using 3 or more concentrations of the solution.

The quantum yield of the photo-reaction (Sec.2.10.2)

Use a dip type low pressure mercury lamp, provided with a quartz thimble and circulate in the annular space on the inner side of the thimble water from a thermostat at $30^\circ \pm 1^\circ C$. Prepare a solution 0.5 M in ammonium chloride and in sodium nitrite and check its pH value before filling a cylindrical reaction vessel with a measured volume of the solution so that its level is above the level of the mercury arc. Connect the reaction vessel to a water-filled gas burette provided with a tap and a levelling device as in Fig.2.13. Keeping the solution magnetically stirred, observe the level of liquid in the burette. At intervals, measure the volume of gas evolved at the pressure and temperature prevalent. The temperature is read on a sensitive thermometer fixed near the gas burette. Calculate the pressure from the atmospheric pressure (read on a manometer) and corrected for the saturated vapour pressure of water at the measured temperature. Continue this process for a period of 3-5 hours. Repeat the procedure, switching on the low pressure mercury lamp for the same period. Subtract the volume of gas at the end of the thermal reaction from the corresponding volume of gas at the end of the corresponding photo-reaction. The difference is the volume ascribed to the photo-reaction. Replace the nitrite solution in the reaction vessel by an equal volume of a solution 0.02 M in uranyl(VI) nitrate and 0.1 M in oxalic acid and irradiate for a short known period (~20 minutes). After irradiation titrate an aliquot of the irradiated solution with 0.05 M permanganate and carry out another titration of the original actinometer solution. Measure the absorbance of that solution at 254 nm. If either this solution or the ammonium nitrite solution in the irradiated layer of solution is not completely absorbing at 254 nm, allow for the fraction of light absorbed in your calculation of the quantum yield. Carry out duplicate titrations and more than one irradiation time. From the difference in the titres of the actinometric solution before and after irradiation, calculate the mols of oxalic acid decomposed s^{-1}

and hence the output of the lamp used in quanta s^{-1}, using the actinometer quantum yield of 0.62. Then calculate the number of mols of nitrogen produced s^{-1} from the photoreaction. Hence calculate the quantum yield of nitrogen production. Repeat the process and find the average yield.

6.5 PREPARATION AND REACTIONS OF DINITROGEN TETROXIDE

Dinitrogen tetroxide and nitrogen dioxide exist in equilibrium:

$$N_2O_4(g) \text{ (nearly colourless) } \leftrightharpoons 2NO_2(g) \text{ (brown)} \tag{6.2}$$

The gas mixture becomes darker as the temperature is raised (the equilibrium shifts to the right). The gas mixture can be obtained by heating heavy metal nitrates e.g.

$$2Pb(NO_3)_2(s) \xrightarrow{\text{heat}} 2PbO(s)+4NO_2(g)+O_2(g) \tag{6.3}$$

By passing the gases through an ice/salt freezing mixture (~23% NaCl) liquid N_2O_4 can be obtained. Since the gas and the liquid are reactive towards H_2O, the apparatus used should be dry and the powdered $Pb(NO_3)_2$ should be previously dried.

Since the gas and liquid are poisonous and since the liquid is corrosive, the preparation should be carried out in the fume cupboard and the gases should not be breathed in and the liquid should not come in contact with your skin. Since the gas and liquid attack rubber, an all glass set up has to be used with ground joints lubricated by silicone grease.

Dry 10 g lead nitrate to 100°C before placing it in a boiling tube. Dry in an oven at 100°C, an all glass set-up consisting of a boiling tube A with a delivery tube ending in another tube B whose side-arm carries a drying tube filled with P_4O_{10}/soda lime, keeping the components in a desiccator before use. Assemble the set-up, surrounding the tube B in a beaker filled with salt/ice mixture. Heat the $Pb(NO_3)_2$ and note the change in its colour. Observe the difference in colour between the gas in the hot boiling tube and in the cool collecting tube. Stop when enough liquid has collected and note its colour (a green/blue colour may be due to N_2O_3 contamination).

Properties

Using a teat (Pasteur) pipette, add some drops of the liquid to about 3 cm^3 distilled water and note any colour or temperature change. Divide the solution into 3 parts: add to one part a few drops of universal indicator; add to another part $FeSO_4$ solution and then gently warm. Boil gently the third part and then cool and add a little Cu metal and warm if necessary. Draw your conclusions.

If a cylinder of dinitrogen tetroxide is available, prepare anhydrous copper(II) nitrate.

Preparation of anhydrous copper(II) nitrate

Copper(II) nitrate is available as the hydrated crystals. When heated, they do not produce the anhydrous salt but decompose. However, dinitrogen tetroxide can react with copper, behaving as if it consists of NO^+ and NO_3^- and the reaction is represented by:

$$Cu+2N_2O_4 \rightarrow Cu(NO_3)_2+2NO \tag{6.4}$$

Assemble in a fume cupboard a dried tube whose socket carries a fitting joint of a drying tube packed with phosphorus(V) oxide. Dispense 2 cm^3 of purest ethyl acetate previously dried by distilling over phosphorus(V) oxide. Then dispense 2 cm^3 of liquid

N_2O_4 from the cylinder. Surround the tube with an ice bath. After sufficient cooling and magnetic stirring, add 0.9 g of purest copper powder and stir for a quarter of an hour. Then add another 2 cm^3 of the oxide from the cylinder and continue stirring while cooling at 0°C until all the copper dissolves. Remove the solvent by evacuation and examine the solid left.

6.6 INVESTIGATING THE REACTIONS OF HYDRAZINIUM AND HYDROXYLAMMONIUM SALTS

In these compounds, the general reaction is with oxidants e.g. permanganate and Ce(IV). Since permanganate oxidations are generally carried out in acid solution and at temperatures 70°-80°C, titration can be carried out with the permanganate acting as self indicator.

Prepare 2 x 10^{-2} M solution of either hydrazinium sulphate or hydroxylammonium chloride in 1 M sulphuric acid and prepare 0.01 M potassium permanganate in the same acid. Pipette 25.0 cm^3 of either reductant solution into a Buchner flask with a rubber bung into which the tip of a burette is inserted. Place on a hot plate/magnetic stirrer. Fill a burette with the permanganate solution. Apply gentle suction to the Buchner flask to exclude air and warm to 70°C. Titrate with the permanganate, while stirring magnetically, until the first permanent, faint pink colour persists. Repeat to obtain concordant results. Carry out duplicate titrations with the other reductant using the same procedure. Calculate in each case the molar ratio of reactants.

6.7 AMMONIA AND NITRITE AS LIGANDS

A chloride ligand in *trans*-$[Co(en)_2Cl_2]Cl$ (Sec.14.8.1) can be readily replaced by other ligands. Ammonia or nitrite can easily replace the chloride. Since they are both higher in the spectrochemical series, the ligand exchange is accompanied by a change in the absorption spectrum and the colour of the complex.

Prepare a 10^{-2} M solution of the complex salt, a 1 M solution of sodium nitrite and 2.5 x 10^{-2} M ammonia solution. Mix equal volumes of the complex solution and the nitrite or ammonia solution and note the change in colour.

To study the reactions kinetically, use the apparatus in Fig.2.12 placing a 5 x 10^{-3} M complex solution in flask A and 10-fold diluted nitrite solution or ammonia solution in flask B and collecting in C aliquots of the mixture cooled in ice/salt. The absorbance of these aliquots is measured at 620 nm, wavelength of maximum absorption of the complex. Use a suitable thermostatically controlled temperature in the range 20°-35°C.

6.8 LIQUID AMMONIA

Cylinders of liquid ammonia are available commercially. Because its boiling point is -33°C, when the liquid is used as a solvent or as a reactant, the process has to be carried out in unsilverised Dewar vessels so as to minimise loss by vaporisation while being able to observe the changes in the system. However, it is necessary to work in a well-ventilated fume cupboard.

6.8.1 Preparation of $[Cr(NH_3)_6](NO_3)_3$ in liquid ammonia *(Inorg.Synth.*3(1941)153).

This complex cannot be prepared in aqueous solution. Even when anhydrous $CrCl_3$ reacts with ammonia, the major product is $[Cr(NH_3)_5Cl]Cl_2$. To replace the coordinated Cl by NH_3, a catalyst $NaNH_2$ is needed. This is generated by adding Na to the liquid.

Cut a small piece of Na to remove the oxidised and carbonated surface layer after surrounding the metal with tissue paper and removing the liquid in which it is stored. Place 0.1 g of the metal in a small Dewar vessel in which 35 cm^3 of liquid ammonia have been delivered from a cylinder by carefully operating a needle valve connected to the main valve of the cylinder. Use a rubber tube connected to the needle valve and directed to the Dewar. Note the blue colour of the solution of Na in liquid ammonia. Add a small crystal of iron(III) nitrate and shake to discharge the blue colour. This iron salt crystal catalyses the reaction to give $NaNH_2$. Prior to this operation, grind anhydrous $CrCl_3$ (Sec.11.5.6) to a fine powder. Weigh out 2.5 g of the powder, and add in small portions to the ammonia solution. Allow the precipitate to settle, decant off the liquid. Transfer the brown precipitate to an evaporating basin and allow any ammonia to evaporate. Dissolve quickly in 10 cm^3 0.75 M HCl preheated to 40°C. Filter under suction and immediately add 4 cm^3 16 M HNO_3 to the filtrate when the yellow complex separates. Cool in ice/salt to complete the precipitation. Filter the crystals under suction, wash with water slightly acidified with nitric acid then with small volumes of ethanol and then with a little ether. Dry by continued suction and store in a dark stoppered container wrapped in Al foil.

6.9 QUALITATIVE TESTS ON PHOSPHORUS AND ITS COMPOUNDS

6.9.1 White phosphorus

(a) Remove a small piece of white P from water (in which it is stored). Examine its appearance in the dark and test its solubility in water and in carbon disulphide.*

(b) Add dilute NaOH to a small piece, heat in the fume cupboard and expose a flame to the mouth of the tube. Decant the solution and add to it silver nitrate solution.

6.9.2 Phosphorus binary compounds

(a) Add water to a little calcium phosphide, expose a flame near the mouth of the tube. Test the solution or suspension with red litmus paper.

(b) Repeat and suck the gas with a Pasteur pipette and press the gas into a silver nitrate solution.

(c) Mix phosphorus(III) chloride with water, note any change in temperature. Test with a pH stick. Then divide into two parts. Add silver nitrate solution to one part and diluted acidified permanganate to the second part.

(d) Add water to a little phosphorus(V) chloride and note any changes in temperature. Test the solution with a pH paper. Then add silver nitrate solution.

(e) Add water gradually to a little phosphorus(III) oxide and test the solution as in (c).

(f) Add a little phosphorus(V) oxide carefully to 20 cm^3 water in a basin. Feel the outer surface of the basin. Add to the solution a piece of magnesium in a test tube and apply a flame to the mouth of the tube.

6.9.3 Phosphate(V)

(a) To a solution of either orthophosphate e.g. Na_2HPO_4, pyrophosphate e.g. $Na_4O_2O_7$ or metaphosphate e.g. $NaPO_3$, add separately:

  (i) silver nitrate solution and allow to stand, test the solubility of any precipitate in dilute ammonia, dilute acetic acid or dilute nitric acid;

  (ii) copper sulphate solution;

  (iii) magnesium and ammonium nitrates in presence of ammonia, check the effect of excess and of boiling;

  (iv) zinc sulphate solution, heat if necessary, check the solubility of any precipitate in dilute acetic acid.

(b) To a solution of an orthophosphate, add separately:
   (i) 3 cm^3 of ammonium molybdate acidified with nitric acid to 0.5 cm^3 of phosphate, warm if necessary, test the solubility of any precipitate in ammonia or in NaOH solution;
   (ii) iron(III) chloride solution after buffering at pH 5;
   (iii) zirconyl nitrate reagent (10% w/v in M nitric acid, boiled with stirring and decanting the clear solution).

6.9.4 Reducing oxosalts of phosphorus

Carry out the following tests on $NaH_2PO_2.H_2O$ (hypophsphite) and separately on $Na_2HPO_3.5H_2O$ (phosphite).

(a) Heat the solid and expose a flame and a silver nitrate paper. Test the residue after cooling with test 6.9.3 a (i) above.
(b) To portions of solutions of either of the above salts, add separately:
   (i) diluted acidified permanganate solution;
   (ii) silver nitrate solution, warm if necessary;
   (iii) copper sulphate solution, warm if necessary;
   (iv) mercury(II) chloride solution, then warm;
   (v) barium chloride solution, then add dilute HCl.
(c) To a little solid of either salt, add 1 cm^3 of conc. sulphuric acid and carefully heat exposing at the mouth of the tube an acidified dichromate paper or a flame.*
(d) To either solid, add a piece of zinc and 1 cm^3 dilute sulphuric acid and expose a flame and a silver nitrate paper at the mouth of the tube.
(e) Add to solid hypophosphite or phosphite conc. NaOH, warm and test with a flame.

6.10 ANALYTICAL CHEMISTRY OF PHOSPHATES AND ORTHOPHOSPHORIC ACID

In absence of interfering ions, orthophosphates are precipitated by magnesia mixture (a solution of magnesium and ammonium chlorides in ammonia solution) giving $Mg(NH_4)PO_4$. This can be weighed after washing with ethanol and drying. Alternatively, it can be transformed to MgP_2O_7 at 1100°C and weighed. High frequency titration of orthophosphates with magnesia mixture is a quicker volumetric method based on precipitating the same orthophosphate. Two alternative spectrophotometric methods are also available based on the formation of coloured complexes. The phosphovanadomolybdate method is based on the formation of a yellow complex obtained in acid solution of orthophosphate, vanadate and molybdate. The alternative method is based on the reduction of molybdophosphoric acid (formed in acid solution of phosphate and molybdate) to give a blue complex. Ortho-phosphoric acid is a tribasic acid and its titration curve is expected to exhibit 3 inflection points. The first neutralisation stage can be titrated with an indicator whose colour change overlaps with the pH of inflection 3.5. The second stage at pH 9.7 can be titrated with phenolphthalein mixed with 1-naphtholphthalein. No indicator is suitable for the third stage. However, pH potentiometric titration reveals the ionisation stages more clearly.

6.10.1 High frequency titration of orthophosphate with magnesia mixture

Prepare a solution which is 0.25 M in magnesium chloride or nitrate and 0.25 M in ammonium chloride or nitrate and 0.75 M in ammonia. Using purest K_2HPO_4 prepare a 0.3 M solution in deionised water. Deliver from a burette 75-80 cm^3 of this solution in the titration vessel provided with a bar magnet. Add, while stirring well, the magnesia mixture solution from a microburette and plot the instrument reading against the volume added. Resolve the plot to two linear parts and from the point of intersection, find the end-point and establish the molar ratio of PO_4^{3-}:Mg^{2+}:NH_4^+ is 1:1:1. Repeat to obtain concordant results.

6.10.2 Gravimetric determination of orthophosphate

Prepare a solution of 0.6 g purest magnesium sulphate, acidify with conc. HCl and make up to 150 cm^3. Add a few drops of methyl red indicator and then pipette 10.0 cm^3 of freshly prepared 0.02 M diammonium hydrogen phosphate. Then add concentrated ammonia solution while vigorously stirring until the colour changes to yellow. Continue stirring and dropwise addition of ammonia (to keep the solution yellow) for a few minutes and finally add a few cm^3 of ammonia and allow to stand for a few hours. Filter through a prepared G4 glass sintered crucible. Wash on the filter with small volumes of dilute ammonia until the filtrate is chloride-free. Then wash with small volumes of ethanol followed by ether (no flames!). Dry by continued suction and keep in desiccator before weighing.

In an alternative procedure, filter through a prepared G4 sintered porcelain crucible, wash with dilute ammonia as above. Then dry the crucible first in an oven at 150°C then in a muffle furnace at 1100°C to constant weight. Calculate from either method the concentration of PO_4^{3-} in mol dm^{-3}.

6.10.3 Investigating the yellow complex formed from phosphate, molybdate and vanadate

A yellow complex is formed when acidified solutions of ammonium vanadate, ammonium molybdate and an orthophosphate are mixed.

Prepare stock solutions of 0.02 M purest ammonium vanadate, 0.1 M ammonium molybdate and 0.01 M of purest orthophosphate. Pipette 5.0 cm^3 of the phosphate solution, into a 100 cm^3 volumetric flask, add 15 cm^3 60% purest perchloric acid, 10 cm^3 of the vanadate solution and variable volumes (3-9 cm^3) of the filtered molybdate solution. Then make up to the mark and shake well. Record the spectrum of the yellow solution of the highest [Mo] in a 10 mm cell over the range 400-500 nm and locate the wavelength of maximum absorption. Then measure accurately the absorbance at this wavelength of the other solutions (similarly treated) and plot it against [molybdate] and find the volume required for maximum colour formation. Using this volume of molybdate and the same volumes of phosphate and acid but 5-12 cm^3 of vanadate, measure the absorbance as above and determine the volume of vanadate required for maximum colour production. Use the same procedure to find the volume of perchloric acid needed for maximum colour production. After establishing these volumes, use these with a range of lower phosphate concentrations and plot the absorbance against [phosphate] to check the applicability of Beer's law.

6.10.4 Spectrophotometric determination of phosphate by the molybdenum blue method

When orthophosphates in acidified solution react with ammonium molybdate, phosphomolybdic acid is formed. When this is reduced by a suitable reductant, an intense blue complex is formed. The absorbance at the wavelength of maximum absorption is proportional to the phosphate concentration.

Prepare a stock solution of 0.01 M purest orthophosphate. By successive dilution, prepare a series of solutions in the range 2 x 10^{-4}- 5 x 10^{-5} M. Pipette 20 cm^3 of each solution, add 4.0 cm^3 of a reagent solution and make up to 25 cm^3. The reagent solution is made up by mixing 75 cm^3 of 0.03 M ammonium molybdate solution, 250 cm^3 2.5 M sulphuric acid and 150 cm^3 of 0.1 M ascorbic acid solution and making up to 500 cm^3 with boiled-out distilled water. Using the most concentrated phosphate solution, mix up 20 cm^3 with 4 cm^3 of the reagent solution, shake well and record the spectrum in a 4 or 10 cm cell over the range 500-1000 nm. Locate the wavelength of maximum absorption and note the absorbance of the test solution at this wavelength. Measure the absorbance of the other phosphate solutions at this wavelength after mixing with the reagent as above. Plot absorbance against phosphate concentration. Use the calibration plot to determine the concentration in an unknown solution. For more accurate calibration, determine the reagent blank by diluting 4 cm^3 to 25 cm^3 in a volumetric flask and measuring the absorbance as above. (*Phosphorus in Waters, Effluents and Sewage, H.M.Stationery Office, 1980).*

6.10.5 Potentiometric titration of orthophosphoric acid

Dilute 69 cm^3 of purest syrupy phosphoric acid to 1 dm^3 to obtain ~ 1 M solution and by 10-fold dilution, prepare ~0.1 M solution. Pipette 20.0 cm^3 of the acid into a 250 cm^3 conical flask. Calibrate the pH meter with a combined glass electrode and two buffer solutions at pH 4 and at 7. Dip the rinsed electrode into the flask, introduce a magnetic bar and add from a burette 0.1 M KOH solution in 2 cm^3 aliquots, reading the pH on the meter when it settles. When the pH change becomes more rapid as the titration proceeds, decrease the volume down to 0.5 cm^3 and then to 0.1 cm^3. After noting the first inflection point, continue with 2 cm^3 additions of KOH and eventually to 0.1 cm^3 addition until the second inflection point is reached. If a facility is available record the titration curve and preferably the derivative titration curve.

6.11 POTENTIOMETRIC TITRATION OF PHOSPHONIC ACID

Prepare 0.1 M solution of purest acid: $HP(OH)_2O$ in water. Use a similar procedure as above and titrate using 0.1 M KOH solution. Note the total volume of alkali required for the two steps. Add this volume to a similar volume of acid used above and test a portion of the neutralised solution with silver nitrate solution. Draw your conclusions about the basicity of the acid.

6.12 QUALITATIVE TESTS ON ANTIMONY AND BISMUTH

6.12.1 Antimony(III) or antimony(V)

(a) to separate portions of antimony trichloride in dil. HCl or potassium dihydrogen antimonate(V) add:
  (i) H_2S solution, test the solubility of any precipitate in ammonium sulphide or polysulphide solution followed by adding KOH solution;
  (ii) pieces of Sn or Fe;
  (iii) excess water;
  (iv) KI solution;
(b) To separate portions of antimony(III) chloride in dil. HCl, add:
  (i) NaOH solution, test the effect of excess NaOH;
  (ii) repeat using dilute ammonia;
  (iii) sodium thiosulphate solution;

(iv) 8-hydroxyquinoline solution.

6.12.2 Tests on bismuth compounds

(a) Acidify a solution of bismuth nitrate with dilute nitric acid to stop hydrolysis and add to separate portions:
   (i) ammonium sulphide solution, test the solubility of any precipitate in hot dilute nitric acid or hot conc. HCl;
   (ii) NaOH solution, test the effect of excess reagent and of boiling;
   (iii) sodium carbonate solution;
   (iv) excess water;
   (v) KI solution, test the effect of adding excess reagent; if a clear solution is formed add isobutylmethyl ketone and shake;
   (vi) diammonium hydrogen phosphate solution;
   (vii) potassium hexathiocyanatochromate(III) solution (Sec.11.6.1);
   (viii) tin(II) chloride solution after adding NaOH until the white precipitate just redissolves;
   (ix) ammoniacal solution of dimethylglyoxime;
   (x) 8-hydroxyquinoline in acetic acid solution;
   (xi) iron wire and heat.

(b) Add solid sodium bismuthate $NaBiO_3$ to a cold solution of manganese(II) sulphate or chloride in dilute nitric acid stir well and then filter the excess solid through a glass wool plug and examine the filtrate.

6.12.3 Micro test for As or Sb

To a few cm^3 of dilute sulphuric acid, add a piece of purest zinc then add a few drops of a solution of arsenic or antimony salt solution in a test tube in the fume cupboard. Place a glass wool plug near the top of the tube and cover the tube with a piece of filter paper moistened with 20% silver nitrate solution. Warm if necessary.*

6.13 ANALYTICAL CHEMISTRY OF ANTIMONY AND BISMUTH

6.13.1 Antimony(III) and antimony(V)

Gravimetric methods for the determination of Sb(III) as trisulphide or as Sb_2O_4 are not very specific. A quick volumetric method for Sb(III) is based on its oxidation by iodine, using starch as indicator. On the other hand, Sb(V) oxidises iodide to iodine which can be titrated against thiosulphate. Antimony as well as arsenic and bismuth can be determined by atomic absorption spectroscopy, the suitable wavelengths and concentration ranges and other conditions are usually supplied by the manufacturer. A useful spectrophotometric method is based on the yellow complex tetraiodobismuthate(III).

6.13.1.1 Determination of Sb(III) by iodine solution

Since antimony(III) compounds only dissolve in acid solution, the reaction of iodine produces HI. To remove this excess, sodium bicarbonate is added. To prevent the precipitation of Sb(III) in this case, tartrate is added. This forms a soluble compound: $K(SbO)C_4H_4O_6$.

Weigh out accurately 2.0 g of the purest potassium antimonyl tartrate, dissolve and make up to 250 cm^3 with water. Safely pipette 50.0 cm^3 of the solution into a conical flask add 20 cm^3 of a saturated solution of sodium bicarbonate and 2 cm^3 of freshly prepared starch solution. Titrate with standardised 0.05 M iodine solution until first appearance of the blue iodine-starch adsorption complex. Repeat to obtain concordant results and calculate [Sb(III)] in mol dm^{-3}.

6.13.1.2 Iodometric determination of Sb(V)

Sb(V)/Sb(III) reduction potential changes sign when the pH of the solution changes from alkaline to acidic. Hence in acidic media, Sb(V) will oxidise iodide to iodine. The liberated iodine is equivalent to [Sb].

Weigh out accurately about 0.4 g of purest potassium antimonate(V), add 30 cm^3 conc. HCl then add a large excess of KI solution in a distilling flask connected to 2 U tubes containing dilute KI. Heat to boiling until all the iodine passes to the U tubes. Combine their contents and rinsings in a conical flask. Titrate with standard 0.05 M thiosulphate solution until the solution is straw yellow. Add 2 cm^3 of fresh starch solution and continue titration until the blue colour disappears for 1 minute. Repeat to obtain concordant results and calculate from the average titre, [Sb(V)] in mol dm^{-3}.

6.13.1.3 Determination of Sb(III)

Prepare a stock solution of Sb(III) by dissolving 0.27 g purest potassium antimonyl tartrate in water, add gradually, with cooling in an ice bath, 160 cm^3 conc. sulphuric acid. When cold, make up to 1 dm^3 in a volumetric flask. By successive dilution, using water acidified with dilute sulphuric acid, prepare a series of solutions in the range: 1.5×10^{-5}- 1.5×10^{-4} M in [Sb(III)]. Pipette safely 10 cm^3 of each solution into a 50 cm^3 volumetric flask. Add 25 cm^3 of KI/ascorbic acid solution, made up by dissolving 14.0 g purest KI and 1.0 g purest ascorbic acid in boiled-out water, and making up to the mark. After thorough mixing run the spectrum of the most concentrated solution in a 10 mm u.v. cell over the range 300-500 nm. Locate the wavelengths of maximum absorption and note the absorbance at these wavelengths. Repeat with the other antimony solutions, but only measuring the absorbance at the wavelengths found. Use the calibration curve to find [Sb(III)] in unknown solutions.

6.13.2 Bismuth(III)

Bismuth(III) compounds in solution can be titrated with EDTA solution or precipitated as orthophosphate or they can be electrolytically determined as Bi. A suitable spectrophotometric method is based on complex formation with iodide.

6.13.2.1 Complexometric titration of Bi(III)

At a pH of 2.5-3.5, bismuth salt solutions can be titrated with EDTA solution using pyrocatechol violet indicator.

Prepare 0.05 M bismuth nitrate solution by weighing out 6 g of purest salt, adding water and 25 cm^3 concentrated nitric acid and making up to 250 cm^3 with water. Pipette 25.0 cm^3 of the solution into a 250 cm^3 conical flask, add an equal volume of water. Adjust the pH to the optimum range using dilute alkali with a narrow range pH stick dipping in the solution. Add a few drops of the indicator solution and titrate with standardised 0.05 M EDTA solution until the colour changes from blue to violet and then yellow at the end-point. Repeat to obtain concordant results and calculate from the average titre [Bi] in mol dm^{-3}.

6.13.2.2 Gravimetric determination of Bi(III) as orthophosphate

Although the gravimetric electrodeposition is quicker, the recommended silverising the platinum cathode from cyanide solution represents a safety problem. Precipitation of bismuth nitrate as phosphate may be carried in the usual way or by precipitation from homogeneous solution. In this case a solution of metaphosphoric acid is used. This should be prepared freshly by dissolving 10 g of the purest solid in 100 cm^3 water in which 1 cm^3 of conc. nitric acid is added. Precipitation is followed by filtration and eventually drying.

Prepare a solution of 0.33 g of purest bismuth nitrate, add 10 cm^3 concentrated nitric acid and 20 cm^3 of water in a 400 cm^3 beaker. Add 1:1 ammonia solution, slowly with stirring, until the solution is turbid. Then add 10 cm^3 of conc. nitric acid and 25 cm^3 of the metaphosphoric acid solution and dilute to 300 cm^3. Cover with a watch glass and heat to the boil on a hot plate and continue for an hour. Allow to cool and decant the supernatant into a prepared porcelain sintered crucible. Transfer the precipitate to the crucible quantitatively with a 10% ammonium nitrate solution. Dry at 110°C and then in a muffle furnace at $800^{oC.}$ Carry out duplicates and calculate the concentration of Bi(III) in mol dm^{-3}.

6.13.2.3 Spectrophotometric determination of bismuth

In absence of coloured compounds and metal ions which react with iodide, Bi can be determined as the yellow iodo-complex.

Prepare a stock solution by dissolving 1.2 g purest bismuth(III) oxide in 200 cm^3 conc. sulphuric acid and making up to 1 dm^3 in a volumetric flask.

Prepare a series of solutions by successive dilution in the range 8×10^{-5} - 8×10^{-4} M using 1 M sulphuric acid for dilution. Pipette 10 cm^3 of each solution into a 25 cm^3 volumetric flask. Add 1 cm^3 of 30% H_3PO_2 and 1 cm^3 of 10% KI solution shake well after making up to the mark. Using the most concentrated solution, run its spectrum in a 10 mm cell over the range 380-580 nm and locate the wavelength of maximum absorption and determine the absorbance at this wavelength. Repeat the colour development in the other solutions and measure the absorbance at this wavelength. Plot absorbance against Bi concentration and use the calibration plot to determine the concentration of unknown solutions.

6.14 PREPARATION AND REACTIONS OF $[PCl_4][SbCl_6]$

Solid PCl_5 exists in the lattice as tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ but $SbCl_5$ is a liquid and acts as a strong Lewis acid and powerful Cl acceptor. Both chlorides are very sensitive to moisture. In absence of moisture, they react forming the solid tetrachlorophosphonium hexachloroantimonate(V) which is also sensitive to moisture. Hence the reaction has to be carried out in a moisture-free nitrogen atmosphere in a glove box (Sec.2.9.1) or in a dry bag.

Purge the glove box with nitrogen (freed from moisture by bubbling through conc. sulphuric acid) after introducing all the necessary chemicals and glassware into the box. Mix 1.3 cm^3 of antimony pentachloride with 10 cm^3 of methylene chloride. Dissolve 2.1 g photphorus pentachloride (previously quickly weighed in a stoppered weighing bottle) in 50 cm^3 of the same solvent. Mix the two solutions with stirring and filter the solid produced preferably using a Buchner flask with the flask being partially evacuated by a pumpet. Wash with a little ether and allow to dry and carry out the following tests on the product.

(a) Expose a little solid a to air for some time.

(b) Add a little compound carefully to a few cm^3 of water. To separate portions add:
    (i) silver nitrate solution;
    (ii) NaOH solution added gradually with shaking.

6.15 EFFECT OF Bi(III) ON THE OXIDATION OF Cr(III) EDTA COMPLEX BY PERMANGANATE

When Cr(III) nitrate is boiled with the sodium salt of EDTA, a complex is formed in which a water molecule occupies the sixth coordination position of the Cr(III). The rate of oxidation of EDTA by permanganate is reduced when it coordinates to a metal ion e.g. Cr(III). It is interesting to investigate the effect of Bi(III) on the rate.

Prepare 5 x 10^{-2} M solution of purest EDTA (disodium salt) and 5 x 10^{-2} M solution of purest Cr(III) nitrate enneahydrate in water. Mix equal volumes of the two solutions in a flask provided with an upright water-cooled condenser. Heat to boiling until maximum colour change takes place. Dilute an aliquot to obtain a 0.01 M solution of the Cr(III) complex. Quickly mix 20.0 cm^3 of this solution with 0.4 cm^3 of 0.02 M permanganate solution and 20.0 cm^3 M sulphuric acid and make up to 200 cm^3. Fill a 1 cm cell with the mixture and measure the absorbance at 545 at short intervals. In some instruments the kinetic plot is recorded. Otherwise plot absorbance against time. Repeat the kinetic run but replace the sulphuric acid by 20 cm^3 of 0.01 M Bi(III) nitrate in 1 M sulphuric acid and plot absorbance against time. What conclusions can be drawn from your results?

7

The sulphur group

7.1 INTRODUCTION

Group 16 contains the elements O, S, Se, Te and Po. Oxides of metals or non-metals are usually considered in the respective groups of the Periodic Table. Hence the chemistry of this group is dominated by the compounds of sulphur, which exhibits the widest range of oxidation numbers including fractional numbers. However, the general feature of the whole group is the formation of binary compounds in which they exhibit an oxidation number of -2:sulphides, selenides and tellarides, collectively called chalkogenides. Since the elements of this group have an electronic configuration which is two electrons short of the following noble gas, they have a tendency to acquire two electrons to complete the octet. However, only sulphides of groups 1 and 2 are typically ionic. With most other metals, there is clear departure of the sulphides from ionic character. This trend is more apparent in the chalcogenides down the group. Most metal sulphides have very low solubility products. Their solubility in acids varies, depending on the metal and its oxidation state as well as the nature of the acid. An interesting group of chalcogenides, referred to as (II)/(VI) compounds, are formed with metals of group 12. They are semiconductors and have interesting technical properties including photocatalytic activity. The maximum oxidation number of +6 is common to the elements of this group except O and Po. The main compounds of this oxidation number are the oxides EO_3, the derived oxoacids and their salts. Among the halides, only the hexafluorides are known for S, Se and Te since the strong short bonds to the highly electronegative fluorine stabilise the highest oxidation state. The next common oxidation state is +4 which is represented by the dioxides EO_2(E=S-Po) and the tetrahalides EX_4 or more usually E_4X_{16}. The lower oxidation numbers are less important. However, S_2Cl_2 and the less stable SCl_2 are the more important chlorides of sulphur. A unique feature of S is catenation i.e. its tendency to form chains and rings due to the strong S-S bonds. Most of these bonds are single σ bonds but S=S double bonds are found e.g. in the tetrahedral thiosulphate ion in $S_2O_3^{2-}$. The tendency to catenate decreases down the group as the E-E σ bonds become longer and weaker. The weakness of the O-O σ bond is ascribed to interelectronic repulsion in the compact 2p orbitals of oxygen. This weakness explains the instability of hydrogen peroxide and the oxidising power of peroxo-compounds including persulphates e.g. $S_2O_8^{2-}$. The oxidising power of the higher acids decrease in the series: $H_2SeO_4 > Te(OH)_6 > H_2SO_4$. This is an example of what is termed "mid row anomaly". The oxidising power of these acids contrasts the behaviour of the lower acids.

Thus SO_2 and H_2SO_3 and its salts are usually reducing agents, except when they react with powerful reductants. The volt-equivalent-oxidation number diagram (Fig.7.1) shows these features as well as the greater stability of the oxoanions of S in alkaline media compared to acid solution. It also demonstrates the instability of H_2Se and H_2Te and the stability of H_2S which is exceeded by the stability of water. This is a reflection of the weakness of the bonds to hydrogen as the atoms of this group become larger and generally less electronegative down the group.

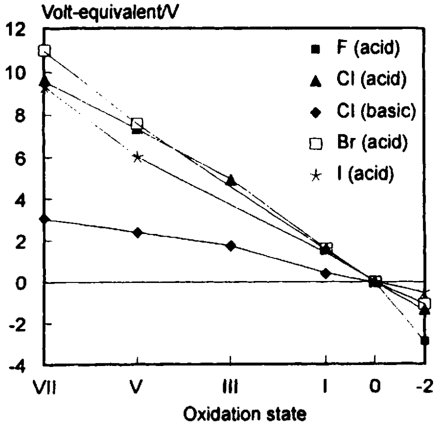


Figure 7.1 Volt-equivalent versus oxidation number for the sulphur group.

7.2 QUALITATIVE TESTS

7.2.1 Sulphur and its binary compounds

(a) Heat in a small borosilicate tube a little finely ground sulphur and notice the changes taking place. When the liquid is mobile, pour it into some water and examine the product.

(b) Mix finely ground S with iron filings and heat in a small crucible. When the two powders react, cool the product and grind to a fine powder. Sprinkle some on a paper placed over a bar magnet. Add dil. HCl to the remainder in a test tube and expose a moist lead acetate paper at the mouth of the tube.

(c) Test the solubility of sulphur in (i) pyridine, (ii) water.

(d) To a little sulphur, add 1 cm^3 fuming sulphuric acid, warm and shake.*

(e) To a little sulphur, add 1 cm^3 of concentrated nitric acid, heat carefully and expose to the mouth of the tube a moist blue litmus paper. When cold, decant the clear liquid and add barium nitrate solution.*

(f) Repeat (d) using conc. sulphuric acid instead of nitric acid, heat and expose at the mouth of the tube acidified dichromate paper.*

(g) Add a drop of mercury to a solution of sulphur in pyridine and shake.

(h) Warm a little sulphur with sodium sulphite solution until it dissolves and then add silver nitrate solution dropwise with shaking.

(i) Boil some sulphur with NaOH solution. When dissolved, add to separate portions: (i) silver nitrate solution, (ii) sodium nitroprusside solution (Nitrosylpentacyanoferrate (II)).

(j) Repeat (i) but using mercury(I) nitrate solution and note any changes.

(k) To a little S_2Cl_2 add water and shake and test with blue litmus and with dichromate paper.

7.2.2 Tests on sulphides

(a) Add to a little solid sulphide e.g. FeS dil. HCl, warm and expose at the mouth of the tube a moist lead or cadmium acetate paper.

(b) Prepare a solution of sodium sulphide in water and add to separate portions:

- (i) silver nitrate solution, test the solubility of any precipitate in dilute nitric acid, heat if necessary;
- (ii) lead acetate solution and test as in (i);
- (iii) sodium nitroprusside solution made alkaline with NaOH;
- (iv) a piece of silver or silver plated article after slightly acidifying with dil.HCl. Then rub with moist lime.

7.2.3 Tests on sulphites

(a) Add to a solid sulphite dil. HCl. Use a teat pipette to suck the gas and then deliver its contents into acidified dichromate solution.

(b) Repeat (a) but deliver into a little lime water.

(c) Add to a solution of sodium sulphite separately:

- (i) barium chloride solution, test the solubility of any precipitate in dil. HCl;
- (ii) repeat (i) but test after adding hydrogen peroxide;
- (iii) silver nitrate solution, test the solubility of any precipitate separately in excess reagent or in ammonia solution;
- (iv) permanganate solution (acidified with sulphuric acid);
- (v) potassium dichromate solution acidified with sulphuric acid;
- (vi) lead acetate solution, test the solubility of any precipitate in dilute nitric acid before and after boiling;
- (vii) iodine solution in KI;
- (viii) dilute sulphuric acid and a piece of zinc, expose at the mouth of the tube a lead acetate paper.

7.2.4 Tests on dithionites $(O_2S\text{-}SO_2)^{2-}$

(a) Add to a little of the solid sodium dithionite dilute HCl or sulphuric acid and expose an acidified dichromate paper at the mouth of the tube.

(b) Repeat (a) using conc. sulphuric acid.

(c) Add to a solution of the sodium salt separately:

- (i) silver nitrate solution;
- (ii) copper sulphate solution, discard the supernatant and add dilute nitric acid to the residue;
- (iii) mercury(II) chloride solution;
- (iv) mercury(I) nitrate solution;
- (v) acidified permanganate solution;
- (vi) potassium hexacyanoferrate(III);
- (vii) nickel(II) salt solution to which ammonia solution had been added in excess, then heat;
- (viii) acidified Cr(VI) solution, shake and then add barium chloride solution;
- (ix) iron(III) chloride solution.

(d) Heat a little solid dithionite in a dry test-tube, apply a blue cobalt paper to any condensate. Expose at the mouth of the tube an acidified dichromate paper. Cool the residue, dissolve it in water and add silver nitrate solution.

7.2.5 Tests on thiosulphates (trioxothiosulphate(VI)

(a) Heat some sodium thiosulphate crystals gradually in a dry test tube and then heat more strongly. When cold, add dil. HCl to the residue and expose a moist lead acetate paper.

(b) Add to a solution of sodium thiosulphate separately:

- (i) iodine solution in KI;

- (ii) silver nitrate solution, added dropwise with shaking; then warm;
- (iii) lead acetate solution, test the effect of adding an excess reagent and of boiling;
- (iv) ammonium molybdate solution, mix well and pour on the sides of a dry test tube containing a little conc. sulphuric acid;
- (v) iron (III) chloride solution added slowly;
- (vi) acidified permanganate solution;
- (vii) acidified dichromate solution;
- (viii) copper sulphate solution, then boil.

(c) Add a little dil. HCl to the solid thiosulphate, expose at the mouth of the tube an acidified dichromate paper.

7.2.6 Tests on dithionates ($S_2O_6^{2-}$)

(a) Heat a little sodium dithionate in a test tube strongly, exposing an acidified dichromate paper at the mouth of the tube. When cold, dissolve the residue and add barium chloride solution.

(b) Add conc. HCl to the solid salt, test as in (a).

(c) To a solution of the sodium salt, add separately:
- (i) barium chloride solution;
- (ii) 0.2 M iodine solution;
- (iii) iron(III) chloride solution;
- (iv) NaOH solution, then boil. When cold divide into two parts: Add to one part barium chloride solution and add to the other part acidified dichromate solution;
- (v) concentrated lead nitrate solution;
- (vi) acidified permanganate solution and then boil;
- (vii) nickel(II) nitrate solution to which diaminoethane had been added until a violet colour is produced.

7.2.7 Tests on sulphates

(a) Make up a solution of a soluble sulphate e.g. the sodium salt and add separately to portions:
- (i) barium nitrate solution, acidified with dil. HCl, test the solubility of any precipitate separately in: boiling conc. HCl, and in an alkaline solution of EDTA;
- (ii) lead acetate solution, test the solubility of any precipitate separately in alkaline EDTA and in a concentrated solution of ammonium acetate;
- (iii) silver nitrate solution to a concentrated solution of sulphate.

(b) Mix a powdered sulphate with powdered sodium carbonate and fuse the mixture on a charcoal block. When cool, add 2 drops of very dil. HCl and cover with a lead acetate paper.

7.2.8 Tests on sulphuric acid, sulphamic acid and its salts

(a) To a little glucose or other sugar add 1 cm^3 conc. sulphuric acid.

(b) To a dilute solution of sulphamic acid, add bromine water dropwise.

(c) Mix sulphamic acid solution with sodium nitrate solution, then add barium nitrate solution.

7.2.9 Tests on persulphates (peroxodisulphates)

(a) Boil a solution of the potassium salt and expose a glowing splint after inserting a glass wool plug near the mouth of the tube.

(b) Heat the solid salt and test with a glowing splint.

(c) To a solution of manganese(II) salt acidified with dilute nitric acid, add 2 drops of silver nitrate solution and a solid ammonium persulphate, boil for a few minutes.

(d) Repeat (c) using a solution of Cr(III) salt.

(e) To a solution of a persulphate, add separately:
- (v) silver nitrate solution to a concentrated solution;

(vi) barium chloride solution, boil if necessary;
(vii) KI solution, warm and dip a starch paper;
(iv) nickel (II) solution after adding KOH solution.

7.3 ANALYTICAL CHEMISTRY OF SULPHUR ANIONS

7.3.1 Hydrogen sulphide and soluble sulphides

These can be titrated by adding a known excess of an iodine solution, back titrating the excess iodine against standardised thiosulphate. Alternatively, sulphides may be precipitated after oxidation to sulphate.

Prepare a 0.1 M solution of purest sulphide and dilute 10-fold. Add 25.0 cm^3 of the solution to 35.0 cm^3 of 0.01 M iodine solution (measured by burette) in a conical flask. Determine the excess iodine by titration against standardised 0.01M thiosulphate solution (obtained by 5-fold dilution of 0.05 M solution) until the solution is pale yellow. Add 2 cm^3 freshly prepared starch solution and continue titration until the blue colour is discharged.

7.3.2 Sulphur dioxide and sulphites

Similar to hydrogen sulphide and sulphides, sulphur dioxide and sulphites can be determined by titration with iodine or by oxidation to sulphate followed by gravimetric determination as barium sulphate. Additionally a spectrophotometric method was developed based on the colour of *p*-nitroaniline which is discharged on acidification but is restored by adding formaldehyde and sulphur dioxide or sulphite.

7.3.2.1 Iodometric titration of sulphites

The reaction is rather slow but is best carried out in dilute solution. To avoid the aerial oxidation of the sulphite, it is added to a known excess of standardised iodine solution, back titrating the excess with thiosulphate.

Prepare freshly 0.05 M iodine solution. Pipette 25.0 cm^3 of this solution into a 400 cm^3 conical flask, add 5 cm^3 2 M HCl and dilute with water to ~180 cm^3. Prepare freshly a solution which is 0.05M in sulphite or SO_2. Add from a burette 15-20 cm^3 of this solution to the iodine solution. This should be done slowly with stirring and keeping the tip of the burette close to the iodine solution. Then titrate the excess of iodine against standardised 0.01 M thiosulphate solution prepared by 5-fold dilution of 0.05 M solution. Follow the procedure in Sec.7.3.1. Alternatively weigh out accurately 0.09-0.13 g of the purest sulphite and dissolve it in the acidified diluted iodine solution and continue as above.

7.3.2.2 Gravimetric determination of sulphite

Sulphites are oxidised when boiled with an excess of ammoniacal hydrogen peroxide. The sulphate is then precipitated as barium sulphate.

Mix 20 volume hydrogen peroxide with an equal volume of 1:1 ammonia solution.

Weigh out accurately about 0.2 g of purest sodium sulphite into a 400 cm^3 beaker and dissolve it in a minimum of water. Add 5 cm^3 20 volume hydrogen peroxide and 5 cm^3 1:1 ammonia solution and allow the reaction to proceed with shaking. Heat the mixture gradually to the boil and ensure that all the ammonia has been removed by exposing to the vapour a mercury(I) nitrate paper. Then add ½ cm^3 conc. HCl and dilute to 200 cm^3. Heat the solution to boiling and add, dropwise, with stirring, 12 cm^3 of 5% w/v (0.2 M) barium chloride solution. When the precipitate settles, test for complete precipitation by adding the precipitant dropwise, ensuring that a slight excess has been added. Cover with a watch glass and keep on a steam bath for an hour, maintaining a volume >150 cm^3. Filter through a prepared sinter glass crucible and weigh after washing. Wash with hot water until the washings are chloride-free, then wash with small volumes of ethanol and small volumes of ether (away from flames). Suck dry for 10 minutes and weigh after wiping the outside of the crucible. Repeat and calculate, from the average, [sulphite] in mol dm^{-3}. Alternatively filter through a prepared sinter porcelain crucible. Wash with small volumes of water as above. Dry initially in an oven and then in a muffle furnace at 800°C to a constant weight. Calculate the percentage purity of the solid from duplicate results.

7.3.2.3 Spectrophotometric determination of sulphite.

Dissolve 0.138 g of purest *p*-nitroaniline in 25 cm^3 ethanol and make up to 1 dm^3 with water. Dilute formaldehyde to make a 0.1 M stock solution.

Prepare a stock solution which is 5 x 10^{-2} M in sulphur dioxide or sulphite. By successive dilution prepare a series of solutions in the range 0.15-5.0 x 10^{-4}M. Pipette 10.0 cm^3 of each solution into a 50 cm^3 volumetric flask. Add 1 cm^3 of freshly prepared 0.6% sulphamic acid solution, 10 cm^3 of 4 M HCl, 15 cm^3 of the aniline solution and 10 cm^3 of the formaldehyde solution and make up to 50 cm^3 with water after mixing the component solutions. Prepare a blank solution which excludes the sulphur solution. Record the spectrum of the strongest sample against the blank in 10 mm uv cells over the range 200-500 nm and locate the absorbance at the wavelength of maximum absorption. Determine the absorbance of the other prepared solutions at this wavelength, plot absorbance against concentration and use the calibration plot to determine [SO_2] in any unknown.

7.3.3 Thiosulphates (trioxothiosulphates(VI)

Similar to sulphites, thiosulphates can be titrated against standardised iodine solution. Following oxidation to sulphate by hydrogen peroxide/ammonia solution, thiosulphates can be determined gravimetrically as $BaSO_4$ (See above section for details).

Standardisation of thiosulphate solutions

Because of the uncertainty in the exact water content of the purest sodium thiosulphate and because of the instability of its solutions due to traces of carbon dioxide in distilled water etc., it is essential to standardise solutions before use. Any turbidity in solutions due to the deposition of sulphur necessitates discarding the solution. The purest potassium iodate is >99.9% pure and can be dried at 120°C to remove any moisture. Weigh accurately about 3.5g of dried purest iodate, dissolve in water and make up to 1 dm^3 in a volumetric flask. Pipette 25.0 cm^3 of the solution into a conical flask, add 2 g of purest KI and shake well before adding 5 cm^3 1M sulphuric acid solution. Titrate the liberated iodine with the thiosulphate solution as in Sec.7.3.1. Repeat to obtain concordant results and calculate the molar concentration of the thiosulphate solution.

7.3.4 Sulphates

Sulphates in solution may be determined by complexometric titration. After precipitating sulphate as barium sulphate, a known excess of standard EDTA solution is added. The excess is then titrated against standard magnesium salt solution. Gravimetric analysis is also carried out by precipitating and weighing barium sulphate. Among the instrumental methods of analysis, amperometric titration using standard lead nitrate solution will be described. Ion chromatography is suitable for low sulphate concentrations.

7.3.4.1 Complexometric determination of sulphate

Prepare a 0.05 M standard EDTA solution and 0.05 M magnesium chloride solution. Using purest sodium or potassium sulphate, prepare a 0.02 M solution and pipette 25.0 cm^3 into a beaker, add an equal volume of water and 2M HCl to bring the pH to 1. Heat nearly to boiling and add 10 cm^3 of 0.05 M solution of barium chloride which had been similarly heated while stirring well. Keep the beaker on the steam bath for an hour and check for complete precipitation. Filter through No.42 paper (supported on a porcelain disc) under suction and wash with water, ensuring no precipitate is lost during filtration. Transfer the precipitate quantitatively to the original beaker, add from a burette 35-40 cm^3 of 0.05 M EDTA solution, add 5 cm^3 concentrated ammonia and heat to boil for 20 minutes, then add 2 cm^3 of ammonia and repeat the heating. After cooling, add 10 cm^3 of buffer solution (pH 10), a few drops Eriochrome T indicator and titrate with the magnesium solution until the colour changes to red. Repeat to obtain concordant results and calculate from the average the concentration of sulphate in mol dm^{-3}.

7.3.4.2 Gravimetric determination of sulphate

Sulphate can be precipitated as barium sulphate in a similar way to that described in Sec.7.3.2 but without the initial step of oxidation.

7.3.4.3 Amperometric titration of sulphate (Sec.2.5.5)

In this titration with standard lead nitrate, ethanol is added to reduce the solubility of the precipitated lead sulphate. There is no need to add a supporting electrolyte since the salt formed during the titration suppresses the migration current.

Prepare a 0.01 M solution using the purest sulphate. Using an exact weight of purest lead nitrate, prepare ~0.01 M solution. Pipette 25.0 cm^3 of the sulphate solution in the titration cell and add 3 drops of thymol blue indicator and concentrated nitric acid dropwise to change the colour to red. Use a pH stick to indicate a pH of 1-2. Then add 25 cm^3 ethanol. Connect a calomel electrode to the cell. Purge the solution with nitrogen for 20 minutes then pass the gas over the surface of the liquid. Make the necessary electrical connections and apply -1.2 V against the saturated calomel electrode. Use an available polarograph and dropping Hg electrode. Add the lead solution from a burette (at 0.5 cm^3 each addition) noting the current and passing nitrogen after each addition. Reduce the volume of titrant added gradually when the current shows a clear increase near the end-point. Beyond this point, use 0.5 cm^3 additions and plot the current against the volume added. Resolve the plot into 2 straight lines and locate the end-point as the point of intersection. Repeat and calculate from the average titre the concentration of sulphate in mol dm^{-3}.

7.3.5 Persulphates (peroxodisulphates)

7.3.5.1 Volumetric determination of persulphates

Persulphates (e.g. $K_2S_2O_8$ or $(NH_4)_2S_2O_8$) may be determined in acidified aqueous solution by adding a known excess of an iron(II) salt solution and back titrating the excess against a standardised $KMnO_4$ solution. The standardisation can be conveniently carried out by titrating $KMnO_4$ against the iron(II) solution whose concentration should be accurately known.

The relevant standard redox potentials, $E_{298}{}^{o}$at H^+ activity=1 are:

	E°/V	
MnO_4^-/Mn^{2+}	1.51	(7.1)
Fe^{3+}/Fe^{2+}	0.77	(7.2)
$S_2O_8^{2-}/SO_4^{2-}$	2.01	(7.3)

and the relevant equations are:

$$MnO_4^-+8H^++5Fe^{2+}\rightarrow Mn^{2+}+4H_2O+5Fe^{3+} \quad (7.4)$$

$$S_2O_8^{2-}+2Fe^{2+}+2H^=\rightarrow 2Fe^{3+}+2HSO_4^- \quad (7.5)$$

$KMnO_4$ acts as a self indicator in the standardisation and in the back titration. By adding H_3PO_4, the reduction is complete in a few minutes.

Using purest potassium or ammonium persulphate prepare 0.03 M solution. Pipette 25.0 cm^3 of the solution into a 250 cm^3 conical flask, add 3 cm^3 of H_3PO_4 (syrupy), 10 cm^3 dil. H_2SO_4 and 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) solution. After 5 minutes, titrate the excess Fe(II) with 0.02M $KMnO_4$ solution to the first permanent faint pink colour. Repeat to obtain concordant results.

Standardise the $KMnO_4$ solution by the following method: Pipette 25.0 cm^3 of the iron(II) solution, add 3 cm^3 H_3PO_4, 10 cm^3 dil. H_2SO_4 and titrate against the $KMnO_4$ solution in the burette to the first permanent faint pink colour. Repeat to obtain concordant results.

Calculate: (a) the concentration of $KMnO_4$, from the average titre, in mol dm^{-3}; (b) the concentration of $S_2O_8^{2-}$ in the solution, in mol dm^{-3}.

7.3.5.2 Alternative titrimetric method

Instead of using iron(II) solutions to reduce persulphate to sulphate, oxalic acid can be used as a reductant. Here and as in other reactions the rate of reduction is even slower than in the above procedure and the addition of silver ions catalyse the reaction.

Weigh out accurately about 0.38 g of the purest potassium salt, add 50.0 cm^3 (by burette) of 0.05 M oxalic acid solution and 20 cm^3 of 10% sulphuric acid in which 0.2 g silver sulphate had been dissolved, and dilute to 100 cm^3. Heat on a water bath until no more carbon dioxide is evolved (20-30 minutes). Dilute to about 100 cm^3 using hot water. Heat to about 80° before titrating the excess oxalic acid against standardised 0.02M potassium permanganate. Calculate the % purity of the salt used.

7.3.6 Dithionite, sulphite and thiosulphate *(Acta Chim.Hung.*20(1959)399).

Although dithionites can be determined by reaction with iodine in a similar way to that described above for sulphites, and thiosulphates, the problem is the disproportionation of the dithionite.

$$2S_2O_4^{2-}+H_2O = 2HSO_3^-+S_2O_3^{2-} \quad (7.6)$$

A method was therefore devised to determine the three anions simultaneously. This is based on their oxidation by hexacyanoferrate(III) under different alkali concentration and using osmium tetroxide as a catalyst. The corresponding reactions are:

$$Na_2SO_3+2K_3[Fe(CN)_6]+2KOH=Na_2SO_4+2K_4[Fe(CN_6]+H_2O \tag{7.7}$$

$$Na_2S_2O_3+8K_3[Fe(CN)_6]+8KOH=Na_2SO_4+8K_4[Fe(CN)_6]+3H_2O+H_2SO_4 \tag{7.8}$$

$$Na_2S_2O_4+2K_4[Fe(CN)_6]+2KOH+2NaOH=2Na_2SO_3+2K_4[Fe(CN)_6]+2H_2O \tag{7.9}$$

The tetrathionate formed from the reaction of thiosulphate with iodine is also oxidised by the iron(III) complex:

$$Na_2S_4O_6+14K_3[Fe(CN)_6]+14KOH=Na_2SO_4+14K_4[Fe(CN)_6]+4H_2O+3H_2SO_4 \tag{7.10}$$

When the alkali concentration is 0.5-1.0M, dithionite can be titrated with standard hexacyanoferrate(III) solution. Because of the possibility of oxidation in air, the titration vessel should be provided with an inlet and an outlet for purging and maintaining an oxygen-free nitrogen atmosphere. Under these conditions, the dithionite is oxidised to sulphite. When the alkali concentration is raised to 4-4.5 M and the temperature is raised to 50°-60°C, the sulphite thus produced or already present together with the thiosulphate, the anions are oxidised by the iron(III) complex to sulphate. Titration is carried out in presence of osmium tetroxide as a catalyst. A second titration with iodine in acid solution oxidises the thiosulphate to tetrathionate. This can be titrated with the iron(III) complex at 50°C when the alkali concentration is 5 M. The end-point could be detected potentiometrically or by the dead-stop set up.

Prepare a solution which is 0.1 M in sodium sulphite using 1M NaOH for making up the solution. Prepare another solution which is 0.1M in sodium dithionite in 1 M KOH. Pipette 25.0 cm^3 of each freshly prepared solution into a titration vessel equipped with magnetic follower and two platinum electrodes as well as an inlet and an outlet for purging with nitrogen. Weigh out accurately about 0.16 g of purest sodium thiosulphate and dissolve it in the mixed solution. Purge with nitrogen for 15 minutes before starting the titration with 0.1 M purest potassium hexacyanoferrate(III). The end-point is indicated when the current is practically zero. Add 9.8 g of KOH and 2-3 drops of osmium tetroxide and heat to 60°C. Continue titration under nitrogen atmosphere and note the volume required at the end-point.

Pipette 25.0 cm^3 of each solution in the same cell and dissolve 0.16 g of sodium thiosulphate. Acidify weakly with HCl and titrate with 0.05 M iodine solution using potentiometric detection of the end-point. At the end-point, the solution only contains sulphate and tetrathionate. Add concentrated alkali solution until its concentration is 5 M in the final solution. Then titrate with 0.1 M hexacyanoferrate(III) at 60°C in presence of the catalyst. Calculate from the results the concentrations of the three oxoanions in the original solution. Carry out titration in duplicate and use the average for the calculation.

7.4 PREPARATION OF SULPHUR OXOSALTS

7.4.1 Preparation of dithionates *(Canadian J.Chem.*11(1963)201)

When sulphur dioxide reacts with an aqueous suspension of manganese dioxide, manganese dithionate is formed. When this is treated with barium hydroxide, the barium dithionate is left in solution when manganese(II) hydroxide separates. Alkali metal or ammonium dithionates are prepared from a solution of the barium dithionate in an ion-exchange column.

Pass sulphur dioxide through a stirred suspension of 10 g precipitated manganese dioxide in 50 cm^3 water cooled in an ice bath until the powder dissolves (in a few hours). Dilute to 300 cm^3 with water and boil until sulphur dioxide has been expelled, indicated by no change in colour of an acidified dichromate paper. Add solid barium hydroxide to the boiling solution to precipitate the manganese(II) ions (~40 g). Filter the precipitated manganese(II) hydroxide under suction, collecting the filtrate in a clean Buchner flask. Evaporate the filtrate until the volume is about 80 cm^3. Cool slowly and allow the barium dithionate to crystallise. Filter the crystals under suction and dry by continued suction while pressing between filter paper. Record the infrared spectrum of the product using a KBr disc over the range 900-1400 cm^{-1}. Measure the refractive index of your product.

Preparation of potassium dithionate

When alkali metal sulphites are mixed with silver nitrate solution in equimolar ratio, and the solution heated to boiling, the alkali metal dithionate is formed together with finely divided silver. The initial stage is preparing potassium sulphite.

Dissolve 4.4 g purest $K_2S_2O_5$ in 20 cm^3 of 10% KOH solution. Add a few drops of phenolphthalein indicator and then add the KOH solution dropwise until a permanent pink colour is obtained. Then add to this solution, slowly and with stirring, a concentrated solution of 6.5 g silver nitrate. After continuous stirring to make the precipitate granular, heat on a boiling water bath for half an hour, with occasional stirring, when a yellowish grey product is formed. Compact the precipitate, filter into an evaporating basin. Check that the filtrate is Ag^+-free and then concentrate the solution on a water bath nearly to dryness. Dissolve the mass in 36 cm^3 hot water and, if necessary, filter through pleated paper. Reheat the filtrate (or the original unfiltered solution) to 70°-80°C in a water bath and add 10 cm^3 ethanol. Cool to room temperature and allow to crystallise; filter under suction. Wash on the filter with equivolume aqueous ethanol and dry by continued suction while pressing between filter paper. If traces of nitrate are detected, recrystallise. Weigh your product and calculate the % yield based on S.

7.4.2 Preparation and analysis of zinc dithionite

Weigh out 2 g purest zinc dust into a 100 cm^3 conical flask and add 10 cm^3 equivolume of water and ethanol or 10 cm^3 ethanol. Place in the fume cupboard and pass a slow stream of sulphur dioxide until the zinc dissolves and crystals of the dithionite forms. Cool and quickly filter the product under suction. Wash with a small volume of ethanol and dry by continued suction. Weigh your product and calculate the % yield.

Dithionites reduce diammine silver nitrate to silver, which is dissolved in nitric acid and the solution titrated against standardised thiocyanate solution.

Pipette 25.0 cm^3 of 0.5 M silver nitrate into a 250 cm^3 beaker and add dilute ammonia until the precipitate formed redissolves and then add 5 cm^3 more of ammonia. Weigh out accurately about 0.1 g of your preparation, add it to the silver solution and allow it to stand for 10 minutes so that all the silver precipitates together with zinc hydroxide. Filter through acid-washed filter paper or a sintered glass crucible. Wash the precipitate with dilute ammonia containing a little ammonium nitrate. Transfer the paper to a conical flask and dissolve the silver in hot dilute nitric acid or preferably treat the precipitate on the crucible with hot dilute nitric acid until all the black silver has dissolved. Boil gently to remove nitrogen oxides and titrate the silver nitrate solution obtained with 0.1 M thiocyanate solution after adding 5 cm^3 10% ammonium iron(III) sulphate indicator until a faint brown colour appears in the supernatant liquid. Repeat and calculate the % dithionite in your preparation and hence its % purity.

7.4.3 Conversion of sulphite to thiosulphate

Sulphur dissolves in boiling sulphite solution to form thiosulphate.

Grind flowers of sulphur to a fine powder and weigh out 2 g and add it to a hot solution of 6 g sodium sulphite in 30 cm^3 water. Boil the suspension until most of the sulphur has dissolved. Filter while hot under suction collecting the filtrate in a clean receiver. Evaporate the filtrate until crystallisation starts. Cool in an ice bath to allow further crystallisation. Filter under suction and dry in an oven at 40°C. Record the weight of your product and calculate the % yield based on sulphite. The purity of the thiosulphate produced can be assayed by titration as in Sec.7.3.3.

7.4.4 Conversion of thiosulphate to tetrathionate

When iodine solution in alcohol reacts with a saturated solution of thiosulphate, tetrathionate forms as a crystalline product.

Prepare a saturated solution of sodium thiosulphate in water and a solution of iodine in ethanol. Add the thiosulphate solution dropwise to the iodine solution cooled in an ice bath, shaking the mixture after each addition until the colour of the iodine fades to a very pale yellow. Allow the tetrathionate formed to crystallise. Collect the crystals by filtration under suction. Wash on the filter with small volumes of ethanol. Dissolve the product in the minimum amount of water and add ethanol to reprecipitate the tetrathionate. This is filtered under suction and washed with small volumes of ethanol and dried by continued suction and then kept in a desiccator with concentrated sulphuric acid as a desiccant. It can be analysed as in Sec.7.3.5.

7.4.5 Preparation of potassium peroxodisulphate

On electrolysing a cool solution of potassium hydrogen sulphate, the discharged anions combine to form peroxodisulphate (persulphate) ions.

Prepare a saturated solution of potassium hydrogen sulphate, cool in ice for 30 minutes and quickly filter, collecting the filtrate in a receiver cooled in ice. Measure 20 cm^3 of the cooled filtered solution into a small beaker cooled in ice. Suspend in the solution a coil of platinum wire as anode and another coiled platinum wire as cathode. Connect the electrodes to a 6V dc supply in a circuit containing a variable resistance, an ammeter in series and a voltmeter in parallel to the electrolytic cell. Adjust the position of the electrodes so that a current of 0.4A passes through the solution. Electrolyse for 60 minutes. Then filter the crystals produced under suction using a sinter glass filter. Wash with small volumes of ethanol and then ether. Dry by continued suction.

7.5 METAL COMPOUNDS CONTAINING THIOSULPHATE

7.5.1 Preparation and analysis of sodium copper(I) thiosulphate

When copper sulphate solution reacts with sodium thiosulphate, copper(II) is reduced to Cu(I) and its thiosulphate crystallises out with the sodium thiosulphate. The crystals can be analysed for copper by oxidising Cu(I) using persulphate and then determining Cu(II) iodometrically. Thiosulphate is determined as in Sec.7.3.3.

Dissolve 10 g of copper(II) sulphate pentahydrate in 50 cm^3 warm water and dissolve 18 g of sodium thiosulphate pentahydrate in 30 cm^3 of warm water. Heat each solution to 40°C. Stir the copper solution well while adding the solution of thiosulphate. Allow the mixture to settle so that complete precipitation of the yellow crystals takes place in about an hour. Filter the crystals under suction and wash them with distilled water and then with acetone. Dry by continued suction while pressing between filter paper and then dry in an oven at 50°C. Weigh your product and calculate the % yield based on copper.

Weigh out accurately about 0.5 g of your preparation and dissolve in 50 cm^3 water in a glass stoppered bottle. Add a few cm^3 of acetic acid and 2 cm^3 of freshly prepared starch solution. Run from a burette 0.05 M iodine solution until a deep blue colour persists. Note the titre and then titrate the excess iodine with 0.02 M standardised sodium thiosulphate until the blue colour has been just discharged. In this case all the thiosulphate of the compound had reacted with iodine whereas copper remains as CuI precipitate.

For the determination of copper, weigh out accurately about 0.5 g of your preparation into a conical flask. Add 30 cm^3 dilute sulphuric acid and 2.5 g ammonium persulphate and shake well to dissolve the solids. Heat the solution gradually to the boiling point. Continue until all the copper appears as the blue copper(II) sulphate disregarding a small residue of sulphur which floats on the surface. Continue boiling for 15 minutes to decompose any remaining persulphate. Filter into a clean conical flask and wash on the filter with water. Add to the filtrate concentrated ammonia until the deep blue copper(II) complex is formed. Then add dilute acetic acid to restore the pale blue colour of aqueous Cu(II) ions and then add an equal volume of the acid already added. Dissolve 2 g of KI and titrate the liberated iodine with standardised 0.05 M sodium thiosulphate until the solution is straw yellow. Dilute with 100 cm^3 water, add 2 cm^3 freshly prepared starch solution and continue titration. When the blue colour fades add 1 g of purest ammonium thiocyanate and continue titration rapidly until the blue colour disappears for 1 minutes. The pale flesh-coloured CuI remains as a precipitate. Calculate the molar ratio Cu:thiosulphate.

7.5.2 Preparation of tris(diaminoethane) nickel(II) thiosulphate

When a solution of a nickel salt is treated with diaminoethane, coordinated water is replaced by the chelating ligand. When the molar ration is 1:3, three ligand molecules replace the six water molecules. The complex cation formed can be precipitated by thiosulphate. The crystalline product is not hygroscopic and has no water of crystallisation and is a suitable magnetic standard.

Dissolve 2.38 g of nickel chloride hexahydrate in the minimum of water, add 2.0 cm^3 of diaminoethane gradually and with stirring until maximum colour change is achieved. Dissolve 2.48 g sodium thiosulphate pentahydrate in the minimum of water and mix the solution with the nickel solution. Allow to stand while cooling in an ice bath. When crystallisation seems to be complete, filter under suction and wash with a little water and dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on Ni. Characterise your product by recording its ir spectrum in a KBr disc and by measuring its magnetic susceptibility and comparing the value with the literature value *(J.Chem.Educ.*49(1972)117).

7.6 KINETICS AND MECHANISMS OF REACTIONS INVOLVING SULPHUR OXOANIONS

A number of kinetic experiments in which a sulphur oxoanion participitate can be studied since they take place at a measurable rate without use of fast reaction facilities.

7.6.1 Kinetics and mechanism of the oxidation of iodide ions by persulphate ions

As with other redox reactions, the reaction is second order i.e. the rate depends on the concentration of both reactants:

$$\text{Rate}=k[S_2O_8^{2-}][I^-] \qquad (7.11)$$

This relation can be established by keeping the concentration of one reactant constant and varying the concentration of the second reactant and observing how the rate changes. Under all conditions, the ionic strength should be kept constant, since rates of reactions between ions depend on the ionic strength. The reaction may be followed by adding an aliquot of thiosulphate which reacts with the iodine liberated from the redox reaction. When all the thiosulphate is consumed, the liberated iodine is detected visually by starch *(J.Chem.Educ.*41(1964)549).

Prepare the following stock solutions: 0.01 M sodium thiosulphate, 0.2% starch solution, 0.2 M potassium nitrate and 0.2 M ammonium sulphate. Use the latter two solutions to dilute 0.2 M potassium iodide and 0.2M ammonium persulphate to prepare 0.1 M and 0.05 M solutions, maintaining the ionic strength constant. Use a large 4 dm^3 beaker with water kept at a known temperature on a hot plate/magnetic stirrer. Pipette 25.0 cm^3 0.2 M KI, 5 cm^3 of the starch solution and 10 cm^3 of the thiosulphate solution and allow time to reach thermal equilibrium, placing some persulphate solution separately in the thermostatting beaker. Then quickly pipette 25.0 cm^3 of the latter solution to the mixed solution, starting a stopwatch and the stirrer at the same time and note the time of the appearance of the blue iodine/starch complex. Repeat by varying the [persulphate]e.g. 0.1 M and 0.05 M. Keeping [persulphate] at 0.2 M, repeat using 0.1 M and 0.05 M iodide solution. Using the first mixture but at 3 or more other temperatures, the activation energy of the reaction can be calculated. The effect of Cu(II) catalyst and ionic strength are also suggested in the reference.

7.6.2 Clock reactions

Consider reactants A and B which produce a product C. If a chemical species D is added to transform the product C to the reactant B, the product C is observed in presence of excess A when D has been consumed. Thus in the above experiment A is persulphate, B is iodide, C is iodine and D is thiosulphate. Since the reaction is catalysed by Cu(II) ions, it can be used for their determination.

7.6.3 The oxidation of hydrogen sulphite ions by potassium iodate

Here iodate is reduced by sulphite to give iodide which is oxidised by iodate which is reduced to iodide by sulphite.

Prepare a solution 0.02 M in potassium iodate (A) and another solution 0.02 M in sodium hydrogen sulphite (B). Mix the following suggested volumes of A and B and make up to 100 cm^3 (where applicable), adding a few drops of 1% starch solution.

Volume of A/cm^3	25	25	25	40	45	50	60	65	50
Volume of B/cm^3	25	35	75	25	25	25	25	25	50

Place each mixture in a shaking thermostat at 25°C (or a large 2-4 dm^3 beaker containing water at room temperature) as quickly as possible after mixing and note the time on a stopwatch when the blue colour of iodine/starch adsorption complex appears. Plot the time against 1/[A][B].

7.6.4 The reaction between hydrogen peroxide and iodide ions

Hydrogen peroxide can react as an oxidant or a reductant. In the titrimetric determination of hydrogen peroxide, it usually reacts as a reductant when a strong oxidant is used as a titrant. In the reaction with iodide, hydrogen peroxide reacts as an oxidant. The iodine produced in this reaction can be reduced by thiosulphate back to iodide. In presence of thiosulphate, the reaction is similar to the reaction in Sec.7.6.1. It was found that molybdates act as catalysts. This fact is the basis of a titrimetric method for determination of the latter ions.

7.6.4.1 Standardisation of hydrogen peroxide solution

The decomposition of hydrogen peroxide to water and oxygen, although favoured thermodynamically, is not fast at low temperature, especially in absence of a catalyst. For this reason, the commercial solution is kept in smooth plastic bottles (to avoid the catalytic effect of rough glass surfaces) and should be stored in the fridge. The commercial product is labelled as 20 or 100 volume. These contain 6% or 30% H_2O_2 respectively. When freshly diluted, a solution should be standardised against permanganate or Ce(IV) solution.

Prepare a solution of hydrogen peroxide by diluting 25.0 cm^3 (100 volume) (measured by a burette) to 250 cm^3. Use a burette to deliver 50.0 cm^3 of the freshly diluted solution to a conical flask, acidify and titrate against standardised 0.02 M permanganate to the first permanent pink. Repeat and calculate, from the average titre, the concentration of hydrogen peroxide in mol dm^{-3}.

Follow the same procedure as in Sec.7.6.1 replacing persulphate by hydrogen peroxide, remembering to add ammonium sulphate to the initial solution to maintain the ionic strength constant. After studying the effects of the concentrations of the reactants and temperature on the rate of reaction, investigate the effect of adding different [molybdate].

7.7 SELENIDES AND TELLURIDES

Metal selenides and tellurides are formed by some metals especially those of group 12 (the zinc group) and these are generally semiconductors which have photocatalytic activity. Some are hydrolysed by water or dilute acids to give H_2Se(or H_2Te) and the metal hydroxide or salt. The two hydrides have acidic properties and unpleasant smells.

7.8 SEMICONDUCTING CHALCOGENIDES

Many metal sulphides, selenides and tellurides have been prepared either as powders or as thin films. Sulphides like CdS can be also formed in colloidal suspension, whose optical properties depend on their particle size.

Preparation of thin films of semiconducting chalcogenides *(J.Chem.Educ.***68** (1991)872; **74**(1997)1205).

The methods described in these references are based on the electrodeposition on a conducting glass slide either by anodic deposition in a solution of the chalcogenide ion or by vacuum deposition. Band gap determination can be carried out by absorption spectroscopy.

7.9 QUALITATIVE TESTS ON (IV) AND (VI) OXIDATION STATES OF Se AND Te

7.9.1 Selenites and tellurites

Te compounds have a nasty smell and should be handled in a well-ventilated fume cupboard. Use the sodium or potassium salts of each:

(a) Prepare a solution of either selenite or tellurite and add to portions separately:
  (i) hydrogen sulphide then heat, test the solubility of any precipitate in yellow ammonium sulphide;
  (ii) barium chloride solution; test the solubility of any precipitate in dil. HCl;
  (iii) silver nitrate solution, after adjusting the pH to 5-9 using bicarbonate;
  (iv) mercury(II) chloride solution at pH 4-10 (for selenite);
  (v) sulphur dioxide in dil.HCl solution;
  (vi) HI solution, then add thiosulphate (in case of selenite) or excess reagent (in case of tellurite);
  (vii) acidified permanganate solution, H_2O_2 or bromine water (for Se(IV));
  (viii) hydroxylammonium or hydrazinium salt in HCl solution, heat if necessary;
  (ix) tin(II) chloride solution;
  (x) zinc in acid solution;
  (xi) sodium thiosulphate solution;
  (xii) thiourea in HCl solution.

(b) To a solution of selenite, add iron(II) sulphate solution.

(c) Add to a solution of tellurite phosphonic or phosphenic acid solution.

7.9.2 Selenates and tellurates

(a) Use a solution of sodium selenate or tellurate. Add to separate portions of either solution:
  (i) H_2S in conc. HCl, boil of necessary;
  (ii) barium chloride solution to a concentrated solution, test the solubility of any precipitate in conc. HCl.

(b) To separate aliquots of a solution of selenate, add:
  (i) HCl(<6 M), boil and test the vapour with moist blue litmus paper;
  (ii) thiourea, warm for some time.

(c) To separate portions of a solution of a tellurate, add;
  (i) SO_2 in >2 M HCl;
  (ii) hydrazinium salt solution and boil;
  (iii) phosphenic acid solution;
  (iv) KI solution, then add dropwise thiosulphate solution;
  (v) concentrated silver or calcium nitrate solution.

8

The Halogens

8.1 INTRODUCTION

The halogens (F, Cl, Br, I and At) occupy group 17 of the Periodic Table. The atoms have 7 outer electrons and hence share a pair of electrons between two atoms forming a σ bond in the molecules X_2. The bonds become longer down the group. The bond dissociation enthalpy decreases from chlorine down the group. However, fluorine has a value close to that of iodine. As the Van der Waals forces increase with the size of the molecules, the boiling points of the elements increase. Thus fluorine and chlorine are gases whereas bromine is a liquid and iodine is a solid. These facts and the trend in the dissociation enthalpy explain the high reactivity of fluorine and the decrease in reactivity down the group. The halogen atom requires one electron to complete the stable configuration of the next noble gas. Hence the anions X^- represent the most stable oxidation state of -I. The electron attachment energy becomes less negative from Cl to I as expected from their atomic radii. However, F has a less negative value than Cl. This behaviour and the anomalous dissociation enthalpy of F_2 are ascribed to interelectronic repulsions in the compact 2p sub-shell of F. The halogens tend to form σ bonds with other non-metals as well as between themselves. E-X bonds (where E is a non-metal and X is a halogen) increase in length but decrease in strength from F to I. Because F cannot expand its valence shell beyond 8, it forms one E-F bond whereas the lower halogens have available d orbitals. Hence they can reach a maximum covalence of seven. Fluorine is also unique because of its high electronegativity (the highest in the Periodic Table) and its small radius. Thus it forms strong hydrogen bonds: F-H--E where E=F, O or N. The positive oxidation numbers of the halogens from +1 to +7 increase by two units. Only Cl exhibits species in the +3 state. Fig.8.1 represents the volt-equivalent/oxidation number diagram of the halogens in acidic solution and the diagram of chlorine in alkaline media. The reactivity of the positive oxidation states is determined by kinetic as well as thermodynamic considerations. Generally the oxidising power of a given species is higher in acidic than in alkaline media. In the case of chlorine oxoacids, the acid strength and thermal stability increase with increase in oxidation number. The oxidising power of the elements decreases from fluorine to iodine, mainly due to the highly negative hydration enthalpy of the fluoride ion, which is formed in the oxidation reaction in aqueous solution. No stable F oxoacid is known as expected from its high electronegativity. Among the oxoacids and their anions in the +1 oxidation state, only HOCl and OCl^- are sufficiently stable. OBr^- and OI^- rapidly disproportionate to -1 and +5 species. The oxidising power of the highest acids decreases in the series:

$HBrO_4 > HClO_4 > H_5IO_6$

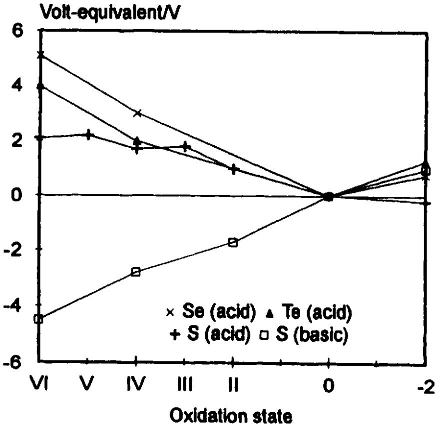


Figure 8.1 Volt-equivalent versus oxidation number for Group 17 elements.

This is an example of the "middle row anomaly" observed among the p block groups. Among the +5 anions, the most useful oxidant is the iodate, whose reactions proceed rapidly and smoothly.

8.2 QUALITATIVE TESTS

8.2.1 Tests on the halides

(a) To a little solid fluoride e.g. NaF, in a dry test tube, add 1 cm^3 conc. sulphuric acid, warm carefully and expose to any gas: a moist blue litmus paper, an open m.p. tube containing a drop of water and a drop of conc. ammonia.

(b) Add to separate portions of a concentrated solution of an alkali fluoride:
  (i)calcium chloride solution;
  (ii)iron(III) chloride solution added gradually;
  (iii)thorium nitrate solution;
  (iv)lanthanum acetate after adding acetate buffer (pH4.5);
  (v)silver nitrate solution.

(c) To a little solid chloride, bromide or iodide in a dry test tube, add 1 cm^3 conc. sulphuric acid, warm and expose to any gas: a moist blue litmus paper, a drop of conc. ammonia on a rod and, for bromides, an acidified dichromate paper and a fluorescein paper, and, for iodides a starch paper and a lead acetate paper.

(d) Repeat (c) using bromide or iodide and syrupy phosphoric acid, exposing to any gas: a blue litmus paper and a drop of conc. ammonia.

(e) To separate portions of a solution of a chloride, bromide or iodide, add:
  (i) silver nitrate solution, test the solubility of any precipitate in dilute ammonia and then conc. ammonia, or in KI solution;
  (ii) lead acetate solution, add excess water to a portion of any precipitate, boil and then allow to cool.

(f) Mix solid chloride, bromide or iodide with a little manganese dioxide and add a little conc. sulphuric acid, heat and expose to any gas: a moist blue litmus paper (for chloride), a fluorescein paper (for bromide) and a starch paper (for iodide).

(g) Mix solid chloride or bromide with potassium dichromate, add conc. sulphuric acid, warm and pass any vapour through a little water, then add NaOH solution.

(h) Add some chlorine water to a solution of chloride, bromide or iodide, then add a little chloroform and shake.

(i) To a solution of an alkali metal iodide, add separately:
  (i) copper sulphate solution, then add sodium thiosulphate;
  (ii) sodium nitrite solution acidified with acetic acid then test with starch paper;
  (iii) mercury(II) chloride solution, then add excess iodide;
  (iv) palladium(II) chloride solution.

8.2.2 Tests on the halogens

Fluorine is a very reactive gas and attacks most containers and is excluded from these tests.

(a) To ~0.2 g permanganate, add 2 cm^3 conc.HCl, warm and expose to any gas a moist blue litmus paper and a KI/starch paper.

(b) Repeat (a) passing the gas through a little water and then add KI solution and shake with a little chloroform.

(c) Add a drop of mercury to some chlorine water.

(d) Test the solubility of bromine in water and in chloroform.

(e) Add to portions of bromine water separately:
  (i) KI solution, test with a starch paper;
  (ii) thiosulphate solution;
  (iii) silver nitrate solution and warm;
  (iv) phenol red solution;
  (v) litmus paper, allow to stand;
  (vi) NaOH solution.

(f) Test the solubility of iodine separately in water, ethanol and carbon tetrachloride.

(g) Add to separate portions of iodine solution in KI:
  (i) sodium thiosulphate solution;
  (ii) starch solution;
  (iii) NaOH solution then warm;
  (iv) hydrogen sulphide in dilute acid;
  (v) fluorescein solution.

8.2.3 Tests on NaOCl(aq.) (sodium oxochlorate(I)

Only HOCl and its anions are sufficiently stable; HOBr and HOI and their anions rapidly disproportionate. NaOCl is known only in solution but solid bleaching powder is the calcium salt.

(a) To portions of NaOCl solution, add separately:
  (i) dilute sulphuric acid and iron(II) sulphate solution, warm and then add NaOH solution;
  (ii) KI solution and a few drops of dilute sulphuric acid, then test with starch paper;
  (iii) hydrogen peroxide solution;
  (iv) manganese(II) sulphate solution to which NaOH solution had been added:
  (v) chromium(III) sulphate solution and then boil in an evaporating basin;
  (vi) cobalt nitrate solution, warm and expose through a glass wool plug a glowing splint;
  (viii)lead acetate solution and boil.

(b) Heat gently NaOCl solution acidified with hydrochloric acid, expose to any gas a moist blue litmus paper.

8.2.4 Tests on trioxohalates(V)

(a) Heat a little KXO_3 (X=Cl,Br,I) in a dry test tube and test with a glowing splint. Cool, dissolve in water and add silver nitrate solution and test the solubility of any precipitate separately in dilute and then in conc.ammonia.

(b) Add a little conc. sulphuric acid to a little solid KXO_3 (use only a small $KClO_3$ crystal and 2-3 drops of acid).* Expose a glowing splint and a fluorescein paper (in the case of bromate). Add $FeSO_4$ solution (in the case of iodate).

(c) To separate portions of a halate solution, add:
  (i) silver nitrate solution, test the solubility of any precipitate as in (a);
  (ii) iron(II) sulphate solution acidified with sulphuric acid following by a thiocyanate solution;
  (iii) sodium nitrite solution, acidified as in (ii) followed by silver nitrate solution;
  (iv) hydrogen sulphide solution.

(d) Add 2-3 drops conc. HCl to a small chlorate crystal, expose a moist blue litmus paper to any gas.*

(e) Add a solution of chlorate or bromate to a saturated manganese(II) sulphate solution in syrupy phosphoric acid (for chlorate) or in an equal volume of dilute sulphuric acid (for bromate).

(f) To a solution of bromate or iodate, acidified with sulphuric acid, add either KBr or KI solution.

(g) Add to portions of an iodate solution separately:
  (i) barium chloride;
  (ii) lead acetate solution;
  (iii) mercury(II) salt solution;
  (iv) acidified thiocyanate solution.*

8.2.5 Tests on $KClO_4$ and KIO_4 (tetraoxochlorate(VII) or tetraoxoiodate(VII))

(a) Heat the solid in a dry test tube, expose a glowing splint to any gas. Cool, dissolve in water and add silver nitrate solution.

(b) To a solution of $NaClO_4$, add separately:
  (i) concentrated potassium chloride solution;
  (ii) concentrated ammonium salt solution;
  (iii) concentrated cadmium nitrate solution in conc.ammonia.

(c) To a solution of KIO_4, add separately:
  (i) silver nitrate solution then dilute nitric acid;
  (ii) mercury(II) nitrate solution;
  (iii) barium chloride solution then dilute nitric acid;
  (iv) cerium(IV) nitrate solution;
  (v) ascorbic acid in 9 M HCl;
  (vi) iodide in alkaline solution;
  (vii) manganese(II) salt solution in dilute nitric acid.

8.3 ANALYTICAL CHEMISTRY OF HALOGEN COMPOUNDS

8.3.1 Analytical chemistry of halides

Since the silver halides, except AgF, are sparingly soluble, the halides can be determined by precipitation titration or gravimetrically. Among instrumental methods of analysis, ion-selective electrodes and ion chromatography are readily available. The latter is capable of estimating mixtures of anions.

Precipitation titrations

In precipitation titrations, a solution containing a precipitating ion is gradually added to a solution containing an ion which forms a sparingly soluble compound with the precipitating ion. The end-point may be detected by the formation of a coloured precipitate, by the formation of a soluble coloured compound at the equivalence point or by the use of an adsorption indicator. The latter is adsorbed by the precipitate at the equivalence point. During the adsorption, a change occurs in the indicator which leads to a change in colour. A suitable adsorption indicator can be used if the precipitate is in the colloidal condition and the indicator has an opposite charge to the precipitating ion. It should be strongly adsorbed immediately after the end point.

8.3.1.1 Titration of chloride in presence of iodide

Since the two anions have different adsorbability on the silver halides, it is possible to carry out two precipitation titrations using two different adsorption indicators.

Prepare a 0.1 M silver nitrate solution and a solution which is 0.05 M in NaCl and 0.05 M in NaI. Pipette 25.0 cm^3 of the mixed halide solution into a conical flask, add 10 drops of fluorescein indicator. Titrate with the silver nitrate solution while rotating the flask in diffuse daylight until the silver halides coagulate and a pink colour develops locally on the addition of the silver solution. Continue the titration until the precipitate suddenly assumes a permanent pink colour. Repeat to obtain concordant results. The titre gives the total halide concentration. Repeat the titration using diiododimethylfluorescein as indicator, when the precipitated compound assumes a permanent blue red colour. Repeat to obtain concordant results. The average titre in this case is equivalent to the iodide alone. Work out the difference between the titres using the two indicators, which corresponds to the chloride. Calculate [NaCl] and [NaI] in mol dm^{-3}.

Titration of bromide together with iodide can be carried out as above using fluorescein as indicator in the titration with 0.1 M silver nitrate, which gives the total halide. In another titration using diiododimethylfluorescein the titre gives the iodide in the halide mixture.

An alternative titrimetric determination of Cl$^-$ using silver nitrate and chromate indicator is described in Sec.14.6.1.

Titrimetry using mercury(II) nitrate solution is described in Sec.14.8.1.

Gravimetric determination of chloride as AgCl is described in Sec.16.7 and in Sec.11.5.4. In the latter, special conditions are recommended which are unnecessary in normal chloride analysis.

Titrimetric and gravimetric determination of bromide or iodide are carried out in the same way as for chlorides. Silver halides especially the bromide are light-sensitive and if precipitated gravimetrically they should be protected from light until they are weighed.

8.3.1.2 Gravimetric determination of fluoride as PbFCl

At pH 3.6-5.6, fluoride ions can be precipitated by a saturated lead chloride solution. The precipitate can be dried and weighed.

Pipette 50.00 cm^3 of ~0.02 M fluoride solution into a 100 cm^3 beaker. Heat the solution to 60-70°C and add 0.25 cm^3 of 30% (v/v) acetic acid solution. In a 400 cm^3 beaker, heat nearly to boiling a mixture of 200 cm^3 of a saturated lead(II) chloride solution and 0.5 cm^3 of the 30% (v/v) acetic acid solution. Add the hot fluoride solution to the contents of the 400 cm^3 beaker and wash the 100 cm^3 beaker twice with 15 cm^3 portions of the lead solution adding the washings to the larger beaker. Cover with a clock-glass and heat the combined solutions gently to boiling. Cool to room temperature and then stand the beaker in an ice-water mixture for 2 to 2½ hours.

Collect the precipitate of lead(II) chlorofluoride in a prepared No.4 sintered-glass crucible, washing out the beaker twice with 15 cm^3 portions of the lead solution, followed by 20 cm^3 of the lead solution as a jet from a wash bottle. Wash the precipitate three times with 15 cm^3 portions of a saturated solution of lead(II) chlorofluoride and then three times with 15 cm^3 portions of acetone. Suck the precipitate dry, wipe the outside of the crucible and place in an oven at 110°C for 30 minutes. Dry to constant weight. Calculate from duplicate results the concentration of fluoride in the original solution in mol dm^{-3}.

Instrumental determination of halides

Each of the four halides can be determined using an ion-selective electrode specific to the halide. The iodide-sensitive electrode can detect as low as 5×10^{-8} mol dm^{-3} whereas the chloride-sensitive electrode can only detect 5×10^{-5} mol Cl^- dm^{-3}. The operation of these electrodes are mentioned in Sec.2.5.1.

A more useful technique for the determination of mixtures of halides, which may contain other anions, is by ion chromatography using suppressed conductivity and uv absorbance. Some commercial columns claim to determine 1-25 mg anion dm^{-3} in a mixture of 10 anions.

8.3.2 Analysis of NaOCl solution

Iodometry

Titrations involving iodine either as a titrant or as a product of reaction, which is titrated with a reductant, are generally referred to as iodometry. (The term iodimetry is sometimes used when iodine solution is used as a titrant). Iodine is soluble in KI solution forming the triiodide ion I_3^- but for simplicity I_2 is used in equations and in reactions. Solutions of iodine can be conveniently prepared by acidifying a mixture of iodate and iodide (molar ratio 1:5), a slight excess of the latter dissolves the iodine liberated. Iodine is a mild oxidant and the titrations involving it are generally carried out in acid solutions. Standardisation of iodine solution using sodium thiosulphate solutions is described in Sec.7.3.1.

OCl^- ions oxidise iodide in acid solution, to iodine which is titrated with standardised thiosulphate solution.

Pipette 25.0 cm^3 of the commercial NaOCl solution (Freshly supplied) into a 250 cm^3 conical flask and add 50 cm^3 water and 2 g KI, acidify with 10 cm^3 glacial acetic acid and titrate the liberated iodine with standardised 0.05 M thiosulphate solution using starch indicator (Sec.7.3.1). Repeat to obtain concordant results. Calculate, from the average titre, $[OCl^-]$ in mol dm^{-3}.

8.3.3 Analytical chemistry of halates(V)

The three halates can be determined titrimetircally by oxidising iodide to iodine which is titrated as above. If reduced to halide e.g. by iron(II) acidified salt solutions, the halide can be precipitated as silver halide and weighed. A convenient instrumental method is by ion chromatography which is ideal in mixtures of halates with or without halides.

8.3.3.1 Volumetric determination of chlorate

Pipette 25.0 cm^3 of 0.05 M potassium chlorate solution into a conical flask provided with a stopper. Add 3 cm^3 conc.HCl followed by two portions of ~0.3 g sodium bicarbonate to displace air by the carbon dioxide formed. Immediately add ~1 g KI and 25 cm^3 conc. HCl. Stopper the flask, shake and allow to stand for 10 minutes. Titrate the liberated iodine with standardised 0.05 M thiosulphate solution as in Sec.7.3.1. Repeat and calculate from the average titre, the concentration of chlorate in mol dm^3.

8.3.3.2 Titration of iodate against HCl solution

The reaction between iodate and iodide in acid solution produces iodine according to:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \tag{8.1}$$

The iodine reacts with thiosulphate according to:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \tag{8.2}$$

When an excess iodide and an excess thiosulphate are added to an iodate solution, the latter can be titrated against an acid using an acid base indicator. At the end point the indicator will change from the basic to the acidic form when an extra drop of acid had been added.

Pipette 25.0 cm^3 of M/60 iodate solution into a 250 cm^3 conical flask, add 0.5 g KI and 1 g sodium thiosulphate and a few drops of methyl red indicator and shake to dissolve. Titrate with standard 0.1 M HCl with constant stirring until the colour changes sharply from yellow to red. Repeat and calculate from the average titre, the iodate concentration in mol dm^{-3}.

8.3.3.3 Volumetric determination of bromate

Potassium bromate in the purest commercial product is >99% pure. When the powder is dried at 120°C for 2 hours can be used as a primary standard. The solution can be titrated after oxidising iodide to iodine as above.

Prepare a M/60 solution of potassium bromate. Pipette 25.0 cm^3 into a 250 cm^3 conical flask. Acidify liberally with HCl, add 2 g KI and titrate the liberated iodine as above.

8.3.3.4 Gravimetric determination of chlorate

After reducing a chlorate solution with iron(II) sulphate, the chloride formed is precipitated and weighed as AgCl.

Prepare a 0.02 M solution of purest potassium chlorate. Pipette 50.0 cm^3 into a beaker, add 25 cm^3 of 10% solution of purest iron(II) sulphate. Boil for 15 minutes, with constant stirring. Allow to cool and then add nitric acid until any precipitate dissolves. Then add water to a volume of ~150 cm^3 and add ½ cm^3 conc.nitric acid. Then add slowly and with constant stirring a 0.1 M silver nitrate solution until a slight excess has been added. Heat to boiling while stirring until AgCl coagulates and the supernatant is clear. Check for complete precipitation and allow to stand in the dark for 2 hours. Filter through a prepared G4 sintered glass crucible. Wash with 0.01 M nitric acid until the washings are silver free. Dry to constant weight at 130°C,. Calculate from duplicate results, [chlorate] in mol dm^{-3}.

Andrew's titrations

KIO_3 is a stronger oxidising agent than I_2. When KIO_3 reacts with a reducing agent in high concentrations of HCl (3-9 M), IO_3^- is reduced to ICl according to:

$$IO_3^- + 6H^+ + Cl^- + 4e^- \leftrightarrows ICl + 3H_2O \tag{8.3}$$

Since ICl forms a stable complex in HCl solution ($ICl+Cl^- \leftrightarrows ICl_2^-$), the overall half cell reaction may be written:

$$IO_3^-+6H^++2Cl^-+4e^- \leftrightarrows ICl_2^-+3H_2O \tag{8.4}$$

Under these conditions, KIO_3 acts as a powerful oxidant (E^o=1.23 V). Oxidation by KIO_3 proceeds through the stages:

$$IO_3^-+6H^++6e \leftrightarrows I^-+3H_2O \tag*{(8.4),}$$
$$IO_3^-+5I^-+6H^+ \leftrightarrows 3I_2+3H_2O \tag*{(8.5),}$$
$$IO_3^-+2I_2+6H^+ \leftrightarrows 5I^++3H_2O \tag{8.6}$$

Initially I_2 is liberated, but on adding more titrant, oxidation proceeds to ICl and the dark colour gradually disappears. The optimum acidity for a rapid reduction is 2.5-3.5M HCl.

8.3.3.5 Volumetric determination of iodide by Andrew's titration

Since purest potassium iodate can be used as a primary standard, its solution can be used to determine reducing agents like iodide.

Preparation of 0.025 M potassium iodate

Dry the purest solid at 120°C for one hour and allow to cool in a desiccator. Weigh out accurately 5.35 g of the dried solid, dissolve in water in a beaker with stirring. Transfer quantitatively to a 1 dm^3 volumetric flask and make up to the mark with water.

In high concentrations of HCl, the reaction between IO_3^- and I^- may be represented by:

$$IO_3^-+6H^++2I^-+3Cl^-=3ICl+3H_2O \tag{8.7}$$

therefore 1 mol $IO_3^- \equiv$2 mol I^-.

The end-point is detected by adding an immiscible liquid ($CHCl_3$ or CCl_4) which extracts I_2. ICl is not extracted and imparts a yellow colour to the aqueous phase.

Pipette out 25.0 cm^3 of a 0.05 M iodide solution into a 250 cm^3 glass-stoppered bottle (check that the stopper fits properly), add in the order given, ~25 cm^3 H_2O, 60 cm^3 conc. HCl and 4 cm^3 $CHCl_3$. Cool to room temperature and titrate with standard 0.025 M KIO_3 solution, shaking the stoppered bottle vigorously at intervals. Safety goggles must be worn during this titration. The end-point is reached when the organic layer is no longer coloured violet. Repeat to obtain concordant results.

Calculate the concentration of I^- in g dm^{-3} and in mol dm^{-3}.

8.3.4 Analytical chemistry of periodates

Perchlorates can be determined gravimetrically by fusion with ammonium chloride in a platinum crucible, extracting the chloride formed with water and precipitating AgCl as before.

However, analysis of periodates is more important and is therefore discussed below. The procedure is similar to that described for iodates and a mixture of the two can be analysed.

Volumetric determination of periodate and iodate

In a buffered alkaline solution, periodate oxidises iodide to iodine and it is reduced to iodate. On the other hand, in acid solution, iodate oxidises iodide to iodine, which can be titrated against standardised $Na_2S_2O_3$ solution.

(a) Pipette 25.00 cm^3 of a solution which is 0.02 M in IO_4^- and 0.0135 M in IO_3^-. Dilute to about 100 cm^3 and add 2 g of borax and saturate the solution with boric acid by shaking the solid acid with the solution. Dissolve 3 g KI in the solution, allow to stand undisturbed for 3 minutes and then titrate the liberated iodine with standardised 0.1 M $Na_2S_2O_3$ solution. When the colour becomes pale yellow, add 100 cm^3 of boiled-out distilled water, 2 cm^3 of freshly prepared starch solution and continue the titration until the colour disappears for 30 seconds. Record the volume (V_1 cm^3).

(b) Add to the solution an excess of dil. H_2SO_4 to liberate I_2 from IO_3^- ions. Titrate this iodine with the $Na_2S_2O_3$ solution until the blue colour of the iodine/starch adsorption complex disappears for 30 seconds. Record the volume (V_2 cm^3). Repeat the titration once. Calculate from the average titres V_1 and V_2, the concentration of IO_4^- and IO_3^- in mol dm^{-3} of the original solution.

8.4 STUDY OF THE INTERHALOGENS

Because of the reactivity of the halogens and their ability to form σ bonds between themselves, a number of interhalogens of the formula XX_n^1 (X^1 is the more electronegative halogen and n is an odd number) are known. The general preparative method is by reacting the two halogens under specific conditions.

8.4.1 Preparation of ICl *(Inorg.Synth.*1(1939)165)

The combination of chlorine and iodine in a 1:1 molar ratio produces ICl.

Weigh out accurately 12.5 g iodine. Weigh accurately a graduated boiling tube with a ground glass stopper. Cool it in a Dewar vessel containing solid carbon dioxide acetone mixture. Place the tube in a fume cupboard and condense into it 5 cm^3 of liquid chlorine from a cylinder. Add the iodine to the liquid and allow the contents to warm slowly to room temperature, when the uncombined liquid will evaporate. Stopper the tube, reweigh it and work out the weight of chlorine combined and hence the extra mass of iodine needed for the 1:1 molar ratio. Add the calculated amount of iodine, stopper the tube and warm gently until liquid ICl is formed. Stand overnight. Determine the m.p. of the product (pure ICl melts at 27.2°C). To purify your preparation, warm it so that it melts and allow to cool slowly until most of the product solidifies. Discard the liquid.

8.4.2 Preparation of iodine trichloride *Inorg.Synth.*1(1919)167

Using a higher Cl/I ratio, this interhalogen can be prepared in a similar way.

Add 6 g powdered iodine very slowly to 5 cm^3 liquid chlorine condensed as above. Allow the temperature to rise slowly when excess chlorine is lost and the yellow orange solid remains. Quickly pack into an ampoule and seal off.

8.4.3 Electronic spectral study

Add a drop of ICl to 10 cm^3 of chloroform. Run the spectrum of the solution in a 10 mm quartz cell over the range 700-325 nm. Compare the spectrum with those of chlorine and iodine in carbon tetrachloride. Use ~0.013 M solution of chlorine and 0.0009 M solution of iodine.

8.5 EQUILIBRIA INVOLVING IODINE AND IODIDE

8.5.1 The distribution coefficient of iodine between water and tetrachloromethane

The distribution coefficient D

When a solute is in equilibrium with two immiscible liquids at a given temperature, the ratio of the concentrations of a given species of the solute in the two liquids is constant and independent of the amount of solute. This ratio is termed the distribution coefficient

D. When iodine is in equilibrium with water (w) and the immiscible CCl_4 (o), D is given by:

$$D=[I_2]_o/[I_2]_w \tag{8.8}$$

For the determination of D, the volume of water is conveniently taken as 8 times the volume of the organic liquid in which iodine is much more soluble than in water. The concentration of iodine in each liquid can be easily determined by titration against thiosulphate.

Dissolve powdered purest iodine in 500 cm^3 of purest CCl_4 in a bottle kept at a constant temperature in a thermostat (preferably a shaking thermostat or orbital incubator). Add the iodine until a small amount of solid remains undissolved. Carefully transfer the saturated solution to a clean dry bottle, through a glass wool plug if necessary. Keep a large volume of distilled deionised water at the same temperature. Pipette into clean bottles provided with stoppers 175 cm^3 water. Using the organic solvent kept at the same temperature, prepare 4-5 iodine solutions with a range of concentrations starting with the saturated solution. Pipette 25.0 cm^3 of each of these solutions into the bottle containing the water. Shake each bottle, after stoppering, for ½ hour. Pipette a small volume say 2.0 cm^3 of the organic layer into a conical flask, add 10 cm^3 of 20% w/v KI solution and a few drops dilute sulphuric acid. Titrate with standardised 0.01 M thiosulphate solution (Sec.7.3.1). Repeat after a further shaking for 15 minutes. Pipette 50.0 cm^3 of the aqueous layer into a conical flask, using a 25.0 cm^3 or 50.0 cm^3 pipette, and determine $[I_2]$ as above, repeating the withdrawal and analysis after 15 minutes. Calculate from the results of each solution, D and work out an average value.

8.5.2 Determination of the equilibrium constant for: $I_2+I^- \rightleftharpoons I_3^-$ (8.9)

When iodine in the aqueous layer reacts with iodide in the aqueous solution, the triiodide ion is formed in equilibrium with the two reactants. If such an aqueous solution is equilibrated with the organic solvent used above, the constant D applies to molecular iodine. Using the determined D and the results of equilibrium mixtures of iodine and KI in the aqueous layer and in CCl_4, the equilibrium constant of the above reaction can be determined.

Prepare a 0.05 M KI solution using the purest solid after drying at 100°C, then prepare a series of KI solutions of lower concentrations using water, ensuring that all the solutions are kept at the same temperature as that used in the above experiment. Equilibrate 100 cm^3 of each of the KI solutions with 25.0 cm^3 of the saturated iodine solution as instructed above. Withdraw 5.0 cm^3 of the organic layer and determine [iodine] as above, repeating after 15 minutes. Withdraw 25.0 cm^3 of the aqueous layer and determine [iodine] similarly and repeat after 15 minutes. Calculate from the titres $[I_2]$ in mol dm^{-3}. The titres in the aqueous layer are due to $[\Sigma I_2]$ i.e. due to the total iodine, whereas the titrations of the organic layer give $[I_2]_o$. The total [KI] is known and since the organic layer has no I^- or I_3^-, the following relations are applicable.

$[\Sigma I_2]=[I_2]_w+[I_3^-]$ (8.10),
$[KI]=[I^-]+[I_3^-]$ (8.11)
$[I_2]_w=[I_2]_o/D$

Use these relations and the value of D, expressed in (8.8), to calculate the equilibrium constant, K, for reaction (8.9):

$$K=[I_3^-]/[I_2][I^-] \qquad (8.12)$$

and the free energy of the reaction, ΔG, using the relation:

$$\Delta G=-RT\ln K \qquad (8.13)$$

8.6 IODIC ACID AND IODINE PENTOXIDE

Iodic acid is a solid which can be prepared by the oxidation of iodine using fuming nitric acid.

8.6.1 Preparation and analysis of iodic acid

Weigh out 5 g of powdered iodine into a round bottom flask provided with a reflux condenser. Add 50 cm^3 fuming nitric acid and reflux at 90°C on a water bath in the fume cupboard for 30 minutes. Cool the flask and decant the acid solution from the yellow solid formed. Dissolve the solid in an equivolume conc. nitric acid/water to recrystallise it. Heat the crystals gently to remove the acid. Recrystallise from hot water. Filter under suction and dry at 100°C. Store in a vacuum desiccator over conc. sulphuric acid and solid NaOH.

The acid is analysed iodometrically.

Weigh out accurately ~0.1 g of your preparation in 25 cm^3 water, add ~0.6 g KI and titrate the liberated iodine as in Sec.7.3.1. Calculate from duplicate results the purity of your preparation.

8.6.2 Preparation of iodine pentoxide

When iodic acid is heated to 180°C, it loses water leaving I_2O_5. Weigh out accurately ~0.1 g of your prepared iodic acid into a crucible. Heat gently on a small flame and then in an oven at 180°C to constant weight. Calculate from the mass loss, the formula of the solid produced.

Heat a little of the solid oxide strongly and expose a moist starch paper.

8.7 STUDIES OF OXOSALTS OF HALOGENS

Oxosalts of the halogens can be prepared by various methods including electrolytic oxidation, double decomposition and, in the case of iodates, starting with iodine.

8.7.1 Preparation of potassium chlorate (trioxochlorate(V)

On electrolysis of KCl, under controlled conditions, the chlorate is formed at the anode.

Dissolve 30 g KCl in 100 cm^3 water in a 150 cm^3 beaker in the fume cupboard. Add 0.2 g potassium dichromate and ensure that the pH is 6-7 throughout the experiment. Insert two platinum electrodes, preferably rotating the anode. Estimate the area of the electrodes. Heat to 60°C and use a circuit as in Sec.7.4.5) to pass a current, such that the current density is 0.15 A cm^{-2}, continue for a few hours, stirring the solution and maintaining the pH by adding dil. HCl if necessary. Allow to cool when enough solid had separated. Filter under suction, pressing between filter paper. Weigh your product and determine its purity as in Sec.8.3.3.

8.7.2 Preparation of barium iodate monohydrate

Amorphous barium iodate is formed when iodic acid solution is titrated with barium hydroxide or in the reverse titration. In such reactions, atmospheric carbon dioxide has to be excluded since it precipitates barium carbonate. An alternative preparation involves the reaction of iodine with sodium chlorate in presence of nitric acid. The reaction sequences involve the formation of ICl and the generation of chlorine by its reaction with chlorate.

Weigh into a flask with a long neck 5 g sodium chlorate and 5 g powdered iodine. Add 40 cm^3 water, shake to dissolve the chlorate and then add ½ cm^3 conc. nitric acid. Close the mouth of the flask with an inverted beaker. Heat gently with a small flame in the fume cupboard until the iodine has dissolved and then heat the open flask until the chlorine is boiled off, test with a moist blue litmus paper. Pour the contents into a 250 cm^3 beaker. Use 30 cm^3 water to wash the flask and to dilute the solution. Boil the beaker and maintain it on a boiling water bath. Dissolve 5.25 g barium nitrate in 50 cm^3 water and add the solution slowly to the beaker, with continuous stirring. Cool to room temperature. Filter under suction and wash on the filter with small volumes of cold water. Dry by continued suction while pressing between filter paper. Record your yield and calculate the % yield based on Ba.

Heat a little of the solid gently in a dry test tube and test any condensed liquid on the cool sides with a blue cobalt paper. Then heat more strongly inserting a glass wool plug near the mouth of the tube and expose to any gas, a glowing splint and a damp starch paper.

8.7.3 Preparation and analysis of $K[H(10_3)_2]$

This solid can be prepared by the reaction of potassium hydrogen sulphate with barium iodate and discarding the precipitated barium sulphate. Its purity can be assessed by titration with a standard alkali.

Dissolve 4 g of potassium hydrogen sulphate in 60 cm^3 boiling water. Add 10 g of powdered barium iodate (Sec.8.7.2) while stirring and boiling the mixture for an hour, maintaining the volume by adding hot water. Filter the precipitate using pleated filter paper and wash on the filter with 20 cm^3 boiling water. Collect the filtrate and washings in a clean basin and heat on the water bath until a quantity of crystals forms. Filter under suction, wash with small volumes of water and dry by continued suction. Record the yield and calculate the % yield based on iodate.

Weigh out accurately ~1.0 g and dissolve in water in a conical flask. Add a few drops of bromothymol blue indicator and titrate with standard 0.05 M NaOH solution until the colour changes from yellow to blue. Repeat and calculate from average results, the % purity of your preparation.

8.7.4 Preparation and analysis of KIO_4

Potassium iodate can be oxidised with persulphate in an alkaline solution.

Dissolve 5 g of KIO_3 and 5 g of potassium hydroxide in 50 cm^3 of water. Boil, then dissolve in the solution 8 g of potassium persulphate. After 5 minutes add 3 g of potassium hydroxide, pellet by pellet. Heat the solution on a boiling water-bath for 30 minutes and add 50 cm^3 of hot water, stir until all the precipitated potassium sulphate has dissolved, then cool. Filter off any insoluble material through GF paper, place the beaker containing the solution in a bath of cold water, and while stirring well, run in a 1:1 concentrated nitric acid: water mixture from a burette until the solution is acid to methyl orange; then add 1 cm^3 of the acid in excess. Wash the precipitated product with cold water, twice by decantation, and then on a filter. Air dry at normal temperature and weigh your product and calculate the % yield based on I.

Determine the purity of your product using the titration in Sec.8.3.4.

8.7.5 The solubility product of calcium iodate and the dissociation constant of iodic acid

Calcium iodate hexahydrate can be prepared by a procedure similar to the barium iodate (Sec.8.6.2) using 2.5 g calcium chloride in 50 cm^3 hot water to precipitate the calcium iodate. However, it is simpler to prepare it by double decomposition.

Dissolve 3.4 g calcium chloride dihydrate in 100 cm^3 water. Add to the hot solution at 80°C, a hot solution of 6.8 g sodium iodate in a minimum of hot water, while stirring continuously. Allow the mixture to cool and then place in an ice/salt bath to complete crystallisation. Filter under suction, wash on the filter with small volumes of cold water until the filtrate is chloride-free. Dry at 80°C and weigh your product.

The solubility of calcium iodate is represented by the equilibrium:

$$Ca(IO_3)_2(s) \leftrightarrows Ca^{2+}(aq)+2IO_3^-(aq) \qquad (8.14)$$

and its solubility product, K_s, is defined by:

$$K_s=[Ca^{2+}][IO_3^-]^2 \qquad (8.15)$$

$$\therefore \quad [IO_3^-]=(K_s/[Ca^{2+}])^{½} \qquad (8.16)$$

In these relations, activity coefficients are disregarded and molar concentrations are used, and this applies to the following discussion. When the solid dissolves in an acidified solution, another equilibrium is established:

$$H^+(aq)+IO_3^-(aq) \leftrightarrows HIO_3(aq) \qquad (8.17)$$

The equilibrium constant for this is usually termed the acid dissociation constant, K_a, represented by:

$$K_a=[H^+][IO_3^-]/[HIO_3] \qquad (8.18)$$

$$\therefore \quad [HIO_3]=[H^+][IO_3^-]/K_a \qquad (8.19)$$

Equilibria (8.15) and (8.17) represent a competition between H^+ and Ca^{2+} for IO_3^-. However both (8.15) and (8.18) have to be satisfied. From stoichiometry:

$$2[Ca^{2+}]=[IO_3^-]+[HIO_3] \qquad (8.20)$$

Combining (8.17) with a rearranged (8.19) gives the relation:

$$[HIO_3]=([H^+]/K_a)(K_s/[Ca^{2+}])^{½} \qquad (8.21)$$

Substituting into (8.20) from (8.16) and (8.21) we get:

$$2[Ca^{2+}]=(K_s/[Ca^{2=}]^{½}+([H^+]/K_a)(K_s/[Ca^{2+}])^{½} \qquad (8.22)$$

Rearranging the terms leads to:

$$2[Ca^{2+}]^{3/2}=K_s^{½}+(K_s^{½}[H^+]/K_a) \qquad (8.23)$$

The molar solubility of calcium iodate, S, = the molar concentration of Ca^{2+} ions in solution. Hence measurements of S at different $[H^+]$'s and a plot of $2S^{3/2}$ against $[H^+]$ is expected to be linear. From the intercept, K_s is calculated and using this value and the slope, K_a can be determined.

The solubility of calcium iodate in perchloric acid/perchlorate solution is suitable for testing (8.23). The mixtures of perchloric acid and its salt maintains a constant ionic strength while varying $[H^+]$. Prepare 1 M solution of purest perchloric acid and 1 M solution of sodium perchlorate. Using different ratios of acid and salt, prepare 8 or 10 solutions in which the total $[ClO_4^-]$ = 1 M with $[HClO_4]$ varying between 1 M and 0.1 or

0.2 M. Weigh out in dry tubes or flasks ~0.2 g of your preparation, add 25 cm^3 of one of the prepared solutions, stopper and keep in a shaking thermostat or an orbital incubator at 25°C for a conveniently long time (at least overnight). Pipette 5.0 cm^3 of each supernatant solution into a conical flask, add 50 cm^3 20% w/v KI solution, 10 cm^3 1 M HCl and titrate the liberated iodine as in Sec.7.3.1. Hence calculate the solubility of calcium iodate in mol dm^{-3}. Use a pH meter to find the pH of an aliquot of each solution. If an atomic absorption spectrometer is available, determine the concentration of calcium ions in the saturated solutions. Plot $2S^{3/2}$ against $[H^+]$ and calculate K_s and K_a.

8.7.6 Comparing the solubility of calcium iodate in water and in 0.01 M potassium iodate solution

The common ion effect

Equilibrium (8.14) indicates that adding iodate ions to a saturated solution of calcium iodate will shift the equilibrium to the left i.e. will reduce the solubility of the calcium salt. This is an example of the common ion effect.

Use the same procedure as in 8.7.5, replacing the acid solution by water or by 0.01 M potassium iodate solution and determine the solubility in each case as above. Draw your conclusions.

8.8 CATIONIC IODINE

Because of the comparatively low ionisation energy and electronegativity of iodine, cationic iodine compounds can be isolated, especially when iodine is coordinated to a ligand e.g. pyridine.

8.8.1 Preparation of $[I(py)_2](NO_3)$

This compound is formed when a solution of iodine in chloroform is added to a silver nitrate solution in pyridine.

Dissolve 2.5 g of powdered iodine in 50 cm^3 of chloroform. Add the solution to a solution of 1.7 g silver nitrate in 5 cm^3 of $CHCl_3$ with constant stirring. Allow to stand until no more precipitate is formed. Filter and discard the precipitate, collecting the filtrate in a clean dry beaker. Ensure no flames are near, add 50 cm^3 of ether to the filtrate, while stirring. Allow to stand until crystallisation seems to be complete. Filter the yellow crystals under suction, wash with small volumes of ether. Dry by continued suction. Weigh your product and calculate the % yield based on iodine.

8.9 KINETICS AND MECHANISMS OF REACTIONS INVOLVING A HALOGEN SPECIES

The oxo-salts of the halogens are strong oxidants whereas the halides, especially the iodide, may act as reductants. Some of the reactions involving halogen species are sufficiently slow to make kinetic studies possible without the need for special fast reaction techniques.

8.9.1 Investigating the oxidation of iodide by iron(III)

In acid solution, iodide solutions are slowly oxidised by iron(III) salt solutions.

Use boiled-out distilled water to prepare a stock of 0.2 M sulphuric acid. Use the acid to prepare a 0.04 M KI solution and separately a 0.04 M iron(III) solution (from purest ammonium iron(III) sulphate dodecahydrate). Place one solution in flask A (Fig.2.12) and an equal volume of the other solution in flask B and keep in a thermostat at 20°C (purging with nitrogen is advisable). After 20 minutes, mix the two solutions thoroughly while starting a stopwatch. At 5 minute intervals, transfer a small volume into flask C, which is cooled in ice/salt mixture. Continue collecting aliquots, increasing the time interval as the reaction proceeds and the colour of the solution darkness. After 90-100 minutes, run the spectrum of the remaining solution in a 1 cm stoppered cell over the range 380-600 nm and locate the wavelength of maximum absorption. Allow each of the collected aliquots to warm to 15°C and quickly measure the absorbance at the wavelength previously determined. Plot absorbance against time and find the initial slope of the line. Repeat using a 0.02 M iron(III) solution and a 0.04 M KI solution both in 0.2 M acid and determine the initial slope of the kinetic curve. Using a 0.02 M solution of Fe(III) and 0.01 M solution of KI both in 0.2 M acid, repeat the procedure and find the initial slope of the curve. By comparing the initial slopes in the three runs, deduce the order of the reaction with respect to iodide and to iron(III). Dissolve in a volume of the first iron(III) solution, powdered purest ammonium iron(II) sulphate hexahydrate to give a 0.02 M solution in iron(II) and carry out another kinetic run. Compare the curve with the one in which no iron(II) was added and comment on your observation.

8.9.2 Oscillatory reactions in solution

When there is a dual set of solutions to the steady state equations; as one set is established, the resulting concentration changes may cause a change to the other set. At no time is $\Delta G^{\theta}>O$. For a sequence: $A \rightarrow X \rightarrow B \rightarrow C$, if $A \rightarrow X$ is autocatalytic but inhibited by B and if there is a delay between the two processes, concentration oscillations may be observed. Oscillation depends on two feedbacks: positive i.e. catalytic and negative i.e. inhibitory.

8.9.3 The Belousov-Zabotinsky reaction

The best studied homogeneous oscillatory reaction involves the oxidation of propanedioic acid (PDA) by bromate in acidified bromide solution, catalysed by Ce(IV). The overall reaction is:

$$2BrO_3^-+3PDA+2H^+ \rightarrow 2BrPDA+3CO_2+4H_2O$$

where $BrPDA=BrCH(COOH)_2$. The main stages of the reaction are:

1. Reduction of bromate by bromide with the bromination of the acid:

$$BrO_3^-+2Br^-+3PDA+3H^+ \rightarrow 3BrPDA+3H_2O \qquad (8.24)$$

2. Catalysed production of HOBr:

$$BrO_3^-+4Ce^{3+}+5H^+ \rightarrow HOBr+4Ce(IV)+2H_2O \qquad (8.25),$$

3. Reduction of Ce(IV) and oxidation of BrPDA:

$$BrPDA+4Ce(IV)+HOBr+H_2O \rightarrow 2Br^-+3CO_2+4Ce^{3+}+6H^+ \qquad (8.26)$$

Add 30 cm^3 concentrated sulphuric acid slowly to 399 cm^3 cooled water and dissolve in the solution 10 g propanedioic acid, 3.9 g potassium bromate and 0.4 g ammonium hexanitrocerate(IV). Add to the solution drops of 0.025 M ferroin indicator (>½ cm^3) to give a visible colour. Stir magnetically and note the change in colour from blue to red. Alternatively, insert a platinum electrode into the solution and dip a calomel electrode through a salt bridge in the solution. Connect the two electrodes to a mV meter and observe its reading as the mixture is stirred magnetically. If available record the output of the meter.

8.9.4 Other oscillatory reactions

Add 5 cm^3 1 M sulphuric acid to 20 cm^3 acetone followed by 20 cm^3 0.1 M potassium iodate, 5 cm^3 of 100 volume hydrogen peroxide and 5 cm^3 0.075 M manganese sulphate solution. Use a magnetic stirrer and note the oscillation of the colour from yellow to colourless. Otherwise record the mV meter output when it is connected to the platinum and the calomel electrode as above.

9

Titanium

9.1 INTRODUCTION

Ti, the top metal in group 4, exhibits the common oxidation numbers: +2, +3 and +4. The latter is the most stable state and corresponds to the group number. This oxidation state is represented by the solid and ionic TiO_2 and the liquid covalent $TiCl_4$. The ionic character of the former means that it contains Ti^{4+} ions, of [Ar] configuration. This and its high lattice energy account for its stability. However, the high polarising power of Ti^{4+}, makes it energetically more favourable to form the tetrahedral covalent $TiCl_4$. Ti(II) compounds are the least stable and liberate hydrogen from water. On the other hand, Ti(III) compounds in acidified solution can be stored and handled in an inert atmosphere. The d^1 configuration of Ti^{3+} gives it its colour, and its visible absorption spectrum, unlike the colourless Ti(IV). However, TiO_2 is a useful white pigment in its two main crystalline forms: rutile and anatase. They are very inert and are n-type semiconductors, whereas TiO, which is non stoichiometric has metallic conductivity.

9.2 TESTS ON TITANIUM COMPOUNDS

9.2.1 Ti(IV) Compounds

(a) Heat TiO_2 powder in a porcelain crucible, note its colour when hot and when it cools down. Test the solubility of the powder separately in: conc. HCl or in conc. NaOH.

(b) Add to separate portions of $TiCl_4$ in 1:1 HCl:
  - (ii) NaOH solution and test the solubility of any product in conc.HCl;
  - (iii) water, boil gently and test as above;
  - (iv) Zn dust, shake and note any changes in the supernatant liquid;
  - (v) 10 volume H_2O_2, note any colour change and then add powdered NaF;
  - (vi) $K_4[Fe(CN)_6]$ solution.

9.2.2 Ti(III) Compounds

Add to separate portions of freshly dispensed $TiCl_3$ in HCl;
  - (i) NaOH solution and note any changes;
  - (ii) diluted acidified $KMnO_4$ solution dropwise;
  - (iii) warm conc. solution of $NaClO_4$;
  - (iv) acidified Fe(III) sulphate solution.

9.3 ANALYSIS OF Ti(IV) and Ti(III) COMPOUNDS

9.3.1 Analysis of $K_2[TiO(C_2O_4)_2].2H_2O$

Prepare and standardise 0.02M permanganate solution as described in Sec.12.8.2.

Weigh out accurately about 12g of the solid, dissolve in dil. H_2SO_4 and make up to 250 cm^3 with the acid. Pipette a 25.0 cm^3 aliquot of the solution into a 250 cm^3 conical flask, add 100 cm^3 of the acid and heat to 70°-80°C and titrate with standardised 0.02M permanganate solution to the first permanent faint pink colour. Repeat and calculate the average the percentage purity of the solid.

9.3.2 Standardisation of $Ti_2(SO_4)_3$ Solution

Set up the apparatus shown in Fig.9.1. Dispense the Ti(III) solution into the aspirator A so that it nearly fills it, while H_2 (from Kipp's apparatus) displaces air from the system. Fill the burette B completely with the solution by opening the Tap T. Then empty the burette to allow H_2 to displace air from the system. Then fill the burette again with the solution by turning the tap.

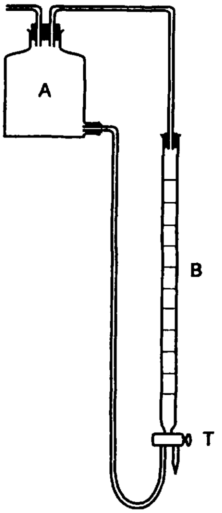


Figure 9.1 The arrangement for storing and dispensing air-sensitive solutions.

Pipette 25.0 cm^3 of standard 0.1 M Fe(III) solution together with 25.0 cm^3 dil. sulphuric acid into a 250 cm^3 conical flask provided with a rubber bung with 2 holes to allow a stream of CO_2 (from a Kipp's apparatus) to circulate and a middle hole for the tip of the burette B. Run in the Ti(III) solution with constant stirring until the colour of Fe(III) nearly disappears. Then add 10 cm^3 of 10% NH_4SCN solution and continue titration until the colour of the Fe/SCN complex just disappears.

Alternatively deliver 25.0 cm^3 of the Ti(III) solution into the conical flask, while circulating CO_2, which is continued throughout the experiment, add 10 cm^3 of 10% NH_4SCN solution and titrate with the Fe(III) solution from a burette until a persistent light brown colour appears.

Calculate from an average titre the concentration of Ti(III) in mol dm^{-3}.

9.4 PHOTOCHEMICAL EXPERIMENTS ON TITANIUM COMPOUNDS

Titanium dioxide is a versatile photocatalyst. U.v. irradiating some organic compounds in presence of anatase or rutile in absence of air leads to the oxidation of the organic species and the partial reduction of Ti(IV) to Ti(III). Similarly irradiating Ti(IV) complexes is expected to lead to the reduction of Ti(IV) and the oxidation of the ligands.

9.4.1 Photo Redox Reactions of Aqueous Solutions of Transition Metal Complexes

(V.Balzani, V.Carassiti; *Photochemistry of Coordination Compounds*, Academic Press, 1970, pp.376-37)

When an aqueous solution of a transition metal complex exhibits a LMCT band(s),usually located in the u.v., irradiation of the solution by a u.v. lamp leads to a reduction of the metal ion and the oxidation of the ligand. This is expected when the metal is in a high oxidation state with a reducing ligand. Numerous oxalato-complexes, when irradiated in the LMCT region, were found to undergo a photoredox reaction e.g.

$$2[M(C_2O_4)_3]^{3-} \rightarrow 2M(C_2O_4)_2^{-} + 2CO_2 + C_2O_4^{2-} \quad (9.1),$$

where M(III) is reduced to M(II) and the oxalate is oxidised to carbon dioxide. The rate of the reaction, which depends mainly on the metal ion, wavelength of irradiation and pH, is expressed as quantum yield, Φ, (Section 2.10.2).

9.4.2 Photoreduction of Acidified $[TiO(C_2O_4)_2]^{2-}$

Prepare a stock solution of 0.064M complex in O.15M H_2SO_4. Pipette 75.0 cm^3 aliquots of the solution into 3 volumetric flasks, dilute to 100 cm^3 with either 0.3M acid, 0.15M acid, or water. Dilute a 5.0 cm^3 aliquot of the first solution 10 fold using 0.15M acid and repeat on an aliquot of the diluted solution. Record the spectrum of the final solution in a 10 mm quartz cell over the range 270-210 nm and measure accurately the absorbance at 254 nm. Calculate the molar absorption coefficient at 254 nm.

For the photochemical experiment use a dip type low pressure mercury lamp provided with a quartz thimble and a cylindrical reaction vessel with a ground joint to match the thimble's joint. The vessel should have a side arm to allow a narrow Tygon rube for nitrogen flow and another arm which is connected to 2 bubblers filled with $Ba(OH)_2$ in NaOH solution. Check the volume of solution which will completely surround the mercury arc and pipette this volume of one of the $[TiO(C_2O_4)_2]^{2-}$ solutions after introducing a magnetic follower. Purge with nitrogen and continue throughout the experiment. Place a safety dark screen in front of the lamp and do not look directly to the lamp except through special dark glasses. This is necessary when a mercury lamp is used. Switch on the lamp and irradiate for 1 hour. Then quickly replace the lamp with a rubber bung with a burette containing the Fe(III) solution used in 9.3.2 and titrate to the end-point as above while stirring continuously. Repeat the experiment but using standardised 0.02 M MnO_4^- solution after quickly adding 25 cm^3 dil. sulphuric acid and titrate the oxalate in solution as in 9.3.1.

Repeat the irradiation for 2 or 3 hours. Use either irradiation time with solutions of varying acidity prepared above. Repeat any experiment after surrounding the lamp thimble with a Cu wire gauze to reduce the light intensity. Repeat using a Cu wire gauze of different mesh size. Carry out a run using the original complex solution and diluting 75.0 cm^3 aliquot with either 0.025 or 0.0125 M oxalate solution in 0.3 M acid and irradiate under similar conditions where no oxalate was added. Determine Ti^{3+} and $C_2O_4^{2-}$ in each case.

9.4.3 Determination of Φ

Prepare a stock solution which is (0.02 M in $UO_2(NO_3)_2$;0.1 M in $H_2C_2O_4.2H_2O$. Dilute 25.0 cm^3 to 250 cm^3. Use a volume of the solution identical to that used in the above irradiations and irradiate for a known short period (no nitrogen atmosphere is required). Titrate the irradiated solution with 0.004M permanganate solution prepared as in 9.3.1 followed by appropriate dilution. Repeat using the same volume of the actinometric solution. Repeat the irradiation and titration of the irradiated solution at least once. Use a stop watch to record the irradiation time. Measure the absorbance of the actinometric solution at 254 nm. By measuring the outer diameter of the quartz thimble and the inner diameter of the irradiation vessel, estimate the length of the irradiation path and work out the percentage of light absorbed at 254 nm by the actinometric solution, then calculate the output of the lamp at 254 nm (in quanta s^{-1}), taking the quantum yield at this wavelength as 0.63. Repeat using the two Cu gauzes mentioned above. Using the calculated output and the absorbance of the complex solution used at 254 nm and the length of the light path determined above, estimate the fraction of light absorbed by the complex solution. From this value and the rate of production of Ti^{3+} ions and the rate of disappearance of oxalate, calculate the quantum yields of those two species under the various conditions used in 9.4.2. Comment on your results.

9.4.4 The Photo-oxidation of Primary Alcohols by Anatase

When primary alcohols are u.v. irradiated in presence of anatase, with nitrogen flowing, the alcohol is expected to be oxidised to aldehyde and Ti(III) is expected to be formed in the suspension and at the surface of the powder. This is an example of a photoredox heterogeneous reaction (*Prog.Org.Coatings*, **1**, (1972) 157).

Use a set up similar to that described in 9.4.2 except by replacing the low pressure lamp with a medium pressure lamp and inserting an outlet stopper carrying a micro-burette containing 0.05 M iodine solution in purest methanol. Measure the volume of liquid which completely surrounds the mercury arc. Introduce this volume of a normal alcohol into the reaction vessel together with a weight of anatase equal to a tenth of that figure in g of powdered anatase. Pass a steady stream of nitrogen (through the lamp if that is necessary) through $CrCl_2$ solution (made by adding Zn to acidified Cr(III) solution) and then through the reaction vessel. Allow the gas stream for about 15 minutes while magnetically stirring the anatase/alcohol mixture. Switch on the lamp and irradiate the mixture for a given period e.g. 60 minutes and then add from the burette a known excess of the iodine solution (about 5-10 cm^3 in excess, after the appearance of the colour of I_2 in the suspension). Then filter through glass fibre filter and titrate the filtrate (and washings with CH_3OH) against 0.05 M aqueous $Na_2S_2O_3$ solution until the yellow colour disappears, or titrate potentiometrically using a Pt electrode and a calomel electrode connected to a potentiometer. Record the end point or plot the potentiometer reading E *vs* the volume V used (or preferably ΔE *vs* ΔV). The end point is indicated by the sharp change in the reading (or the sharp peak in the ΔE *vs* ΔV plot). (Section 2.5.1).

Calculate the number of mols of Ti^{3+} formed from the titre and from the standardisation of the I_2 solution. An independent $I_2/Na_2S_2O_3$ titration gives the exact molarity of the I_2 and is a useful practice for the end point detection. The $Na_2S_2O_3$ solution should be standardised against standard KIO_3 solution.

Repeat the irradiation and titration replacing methanol by ethanol, *n*-propanol or *n*-butanol. Using the latter alcohol, repeat using irradiation times of 2 or 3 hours. Keeping irradiation time to 1 hour, using anatase concentrations = 2,3 or 4 times the previous 1% (w/v).

Determination of the yield of butyraldehyde (butanal)

Using *n*-butanol and 1% (w/v) anatase, irradiate for 1 hour without adding I_2 solution. Filter the reaction mixture through GF/C paper and distil to separate the aldehyde produced using a fractionating 12" column. Collect the first batch of distillate in a weighed receiver. Add a few drops of NaOH, heat on a water bath for 40 minutes and measure the absorbance at 280 nm after cooling an aliquot. Determine the concentration of the aldehyde by interpolation from a calibration plot in which the absorbance is plotted against concentration of purest aldehyde in various concentrations in purest *n*-butanol. Investigate analysis using HPLC (Section 2.8.2).

Examine the appearance of the irradiated P25 and note the change after leaving in air for a few days. Comment on your results and your observations.

9.5 SURFACE CHEMISTRY OF TiO_2

Like other insoluble compounds, the surface of TiO_2, suspended in water is known to be hydroxylated. The surface equilibria can be represented by:

$$Ti_HH^+(surf) \rightleftharpoons Ti(OH)(surf)+H^+ \rightleftharpoons TiO^-(surf)+2H^+ \qquad (9.3),$$

The net charge on the particles = O at the point of zero charge, PZC. At pH's >PZC, adsorption of cations is expected whereas anions would be adsorbed at pH's <PZC. H^+ (aq.) and OH^- ions are said to be potential-determining. Electrostatic considerations predict a stronger adsorption as the charge on the ions increases. However, the pH of the solution also determines the speciation of the ions in solution, which is particularly important for phosphate ions. PZC of anatase is at pH 6.2 and that of rutile is at pH 5.3. It is advisable to convert the surface to the K^+ form by equilibrating with KNO_3 or $KClO_4$ prior to adsorption to minimise the effects of pH changes which would accompany the adsorption process. In the following sections, the adsorption of the alkaline-earth ions or phosphate on an anatase pigment is described. Because adsorption depends on temperature, the experiments should be carried out in a shaking thermostat or an orbital incubator.

9.5.1 Determination of the Point of Zero Zeta Potential of Titania

Sonicate a suspension of 10 mg titania in 1 dm^3 of 0.01 M KCl solution for 2 hours. Decant portions of the suspension in a beaker, adjust the pH to a suitable value by using 0.01 M KOH or 0.01 M nitric acid. Sonicate for 1 hour and measure the pH using a pH meter. Introduce the suspension in the cell, thermostat it by circulating water from a thermostat around the cell. Apply a potential difference of say 50V across the cell and time the movement of a particle through a distance (say 13.0×10^{-3}cm (the distance of 2 divisions on the calibrated divisions of the graticule in the eye piece). Make at least ten measurements at each stationary level, noting to which electrode the particles move. Reverse the polarity of the D.C. supply and make 10 measurements. Take the average of the velocity readings and calculate the mobility from the velocity and the potential gradient i.e. applied voltage/cross-sectional area. Repeat using similar suspensions with pH values in the range of 2-10. Plot the mobility including its sign against pH and estimate the PZZ, where the curve crosses the zero mobility line.

9.5.2 The Adsorption of the Alkaline Earth Cations by TiO_2

Prepare a stock solution of 0.1 M $Ca(NO_3)_2$, $Sr(NO_3)_2$ or $Ba(NO_3)_2$ in 10^{-2} M KNO_3 as well as stock solutions of the latter and 10^{-2} M EDTA using purest solids. Standardise the latter solution against $CaCO_3$ (Sec.3.4.1.2). By successive dilution, prepare solutions of the alkaline-earth nitrates in 0.01 M KNO_3 with a range of concentrations e.g. 0.02, 0.01 and 0.005. Ensure that the pH of all solutions is 7.0. To 2.0 g of anatase or rutile in a round bottom centrifuge tube, pipette 50.0 cm^3 of the KNO_3 solution and equilibrate at 25°C in a shaking thermostat preferably overnight. Use a set of five identical tubes. Centrifuge and carefully withdraw 40.0 cm^3 of the solution and introduce 50.0 cm^3 of 0.1 M $Ca(NO_3)_2$ solution. Shake the suspensions at 25°C for 1, 1.5, 2, 2.5 and 3 hours. Centrifuge and decant the supernatant through GF/C or GF/F filter. Titrate an aliquot of the filtrate against the standardised EDTA solution. Choose the time at which the titres become nearly constant and take it to represent the time for attaining adsorption equilibrium, and use this time for subsequent experiments.

Repeat the experiments using the other Ca^{2+} solutions, and calculate in each case the equilibrium concentration and the amount adsorbed g^{-1} and plot an adsorption isotherm. Repeat using a lower and a higher temperature for adsorption say 10° and 45°C. Carry out the same runs using Sr^{2+} or Ba^{2+} ions and comment on your results.

9.5.3 The Adsorption of Phosphate by Anatase

Prepare a stock solution of 0.05 M KH_2PO_4 in 0.1 M $NaClO_4$. By successive dilution, using 0.1 M $NaClO_4$ for dilution, prepare: 2.5, 1.0, 0.5, 0.25 and 0.125 x 10^{-4} M solutions of KH_2PO_4. Adjust the pH of each solution to 5.0 (check using a pH meter). Equilibrate 1.00 g of anatase powder with 25.0 cm^3 of 0.1 M $NaClO_4$ in a round bottom centrifuge tube overnight in a shaker or preferably in a shaking thermostat. Centrifuge and carefully withdraw 20.0 cm^3 of the clear supernatant replacing it by 25.0 cm^3 of the phosphate solution. Using the thermostat at 25°C (or an orbital incubator) agitate the suspension for 1-2 days. Centrifuge and withdraw an aliquot of the clear supernatant for determining the phosphate concentration (Sec.6.10.3). Repeat with suspensions containing the five phosphate solutions prepared. Construct an adsorption isotherm as described above. Repeat using two other temperatures e.g. 5°C and 45°C. Repeat the runs using solutions adjusted to two pH values e.g. 1 and 3. Comment on your results. If the surface area S of the anatase is known, calculate the area A occupied by a phosphate species using the relation:

$$A=S/N_AX_m \qquad (9.4),$$

where N_A is the Avogadro constant and X_m from the Langmuir isotherm.

10

Vanadium

10.1 INTRODUCTION

Vanadium, like the other 3d transition metals, exhibits the common low oxidation state of +2 by the loss of its two s electrons. In the highest oxidation state of +5, which corresponds to the group number, all the valence electrons are involved in bonding. As usual, O or F stabilise this state and the oxide V_2O_5 is the most common oxide and is more ionic than the only +5 halide: VF_5. As the Ebsworth diagram in acid solution (Fig.10.1) shows, the +3 state is the most stable thermodynamically. However, it is susceptible to oxidation in air. The +4 state is stable in air.

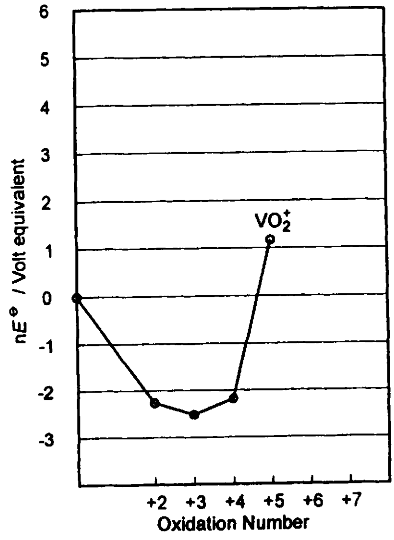


Figure 10.1 Volt-equivalent versus oxidation number for V in acid solution.

As expected, V(II) compounds are strong reductants whereas V(V) compounds are mild oxidants. All the oxides representing the four oxidation states are known. As the oxidation number and electronegativity increase, the basic character of the oxide decreases and its acidic character increases. Thus VO and $V(OH)_2$ are basic whereas V_2O_4 is amphoteric and so is V_2O_5 although it is more acidic than V_2O_4. Parallel to this trend, the ions $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$ are found in aqueous solution whereas the oxocations: VO^{2+} and VO_2^+ are the stable forms in acid solution. The latter is formed on dissolving V_2O_5 in acids whereas vanadates are formed in alkaline solution. The solid vanadates are represented by NH_4VO_3 and Na_3VO_4. Complex compounds are known for the four oxidation states. V(II) and V(III) usually form octahedral complexes whereas the V(IV) complexes are usually square pyramidal with a V=O group above the square plane. Because of the d^1, d^2 and d^3 configuration of V(IV), V(III) and V(II) compounds respectively, they are paramagnetic and coloured.

10.2 ANALYTICAL CHEMISTRYOF VANADIUM COMPOUNDS

10.2.1 Tests on Vanadium Compounds

10.2.1.1 V(V)

(a) Heat in a dry test tube NH4VO_3. Expose to any gas(es): a moist red litmus paper and a dry cobalt blue paper. Examine the residue and add to it, when cool dilute sulphuric acid or dilute NaOH solution.

(b) Dissolve NH_4VO_3 in dilute NaOH and then add dil. sulphuric acid liberally. Add to separate portions of the solution:
  (i) a crystal of sodium sulphite and note the colour;
  (ii) a few magnesium turnings carefully, test for the gas evolved;
  (iii) zinc dust or amalgam and more sulphuric acid, shake well and allow to react, note the colour of the supernatant or filtrate;
  (iv) hydrogen sulphide gas or solution and warm in the fume cupboard;
  (v) ammonium sulphide, acidify, test any precipitate with alkali solution and note the colour of supernatant or filtrate;
  (vi) hydrogen peroxide in 20% sulphuric acid added dropwise and then in excess;
  (vii) lead acetate solution, test the solubility of any precipitate in dilute nitric acid;
  (viii) barium chloride solution, test the solubility of any precipitate in dilute HCl;
  (ix) copper (II) sulphate solution;
  (x) iodide solution, boil gently until no more vapour is evolved;
  (xi) silver nitrate solution, boil and test the solubility of any precipitate in dilute ammonia;
  (xii) periodic acid.

10.2.1.2 Tests on Vanadium (IV)

Prepare a solution of $VOSO_4$ in dilute sulphuric acid and add to separate portions;

(a) potassium permanganate dropwise;
(b) magnesium turnings carefully;
(c) zinc dust, shake and allow to react, note the colour of the supernatant;
(d) hydrazine hydrate or hydrazinium salt solution and heat;
(e) iron (III) chloride solution, after adjusting the pH to >6, testing for Fe^{2+} by dipyridyl (2% in 0.1 M HCl)
(f) an alkali solution;
(g) thiocyanate solution.

10.2.1.3 Tests on Vanadium (III)

Add Mg turnings gradually to an acidified VO^{2+} solution and add separately the supernatant to each of the following:

(a) an alkali solution;
(b) iron (III) chloride solution;
(c) thiocyanate solution;
(d) powdered sodium dithionite $Na_2S_2O_4$;
(e) acidified potassium permanganate added dropwise.

10.2.1.4 Tests on Vanadium (II) solutions

Place zinc dust in a separating funnel, add acidified vanadyl (IV) solution and close with a stopper carrying a Bunsen valve. Shake well and allow to stand with intermittent shaking. Add to aliquots of the filtrate, each of the following solutions:

(a) alkali solution, check the effect of excess;
(b) iron (III) chloride solution;
(c) acidified potassium permanganate added dropwise;
(d) acidified vanadate solution;
(e) a warm solution of potassium oxalate/oxalic acid.

10.2.2 Determination of the Water of Crystalisation $VOSO_4.xH_2O$

Weigh out accurately about 0.9 g of the blue crystals . Dissolve in dilute sulphuric acid and make up to 250 cm^3 with the acid in a volumetric flask. Pipette 25.0 cm^3 of the solution into a conical flask, add an equal volume of the acid and titrate with standardised (about 0.02 M permanganate) until a drop produces a faint permanent pink colour superimposed on a faint yellow. Repeat to obtain concordant results and calculate from the average titre the molar concentration of $VOSO_4$ and its mass. Hence calculate x in the formula.

10.2.3 Titrimetric Study of the Oxidation States of Vanadium

(i) Weigh out accurately about 2.0 g of purest NH_4VO_3 and dissolve in 50 cm^3 of IM NaOH. Add 80 cm^3 dilute sulphuric acid while agitating the solution and when it is clear make up to 250 cm^3 with distilled water. Pipette 25.0 cm^3 of the solution into a conical flask, add an equal volume of acid and a few crystals of sodium sulphite. Heat to boiling to expel SO_2 until an acidified dichromate paper no longer changes to green. Then titrate with the standardised permanganate solution as above. Find the oxidation state of V in the reduced solution.

(ii) Pipette 25.0 cm^3 of $VOSO_4$ solution, prepared as in 10.2.2, into a separating funnel as in Fig.2.10. Add a couple of Zn granules and 1.0 g of Zn dust (use a spatula to break any lumps). Shake the mixture carefully and intermittently until the colour does not change further. Place 40 cm^3 of the prepared vanadate solution into the Buchner flask. Apply gentle suction to evacuate the flask and then open the tap of the separating funnel carefully to run the reduced vanadium solution into the vanadate solution. Then disconnect the vacuum, dismantle the apparatus and titrate the final solution with the standardised permanganate as above. Calculate the valance state of V in the reduced solution.

(iii) Pipette 25.0 cm^3 of the $VOSO_4$ solution and an equal volume of the acid into a conical flask and gradually add 0.5 g Mg turnings. When no further colour change takes place, quickly filter off any unreacted Mg and collect the filtrate into a conical flask. Rinse with acid and add to the conical flask. Then titrate with standardised permanganate as above and calculate the valence state (or oxidation number) of the reduced V solution.

10.3 STUDY OF THE OXALATO-COMPLEXES OF VANADIUM

10.3.1 Preparation and Analysis of $(NH_4)_2[VO(C_2O_4)_2].2H_2O$

(*School Sci. Rev.* **56**(1975), 197)

The complex compound is prepared by reducing ammonium vanadate by oxalic acid. This, together with oxalate, form the vanadyl (IV) oxalato-complex.

The complex is analysed by permanganate titrimetry. This oxidises both VO^{2+} and oxalate. Following this, the produced V(V) is reduced by sulphite whose excess is removed by boiling. The V(IV) produced is determined by permanganagte titrimetrically.

Dissolve 10 g of $H_2C_2O_4.2H_2O$ in 15 cm^3 of water heated to boiling and then add 2.4 g of $(NH_4)_2C_2O_4$ and, in small portions, 4.6 g of NH_4VO_3. Gently boil the solution to reduce the volume to half its original volume. Stop heating and immediately add 20 cm^3 water, stir well and place in a large separating funnel and then add 200 cm^3 ethanol and shake well for 5 minutes. Decant off any formed dark oil from the blue solution. Leave overnight so that crystals are formed. Collect these by filtration under vacuum. Wash with small amounts of ethanol and acetone. Dry by continued suction while pressing between filter paper. Calculate the percentage yield based on the vanadate mass, after weighing your product.

To analyse the product, weigh accurately about 0.2 g, dissolve in dilute sulphuric acid, heat to 80°C and titrate with standardised permanganate as described before. Add to the titrated solution, sodium sulphite, warm to obtain the blue colour of the complex. Check that complete reduction has taken place by adding another crystal to ensure maximum colour production. Boil gently to expel SO_2 and check that no more is evolved as mentioned before. Then titrate with the same permanganate solution. It is advisable to repeat the operations. Work out the molar ratio of V(IV)/(oxalate).

10.3.2 Preparation and Analysis of $K_3[V(C_2O_4)_3].3H_2O$

This complex is prepared by reducing the alkali vanadate (formed from the ammonium salt) by hydrazine hydrate in acetic acid. The addition of potassium oxalate in presence of ethanol precipitates the complex.

The complex is analysed by permanganagte titrimetry where both V(III) and oxalate are oxidised. If V(III) is first precipitated as hydroxide, the filtrate containing only oxalate can be titrated against permanganate.

Dissolve 8.5 g of NH_4VO_3 in 25 cm^3 of water in which 3.8 g KOH had been dissolved. Heat to boiling very gently in the fume cupboard (preferably over a sand bath). Continue until all the ammonia has been expelled, test by exposing to the vapours moist red litmus or moist $Hg_2(NO_3)_2$ paper. Prepare a solution by the gradual addition of 7.5 cm^3 $N_2H_4.H_2O$ to 27 cm^3 of glacial acetic acid in the fume cupboard. Add this solution to the V solution and heat carefully until no more N_2 is evolved. Dilute two fold with water. If the colour is not clearly green, add more of the reducing mixture to attain maximum colour production. Filter and add to the filtrate 4.0 g $K_2C_2O_4.H_2O$ dissolved in 100 cm^3 water. Then add 100 cm^3 ethanol and cool in an ice/salt bath until crystallisation of the complex seems to be complete. Filter off the green crystals under suction, wash with a few cm^3 water and small volumes of ethanol. Dry under suction while pressing between filter paper. Weigh your product and calculate the percentage yield.

To determine the purity of your product, weigh accurately about 0.2 g into a Buchner flask fitted with a rubber bung with a hole to accommodate the tip of a burette containing standardised 0.02 M permanganate. Add 40 cm^3 dilute sulphuric acid, replace the bung, and connect the Buchner to the vacuum line. Warm the flask on a sand bath and titrate with the permanganate solution as before. Repeat the determination and calculate the percentage purity.

Repeat the procedure but replacing the burette with a separating funnel containing dilute sodium hydroxide solution. After dissolving the preparation as above and connecting to vacuum and warming, add slowly with stirring an alkali solution to precipitate the vanadium. When precipitation seems complete, filter under suction. Collect the filtrate and washings (which should be colourless) in a clean conical flask. Acidify liberally with dilute acid and titrate with permanganate as above. Compare the titres in this case and that obtained above and draw your conclusions.

Determination of the water of crystallisation

Weigh out accurately about 0.2 g of your preparation into a weighed container. Place in a drying oven set at 105° and dry to constant weight. Calculate the percentage loss in weight and hence the number of molecules of water of crystallisation.

10.3.3 Kinetic Study of the Oxidation of Aqueous $[V(C_2O_4)_3]^{3-}$ by persulphate

Prepare by accurate weighing about 0.08 M stock solution of the V complex and about 0.80 M solution of ammonium persulphate, both dissolved in 1M HCl. Pipette a suitable volume of the V complex into A and an equal volume of the persulphate into B (Fig.2.12). Keep the two solutions thermostatted at say 30°C before mixing them thoroughly as you start a stopwatch. At intervals, say 5, 10, 15, 20, 30, 40, 60, 90, 120 minutes, withdraw aliquots of the reaction mixture into the cooled (in ice/salt) flask C by applying pressure at g. Keep the aliquots cooled until you are ready to measure the absorbance in a 10 mm cell at 590 nm (maximum absorbance of the complex) and at 792 nm (maximum absorbance of the product). Repeat at 2 or 3 more temperatures up to 60°C. Plot the logarithms of the absorbances against time and comment on your plots.

10.4 STUDY OF THE COMPLEXES WITH ACETYLACETONE (PENTANE -2,4-DIONE)

This ligand forms stable complexes with V(IV), V(III) and V(II). The anion of the enolic form of the ligand forms chelate rings via two oxygens. These rings are stablised by the delocalisation of the π electron system. The complexes formed are neutral and are soluble in organic solvents.

10.4.1 Preparation of $[VO(C_5H_7O_2)_2]$ (*Inorg. Synth.* 5 (1957), 113).

The vanadium (V) oxide is reduced in sulphuric acid/ethanol hot mixture to V(IV). This forms the complex with the ligand in sodium carbonate solution.

Add 18 cm^3 of conc. sulphuric acid slowly, with cooling and stirring, to 25 cm^3 of water. Weigh out 4.0 g of V_2O_5 into a 400 cm^3 beaker, add to it 20 cm^3 of the diluted acid and 20 cm^3 of ethanol carefully. Heat on an electric mantle or hot plate to boiling. Continue while stirring for 40-60 minutes. If the mixture is too viscous, add a little ethanol to reduce the viscosity. Filter, add 20 cm^3 of acetylacetone to the filtrate and neutralise by the slow addition, with continuous stirring, of a solution of 16 g Na_2CO_3 in 100 cm^3 water. Filter under suction. Recrystallise from chloroform. Weigh and calculate the percentage yield based on V_2O_5. Obtain data on % C and % H.

10.4.2 Preparation and Analysis $[V(C_5H_7O_2)_3]$ (Vanadium *tris* (pentane-2,4-dionate)

This compound was first prepared by reacting VCl_3 with the ligand in alkali ethanol. However, VCl_3 is not readily available and not stable in air. The stable vanadyl (IV) sulphate is a suitable starting material. After reduction of the acidified solution by Mg, the V(III) solution reacts with the ligand in alkaline solution to yield the product.

The product is analysed by titration against dichromate, when V(III) is oxidised to V(IV).

From $VOSO_4.5H_2O$

Dissolve 3.5 g of the sulphate in 30 cm^3 dilute sulphuric acid, warm if necessary. Place the solution in a separating funnel (Fig.2.10). Dissolve 13 g CH_3CO_2Na in 50 cm^3 water, add 4 cm^3 acetylacetone (pentane-2,4-dione) and place in the Buchner flask. Assemble as in Fig.2.10 and add gradually pieces of Mg ribbon until maximum green colour is obtained (about 1 g may be needed). Connect the Buchner flask to the vacuum line and open the stopcock of the funnel, gradually adding the green solution to the magnetically stirred solution in the flask. Filter the precipitate under suction and dry by continued suction while pressing between filter paper. Recrystallise from ether (well away from naked flames). Weigh the final product, calculate the percentage yield based on the vanadium salt and determine its melting point.

From VCl_3

Grind 6 g NaOH and dissolve in 50 cm^3 absolute ethanol by warming on a hot plate and/or by sonication. Add the solution to a solution of 7.9 g VCl_3 (anhydrous) and 15.8 cm^3 of acetylacetone in absolute alcohol. Remove the precipitated NaCl by filtration. Evaporate the alcoholic filtrate on a rotary evaporator under vacuum at about 80°C. Collect the product by filtration, dry and recrystallise as above. Determine its melting point.

Analysis

Weigh out accurately about 0.5 g of your preparation, add about 50 cm^3 of dilute sulphuric acid and place in a Buchner flask, whose rubber bung carries a burette containing standard potassium dichromate solution (about 0.0167 M). Add a few drops of diphenylamine indicator, apply suction and titrate under the reduced pressure until the colour changes to violet. Repeat the determination and determine the percentage purity of your preparation.

10.5 SPECTRAL AND MAGNETIC STUDIES OF VANADIUM COMPOUND

Electronic spectra are very useful to characterise vanadium compounds and complexes. For the complexes prepared, infrared spectra characterise the ligands. Since V(II), V(III) and V(IV) compounds have 3,2 and 1 unpaired electrons respectively, their magnetic moments would confirm the oxidation state.

10.5.1 Electron spectra of V(II) and V(III)

The d^3 configuration of V(II) and d^2 configuration of V(III) suggest the d-d electronic spectra would exhibit 3 spin-allowed bands. In the case of V(II) solutions, the longest wavelength band gives Δ_o, which varies with the ligand.

Prepare VSO_4 and V(II)/oxalate solutions in the glove box as described below. Run their spectra over the range 600-900 nm in a 2 cm vacuum cell. Dilute each solution by an equal volume of acid and record the spectra in 1 cm cell in the range 450-600 nm and in a 2 mm cell over the range 200-450 nm. Work out Δ_o and comment on their relative magnitudes.

Prepare a solution of 0.01 M $K_3[V(C_2O_4)_3]$ in dilute silphuric acid and record the absorption spectrum in a 1 cm cell over the range 600-800 nm. Dilute an aliquot 10 times with the acid and record the spectrum in a 1 cm cell in the range 400-600 nm and in a 2 mm cell in the range 200-400 nm.

10.5.2 Spectrophotometric Determination of the Composition of V Complexes in Solution

The method of continuous variation (Job's method)

When a ligand L is added to an aqueous solution of a metal salt, L replaces water according to:

$$[M(H_2O)_6]^{z+} + n\,L \rightarrow [M(H_2O)_{6-n}L_n]^{z+} \qquad (10.1),$$

assuming that L is unidentate and neutral for simplicity. Generally the electronic absorption spectrum of the solution changes and is often accompanied by colour change. If solutions of different ratios of the metal salt and the ligand are prepared such that their total molar concentration (and preferably ionic strength) are constant, determination of the spectra at a given wavelength will exhibit a maximum absorbance when the molar ratio n:1 gives the composition of the stable complex under the experimental conditions (see *Anal. Chem.*43,1971,1265). If more than one complex is formed, it may be necessary to measure the absorbance at more than one wavelength. The method can be also adapted to calculate stability constants.

Determination of the composition of the complex in acidified V^{2+}/oxalate solutions. The use of the glove box.

Deaerate the following solutions by bubbling O_2-free N_2 for 10 minutes in boiled-out water: dilute sulphuric acid, $VOSO_4.5H_2O$ (20.2 g dm^{-3} dilute sulphuric acid), 0.017 M NH_4VO_3, $K_2C_2O_4$(14.7 g dm^{-3}) and 0.02 M standardised permanganate. Place these solutions together with the necessary glassware and accessories in the box and ensure that it is filled with nitrogen and keep its flow as recommended. To a 200 cm^3 of the $VOSO_4$ solution, add 5 g zinc dust and shake well, and allow to react with intermittent stirring until maximum colour is attained. Filter off the zinc and collect the VSO_4 solution in a clean beaker. If piston burettes are available, titrate an aliquot of the solution against permanganate and calculate its concentration in mol dm^{-3}. Measure aliquots of the solution in the range of 10-35 cm^3 into 50 cm^3 measuring flasks. Measure aliquots of the oxalate solution in the same range and introduce into the flasks so that the total V^{2+}+$C_2O_4^{2-}$ solution is 45 cm^3 and make up to the mark with dilute sulphuric acid. Fill a 4 cm vacuum spectrophotometer cell with the original VSO_4 solution and run its spectrum in the range of 400-900 nm. Fill in turn a 4 cm vacuum cell with one of the mixtures using as a blank a VSO_4 solution (made up of the same volume of VSO_4 as in the mixture and made up to 50 cm^3 with acid). Record the spectra of the mixed solutions using blank solutions as above. Plot the absorbance at a suitable maximum wavelength against the molar ratio : oxalate/VSO_4 and estimate the composition of the complex eventually formed.

Determination of the composition of the complex in acidified $VO^{2+}/C_2O_4^{2-}$ solution
Prepare a stock solution of 0.025 M $VOSO_4$ and 0.025 M $K_2C_2O_4$ both in dilute sulphuric acid. Pipette volumes of the vanadium salt solution in the range of 5-40 cm^3 into a 50 cm^3 volumetric flask and add pipetted volumes of the oxalate solution in the range of 40-5 cm^3 so that the total volume (vanadyl + oxalate) = 45 cm^3, and make up to the mark i.e. a total molar concentration of 0.0125 M. Record the spectra in the range of 350-850nm. Plot the absorbance at the wavelength of maximum absorption against the molar ratio of $C_2O_4^{2-}/VO^{2+}$ and draw your conclusions.

Determination of the composition of the complex in acidified $V^{3+}SCN^-$ solution
Prepare a solution of $VOSO_4.5H_2O$ by dissolving 8.2 g in dilute sulphuric acid and making up to 250 cm^3 with the acid. Add gradually magnesium foil until a maximum green colour is obtained. Filter off on fluted filter paper and keep the filtrate in a clean dry stoppered bottle. Determine the concentration of V^{3+} as described previously. Prepare a solution of KSCN of the same concentration as the vanadium solution. Pipette aliquots of the vanadium solution in the range of 5-35 cm^3. To each aliquot pipette aliquots of the thiocyanate solution in the range 35-5 cm^3 so that the total molar concentration (V^{3+}+SCN^-) is constant. Make up to the mark with the acid. Run the absorption spectra of the solutions in the range of 350-700 nm. Plot the absorbance at the wavelength of maximum absorption against the molar ratio SCN^-/V^{3+} and draw your conclusions.

10.5.3 Solvent effects on the electronic spectra

In the case of $[VO(C_5H_7O_2)_2]$ and $[V(C_5H_7O_2)_3]$, the neutral nature of the complexes and their organic ligands make them soluble in organic solvents. A number of studies of the solvent effects on the electronic spectra of the 2 complexes have been published (*J.Inorg.Nucl.Chem.* **21**(1961)221; *Montsh.Chem.* **114**(1983)1311) relating the spectra to solvent properties.

Prepare approximately 10% solution of each solid in a range of solvents. Run the absorption spectra in the range of 200-900 nm. Locate the wavelengths of maximum absorption. In case of very intense bands, dilute to obtain absorbances within the chart range. Comment on any relation between these bands and the solvent. E_T parameter or Donor and Acceptor numbers of the solvlents as defined in the two references.

10.5.4 Infrared Spectra

Prepare KBr discs of the four vanadium complexes prepared. Run their infrared spectra in the range 400-4000 cm^{-1}. Compare the complexes of V(III) and V(IV) and comment on your results.

10.5.5 Magnetic Measurements

Prepare or use a magnetic susceptibility standard in the Gouy balance or the Evans instrument. Use the standard to find the constant C in the eqn. 2.6 or C in eqn. 2.11. Grind each of the prepared complexes to a fine powder. Pack the balance tube with the powder to the mark and follow the instructions as in Sec.2.1.3. Calculate the magnetic susceptibility and the effective magnetic moment of each powder and comment on your results.

11

Chromium

11.1 INTRODUCTION

Although the ground state electronic configuration of Cr: $3d^545^1$ suggests the formation of Cr(I) compounds, it is energetically more favourable to form Cr^{2+} ions in solution or in solid compounds. However, oxidation states of +1 or lower are stabilised in presence of π-bonding ligands. The +2 is the lowest common oxidation state of Cr but Cr(II) compounds are powerful reductants which are readily oxidised to Cr(III): the most stable state. A solution of $CrCl_2$ is used to remove traces of oxygen from nitrogen. The blue paramagnetic Cr(II) solids or solutions should be handled in an inert atmosphere. The d^4 configuration of Cr(II), especially in octahedral environment, leads to Jahn-Teller distortion. As the Ebsworth diagram of Cr in acid solution, depicted in Fig.11.1, shows, Cr(III) is the most stable state of Cr. This is related to its d^3 configuration, which gives an exactly ½ filled t_{2g} level in octahedral ligand fields.

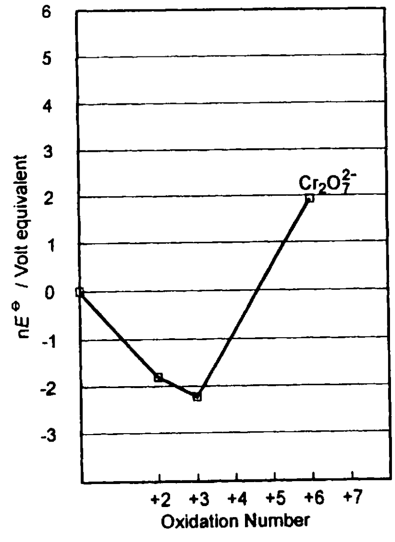


Figure 11.1 Volt-equivalent versus oxidation number for Cr in acid solution.

Numerous co-ordination compounds of Cr(III) are known. Some of these exhibit hydration isomerism or *cis/trans* and/or optical isomerism. Cr(IV) or Cr(V) compounds are rare, like Cr(I) compounds, but CrO_2 is a useful ferromagnetic material used for magnetic recording. The highest oxidation state of +6, which corresponds to the group number, is well represented by the acidic trioxide, its oxoanions: CrO_4^{2-} and $Cr_2O_7^{2-}$ as well as the covalent hexafluoride and the oxohalides CrO_2X_2(X=F,Cl). The stabilisation of the highest oxidation state by F and especially by O is demonstrated in these compounds. Whereas the dichromates are useful strong oxidants in acid solutions, chromates are used for precipitating many divalent cations. The oxidising power is greatly reduced as the pH is raised, which is a common feature of the 3d transition metal series.

11.2 QUALITATIVE TESTS

11.2.1 Tests on Cr(II)

(a) Place a small piece of Cr metal in a mortar, add dil.HCl, break the piece with a pestle to expose a fresh (not passive) surface and note the evolution of gas. Quickly transfer into a test tube and expose a lit splint.

(b) Repeat but transfer to a tube provided with a Bunsen valve. Allow to react and note the colour of the solution. Remove the bung with its valve and blow air and note the change in colour.

(c) Acidify Cr(III) chloride solution (prepared from solid $[CrCl_2(H_2O)_4]$ $Cl.2H_2O$), add Zn dust and allow it to react until there is a maximum change in colour

(d) Repeat test (c) and quickly decant through glass wool into a saturated solution of sodium acetate and note the colour developed, which may be transient.

11.2.2 Tests on Cr(III)

(a) Acidify a solution of $K_2Cr_2O_7$ with dil. H_2SO_4, add a solution of SO_2 and note any colour change. Concentrate the solution by boiling. Transfer to a basin and cool in an ice/salt bath to obtain crystals.

(b) Compare the colours of aqueous solutions of $[CrCl_2(H_2O)_4]Cl.2H_2O$ and $Cr(NO_3)_3$. Attempt an explanation of the difference.

(c) Add to a Cr(III) chloride solution, dil. NH_3 gradually. Shake the precipitate formed with an excess of NH_3 solution and note the colour of the supernatant liquid.

(d) Add to a Cr(III) chloride solution, dil. NaOH solution gradually. Check the solubility of any precipitate in excess NaOH.

(e) To a Cr(III) chloride solution. add a solution of sodium phosphate. Test the solubility of any precipitate in dil. H_2SO_4.

(f) Grind a Cr(III) salt with sodium carbonate, mix a small amount with a little KNO_3 and heat in porcelain basin.

11.2.3 Tests on Cr(VI)

(a) Add to a solution of Cr(III) chloride dil. NaOH solution and then 20 volume H_1O_2. Heat if necessary to observe a change in colour. Repeat using Na_2O_2 instead of $NaOH/H_2O_2$.

(b) To a chrome alum solution $(K_2SO_4.Cr_2(SO)_4)_3.24H_2O)$, add solid$(NH_4)_2S_2O_8$ and a drop of Ag_2SO_4 solution. Boil for some minutes and note the colour changes.

(c) Add dil. NaOH to a solution of $K_2Cr_2O_7$ solution, note the colour change and then add dil. H_2SO_4 and note the colour change.

(d) Dissolve CrO_3 (CARE!) separately in (i) H_2O (ii) dil. NaOH and compare the colours.

(e) Add separately to a solution of K_2CrO_4:

    (i) $BaCl_2$ solution and test the solubility of any precipitate in dil. HCl.

(ii) $AgNO_3$ solution and (after centrifugation and washing) test the solubility of half the precipitate in dil. nitric acid and test the solubility of the other half in dil. NH_3.
(iii) $Pb(CH_3COO)_2$ solution and test the solubility of any precipitate in dil. HNO_3.
(iv) $Hg_2(NO_3)_2$ solution, note any changes and the effect of heat on the mixture.

(f) Acidify $K_2Cr_2O_7$ solution with dil. H_2SO_4, add 2 cm^3 amyl alcohol and add dropwise 20 volume H_2O_2 and shake carefully. Note the colours obtained.
(g) Add conc. HCl to solid $K_2Cr_2O_7$, warm if necessary, in the fume-cupboard and expose a moist blue litmus paper to any gases formed.
(h) Grind small amounts (ie semi-micro scale) of KCl and $K_2Cr_2O_7$ together. Add to a little of the mixture conc. H_2SO_4. Warm, if necessary, *in the fume cupboard.* Note any vapour formed. Suck any vapour into a Pasteur pipette, introduce into a little H_2O and test with a blue litmus paper.*
(I) Add *sym*-diphenylcarbazide to a strongly acidified dichromate solution and note the colour change.

11.3 PREPARATION AND ANALYSIS OF Cr(II) COMPOUNDS

As Fig. 11.1 shows, Cr(II) compounds are readily oxidised to Cr(III). Even traces of oxygen can oxidise the compounds. Hence they should be prepared in special apparatus to exclude oxygen. One of the most stable Cr(II) compounds is the acetate (ethanonate) which is in fact a dimer containing short Cr-Cr multiple bonds.

11.3.1 Preparation and analysis of $CrSO_4$ solution

This can be obtained by reducing Cr(III) solutions eg by Zn and acid. When a Cr(II) solution is run into an excess of Fe(III) solution, the latter is reduced to Fe(II), which is equivalent to Cr(II) and may be determined eg by titration against standard $K_2Cr_2O_7$ solution, using a redox indicator. Fe(II) solutions are only slowly oxidised in air.

$$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+} \quad (11.1),$$
$$Cr^{2+} + Fe^{3+} \rightarrow Cr^{3+} + Fe^{2+} \quad (11.2),$$
$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \quad (11.3),$$
$$Cr_2O_7^{2-} \equiv 6Fe^{2+} \equiv 6Cr^{2+} \quad (11.4).$$

Weigh out accurately about 12.5 g of purest $KCr(SO_4)_2.12H_2O$, dissolve in dilute H_2SO_4 and make up with the acid to 250 cm^3. Using a pipettor, pipette 25.0 cm^3 of the solution into a separating funnel fitted with a bung carrying a Bunsen valve (Fig.2.10). Weigh about 3.5 g of Zn dust. Add a few granules of Zn and the Zn dust to the solution and quickly replace the bung. Shake the suspension carefully and allow to stand, with intermittent shaking, until the colour does not seem to change. Assemble the apparatus with the Buchner flask containing 25 cm^3 0.1M Fe(III) solution (an excess measured by a cylinder). Apply suction for 2-3 minutes and, by opening the funnel's tap, allow the Cr^{2+} solution to mix and react with the Fe(III) solution in the flask. Note the colour change during the experiment. Close the funnel's tap, quickly add about 25 cm^3 dilute H_2SO_4 (to wash the funnel and the Zn) and open the tap under suction so that the washings are added to the solution in the flask. Disconnect the vacuum and the apparatus. Add to the flask about 25 cm^3 dilute H_2SO_4 and 3 drops of diphenylamine indicator. Titrate with M/60 $K_2Cr_2O_7$ solution until there is a sharp colour change from green to dark violet. Repeat the operation and calculate, from the average titre, the concentration of $CrSO_4$ in mol dm^{-3}. Compare this molarity with the molarity of the initial Cr(III) solution and comment on the two values.

11.3.2 Preparation and analysis of Cr(II) acetate (ethanoate)

When a solution of $CrCl_2$, prepared by reducing Cr(III) chloride by zinc (as above), is mixed with sodium acetate, a precipitate of the Cr(II) acetate is obtained. This can be analysed as above.

Assemble in the glove box all the deaerated solutions and all the glassware required and displace the air by nitrogen as described in Sec.2.9.1. Deaerate the following solutions: 10 g chromium (III) chloride in HCl solution (25 cm^3 conc. HCl + 15 cm^3 water); 15 g sodium ethanoate in 35 cm^3 water. Add inside the box 10 g Zn to the Cr(III) solution, allow the reaction to proceed until the maximum blue colour is attained. Fill a vacuum 1 cm spectrophotometer cell with the supernatant solution. Then filter the remaining suspension into the ethanoate solution, which is being shaken, when a red precipitate is formed. Filter the precipitate in a Buchner assembly, wash on the filter with 20 cm^3 water, 20 cm^3 ethanol and finally 20 cm^3 ether. Dry by pressing between filter paper.

Record the spectrum of the reduced Cr solution over the range 800-200 nm, using water as a blank.

Pack the red powder into the Evans tube and measure the magnetic susceptibility as described in Sec.2.1.3.

Transfer about 0.5 g of the powder into a weighed weighing bottle, put on its stopper and weigh accurately. Dissolve the powder in a conical flask in about 15 cm^3 of a 10% iron (III) alum solution, add 25 cm^3 dilute sulphuric acid, 15 cm^3 of syrupy phosphoric acid and a few drops of diphenylamine indicator and mix the solution thoroughly. Titrate with standardised about 0.02 M permanganate until a permanent blue colour appears in the green /violet solution. Repeat with a second weight and calculate the average percentage Cr in your preparation and hence the percentage purity of the preparation. Potentiometric titration is more suitable in this case.

Comment on the spectrum of the blue solution and the magnetic susceptibility of the red solid.

11.4 STUDIES OF THE OXALATO-COMPLEXES OF Cr(III)

There are numerous complexes of Cr(III); their stability is related to the $(t_{2g})^3$ configuration. The chelate effect confers extra stability on the oxalato-(ethanedioato-) complexes. When water in the hexaaqua ion is replaced by three oxalate ligands, a trisoxalato-complex is formed in solution and can be readily prepared as a solid potassium salt. This exhibits optical isomerism. Geometrical isomerism is encountered in the cis- and *trans-* bisoxalato-complexes. The former exhibits optical isomerism. Although no solid containing the monooxalato-cation has been obtained, there is spectral evidence of its formation in solution.

11.4.1 Preparation and analysis of $K_3[Cr(C_2O_4)_3].3H_2O$ *(Inorg.Synth.*1(1939) 37)

This can be prepared by the reduction of potassium dichromate with oxalic acid in presence of oxalate. It is envisaged that the first stage is the reduction of Cr(VI) to Cr(III), followed by the complex formation with the oxalate.

Dissolve 8.8 g $H_2C_2O_4.2H_2O$ in 25 cm^3 warm water. Add *gradually* 3.0 g of *finely ground* $K_2Cr_2O_7$. When the vigorous reaction has subsided, heat nearly to boiling and dissolve in the solution 3.7 g $K_2C_2O_4.H_2O$ (finely ground). After cooling, add 5 cm^3 C_2H_5OH and cool in ice to enhance crystallisation. When no more crystals separate, filter under suction. Wash with 1:1 water/alcohol mixture and then with alcohol. Dry by continued suction while pressing between filter paper. Record the yield and calculate the percentage yield based on Cr.

Recrystallise from water/ethanol mixture, wash with alcohol and ether and dry by continued suction.

Analysis

When the solid is boiled with KOH solution, it decomposes the complex anion precipitating Cr(III) hydroxide. On filtering this off, the acidified filtrate containing the oxalate, is determined by titration with permanganate.

Heat an exactly weighed amount of the preparation at 110°C to a constant weight to determine the % of water of crystallisation.

Weigh out accurately about 0.3 g of the complex. Add 20 cm^3 of 5% KOH solution and boil for 10 minutes to precipitate $Cr(OH)_3$. Filter off $Cr(OH)_3$ and collect the filtrate and washings in a clean conical flask. Add 50 cm^3 dilute H_2SO_4 and heat to 80°C. Titrate the oxalate with~ 0.02 M $KMnO_4$ solution previously standardised against 0.05 M $Na_2C_2O_4$ solution. Repeat and calculate the percentage purity of your preparation.

Prepare 10^{-2} M solution of your complex and run its electronic spectrum over the range 400-800 nm in a 10 mm cell. Dilute an aliquot ten fold and run the spectrum in the same cell over the range 200-400 nm, using water as a blank. From the position of the longest wavelength maximum, calculate Δ_0 and LFSE.

11.4.2 The effect of ionic strength and dielectric constant on the aquation of the complex anion

The mechanism of the reactions of complex ions in solution may be clarified by studying the effect of ionic strength and dielectric constant on the rate of reaction.

Prepare a stock solution of 0.01M in the complex and another solution 0.01 M in HCl. Dissolve in aliquots of each solution known masses of $NaClO_4$ so that the ionic strength is in the range 0.3-1.5. Introduce a suitable volume of the complex in flask A (Fig.2.12) and an equal volume of HCl in flask B. Equilibrate thermally at 90°C for 20 minutes (in a thermostat) before thoroughly mixing the two solutions and starting a stopwatch. Ensure efficient cooling of the condenser. At suitable intervals, withdraw aliquots of the reaction mixture into the properly cooled flask C, as described in 2.11.1. When cool, measure the absorbance A of each aliquot at either of the visible maxima of the electronic spectrum of the complex. Plot log.A against time and calculate the rate constant k. Repeat for the solution of known ionic strength μ and then plot log k against μ and determine its slope. What conclusions can be drawn from your results?

Measurement of the dielectric constant, D, of dioxan/water mixtures

Thermally equilibrate a 1pF capacitance cell filled with air in a thermostat for 20-30 minutes. Measure the capacitance C_0 using a Universal Dielectrometer and record the temperature on a precision thermometer. Fill the cell with a calibrating liquid e.g water, whose dielectric constant, D_c, is accurately known over a temperature range. Thermally equilibrate at the same temperature and then measure the capacitance, C_c. Calculate the measuring capacitance, C_m, of the cell from the relation:

$$C_m = (C_c - C_0)/(D_c - 1) \qquad (11.5),$$

and work out the "spurious" cell capacitance, C_s, from the equation

$$C_s=C_o-C_m \qquad (11.6),$$

Fill the cell with a dioxan/water mixture in the range of 10-60 volume %. Equilibrate at the same temperature and measure the capacitance, C_u. Calculate the dielectric constant, D_u, of the mixture from the relation:

$$D_u=(C_u-C_s)/C_m \qquad (11.7).$$

Repeat using the other dioxan/water solvents.
Prepare stock solutions of 0.01 M in the complex, dissolved in a dioxan/water mixture of known dielectric constant. Prepare a 0.01 M HCl solution in a dioxan/water mixture so that the percentage dioxan by volume is the same as in the solution of the complex. Allow for the water content in conc. HCl when you prepare the latter solutions. Carry out kinetic runs as described above and calculate the rate constant, k, in the solvent mixture. Repeat using different solvent mixtures. Plot log k against the reciprocal of the dielectric constant and comment on the results.

11.4.3 Spectral study of the formation of $[Cr(C_2O_4)_3]^{3-}$-in solution

It is instructive to know the conditions under which this anion is formed either from a Cr(III) salt solution and an oxalate solution or from a dichromate solution with oxalic/oxalate solution. The reactions are likely to be pH-dependent and to be catalysed eg by Mn^{2+} ions.

Prepare the following solutions:
A:0.0194 M in $H_2C_2O_4.2H_2O$; B:0.0306 M in $K_2C_2O_4$; C:as B but 5% in $MnSO_4.4H_2O$; D:0.002 M in $KCr(SO_4)_2.12H_2O$; E:0.00125 M in $K_2Cr_2O_7$. Then mix the following solutions:

(i) 25.0 cm^3 each of A and B and 50.0 cm^3 of E;
(ii) identical to (i) but adjust the pH to 4-5 using dilute HCl or KOH;
(iii) 25.0 cm^3 each of A and C and 50.0 cm^2 of E, adjusting the pH as above.

Heat each solution in a flask, provided with a short upright condenser, in a thermostat at 90°C for 20 minutes on a water bath and allow to cool in ice-water mixture.
Then prepare the following solutions:

(iv) 50.0 cm^3 of D; 120 cm^3 of each A and B, adjust the pH to 4 and make up to 100 cm^3
(v) 50.0 cm^3 of D; 36.0 cm^3 of B, adjust the pH to 6 and make up to 100 cm^3. Heat each solution as above.

When the solutions are cold, measure the absorbance in a 10 mm cell at the longest wavelength band of the prepared complex. Calculate the percentage conversion to $[Cr(C_2O_4)_3]^{3-}$ and comment on your results.

11.4.4 Preparation, analysis and tests on *cis*-$K[Cr(C_2O_4)_2(H_2O)_2].2H_2O$

The solid can be prepared from the same reagents as the trisoxalato-complex but under different conditions. It can be also analysed for oxalate and water of crystallisation as above and for Cr by oxidation to Cr(VI) using bromate.

11.4.4.1 Preparation

Powder separately in a dry mortar 12 g of $H_2C_2O_4.2H_2O$ and 4 g $K_2Cr_2O_7$. Mix the powders intimately by gentle regrinding. Moisten an evaporating basin (10 cm diameter) with water and allow nearly all the water to drain away. Place the mixture in a compact mass in the centre of the basin, then cover with a watch-glass and place the basin on a hot-plate set at 'low'. When the vigorous reaction is complete, immediately pour 20 cm^3 of ethanol over the molten product. Continue to warm the mixture and triturate until a solid is produced.

If solidification does not occur, drain off the liquid and repeat the trituration with a further 20 cm^3 of ethanol. Filter the solid under suction and wash with small portions of ethanol then with acetone and finally suck dry, while pressing between filter paper. Record your yield, and calculate the % yield based on Cr. Determine the percentage water of crystallisation and percentage oxalate as before (11.4.1).

11.4.4.2 Determination of Cr

Weigh out accurately about 0.2 g of your preparation, dissolve by warming with 50 cm^3 of water acidified with 3 cm^3 of conc.H_2SO_4. When complete solution is reached, add 1.5 g of solid potassium bromate, and then boil for 10 min in the fume cupboard. Dissolve 5 g of ammonium sulphate in a small volume of hot water, filter if necessary, and then add to the hot solution, in which Cr is now present entirely as chromic acid. Boil the whole until nearly all the excess of Br_2 has been volatilised (30-45 min.). Then add 20 cm^3 of 1 M HCl, and again boil until starch-iodide paper is not stained when held in the steam. Cool the liquid, add 10 cm^3 of conc. HCl, and 1 g KI. Titrate the liberated iodine with 0.05 M thiosulphate, standardised by means of $K_2Cr_2O_7$. Repeat and calculate the average percentage of Cr in your preparation.

Standardisation of thiosulphate

To a 100 cm^3 of recently boiled-out water, in a 500 cm^3 conical flask, add 3 g of KI and 2 g $NaHCO_3$ and shake to dissolve the salts. Then slowly add 6 cm^3 conc. HCl while shaking to mix the solutions well. Then add from a pipette 25.0 cm^3 of standard M/60 $K_2Cr_2O_7$ and allow the flask to stand in the dark after washing the sides of the flask and covering it. When the liberation of I_2 is complete, dilute to 300 cm^3 and titrate with the thiosulphate solution until the brown colour turns to faint straw colour. Then deliver 2 cm^3 of freshly prepared starch indicator solution. Continue titration until a drop changes the colour from greenish blue to light green. Repeat to get concordant results and calculate from the average titre, the concentration of thiosulphate in mol dm^{-3}. Potentiometric titration would be more suitable.

11.4.4.3 Qualitative tests

Carry out the following tests on small quantities of your preparation

(i) Heat the solid in a dry test tube, gently at first and then more strongly. Test for any products. Add to the residue, when cold dil. H_2SO_4 and test for any products.

(ii) Add to a small quantity of the solid conc. H_2SO_4 and warm gently. Test for any products. Expose a drop of $PdCl_2$ solution near the mouth of the test tube.*

(iii) Carry out a flame test.

(iv) Dissolve the solid in dil. H_2SO_4 and divide into 2 portions:

  (a) add to one portion some Zn dust;

  (b) add to the second portion some solid $K_2S_2O_8$ and a drop of $AgNO_3$ solution. Boil for a few minutes until a clear solution is formed.

(v) To a solution of the solid in water, add NaOH solution gradually. Then add H_2O_2 and heat. Draw conclusions from your observations.

(vi) Place a pinch of compound on a filter paper resting on a watch glass. Irrigate with a few drops of dilute ammonia. Then add dil.HCl.

Determination of % oxalate

Use the same method as in Sec.11.4.1.

11.4.5 Preparation and analysis of the *trans*-isomer

Under different experimental conditions, the *trans*-isomer can be prepared from potassium dichromate and excess of oxalic acid. It can be analysed for % water of crystallisation and percentage oxalate as in (Sec.11.4.1).

Dissolve 12 g of $H_2C_2O_4.2H_2O$ in the minimum quantity of boiling water in a 300 cm^3 beaker. Dissolve 4 g of $K_2Cr_2O_7$ in the minimum of hot water. Add the solution, in small portions, to the oxalic acid solution, which should be covered while the violent reaction proceeds. Then cool the beaker and transfer its contents to a clean wide evaporating basin. Allow spontaneous evaporation until the solution is reduced to about 1/3 of the original bulk (in about 36 hours). The initial crystals are likely to be purer. Collect the crystals on a Buchner funnel by suction. Wash with few portions of cold water, then with C_2H_5OH and a little ether. Dry by continued suction while pressing between filter paper. Record the yield of your product and calculate the % yield. Carry out the above test (vi) on a pinch of your product and compare its result with the test on the *cis*-salt. Weigh out accurately about 0.4 g of your preparation in porcelain basin. Heat at 110°C to constant weight and determine the percentage of water of crystallisation. Record the reflectance visible/near infrared spectrum of the resulting solid and compare it with the spectrum of your preparation.

Alternative preparation

Prepare an approximately 0.5 M solution of the *cis*-isomer. Allow to stand for a few days. Collect the crystals which separate by filtration under suction. Show its *trans*-configuration by chemical or spectral methods.

11.4.6 Spectral study of the kinetics and mechanism of the isomerisation of the *trans*-isomer

Trans-to-*cis*-isomerisation of solutions of transition metal complexes such as the inert complexes of Cr(III), usually proceeds at a conveniently slow rate. Since the electronic spectrum of the *trans*-isomer contains bands of lower intensity than those of the *cis*-isomer, the reactions can be followed by spectrophotometry. Solid state isomerisation may be similarly studied.

Spectral study

Before carrying out the kinetic runs, the electronic spectra of solutions of the two isomers should be recorded and compared with those of the tris-oxalato and mono-oxalato species.

Record the visible spectra of 0.01 M solutions of the two isomeric complexes using 1 cm cells. The *trans*-isomer should be finely ground and the solution made up in cold distilled water at ~15°C; the preparation and measurement should be carried out as quickly as possible. The solutions should be 10-fold diluted before recording the UV spectra in 1 cm quartz cells. The solution of the *trans*-isomer should be quickly prepared and quickly diluted and immediately measured.

Heat an equal volume of 0.01 M solutions of $Cr(NO_3)_3$ and $K_2C_2O_4$ at 90°C for an hour to obtain a solution of $[Cr(C_2O_4)(H_2O)_4]^+$. After cooling, record the electronic spectrum as above and compare it with those of the two isomers and with that of $[Cr(C_2O_4)_3]^{3-}$.

Kinetic experiments

Using stock solutions of 1 M $HClO_4$ in 1 M $NaClO_4$ (A) and 1 M $NaClO_4$ (B), prepare the following solutions by dilution (using the 1 M $NaClO_4$ for dilutions): 0.2 M $HClO_4$ in 1 M $NaClO_4$ (C); 0.001 M $HClO_4$ in 1 M $NaClO_4$ (D); 10^{-4} M $HClO_4$ in 1 M $NaClO_4$ (E). Cool these solutions keeping them at about 15°C. Weigh, to the nearest mg, three portions of 0.089 g of the finely powdered *trans*-complex. Dissolve each in one of the $HClO_4/NaClO_4$ solutions and make up to 25 cm^3. Start a stopwatch when you dissolve in solution (E). Place the solution in a 1 cm glass cell in a spectrophotometer, which has been set with H_2O as blank in a 1 cm cell. Measure the absorbance of the solution at 420 nm and note the time on the stopwatch when you take a reading. Take readings at intervals of 3-5 minutes, increasing the interval as the reaction slows down and continue over a period of 60-80 minutes. Take a final reading after > 2 hours. Plot log $(A_f - A_t)$ against t, where A_f is the final absorbance, A_t is the absorbance at time t and the time t is when a measurement is made (from the time when the solution was made up, as indicated by the stopwatch). Repeat using solution (D) and solution (C).

From the plots, which are expected to be linear, calculate the rate constant (using the slope of the best straight line through the points). Measure the temperature of the solutions and tabulate the rate constants at the three different acid concentrations. Comment on your results.

11.4.7 Solid State Isomerisation

Weigh out accurately two portions of about 180 mg of the *cis*-isomer. Heat one at 110°C for >2 hours. Cool and quickly dissolve in 50 cm^3 of water and measure the absorbance in a 1 cm cell at the previously determined visible wavelengths of maximum absorption at intervals eg 5, 20, 40, 60 minutes and plot each set of readings against time, taking zero time when the solution was prepared. Extrapolate to zero time and estimate the initial absorbances. Dissolve the sample which was not heated in 50 cm^3 water and carry out the same measurements. The two runs should be carried out at the same room temperature unless a thermostatted spectrophotometer cell is available. In that case the same thermostat temperature is used. Compare the two sets of results. Repeat using the finely ground *trans*-isomer instead of the *cis*-complex. Comment on your results.

11.4.8 Infrared Studies of the Oxalato-Complexes

Prepare KBr discs (using purest KBr previously dried and kept in a desiccator) from a mixture of each of the three solid complexes and KBr (~1:10). Record the infrared spectra of the three prepared solids in the range 400-4000 cm^{-1} and tabulate the peaks obtained. Compare the spectra and assign the peaks.

11.5 STUDIES OF THE CHLORO-COMPOUNDS OF Cr(III)

Three compounds of the empirical formula $CrCl_3.6H_2O$ are known. This is an example of **hydration isomerism** where water can be either as a ligand in the inner co-ordination sphere and/or as water of crystallisation in the outer sphere. Chloride may be co-ordinated to Cr or it may be partly or completely in the outer co-ordination sphere. As a result the electronic spectra of the three complexes exhibit shifts in the position of their d-d bands, since chloride and water occupy different positions in the **spectrochemical series.** The isomers can be also distinguished by chemical or physico-chemical methods. The compounds also offer the possibility of testing the **law of average environment.** This relates to the crystal field splitting parameter Δ_o of a mixed ligand complex $[MA_nB_{6-n}]$, where n A ligands and (6-n) B ligands are co-ordinated to the metal M. Assuming that the ligands A and B are unidentate and disregarding charges on M, A or B, Δ_o of the mixed ligand complex is given by:

$$\Delta_o=1/6[n(\Delta_o)_A+(6-n)(\Delta_o)_B]$$

where $(\Delta_o)_A$ refers to $[MA_6]$ and $(\Delta_o)_B$ refers to $[MB_6]$, where the charges on the metal and ligands are disregarded for simplicity.

11.5.1 Purification of the Commercial $[CrCl_2(H_2O)_4]Cl.2H_2O$

The dark green commercially available solid is thought to be the *trans*-isomer. The purification procedure described below is based on a paper by W.B.Guenther; J.J.Stuart in *J.Tennesse Acad.Sci.*, **35** (1960) 244.

Grind the commercial product under pure acetone. Replace the acetone by another aliquot of acetone by decantation. Filter through a sintered glass funnel, wash with acetone until the filtrate is colourless. Then wash well with dry ether. Suck dry and store in a dessicator over solid NaOH in contact with its saturated solution.

11.5.2 Preparation of $[CrCl(H_2O)_5]Cl_2.H_2O$

Dissolve 14 g of $[CrCl_2(H_2O)_4]Cl.2H_2O$ in 20 cm^3 water and reflux for 10 minutes. Cool the solution in ice and saturate it with HCl gas from a cylinder in a fume cupboard, cool 300 cm^3 of ether in ice and saturate it with HCl gas. Add to 200 cm^3 of this solution the cooled chromium solution and cool the mixture in ice and stir mechanically for 30 minutes. Filter the precipitate and wash it with the remainder of the cooled ether solution. Weigh your product and calculate the percentage yield.

11.5.3 Preparation of $[Cr(H_2O)_6]Cl_3$

Prepare a solution of 10 g $KCr(SO_4)_2.12H_2O$ in a mixture of 40 cm^3 conc. HCl and 10 cm^3 water and cool it in ice. Filter the solution into a Drechsel flask cooled in ice. To generate a stream of gaseous HCl, allow conc. sulphuric acid in a separating funnel to drip into NaCl in a dm^3 flask containing NaCl solid. Pass the gas through a desiccant tower containing calcium chloride and through the cooled ether solution in the Drechsel flask whose outlet tube was connected to an inverted funnel dipped in NaOH solution to absorb any emerging gas. Continue for a few hours until the chromium solution seems colourless. Filter the crystals formed through a sintered glass G3 crucible under vacuum. Wash with acetone, then with ether. Dry by continued suction. Weigh your product and calculate the percentage yield.

Alternatively, prepare a saturated solution of $KCr(SO_4)_2.12H_2O$. Decant the supernatant liquid into a suitable container, cool in ice and saturate it with gaseous HCl until nearly colourless. Filter, wash and dry as above. Weigh the product.

11.5.4 Analysis of the Hydration Isomers

11.5.4.1 Determination of ionisable chloride

Add to 25 cm^3 of 0.02 M silver nitrate, 20 cm^3 dilute nitric acid and 30 cm^3 water in a 250 cm^2 beaker. Cool in ice. Weigh out accurately about 0.1 g of one of the isomeric solids and dissolve in the iced solution, stir for 20 s. and filter into a prepared weighed G4 sintered glass crucible. Wash with 0.01 M nitric acid, then with ethanol and with ether. Suck dry and dry at 110°C to constant weight. Carry out a duplicate determination. Repeat with the other prepared solids.

Determination of the total chlorine

Use the same procedure as above without cooling the silver nitrate solution. Weigh out accurately about 0.1 g of $[CrCl_2(H_2O)_4]Cl.2H_2O$ or $[CrCl(H_2O)_5]Cl_2.H_2O$, dissolve in water, boil for half an hour to transform to $[Cr(H_2O)_6]Cl_3$ and add slowly to the silver solution with constant stirring to precipitate AgCl, weighing it as above.

11.5.4.2 Determination of Cr

Weigh out accurately about 0.1 g of your preparation into a 250 cm^3 conical flask. Dissolve in 20 cm^3 water and then add 50 cm^3 of 0.02 M silver nitrate, 8 cm^3 of 10% ammonium persulphate and 35 cm^3 1 M sulphuric acid. Boil for 20 min. so that chromium is oxidised to dichronate. Add 10 drops of N-phenylanthranilic acid indicator and titrate against standardised 0.05 M iron (II) solution until the dark solution turns to green. Repeat and calculate from the average titre the percentage Cr in your preparation. Carry out similar determinations for the other prepared complexes.

11.5.5 Spectral study of the hydration isomers

For Cr^{3+}, Δ_0 can be directly calculated from the longest wavelength spin-allowed d-d band. Hence the absorption spectra of the hydration isomers can be used to test the law of average environment. Because of the possibility of equilibria in solution, it is more useful to obtain spectra of the solids as in (Sec.2.4.1). Spectra of $[CrCl_6]^{3-}$ will be important especially since water and chloride are not far apart in the spectrochemical series. This large anion can be precipitated by a large cation eg $[Co(pn)_3]^{3+}$.

Preparation of $[Co(pn)_3][CrCl_6]$

Mix 5.4 g $CrCl_3.6H_2O$ (the green unpurified salt) with 50 cm^3 conc. HCl to dissolve the salt. Add to the solution of 3.8 g of $[Co(pn)_3]$ Br_3 (Sec.14.10.1) with shaking and allow to stand to induce crystallisation. Collect the crystals by filtration under vacuum, wash with small volumes of water then ethanol and finally ether. Suck dry and then finish drying in an oven at 105°C. Weigh your product and calculate the percentage yield.

Electronic absorption and reflectance spectra

Prepare approximately 10^{-2} M (or 1%) solutions of the three hydration isomers in ice-cold water. For the purified $[Cr(H_2O)_4Cl_2]^+$ prepare solutions in HCl (in the range 1-12 M) and in CH_3COOH (in the range of 1-11 M) and for $[Cr(H_2O)_6]$ Cl_3 prepare a solution in 12 M HCl. Run the absorption spectra over the range 200-800 nm in 10 mm cells, using water or the corresponding acid solution as a blank. Locate the wavelengths of maximum absorption.

Solid state spectra

Impregnate a strip of Whatman No.1 filter paper with nujol, press it against the inner or outer surface of a rectangular 1 cm glass cell. Grind a little of one of your preparations with nujol and impregnate an identical strip of paper with the mixture, and press it against a surface of the sample cell. Run the spectrum over the range 350-700 nm as usual. Repeat with the other preparations. Locate the wavelengths of maximum absorption. Run the second derivative reflectance spectra of each of your preparations as well as $[Co(pn)_3]Br_3$ in the range 400-2500 nm. Locate the positions of the bands in the range 400-800 nm.

Using all the spectral data, check the applicability of the law of average environment. Comment on any features of interest in the recorded spectra.

Explain why the oxalato-complexes are not very suitable for checking the applicability of the law of average environment.

11.5.6 Preparation of anhydrous Chromium (III) Chloride

The hydration isomers contain strongly co-ordinated water which cannot be removed by heating. A common method for dehydrating hydrated chlorides is to reflux with $SOCl_2$. The reaction is most suitable for the hexaaqua-complex, whose dehydration can be represented by:

$$[Cr(H_2O)_6]Cl_3+6SOCl_2 \rightarrow CrCl_3+6SO_2+12HCl \qquad (11.9)$$

To obtain an adequate amount of this isomer, double the amounts in the preparation in Sec.11.5.3. Weigh out ~5 g of the prepared compound, grind to a fine powder. Distil purest thionyl chloride and add 15 cm^3 of the freshly distilled liquid to the powdered solid in a flask fitted with a reflux condenser. Test the evolved gases with acidified dichromate paper and a drop of conc. ammonia. When the evolution of SO_2 and ammonia, as tested, appears to have stopped, reflux the contents under a nitrogen atmosphere for 1-2 hours. Remove the unreacted thionyl chloride by vacuum distillation and store the solid formed in a stoppered bottle in a vacuum desiccator.

An alternative preparation involves the reaction of the Cr(III) oxide with tetrachloromethane. The oxide is available commercially but it is better to prepare it freshly by heating ammonium dichromate carefully. The reactions involved are:

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3+N_2+4H_2O \qquad (11.10)$$
$$Cr_2O_3+3CCl_4 \rightarrow 2CrCl_3+3COCl_2 \qquad (11.11)$$

Weigh about 1.5 g of Cr(III) oxide into the middle of a long silica tube connected via a ground joint to a flask containing CCl_4, through which nitrogen is bubbled. Place the system in a well-ventilated fume cupboard and place the tube in an electric furnace and the flask on a water bath at 50°C. Heat the tube to 650°C while passing nitrogen through the liquid until the colour of the solid changes to red violet. When cool, check the solubility of the solid in water. Then check the solubility in water to which tin(II) chloride has been added.

Because of the high toxicity of $COCl_2$, the experiment should be carried out by mature students under close supervision. The door of the fume cupboard should be closed throughout and it should be served by a water-fed scrubbing tower.

11.6 STUDIES OF THE THIOCYANATO-COMPLEXES OF Cr(III)

Two preparative methods are known for potassium hexathiocyantochromate (III). Both involve the exchange of the ligand water with thiocyanate. In both cases chrome alum, $KCr(SO_4)_2.12H_2O$ reacts with either a solution of KSCN or it is added as a solid to molten KSCN. Since the potassium salts of the complex anions are very hygroscopic, it is advantageous analytically to transform them to the pyridinium salts. For a long time, the complexes were known to be readily partially aquated. However, interest in the spectra of their solutions in various solvents dates from the mid-fifties.

11.6.1 Preparation and analysis of $K_3[Cr(SCN)_6].4H_2O$

Wet Method

Add a hot solution of 12.5 g chrome alum in 45 cm^3 H_2O to a solution of 15 g KSCN in 15 cm^3 H_2O. Heat the mixture to boiling and keep the temperature near the boiling point for 1 hour, without allowing the total volume to fall below 50 cm^3. Cool to room temperature and add 40 cm^3 C_2H_5OH to precipitate the sulphate. Allow to stand for 5-10 minutes and decant the deeply coloured liquid through a Buchner filter. Evaporate the filtrate to ~15 cm^3 on a hot plate away from flames. Allow to cool and crystallise. Filter under suction and dry by continued suction while pressing between filter paper. Weigh your product to the nearest cg. Calculate the % yield.

Dry Method

Heat in a porcelain dish, set over a small flame, 12 g of KSCN just to fusion (m.p.172°C). While continuing to heat gently, sift on the fused salt, in small portions, 10 g of chrome alum, stirring well after each addition. Eventually the red-violet mixture is almost solidified. Allow to cool in a desiccator. Then quickly scrape the solid from the dish into 60-70 cm^3 C_2H_5OH in a mortar and crush and triturate with the solvent. Filter the insoluble K_2SO_4 and quickly concentrate the filtrate on a boiling water bath, until a crystalline crust is formed. Dry in a vacuum desiccator over conc. H_2SO_4. Calculate % yield.

Recrystallise each product from methanol. Store in a desiccator over conc. H_2SO_4/KOH(s). Weigh out accurately about 0.2 g of each product and heat to 110°C for 2 hours. Determine %C and %N in the dried samples.

11.6.2 Preparation and analysis of $[C_5H_6N]_3[Cr(SCN)_6].H_2O$

11.6.2.1 Preparation of the pyridinium salt

Mix 2 cm^3 of redistilled pyridine with 10 cm^3 of 3 M HCl and then add 10 cm^3 H_2O. Weigh out 3.50 g of your crude preparation of $K_3[Cr(SCN)_6].4H_2O$ in a stoppered weighing bottle and dissolve in 15 cm^3 H_2O. Pour the solution into the pyridine solution, briskly shaking the latter during the mixing. The red-violet complex separates as a crystalline precipitate. Filter by suction, wash with water containing a few drops of pyridine. Allow to dry in the dark since it is photosensitive. Record your yield and calculate the % yield.

11.6.2.2 Analysis

Weigh out accurately ~0.1 g of the dry complex into a beaker, add 20 cm^3 H_2O and 5 cm^3 0.1 M NaOH. Boil until most of the pyridine is volatilised. Transfer the beaker into a boiling water bath and add bromine water until the liquid is brown with excess Br_2.

Cover with a watch glass and heat on the bath for >30 minutes. Finally expel the excess Br_2 by boiling. Dilute to ~200 cm^3, add 2 cm^3 HCl, boil and add a solution of 0.4 g $BaCl_2$ in a small volume of hot water. Determine the precipitated $BaSO_4$ gravimetrically in a silica crucible or in a sintered glass crucible Sec.7.3.4. Repeat and calculate from the average the %S.

Weigh out accurately about 0.2 g of your preparation, add 25 cm^3 of 1 M KOH or NaOH, boil for 15 minutes to precipitate $Cr(OH)_3$. Filter the hot solution through a No.4 filter paper and wash twice with hot water. Transfer the filter with the precipitate into a beaker containing 25 cm^3 dilute sulphuric acid to dissolve the precipitate. Filter the green solution formed into a conical flask and wash, in portions, with 30 cm^3 hot water. Then add 1.5 g potassium bromate and boil, in the fume cupboard, for 10 minutes to oxidise Cr to dichromate. Add to the boiling solution a few cm^3 of water in which 5 g ammonium sulphate has been dissolved and continue boiling to drive off all bromine. Then add 10 cm^3 of 1 M HCl and continue boiling to remove traces of Br_2. Test the vapour with fluorescein paper. Cool, acidity with 10 cm^3 conc. HCl, add 1 g Kl and titrate the liberated iodine as in (Sec.11.16). Repeat and calculate from the average the percentage Cr in your preparation. Compare the results of the Cr and S analyses and comment on them.

11.6.3 Preparation of quinolinium aquapentathiocyanatochromate(III) hydrate $(C_9H_8N)_2[Cr(SCN)_5(H_2O)].H_2O$

Dissolve 1.45 g KSCN in 10 cm^3 water and 2.95 g $K_3[Cr(SCN)_6).4H_2O$ in 10 cm^3 water. Mix the two solutions and heat on a boiling water bath for 1 hour. Then add quinoline hydrochloride while agitating the solution, when a purple liquid is formed which crystallises on standing. Filter the solid under suction and keep in a vacuum desiccator with an efficient desiccant. On long standing the anhydrous complex compound is obtained,. Carry out elemental analysis on the product.

11.6.4 Spectral Studies of the Thiocyanate Complexes

Because of the reported partial aquation of the thiocyanate complexes (*J.Amer. Chem. Soc.* **88**, 1966, 394), it is interesting to study the absorption spectra of the prepared complexes in various solvents in freshly prepared or aged or heated solutions. A shift in the bands resulting from change of solvent suggests partial solvation. Prepare approximately 0.012 M solution of the potassium salt in a range of solvents eg water, methyl, ethyl and iso-propyl alcohols, acetone, dimethylformanide, DMF, and dimethylsulphoxide, DMSO. Measure the spectra in the range 200-800 nm in 10 mm quartz cells for freshly prepared solutions, for a week-aged solutions and for solutions heated at 80°C for various periods. Determine the wavelengths of maximum absorption for these solutions. Similarly record the spectra of a solution in 7.7 M $(NH_4)SCN$ over the range 500-600 nm and of 10^{-4} M solution of the latter without the complex (over the range 200-280 nm). Compare the spectra of solutions obtained from the solids with or without water of crystallisation. Repeat using 0.003-0.006 M solutions of the pyridinium salt. For the quinolinium salt, use 0.02-0.04 M solutions in the alcohols, DMF or DMSO over the range 450-650 nm and after 10^3 -fold dilution for the range 300-450 nm. Calculate Δ_0 from the position of the longest wavelength spin-allowed band maxima and comment on your results.

11.7 CHROMATE/DICHROMATE EQUILIBRIA

The well known change of colour of Cr(VI) from yellow in alkaline solution to orange in acid solution is thought to involve the following equilibria:

$$H^+ + CrO_4^{2-} \leftrightarrows HCrO_4^- \qquad (11.12),$$

$$H^+ + HCrO_4^- \leftrightarrows H_2CrO_4 \qquad (11.13),$$

$$HCrO_4^- + HCrO_4^- \leftrightarrows Cr_2O_7^{2-} + H_2O \qquad (11.14),$$

Although $HCr_2O_7^-$ has been reported, its significance is questionable *(Inorganic Reaction Mechanisms,* Pt.II, Ed.J.O.Edwards, Interscience, New York, 1972, p.98 and references therein).

Prepare the following solutions, adjusting the pH with $HClO_4$ and record the absorption spectra in 10 mm quartz cells over the range 200-400 nm.

(i) 10^{-4} M solution in Cr(VI), pH 1-5;
(ii) 10^{-4} M solution in Cr(VI), pH=0 or <0;
(iii) 5×10^{-4} M solution, pH 1.

Locate the absorption maxima and comment on your results.

12

Manganese

12.1 INTRODUCTION

Manganese exhibits more common oxidation numbers than the other 3d transition metals. The Ebsworth diagram, Fig.12.1, for Mn in both acid and alkaline solutions, exhibits all oxidation states from +2 to +7 with the exception of the +5 state. Although this is not represented in Fig.12.1, there are some solids which contain MnO_4^{3-} ions. The diagram shows that the lowest common oxidation state of +2, represented by Mn^{2+}, is the most stable especially in acid solution. This stability is related to its exactly ½-filled d^5 sub level. In the high spin octahedral complexes, the $(t_{2g})^3(e_g)^2$ configuration shows exactly ½-filled levels and the same is true for the $(e)^2(t_2)^3$ configuration of tetrahedral complexes. Only with strong ligands does spin-pairing occur eg $[Mn(CN)_6]^{4-}$. The +2 oxidation state is represented by the basic MnO and $Mn(OH)_2$ and the numerous more ionic salts eg halides, sulphate and nitrate. Lower oxidation states are stabilised by π-bonding ligands.

Mn^{3+}, on the other hand, is represented in Fig.12.1 by a convex point, which indicates its liability to disproportionate to its nearest neighbours: Mn^{2+} and MnO_2. However, the point representing the +3 oxidation number is below the line joining the +2 and +7 states in Fig.12.1 (in acid solution).

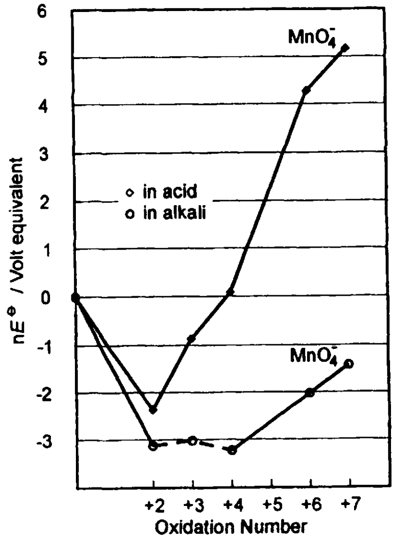


Figure 12.1 Volt-equivalent versus oxidation number for Mn.

Hence the practical preparation of $[Mn(1H_2O)_6]^{3+}$ by the comproportionation ie the oxidation of Mn^{2+} by acidified MnO_4^- Mn(III) forms numerous complexes of which $[Mn(C_5H_7O_2)_3]$ is particularly stable. The steep line joining the +2 and +3 states shows the strong oxidising power of Mn(III) in acid solution which is used titrimetrically. The +4 oxidation state is represented by the sparingly soluble MnO_2. Mn(VI), represented by the anion MnO_4^{2-}, is on a convex point in the diagram 12.1 in acid solution. Hence it readily disproportionates to MnO_2 and MnO_4^- (its nearest neighbours) but it is more stable in alkaline solutions and can be prepared under basic conditions. The highest oxidation state, shown in Fig.12.1 as MnO_4^-, corresponds to the group number. The steep line joining the +2 and +7 states indicates the strong oxidising power of the latter state in acid solution but this is much reduced in alkaline solution, similar to what was found in Cr(VI). The tetrahedral oxoanions $[MnO_4]^{z-}$ (z=1,2 or 3 for Mn VII, VI or V respectively) are structurally similar to $[MO_4]^{z-}$ (z=3,2 or 1 for M=V, Cr or Mn). The basic character of the oxides decreases with increase in oxidation number, a general trend observed in the earlier groups. Thus MnO and $Mn(OH)_2$ are completely basic whereas $Mn(OH)_3$ is less basic but MnO_2 has hardly any acidic/basic properties. When it reacts with acids, it acts as an oxidising agent. On the other hand the unstable oil Mn_2O_7 is an acid anhydride which forms $HMnO_4$ with water. Its covalence contrasts the ionic character of MnO and MnO_2 and is correlated with the decrease in ionic character with increase in oxidation number and increase in electronegativity. MnO_2 is a useful catalyst both in homogeneous and heterogeneous reactions.

12.2 QUALITATIVE TESTS

12.2.1 Mn(II) Compounds

(a) Heat gently in a dry test tube a few crystals of Mn(II) oxalate, test any condensed liquid near the top with cobalt blue paper. Insert a loose glass wool plug midway, heat more strongly and expose a $PdCl_2$ paper near the top. When the crystals become a dark powder, allow to cool. Add dil. HCl and warm.

(b) Make a solution of Mn(II) sulphate or chloride, and add to separate portions:
   (i) NaOH solution; check the solubility of any precipitate in excess NaOH; or dil.HCl allow to stand, add few drops of H_2O_2;
   (ii) dil.NH_3, check the solubility of any precipitate in excess NH_4Cl solution;
   (iii) $(NH_4)_2S$ solution, check the solubility of any precipitate in acetic acid;
   (iv) excess NH_4Cl and then Na_2HPO_4 solution;
   (v) PbO_2, excess $Na_4P_2O_7$ 0.4 M solution (at pH4) nitric acid and heat for 10 minutes, filter through No.42 paper and note the colour;
   (vi) $(NH_4)_2S_2O_8$, dil. sulphuric acid and a drop of Ag_2SO_4, heat carefully for 10 minutes;
   (vii) acidify with H_3PO_4, add a little KIO_4 and boil for a few minutes;
   (viii) repeat (vi) without adding Ag_2SO_4.

12.2.2 Mn(III) Compounds

(a) Add dil. sulphuric acid to a little Mn_3O_4, heat for 5 minutes and note the colour of the supernatant.

(b) Repeat using Mn_2O_3 instead of Mn_3O_4.

(c) Prepare a solution of $Mn_2(SO_4)_3$ by gradually adding 5 cm^3 0.02 M MnO_4^- solution to 40 cm^3 of nearly 0.05 M Mn^{2+} solution in 3 M sulphuric acid. Add to separate portions of your solution:
   (i) excess water and test the solubility of any precipitate in dil. sulphuric acid;

- (ii) an equal volume of 20 volume H_2O_2 and quickly test with a glowing splint;
- (iii) heat some of the solution;
- (iv) add a little normal alcohol and warm, cool and notice the smell.*

12.2.3 Manganese (IV) Oxide

(a) Heat a 50% solution of Mn(II) nitrate in a crucible until the remainder is a dark powder; expose a blue litmus paper to the vapour. Add a little conc. HCl to the powder, warm and expose a blue litmus paper.

(b) To small amounts of MnO_2, add the following:
- (i) 20 volume H_2O_2 in a beaker;
- (ii) conc. HCl and ascorbic acid or its solution;
- (iii) oxalic acid, dilute sulphuric acid and boil gently to dissolve;
- (iv) $N_2H_4.H_2O$.

12.2.4 Mn(VI) Compounds

(a) Mix, on a piece of broken porcelain, a little MnO_2 together with KNO_3, add a pellet of KOH. Heat the mixture. When cold, add a little water and filter through glass wool. Acidify the filtrate with acetic acid and note the change in colour.

(b) Mix together powdered $MnSO_4$, KNO_3 and Na_2CO_3 and heat and treat as above.

12.2.5 Mn(VII) Compounds

(a) Add a single crystal of $KMnO_4$ to 25 cm^3 of purest H_2SO_4 in a clean beaker, stir gently with a glass rod, note the colour of the solution. Then slowly pour onto a large volume of water and note any changes.*

(b) Acidify permanganate solution with dil. sulphuric acid and carry out the following tests on small volumes:
- (i) pass H_2S in a fume cupboard;
- (ii) pass SO_2 gas;
- (iii) add $FeSO_4$ solution;
- (iv) add KI solution and then a little starch indicator;
- (v) add KNO_2 solution;
- (vi) add oxalic acid solution and heat to about 80°C.

(c) Add conc. HCl to solid $KMnO_4$, heat in a fume cupboard and expose a blue litmus paper.

(d) Heat $KMnO_4$ in a dry test tube, test with a glowing splint. When cold, add a little water and filter.

12.3 STUDIES OF Mn(II)

12.3.1 Analysis of Mn(II) Salt Solutions

Mn(II) in solution can be precipitated as ammonium manganese phosphate which can be weighed after drying, or it can be converted to manganese(II) pyrophosphate by heating to 700°-800°C before weighing. However, it is quicker and easier to carry out volumetric or colorimetric analysis. Since Mn(II) forms a stable EDTA complex, complexometric titration is suitable even in presence of other cations eg magnesium. Potentiometric titration of solutions of Mn(II) with permanganate is possible in presence of a large excess of pyrophosphate. Although Mn(II) solutions are faintly coloured, a strongly coloured compound is formed with formaldoxime.

12.3.1.1 Complexometric titration of Mn(II) in solution

Weigh out accurately about 4.50 g purest $MnSO_4.(NH_4)_2SO_4.6H_2O_3$ dissolve in slightly acidified water and make up to 250 cm^3 in a volumetric flask. Pipette 25.0 cm^3 of the solution, add 0.5 g hydroxylammonium chloride (to prevent oxidation) and 100 cm^3 of boiled-out water. Then add NaOH to render the solution neutral and 3 cm^3 triethylamine, together with 2 cm^3 of buffer solution (pH10) and a few drops of Eriochrome black T indicator. Titrate with standardised 0.05 M EDTA solution until the colour changes from red to blue. Repeat to obtain concordant results and calculate from the average titre the concentration of Mn^{2+} in mol dm^{-3}.

12.3.1.2 Complexometric determination of manganese(II) ions in presence of magnesium ions

Both ions can be titrated with EDTA, the titre gives the sum of their concentrations. When NaF is then added, it will form MgF_2 from the Mg complexonate. When excess of Mn(II) ion solution is then added, the excess can be back-titrated against EDTA. Prepare a solution approximately 0.05 M in Mn(II) and 0.05 M in Mg. Pipette 25.0 cm^3 of the mixed solution, treat as above and record the average titre of 0.05 M EDTA. At the end point, add 2.5 g NaF and agitate to dissolve for a minute, then introduce from a burette the standardised Mn(II) solution in 1 cm^3 portions until a permanent red colour is obtained and then add a slight excess. After recording the volume used, titrate with standardised EDTA to the blue end point. Calculate from the titres the concentrations of Mg^{2+} and of Mn(II) in mol dm^{-3}.

12.3.1.3 Potentiometric titration of Mn(II) with permanganate

Solutions of Mn(II) salts can be titrated with potassium permanganate in presence of pyrophosophate. If a Pt and a saturated calomel electrode dip into the solution and connected to a potentiometer (Sec.2.5.1) (or pH-millivolt meter), a large change in the potential of the Pt electrode is observed when the Mn(III) pyrophosphate complex is formed according to:

$$4Mn^{2+}+MnO_4^-+8H^++15H_2P_2O_7^{2-}\rightarrow 5Mn(H_2P_2O_7)_3^{3-}+4H_2O \qquad (12.1)$$

Weigh out 12 g $Na_4P_2O_7.10H_2O$ into a 400 cm^3 beaker. Prepare a saturated solution at room temperature (100-150 cm^3) and add dropwise conc. sulphuric acid to attain a pH of 6-7; use a narrow range pH paper. Then add 25.0 cm^3 of a Mn(II) solution (prepared by dissolving anhydrous $MnSO_4$ in 250 cm^3 water. The purest $MnSO_44H_2O$ is heated to 280°C (to remove its water of crystallisation). Dip a bright pt electrode and a saturated calomel electrode in the solution and connect them to a potentiometer or pH meter (operated on mV scale). Titrate with standardised 0.02 M permanganate solution. A sudden change in the reading indicates the end-point. Repeat to get concordant results and calculate, from the average titre, the concentration of Mn(II) in mol dm^{-3}.

12.3.1.4 Spectrophotometric determination of Mn(II)

Although Mn(II) salt solutions are faintly coloured, a spectrophotometric method of its determination is based on the sensitive qualitative test with formaldoxime. When the two solutions are made alkaline, the red orange coloured compound has an absorption maximum at 450 nm. The solutions obey Beer's law over the range 1-20 μmol dm^{-3} (*J.Amer.Water Works Assoc.*57(1965)107). The method was later developed for measurement of traces of Mn in water in the Water Research Association, at Medmenham.

Prepare a solution of 4 g formaldoxine dissolved and made up to 100 cm^3. Alternatively add to 6.0 g of hydroxylammonium chloride water and make up to 100 cm^3, then add 3.0 cm^3 of 37-41% w/v of formaldehyde solution and store in a stoppered bottle. Prepare a 0.01 M stock solution of either purest manganese sulphate or chloride. Dilute 100-fold by successive dilution. Pipette a volume of this solution into a 100 cm^3 volumetric flask, add 2 cm^3 of the formaldoxine reagent and 3 cm^3 5 M NaOH solution and make up to the mark. Record the absorption spectrum (5 minutes after making up) over the range 350-700 nm using a 10 mm cell. Locate the wavelength of maximum absorption, and note the absorbance at this wavelength. Prepare a set of solutions using varying volumes of the diluted manganese solution eg 10, 15, 20, 25, 30, 40 and 50 cm^3 and measure the absorbance at the predetermined wavelength. Check the applicability of Beer's law. Repeat one determination using boiled-out water for the dilutions and purging the other solutions with nitrogen prior to use and note the effect of this on your absorbance. What conclusions can be drawn from the results?

12.3.2 Preparation, analysis and photolysis of manganese(II) iodide

Manganese (II) iodide is photosensitive but its solution can be prepared and studied when freshly prepared. The simplest preparation is from Mn carbonate and HI solution. However, commercial carbonate is coloured, an indication of partial oxidation. Hence the carbonate has to be prepared freshly by reacting the sulphate solution with sodium bicarbonate solution. Its use, rather than sodium carbonate, is to avoid the formation of a basic solid.

The iodide solution is analysed for iodide by Andrews titration (Sec.8.3.3) ie titration in presence of conc. HCl and a small amount of an organic liquid to indicate the end-points.

When Mn I_2 solution is irradiated by a low pressure mercury lamp, the iodine formed by photolysis can be determined by titration against standardised sodium thiosulphate solution.

Preparation of $MnCO_3$

This is the first stage in the preparation. Commercial samples are impure. Dissolve 19.8 g $MnCl_2.4H_2O$ in 50 cm^3 water. Warm the solution and add slowly with constant stirring 250 cm^3 of a solution containing 16.8 g $NaHCO_3$. Filter quickly the precipitate under suction while pressing between filter paper.

Dilute 20 cm^3 HI solution (nominally 66% HI) to 100 cm^3 and add dropwise a solution of 16.4 g $Na_2SO_3.7H_2O$ until the colour of the contaminating I_2 just disappears.

Place the freshly prepared $MnCO_3$ in a conical flask and gradually add the purified HI solution to dissolve the carbonate. Transfer quantitatively to a 500 cm^3 volumetric flask which is kept stoppered in the dark.

12.3.2.1 Analysis

Dilute a 10.0 cm^3 aliquot of the prepared solution to 100 cm^3. Pipette in a 250 cm^3 reagent bottle. 25.0 cm^3 aliquot of the diluted MnI_2 solution, add 20 cm^3 water, 60 cm^3 conc. HCl and 5 cm^3 $CHCl_3$. Cool to room temperature and run in from a burette standard 0.025 M KIO_3 solution, while shaking vigorously the stoppered bottle. The strong colour of I_2 initially observed gradually changes to pale brown. Continue titration with vigorous shaking after each addition of KIO_3 until the organic layer is faintly violet. Then add the iodate solution dropwise, with vigorous shaking until the last trace of violet disappears. The pale yellow colour is due to ICl. Repeat to obtain concordant results and calculate from the average titre the concentration of MnI_2 in mol dm^{-3}.

12.3.2.2 Photolysis

Pipette 25.0 cm^3 of the MnI_2 solution into suitable containers eg two to four petri dishes (9 cm diameter) and place in reproducible positions under a low pressure mercury lamp. Irradiate for a period (say 30-60 minutes) and collect the solutions quantitatively in a 250 cm^3 volumetric flask. Titrate an aliquot against standardised $Na_2S_2O_3$ solution using starch indicator (Sec.11.4.4).

12.3.3 Photocatalysed oxidation of Mn(II) to MnO_2

When Mn(II) salt solutions in which a photocatalyst is suspended are uv irradiated in air, the electrons photopromoted to the conduction band react with oxygen at the surface, whereas holes formed in the valence band react with the hydroxylated surface producing OH radicals. These react with Mn^{2+} ions in solution forming the stable manganese dioxide. Use a dip type medium pressure mercury lamp provided with a quartz thimble and a cylindrical reaction vessel with a magnetic follower. Measure a volume of 0.0447 $MnSO_44H_2O$ g dm^{-3} so that its level in the vessel is above the mercury arc. Weigh out a mass of anatase so that the solid:liquid ratio is 0.67:100 (w/v) and sonicate the suspension for 30 minutes. Then irradiate while stirring magnetically for 3 hours. Filter through a G4 weighed sinter, wash well and dry to constant weight at 105°C. Weigh the dried product and calculate the mass of MnO_2 deposited g^{-1} of anatase.

12.4 THE CHEMISTRY OF Mn(III)

Although Mn(III) solid salts are not readily available, they can be prepared in solution under regulated conditions. However, Mn_2O_3 is an available oxide and many Mn(III) complexes can be prepared and analysed. Mn(III) compounds are intensely coloured and studying their reactions is interesting and instructive.

12.4.1 Analytical Chemistry of Mn(III)

Investigating the reaction between Mn^{2+} and MnO_4^-

Fig.12.1, the Ebsworth diagram of Mn, shows that, in acid solution, Mn(III) is on a concave point between Mn^{2+} and MnO_4^-, suggesting that it is feasible to prepare it by comproportionation:

$$4Mn^{2+}+MnO_4^-+8H^+\rightarrow 5Mn^{3+}+4H_2O \qquad (12.2)$$

However, compared to Mn^{2+} and MnO_2, Mn^{3+} is on a convex point indicating its tendency to disproportionate, according to:

$$2Mn^{3+}+2H_2O \leftrightarrows Mn^{2+}+MnO_2+4H^+ \qquad (12.3)$$

This shows that in order to prepare Mn(III) solution, an excess of acid and of Mn^{2+} ions should be present to favour the back reaction of (12.3).

Preparation and analysis of manganese (III) sulphate solution

Prepare 0.05 M $MnSO_4$ solution in 3 M sulphuric acid. Gradually add to an aliquot of the solution freshly prepared 0.02 M $KMnO_4$ until the wine colour of Mn(III) is fully developed. Avoid adding excess $KMnO_4$, otherwise $Mn_2(SO_4)_3$ disproportionates with the formation of colloidal MnO_2 producing a turbid solution. If this happens, the suspension is discarded and a fresh preparation is attempted. The solution should be kept in clean stoppered bottles in the dark.

Analysis (Standardisation)

The standard reduction potential E° of Mn^{3+} in acid solution is:

$$Mn^{3+} + e^- \rightarrow Mn^{2+} \qquad E^\circ = 1.5V \qquad (12.4)$$

Hence manganese (III) sulphate solution can be standardised with a standard solution of a reductant eg iron (II) in acid solution. The end-point can be found potentiometrically or by using a suitable redox indicator eg ferroin (iron (II) complex with 1,10-phenanthroline) which is red but turns blue when oxidised.

Pipette 25.0 cm^3 of standard 0.020 M Fe(II) solution into a conical flask. Add 25 cm^3 dilute H_2SO_4, 5 cm^3 H_3PO_4 and a few drops of ferroin indicator. Titrate with the prepared Mn(III) solution in the burette until the colour suddenly changes to blue. Repeat the titration and calculate from the average titre the concentration of Mn(III) in mol dm^{-3}.

Spectrophotometric investigation of the stoichiometry of the Mn(II)/permanganate reaction

Because manganese (II) solutions are faintly coloured unlike the strongly coloured permanganate, it is possible to study the reaction by spectrophotometry. Since the wine colour of the product (Mn(III)) is different from that of permanganate, a spectrophotometric titration is feasible (Sec.2.4.1). Even when the right equipment is not available, the following procedure can be used.

Prepare a solution of 0.4 M $MnSO_4$ in 6 M sulphuric acid and run its spectrum, preferably in a 4 cm cell. By successive dilution using the same acid, prepare a 0.004 M solution.

Prepare a 0.02 M $KMnO_4$ in 3 M sulphuric acid. By successive dilution, using the 3 M acid, prepare 4 or more solutions in the concentration range 0.002-0.0002. Run the spectrum of the 0.002 M solution and then measure the absorbance of all the prepared solutions at 400 and at 500 nm. Check the applicability of Beer's law over the concentration range.

Prepare a stock solution of $Mn_2(SO_4)_3$ solution, as above (Sec.12.4.1) in 6 M sulphuric acid. Standardise the solution as above and run its absorption spectrum. By successive dilution of your stock solution, using 6 M acid, prepare 3 more dilute solutions and measure the absorbances of these solutions at 400 nm and at 500 nm. Check the applicability of Beer's law. Pipette 20.0 or 25.0 cm^3 of 0.004 M of Mn(II) sulphate in 6 M acid into clean dry conical flasks (preferably with stoppers). Using a microburette, add the 0.02 M permanganate solution, using different volumes (0.2-1.6 cm^3) added to the sulphate solution, shake well and then measure the absorbance at 400 nm and at 500 nm in 10 mm cells. Calculate for each solution the molar ratio MnO_4^-/Mn^{2+} and plot the absorbance at the two wavelengths against the molar ratio. What conclusions can be drawn from the plots?

Solvent extraction of manganese (III) and its spectrophotometric determination

It was found that Mn(III) can be extracted from aqueous solution by dibutylphosphate in xylene and that the intensely coloured extracted solution has an absorption maximum at 537 nm *(Polyhedron* **13/14** (1989) 1874).

Prepare a solution of $Mn_2(SO_4)_3$ by carefully adding to a volume of 0.05 M $MnSO_4$ in 3 M sulphuric acid, a quarter of this volume of 0.02 M $KMnO_4$. Standardise as above. Mix 16 cm^3 of dibutylphosphate with 80 cm^3 xylene by shaking thoroughly in a separating funnel. Pipette increasing volumes of the Mn(III) solution (2-10 cm^3) into a separating funnel and add from a pipette 10 cm^3 of the organic solution. Shake well and separate the two layers and note their colours. Run the spectrum of the most concentrated solution in a 1 cm cell over the range 350-650 nm. Locate the wavelength of maximum absorption and check the applicability of Beer's law at this wavelength over the concentration range covered.

Investigating other solvent systems

Try other water-immiscible solvent/water mixtures, checking the solubility of dibutylphosphate in them and the extractability of Mn(III). If extraction is achieved, run the spectrum of the extracted species and compare this with the spectrum in xylene.

Investigating the stoichiometry of the reaction of ascorbic acid with Mn(III)

Ascorbic acid is a powerful reductant and reacts with different oxidants by 2,4 or even 6 electron changes. It is important to establish the stoichiometry of its reaction with Mn(III) sulphate solution. However since ascorbic acid solutions are oxidised in air, its solutions should be freshly prepared in boiled-out water and freshly used.

Prepare 0.025 M *L* ascorbic acid solution by weighing accurately about 1.1 g of the purest solid, dissolving it and making up the solution in a 250 cm^3 volumetric flask using boiled-out distilled deionised water. Pipette 10 cm^3 of the solution into a conical flask, acidify with dilute sulphuric acid and add a few drops of N-phenylanthranilic acid indicator. Titrate with standardised freshly prepared Mn(III) sulphate solution (as above) until the colour changes sharply to violet. Repeat to obtain concordant results and calculate, from the average titre, the ascorbic acid:Mn(III) molar ratio.

Investigating the stoichiometry of the reaction of hydrazine with Mn(III)

Hydrazine and its salts react with oxidants in different molar ratios under different conditions. It is therefore necessary to establish the stoichiometry of its reaction with Mn(III) sulphate solution.

Prepare a 0.025 M solution of purest hydrazinium sulphate, pipette 25.0 cm^3 of the solution, acidify with sulphuric acid and add drops of N-phenylanthranilic acid indicator. Titrate with the prepared and standardised Mn^{3+} solution until the colour changes suddenly to violet. Repeat to obtain concordant results. Calculate from the average titre the number of mols of Mn^{3+} and compare this with the number of mols of N_2H_4.

12.4.2 Kinetics and mechanism of the oxidation of Cr(III) by Mn(III)

The oxidation of Cr(III) by Mn(III) is thermodynamically feasible as can be seen from the standard redox potentials, E^o at 298 K in acidic solution (pH=0):

$$Cr_2O_7^{2-}+14H^++6e^-=2Cr^{3+}+7H_2O \quad +1.33V \qquad (12.5),$$
$$Mn^{3+}+e^-=Mn^{2+} \quad +1.5\ V \qquad (12.6),$$

The stoichiometry of the reaction is:

$$6Mn^{3+}+2Cr^{3+}+7H_2O=Cr_2O_7^{2-}+6Mn^{2+}+14H^+ \qquad (12.7)$$

The kinetics of the reaction has been followed by measuring the absorbance at 480 nm (λ_{max} for Mn(III)) and at 580 nm (λ_{max} for Cr(III) and the reaction was reported to be second-order. However, since both reactants and the $Cr_2O_7^{2-}$ ions produced absorb at the two wavelengths, it is preferable to separate the reactants before measuring the absorbance. Mn(III) can be extracted by a solution of dibutylphosphate in toluene or xylene. A stable blue-violet organic layer (λ_{max} 537 nm) is formed and contains all the Mn(III). When the organic layer is dried with Na_2SO_4, its absorbance was found to vary linearly with the Mn(III) concentration. Thus a convenient accurate method of following the reaction is available.

Prepare a stock solution of $Mn_2(SO_4)_3$ in 3 M sulphuric acid as described before and standardise it. Prepare a solution of $KCr(SO_4)_2.12H_2O$ in the same acid such that the ratio $[Mn^{3+}]/[Cr^{3+}]$ is close to 3. Record the absorption spectra of this solution and of a solution of $K_2Cr_2O_7$ in the same acid whose [Cr(VI)] is half of the above solution and record its spectrum (over the range 250-650 nm, use a 10 mm cell). Compare the two spectra with that of $Mn_2(SO_4)_3$.

Pipette a suitable volume of the Mn solution into flask B (Fig.2.12) and pipette an equal volume of the Cr solution into flask A. Immerse flask A in a beaker containing water at appreciably higher temperature than that planned for a run, keeping flask B at room temperature. After thermal equilibration, mix the contents of the two flasks thoroughly and keep in a thermostat, as you start a stopwatch. Check in a blank test the temperature of a similar mixture treated similarly and use it as the thermostatting temperature. At intervals, say 5, 10, 20, 40, 60 and 80 minutes, withdraw aliquots into flask C, cooled in ice/salt mixture. Keep these cold until it is convenient to determine [Mn(III)]. Extract 5.0 cm^3 of each aliquot with 5.0 cm^3 dibutylphosphate/xylene, as described above and hence find the absorbance at the wavelength of maximum absorption and hence [Mn(III))]. Carry out a duplicate run as soon as convenient.

Repeat the procedure at two or three more temperatures in the thermostat. Plot the reciprocal of [Mn(III))] against time, calculate the rate constants and the activation parameters.

Alternatively use the same Mn solution but a Cr solution three times as concentrated as the solution above and repeat the runs at 3 or 4 temperatures. Plot log absorbance against time and calculate as above.

Repeat one of the above runs, purging the system with nitrogen before and during the experiments. Dissolve $MnSO_4$ in a solution 2.5 M in sulphuric acid and 0.5 M in Na_2SO_4 and repeat one of the above runs. What general conclusions can be drawn from your results?

12.4.3 Preparation, tests and analysis of Mn(III) Compounds

Generally manganese (III) complexes are prepared by oxidising a manganese (II) compound with permanganate in presence of the ligand. The conditions depend on the stability of the product and the reactivity of the reagents.

A useful method of analysis is to dissolve a known mass of the compound in a known excess of standardised ascorbic acid solution, back-titrating the excess with standardised Mn(III) sulphate solution or other oxidants. Alternatively, a known mass of the compound is treated with an excess of iodide solution, titrating the liberated iodine with standardised thiosulphate.

12.4.3.1 Preparation, tests and analysis of manganese (III) acetylacetonate (pentane-2,3-dioate)

This is one of the more stable complexes of Mn(III), whose stability is related not only to the chelate and resonance effects but also to its non-ionic character and hence its insolubility in water. However it is soluble in organics.

Dissolve 5 g $MnCl_2.4H_2O$ and 13 g $NaCH_3COO.3H_2O$ in 200 cm^3 H_2O. Add to the solution, slowly and with constant stirring, 21 cm^3 pentan-2, 4-dione. To the two phase system thus obtained, add a solution of 1 g $KMnO_4$ in 50 cm^3 H_2O. Then after a few minutes, add a solution of 13 g $NaCH_3COO.3H_2O$ in 50 cm^3 H_2O, and heat the mixture at 60°C, on a hot plate for 10 minutes. Cool in ice-cold water and then filter off the dark crystals under suction. Wash with small quantities of ice-cold H_2O and then small quantities of acetone. Dry by continued suction while pressing between filter paper. Record your yield and calculate the percentage yield based on the dione.

12.4.3.2 Analysis

Use either of the two methods described later to determine the % Mn in your preparation and hence its % purity.

12.4.3.3 Qualitative tests

To about 0.1 g portions add separately 3 cm^3 of each of the following solutions and shake:

(a) $SnCl_2$;
(b) diluted $N_2H_4.H_2O$;
(c) KI and then dil. sulphuric acid, then CCl_4;
(d) sodium oxalate acidified with dilute sulphuric acid and heat.

12.4.3.3 Preparation, tests and analysis of $K_3[Mn(C_2O_4)_3].3H_2O$

Unlike the previous complex, the trisoxalato-complex is moisture- and light-sensitive. Hence the necessity to adhere strictly to the instructions for the preparation, which involves the oxidation of the manganese (II) formed in the initial step (reduction of permanganate by oxalic acid). The second step ie the oxidation of Mn(II) by permanganate has to be done at below 0°C to avoid the thermal decomposition of the complex formed. Analysis is similar to the earlier complex.

Dissolve 10.5 g oxalic acid dihydrate in 75 cm^3 of water in a 250 cm^3 beaker. Heat the solution to 70°-75°C and slowly add 2.1 g potassium permanganate. When the solution is colourless, add 2.3 g of potassium carbonate. Ignore any white precipitate which forms. Cool to -4°C in an ice/salt bath and add 50 cm^3 water. Maintaining the temperature in the range 0°C to -2°C, add, in small portions, 0.5 g of potassium permanganate. Filter through a sintered-glass filter. Transfer the filtrate to a 250 cm^3 beaker already cooled in ice and add 75 cm^3 ice-cold ethanol. Allow the cooled solution to stand in the dark for 2 hours.

Filter by suction, wash the product with small portions of alcohol and then ether (CARE!) and dry by continued suction while pressing between filter paper. Weigh and store the product in the dark in a fridge. Calculate the % yield.

Analysis

Weigh accurately about 0.5 g of your prepared complex into a 250 cm^3 beaker. Add from a burette a freshly prepared 0.025 M ascorbic acid solution with continuous shaking until the colour of the Mn(III) complex disappears and then add about 5-10 cm^3 in excess. Record the burette reading V_1. Dilute the contents of the beaker, which contain the sparingly soluble MnC_2O_4, with 25 cm^3 H_2O and then add slowly, with continuous shaking 0.5 M $CaCl_2$ solution until precipitation seems complete. Filter through No.40 paper, washing the precipitate twice by decantation. Collect the filtrate and washings in a clean conical flask and add a few drops of ferroin indicator. Titrate with standardised Mn(III) solution from a burette until the colour changes sharply to blue. Note the titre V_2. Calculate:

The excess of ascorbic acid solution, after reacting with the complex and the percentage of Mn(III) in your preparation and hence its % purity.

12.4.3.4 Qualitative tests

(a) To 2 cm^3 of a solution of your preparatio in water at ~0°C, add separately:
  (i) dil. sulphuric acid dropwise and shake;
  (ii) an equal volume of K1 solution, 2 cm^3 CCl_4 and shake carefully;
  (iii) an equal volume of calcium chloride solution, shake and then gradually add 0.1 M EDTA solution;
  (iv) an equal volume of freshly prepared iron (II) sulphate solution and then a few drops of KSCN.

(b) Heat, gently a small quantity of your preparation in a dry test tube and test with cobalt blue paper. Then heat more strongly and test with $PdCl_2$ paper and lime water. Cool the residue and add dilute sulphuric acid.

12.4.3.5 *Conversion to* $K[Mn(C_2O_4)_2(H_2O)_2]$

Prepare a concentrated solution of your preparation in ice-cold water. Cool to 0°C in ice/salt mixture and gradually add cooled dilute sulphuric acid with shaking until the colour changes to golden yellow. Add ethanol to precipitate $K[Mn(C_2O_4)_2(H_2O)_2]$ while cooling in ice/salt. Allow to crystallise while keeping it cold. When crystals form, quickly filter under suction, wash with small volumes of ice cold ethanol and dry by continued suction while pressing between filter paper. Weigh your product and store in a vacuum desiccator kept in the fridge.

12.4.3.6 Preparation of the EDTA complex of Mn(III): $K[Mn(C_{10}H_{12}O_8N_2)(H_2O)]1\frac{1}{2}H_2O$

In the first step of the reaction, permanganate is reduced by ethanol to the dioxide. The freshly obtained dioxide reacts in the second stage with the sodium EDTA salt which reacts forming the Mn(III) EDTA complex.

Slowly add 12 g $KMnO_4$ to a mixture of 20 cm^3 ethanol and 80 cm^3 water. Carefully shake the suspension and warm. After the vigorous reaction has subsided, warm intermittently to expel the excess ethanol and the aldehyde produced. Cool in an ice bath and add, with continuous stirring, a slurry of 23 g disodium EDTA in glacial acetic acid and allow to warm to room temperature. Filter off on a sinter any manganese dioxide and add to the cherry red filtrate an equal volume of cold ethanol and cool in an ice bath for 1 hour and then filter the crystals produced under suction. Wash with 3 x 30 cm^3

ethanol and 40 cm^3 absolute ethanol and an equal volume of ether and dry by continued suction. Weigh your product and calculate the percentage yield based on EDTA.

Analysis by ascorbic acid

Weigh out accurately about 0.5 g of your preparation, dissolve in known excess of 0.1 M ascorbic acid solution and back titrate the excess with standardised Mn^{3+} solution as in Sec.12.4.1.

12.4.3.7 Alternative analysis

This method is the usual one for analysing the manganese content of steel. The initial step is to oxidise and remove organic matter (or O in steels). Persulphate then oxidises Mn to permanganate. The latter is then determined spectrophotometrically when dilution is necessary to obtain an optimum absorbance. The modification discussed in Sec.2.4.1 for strongly absorbing solutions could be used here.

Weigh out accurately about 0.1 g of your preparation. Carefully prepare a mixture of concentrated nitric and sulphuric acids in the fume cupboard. Add the mixture to your sample and heat on a sand bath or hot plate behind a screen to dissolve the solid, boiling if necessary. Then add $(NH_4)_2S_2O_8$ when the mixture is cool and heat again to boiling temperature. Remove any coloured species if observed by gradual addition of sulphite. Then add KIO_4 and about 5 cm^3 of orthophosphoric acid and boil until maximum colour of permanganate is developed. Cool the clear solution and make up to 100 cm^3 in a volumetric flask. Dilute an aliquot of this solution tenfold and measure the absorbance of the solution in a 10 mm cell at 545 nm. Prepare a standard $KMnO_4$ solution by accurately weighing about 0.6 g and making up to 100 cm^3 in a volumetric flask. Dilute an aliquot in stages a hundred fold and measure the absorbance as above. From this absorbance of the standard solution and of your final solution obtained as above, calculate the concentration of Mn in the latter and hence the % Mn in your preparation and its percentage purity.

A quick alternative method is based on the reduction of Mn(III) by an excess of KI, titrating the liberated iodine with standardised thiosulphate.

12.4.3.8 Preparation and analysis of Mn(III) dibutylphosphate

If the solvent extraction of Mn(III) described above is repeated with fresh Mn(III) sulphate solution and the coloured organic layer is allowed to evaporate in a vacuum desiccator, a solid compound is obtained.

Thoroughly mix 12 cm^3 of dibutylphosphate with 60 cm^3 of toluene in a separating funnel. Add 50 cm^3 of $Mn_2(SO_4)_3$ solution prepared as above and shake well. Discard the aqueous layer and use a fresh aliquot of Mn(III) solution and extract as before. Repeat the extraction to obtain maximum colour production in the organic layer. Transfer to an evaporating basin and allow to evaporate in a vacuum desiccator with an efficient desiccant. Separate the solid by filtration under suction, quickly weigh the solid and store in a vacuum desiccator since it is sensitive to moisture.

Analysis

Weigh accurately a portion of the solid into a conical flask, add 10% KI solution until no more iodine is liberated. Titrate against standardised 0.01 M thiosulphate, adding the freshly prepared starch solution when the colour is straw yellow. Continue titration until the blue adsorption complex colour disappears. Repeat and calculate from the average titre the % purity of your preparation.

Alternatively add to the weighed solid a known excess of standard freshly prepared ascorbic acid solution. Ensure that more ascorbic acid solution is added after the complete solubility of the solid, recording the volume used. Back titrate the excess against standardised Mn(III) solution. Calculate the percentage purity.

12.4.4 Reactivity of Mn(III) Compounds

The important reactions of Mn(III) compounds and complexes are oxidations during which the reductant is oxidised and Mn(III) is reduced. If the reactions are not too fast, their kinetics can be easily studied.

Another interesting reaction is ligand replacement which may take place at a measurable rate. The process is then sometimes referred to as leaching.

12.4.4.1 Kinetics of the oxidation of Cr(III) by Mn_2O_3

Mn_2O_3 is commercially available and is expected to oxidise Cr(III) to dichromate in acidified solution. Since this is more strongly absorbing than Cr(III) solutions and since their spectra do not overlap, the kinetics of the reaction can be readily studied by withdrawing aliquots of a thermostatted suspension and measuring [Cr(VI)] spectrophotometrically.

Applicability of Beer's law to $K_2Cr_2O_7$ solution

Prepare a stock solution of 0.01 M $K_2Cr_2O_7$ solution. By successive dilution, prepare solutions of a concentration range from 0.00025 to 0.000025 M and run the spectrum of the most concentrated solution over the range 300-600 nm and locate the wavelength of maximum absorption. Measure accurately the absorbance at this wavelength of your prepared solutions and check the applicability of Beer's law.

Weigh out accurately 12.8 g of Mn_2O_3 into a double-walled beaker provided with a thermometer (0°-100°C) and a sintered glass disc (Fig.2.1), add 100 cm^3 of 0.1 M solution of $KCr(SO_4)_2.12H_2O$, whose pH has been adjusted to 3.0 using a pH meter, and stir magnetcally. Pass water from a thermostat set at say 50°C prior to the experiment and keeping the thermostatting throughout the experiment. At intervals, withdraw small aliquots through the sinter and pipette an adequate volume for measuring the absorbance at the determined wavelength. Repeat using at least two more higher temperatures. Repeat one run using a Cr solution whose pH is 2.0. Calculate for each aliquot the fraction of Cr oxidised and plot it against time. Estimate the time, t, at which a certain fractional oxidation has been achieved Check the relation between log t and the reciprocal of the absolute temperature. Repeat one run after purging with nitrogen.

12.4.4.2 Leaching Mn_2O_3 with pyrophosphate solution

Pyrophosphate forms a strongly coloured complex in Mn(III) solutions and it is interesting to study leaching of Mn^{3+} from the solid oxide.

Preparation and the absorption spectrum of $[Mn(H_2P_2O_7)_3]^{3-}$ (aq)
Ind. Eng. Chem., Anal. Ed. **15** (1943) 8)

Prepare 0.27 M $Na_4P_2O_7$ solution, adjust the pH to 2 and add 140 cm^3 of the solution to 50 cm^3 of 0.1 M $MnSO_4$ solution and 5.5 g PbO_2. Use a magnetic stirrer/hot plate to stir the solution at 45°-60°C for 45 minutes. Filter the suspension through Whatman 42 paper. Record the electronic spectrum in the range of 350-650 nm using a 10 mm cell. Use the literature value of ε at 480 nm to calculate its concentration. Compare its oxidising power with that of Mn(III) sulphate solution (Sec.12.4.3).

Prepare 0.27 M solution of $Na_4P_2O_7$ at pH6. Add 0.32 g Mn_2O_3 to 50 cm^0 of the phosphate solution in a rounded centrifuge tube and shake in a shaking thermostat or orbital incubator at 65°C for 10 minutes. Quench in ice/salt bath, filter after centrifuging and determine the absorbance of the filtrate at 480 nm. Repeat using increasing times. Calculate the percentage Mn leached and plot it against the exact time.

12.4.4.3 Interaction of Mn(III) acetylacetonate with pyrophosphate solution

Since this insoluble Mn(III) complex is one of the stable Mn(III) complexes, it was worth examining whether its Mn^{3+} can be leached by pyrophosphate or not. Prepare 0.1 M solution of $Na_4P_2O_7$ at pH6. Add 0.2 g of your prepared Mn complex to 50 cm^3 of the phosphate solution, stir magnetically for 5 minutes. Filter off any solid and run the spectrum of the filtrate in a 1 cm cell over the range 350-650 nm and compare it with the spectrum of $[Mn(H_2P_2O_7)_3]^{3-}$ solution previously recorded.

12.5 STUDIES OF MIXED VALENCE MANGANESE COMPOUNDS

Mn_3O_4 is a commercial product which has a normal spinal structure with one Mn(II) and two Mn(III) ions per formula. However, some complexes contain one Mn(III) and one Mn(IV) per formula and they are also considered mixed valence complexes. Most of the reactions of these compounds are oxidations in which Mn is reduced to the most stable state of +2.

12.5.1 Kinetics of the Oxidation of Cr(III) by Trimanganese Tetroxide

Use a similar procedure as that used for manganese (III) oxide but weigh 0.42 g portions of Mn_3O_4. When the reaction has been followed for the longest time, wash the residue on the filter with water until the filtrate is colourless, dry at 105°C to constant weight. Grind to a very fine size and submit for X-ray powder diffraction and obtain also a diffraction pattern of the original oxide. Compare the two patterns and comment. If surface area determination is available, measure the surface area of Mn_3O_4 and of Mn_2O_3 and comment on the result and its relevance to the rates of oxidations of Cr(III).

12.5.2 Preparations, Tests and Analysis of $[MnO(phen)_2]_2(ClO_4)_3.2H_2O$

This complex is obtained by the oxidation of Mn(III) by permanganate in presence of the ligand. It can be analysed by dissolving in a known excess of freshly prepared standard ascorbic acid solution and back titrating the excess with Mn(III) sulphate solution.

12.5.2.1 Add 3.0 g $Mn(CH_3CO_2)_2.4H_2O$ in 40 cm^3 water to a solution of 10 g of 1, 10-phenanthroline hydrate in 40 cm^3 acetone and 60 cm^3 of acetate buffer (pH4.5). Then add glacial acetic to adjust the pH to 4.5 Cool the mixture to 0°C in an ice/salt, then add 1.1 g of $KMnO_4$ in 50 cm^3 water, added dropwise keeping the temperature between 0°C and -5°C. Allow the mixture to stand in the ice bath for 15 minutes. Filter under suction and add to the filtrate 40% w/w of $NaClO_4$ dropwise to precipitate the required complex. Collect the solid by filtration under suction, wash with 15 cm^3 of 50/50 ethanol/ether mixture and dry by continued suction while pressing between filter paper. Record the mass of the product and calculate the percentage yield based on phenanthroline (phen).

12.5.2.2 Analysis

Weigh out accurately about 0.25 g of your preparation into a conical flask. Cover with water and add from a burette freshly prepared and standardised 0.05 M ascorbic acid. Shake well until the solid dissolves and then add 10.0 cm^3 acid in excess. Back titrate the excess ascorbic acid against freshly prepared and standardised Mn(III) solution using ferroin as indicator. Repeat and calculate from the average results the percentage Mn in your preparation and hence its percentage purity.

12.5.2.3 Qualitative tests

(a) Check the solubility of the solid in:
  (i) dilute and then concentrated HCl;
  (ii) dilute and then concentrated sulphuric acid (CARE!);
  Compare the colours of the solutions with an aqueous solution.
(b) Add to separate portions of the aqueous solution:
  (ii) methanol and then warm in a water bath;
  (iii) 20 volume hydrogen peroxide;
  (iv) hydrazine hydrate;
  (v) $Na_4P_2O_7$ solution (pH6);
  (vi) acidified KI solution and test with a starch paper.

12.5.3 Preparation, Tests and Analysis of $[MnO(bipy)_2]_2(ClO_4)_3.2H_2O$

Similar procedures are used as for the above complex.

Follow the procedure as above using 10 g 2,2-dipyridyl (bipy) in 40 cm^3 acetone and 100 cm^3 acetate buffer and 5.2 g $Mn(CH_3CO_2)_2.4H_2O$ in 75 cm^3 water and 1.4 g $KMnO_4$ in 60 cm^3 water. Analyse in the same way as for the complex prepared above.

Carry out the same qualitative tests as above.

12.5.4 Kinetics of the Reaction of Hydrazine Hydrate with Either of the Above Mixed Valence Complexes

The reactions produce nitrogen gas and the kinetics can be followed by measuring its volume at different times. Since the rate is relatively fast, it is convenient to record the volume as a function of time.

Use the apparatus in Fig.2.14. Weigh out accurately 0.35 g of either $[MnO(phen)_2]_2(ClO_4)_3.2H_2O$ or $[MnO(bipy)_2]_2(ClO_4)_3.2H_2O$ into flask F and add 10 cm^3 water and keep at a constant temperature by surrounding it with a large beaker containing water at the required temperature. While keeping the mixture magnetically stirred, prepare a hydrazine hydrate solution (either 2.5 or 5.0 M) freshly obtained from the purest liquid by dilution using boiled-out cold water. Either solution is standardised by titration against standardised $Mn_2(SO_4)_3$ solution. Pipette 2.0 cm^3 of this solution into flask E and transfer the solution into flask F by rotation at the ground joint as the chart recorder is started. Work out the volume of gas, V_t, evolved at various times, t, from the smoothed chart and the final volume V_f. Plot $\ln V_f/(V_f - V_t)$ against t to check that first-order kinetics is applicable. Repeat at 2 or more temperatures and estimate the activation energy from the results at different temperatures.

12.6 SPECTRAL AND MAGNETIC STUDIES OF MANGANESE COMPOUNDS

12.6.1 Mn(II) Compounds

Most of Mn(II) compounds are high spin. Whether they are octahedral or tetrahedral they have 5 unpaired electrons and hence they have the highest magnetic susceptibility in the transition series. Some salts are used as susceptibility standards.

Since the ground state configuration is $^6A_{1g}$ in O_h symmetry, any transition to higher states will be spin- and Laporte-forbidden. Hence the d-d electronic spectrum is expected to exhibit weak bands but some of these may be sharp.

Grind a very pure Mn(II) sulphate or chloride to a very fine size. Pack in the Gouy tube and measure the susceptibility by the Gouy or Evans methods (Sec.2.1.3) and calculate the magnetic moment.

Prepare a concentrated solution of Mn(II) nitrate and run its spectrum in a 4 cm cell (or a 10 cm cell if available) over the range 300-700 nm.

Draw your conclusions from your results.

12.6.2 Mn(III) Compounds and Mixed Valence Complexes

High spin (Mn(III) complexes have 4 unpaired electrons. The octahedral ground state configuration is $(t_{2g})^3(e_g)^1$ indicating strong Jahn Teller distortion. Magnetic measurements would indicate the high spin state. The electronic spectrum is expected to show one d-d band of medium intensity. A broad or distorted or split band is expected and its position would follow the position of the ligand in the spectrochemical series. Complexes with organic ligands can be characterised by their ir spectra and elemental analysis.

The mixed valence complexes are similarly characterised but their spectral and magnetic behaviour is not as simple as the Mn(III) complexes.

Use the oxalato-complex as soon as it is prepared. Dissolve in an oxalate solution at 15°C and run its visible spectrum in the range 370-600 nm. Measure its magnetic moment quickly and prepare a mull in Nujol and run its infrared spectrum. The compound is sensitive to moisture and light and is unstable on heating.

Run the spectrum of $[Mn(acac)_3]$ in $CHCl_3$ in the uv/visible region and its i.r. spectrum in a KBr disc. Measure its magnetic susceptibility and obtain results of elemental analysis.

Similarly obtain results for the EDTA complex but record the spectrum using 1.4×10^{-4} M solution in acetic acid/acetate buffer at pH 2.5-4.0. Compare the absorption spectra with the spectra obtained earlier for the other Mn(III) compounds.

Subject the mixed valence complexes to the same but use 0.05 M solution in aqueous bipyridyl buffer (pH4.5) or phenanthroline buffer. Compare the results for the two complexes.

12.7 STUDIES OF MANGANESE DIOXIDES

Several forms of manganese dioxide are known, most of which are non-stoichiometric and contain variable amounts of constitutional water *(Chem. Ind.* (1977) 446). A range of interesting surface and kinetic studies of well-characterised powders are described.

12.7.1 Surface Chemical studies of Manganese Dioxides

12.7.1.1 Preparation, analysis and characterisation of βMnO_2

The stoichiometric form has the rutile structure and is easily obtained by heating Mn(II) nitrate (Sec.12.2.3(a). It is characterised as described in Sec.2.1 and analysed by reduction to Mn(II) by a known excess of standard oxalate, back titrating the excess with permanganate. To confirm its stoichiometry, combined iodometric and complexometric titration is required *(G.Gattow, Batterien,* **15** (1961) 163).

Preparation and characterisation

Heat $Mn(NO_3)_2$ in a porcelain dish until no more NO_2 fumes are produced. Grind the product well, reheat in a muffle furnace at 673 K to constant weight. Using standard sieves, separate the fraction -0.037+0.010 mm. Characterise the powder with the available instrumental techniques. For X-ray diffration, regrind to a very fine powder and keep in a desiccator prior to analysis. For thermogravimetric or differential thermal analysis (Sec.2.6.1; 2.6.3) use a rate of heating of 5° or 10°C per minute.

12.7.1.2 Analysis by the oxalic acid method

Weigh out accurately 0.20 g of your preparation into a 250 cm^3 conical flask. Add 50 cm^3 of standard 0.050 M sodium oxalate solution and 80 cm^3 dilute sulphuric acid. Place a short funnel in the mouth of the flask and boil gently eg on a sand bath until all the black particles have dissolved. Allow to cool to 80°C and titrate the excess oxalate against 0.02 M permanganate standardised against the oxalate solution. Repeat and calculate from the average results the percentage of MnO_2 in your preparation.

12.7.1.3 Determination of χ in the formula $MnO_{1+\chi}$

Weigh accurately 0.2 g of your preparation into a 500 cm^3 conical flask provided with a stopper, dissolve it in 80 cm^3 of 0.1 M KI solution, acidified with 20 cm^3 orthophosphoric acid. Add four portions of 0.5 g sodium bicarbonate in succession to exclude air from the flask. Stopper the flask and shake it well until all the iodine is liberated. Then titrate using a microburette with standardised 0.05 M thiosulphate solution using starch as indicator. Then add 0.2 g of hydroxylammonium chloride, heat to 80°C and add a known excess of standardised 0.01 M EDTA solution. Neutralise by the dropwise addition of NaOH, dilute by 100 cm^3 water. After adding 5 cm^3 of NH_3/NH_4Cl buffer (pH=10) titrate the excess EDTA against standardised 0.01 M Zn^{2+} ion solution using Erio T as indicator. Repeat and calculate from the average result the formula $MnO_{1+\chi}$.

The point of zero zeta potential or point of zero charge of Mn dioxides

To establish the optimum pH conditions for studying the adsorption of cations or anions on a manganese dioxide, the PZZ and/or PZC of the powder has to be determined. Cations are adsorbed at pH's above these points and anions at pH's below them.

The point of zero zeta potential of β MnO_2

Select by sedimentation a size fraction of your preparation fine enough not to settle under gravity in a cylindrical cell. Use 0.001 M KNO_3 as supporting electrolyte. Plot the electrophoretic mobility (or the zeta potential) against pH and hence find PZZ. Follow the instructions in Sec.2.1.4.

12.7.1.4 Effect of doping on PZZ

Preparation of doped MnO_2

Heat $Mn(NO_3)_2$ with $Cr(NO_3)_3$ or NH_4VO_3 such that the atom percent of dopant is around 0.1. Follow the same procedure as above for the preparation of βMnO_2. Use a fine fraction of the doped samples to measure the electrophoretic mobility at different pH values as above and plot the measured mobility against pH and estimate PZZ. Comment on the effect of doping on the PZZ.

12.7.1.5 Determination of PZC of manganese dioxides

Suspend 4.0 g of commercial MnO_2 eg γMnO_2 (International Common Sample No.5) in 200 cm^3 of 0.01 M KNO_3 solution in double-walled beaker, Fig.2.1 and follow the procedure described in (Sec.2.1.4) and calculate from the results the net adsorption density and plot against pH. Hence determine PZC of the sample used.

Measure the electrophoretic mobility of the same sample at the temperature and the concentration of supporting electrolyte as used above and determine PZZ and comment on the comparative values of the two points: PZC and PZZ.

12.7.1.6 The rate of adsorption of calcium ions onto β manganese dioxides

Since Ca ion-sensitive electrode shows a quick response to calcium ion concentration, it is useful to study the rate of adsorption of these ions on Mn dioxide. Convert the powder to the Na^+ form by equilibrating in 0.1 M NaCl at pH~9 for 10 hours. Use 2.0 g in the beaker in Fig.2.1 and add 100 cm^3 of a solution 0.0025 M in $CaCl_2$ and 0.01 M in NaCl. Adjust the pH to 9.0 and circulate water at 20°C from a thermostat. The beaker should have holes to allow a Ca^{2+}-ion selective electrode (Sec.2.5.1) and a saturated calomel electrode, to dip into the suspension besides nitrogen gas inlet and outlet. Connect the two electrodes to a pH or ion meter. Measure the e.m.f. as a function of time. Use standard $CaCl_2$ solutions to relate the e.m.f. to calcium in concentration. Hence calculate their concentration at various time intervals. Plot log $[Ca^{2+}]$ against time and comment on the shape of the plot. Repeat at 2 or more temperatures and estimate activation energies

The adsorption of manganese (II) ions on β MnO_2

Transform the powder to the Na^+-form at pH7.0 as described above. Check the time required to reach adsorption equilibrium (Sec.9.4.2) and prepare $MnCl_2$ solutions in the range of 0.1 to 0.0001M which are all 0.01 M in NaCl and at pH7. Standardise the most concentrated solution by EDTA titration (Sec.12.3) and prepare the more dilute solutions by successive dilution. For each run, suspend 5.0 g of the Na^+ form in 100.0 cm^3 Mn^{2+} solution and agitate in a thermostat 10°C. After equilibration, measure $[Mn^{2+}]$ in the centrifugate or filtrate. Plot the amount adsorbed g^{-1} or m^{-2} against the equilibrium concentration. Repeat at, at least two higher temperatures. Check the applicability of Langmuir's adsorption isotherm and attempt to estimate the heat of adsorption.

12.7.2 Reactivity of manganese dioxides

The main reactions of the dioxides are related to their oxidising power. They oxidise hydrazine to nitrogen and they are reduced to MnOOH. The reduced products are leached with pyrophosphate giving the coloured Mn(III) pyrophosphate complex. The solubility of the solids in acidified ascorbic acid is due to reduction to Mn(II). Manganese dioxides oxidise Cr(III) to dichromate. Even their catalytic role in the decomposition of hydrogen peroxide involves a redox catalytic cycle.

12.7.2.1 The reduction of manganese dioxides by hydrazine hydrate

This is a fairly fast reaction and its kinetics can be followed by measuring the volume of nitrogen produced as a function of time. For battery active samples, the kinetics of the reaction is thought to be related to their battery activity where they act as depolarisers in the common dry batteries.

Place 2.00 g of MnO_2 eg ICS5 into flask F of a larger scale version of Fig.2.14 add 20 cm^3 water and keep stirring magnetically. Pipette into E 20.0 cm^3 of hydrazine solution made by successive dilution (50-fold in the final solution) from purest $N_2H_4.H_2O$. Mix the solutions as previously described (Sec.12.5.4) while starting the chart recorder.

12.7.2.2 Effect of doping on the kinetics of the reaction

Using ^{56}Mn-labelled dioxides, it was found that the solids exchanged with transition or p block metal cations, liberating Mn(II) ions in solution. This is suggested as a method of preparing doped samples. Their reactivity towards hydrazine is expected to depend on the dopant.

Prepare doped samples by shaking 2.00 g of the solid with 15.0 cm^3 of a 0.1 M solution of $GaCl_3$, $Fe_2(SO_4)_3$ or $CoSO_4$ in a thermostat at 65°C for 80 minutes. After cooling, filter through GF and wash thoroughly prior to study the reduction by hydrazine. Compare the results of the powders studied.

Kinetics of leaching the reduced products by pyrophosphate

Suspend 10.0 g of MnO_2 in 100 cm^3 water, add 100 cm^3 of hydrazine hydrate solution, (0.57 g/100 cm^3) stir for 2 hours to produce partial reduction. After filtration and thorough washing, dry at 30°C and store in a vacuum desiccator. Analyse as described in (Sec.12.7.1) to find out the formula MnO_{1+x} and hence calculate the percentage of Mn(III) in your reduced sample.

12.7.2.3 The applicability of Beer's law to $[Mn(H_2P_2O_7)_3]^{3-}$ solutions

Prepare $[Mn(H_2P_2O_7)_3]^{3-}$ solution as described in (Sec.12.4.4) and determine its concentration by titration against standardised Fe(II) solution in Sec.12.4.1. Prepare a series of solutions of $[Mn(H_2P_2O_7)_3]^{3-}$ by successive dilution and measure the absorbance of each solution at 480 nm and plot the absorbance against concentration.

12.7.2.4 Kinetics of leaching

Weigh out 0.50 g of the reduced powder, shake for a known time say 10 minutes at 25°C with 10.0 cm^3 freshly prepared 0.27 M $Na_4P_2O_7$ solution whose pH is adjusted to 6.0. Filter through Whatman GF/F and Nu Flow (47μm) membrance filter and measure the absorbance of the filtrate at 480 nm in a 20 mm or 2 mm cell. Repeat using increasing shaking times up to 100 minutes. From the Beer's law plot obtained above, calculate the Mn(III) concentration. Using the calculated Mn(III) content of the reduced powder, calculate the percentage of Mn(III) leached and plot it against the square root of time. Repeat the run but carrying out the reduction slowly eg by allowing the hydrazine solution to drip from a separating funnel over a period of 3 days. Compare the two results and comment on their significance.

12.7.2.5 The oxidation of Cr(III) to dichronate by manganese dioxides
(J.Inorg. Nucl. Chem. 39 (1977) 1081).

When a manganese dioxide was shaken with a Cr(III) solution at 65°C, the solution turned gradually green. Passing the filtrate through a cation-exchange resin or an anion-exchange resin showed that the green colour was a mixture of dichromate with the original solution.

Separating the products of the reaction of MnO_2 with $Cr^{3+}(aq)$

Prepare a column of a resin (H^+ form, 50-100 mesh). You can use a 50 cm^3burette whose stopper was broken and replaced by a tapering glass tube connected to the burette by a short rubber or Tygon tubing provided with a metal clip. Clean the column thoroughly before filling with distilled water. Push a small glass wool plug down the column with a glass rod. Run the water to about 30 cm^3 level. Make a slurry of the resin and water and pour the slurry until the level is about the 30 cm^3 mark. Rinse with water keeping the height of the liquid at the same level as the resin and never allow the liquid to be below that level.

To 2.0 g of MnO_2 (preferably of γ type) in a round bottom centrifuge tube, add 15 cm^3 of 0.5 M solution of $KCr(SO_4)_2.12H_2O$ whose pH is adjusted to 2.0 and heat in a water bath at 65°C for 60-80 minutes. When cold, centrifuge and filter the suspension. Put 10 cm^3 of the filtrate into the column and allow the liquid out at the rate of 50 drops per minute. Collect the coloured fraction and run its absorption spectrum over the range of 300-600 nm. After the liquid level reaches the resin level, add 10 cm^3 of dilute HCl and elute as above and run the spectrum of the coloured fraction in the range 350-650 nm. Comment on your results.

The kinetics of oxidation

Repeat the above procedure using 0.3 M solution and a time of shaking at a constant rate for 10 minutes. To exclude the possibility of the effect of O_2, purge with nitrogen by using a bung with a gas inlet and a gas outlet. When the tube is cold, centrifuge, filter and measure the absorbance of the filtrate at 350 nm. Repeat at different times say 20, 30, 40, 60 and 80 minutes.

Calculate the percentage of Cr oxidised or the concentration of Cr(III) at each time and plot against time. Repeat using at least two other temperatures. Repeat using a solution at pH 3.0. Repeat using another type say βMnO_2. Draw conclusions from your results.

12.7.2.6 Investigation the reaction of manganese dioxide and ascorbic acid solution

Stoichiometry of the reaction

Weigh out accurately portions of battery-active MnO_2 in the range 0.4-4.5 g into 100 cm^3 conical flasks fitted with rubber bungs and tubes to allow circulation of nitrogen, add 25.0 cm^3 of freshly prepared purest ascorbic acid in boiled-out water and 2.0 cm^3 of dilute HCl (the solutions of the ascorbic acid should be in the range 0.1-1.0 M such that there is an excess of MnO_2 in the flasks). Place the flask in a shaking thermostat at 25°C and shake for 30 minutes, while bubbling nitrogen. Then filter through a weighed prepared No.4 sintered crucible, wash thoroughly with distilled water. Collect the filtrate and washings in a conical flask and titrate with freshly prepared and standardised manganese (III) solution (as in Sec.12.4.1). Calculate the amount of ascorbic acid solution consumed. Dry each crucible to constant weight at 105°C and calculate the amount of MnO_2 consumed in the reaction. Find the molar ratio as ascorbic acid:MnO_2.

12.7.2.7 Kinetics of the reaction

Use the apparatus shown in Fig.2.1 provided with gas inlet and outlet, a sintered stick and a thermometer. Deliver 200 cm^3 of freshly-prepared 0.025 M ascorbic acid into the beaker containing 2.00 g manganese dioxide. Circulate water from a thermostat at 7°C prior to the experiment, keeping the suspension purged with nitrogen and magnetically stirred throughout. At intervals, withdraw an aliquot through the filter and pipette 2-5

cm^3, quench in an ice/salt bath and titrate as soon as possible with the standardised Mn(III) solution. Repeat at three or more temperatures up to 30°C. From the titration results, calculate the concentration of ascorbic acid at each time. Plot the function $\chi/a(a-\chi)$, against time where a is the initial concentration $(a-\chi)$ is the concentration at time t (χ is the difference between the two). A linear plot indicates second-order kinetics in ascorbic acid. From the rate constants at various temperatures, calculate the activation parameters.

Repeat one of the runs, say that at 20°C using ascorbic acid solution freshly prepared in boiled-out 0.01 M HCl and comment on the effect of the acid on the rate of reaction.

12.7.1.8 Isolation and identification of a solid product

Prepare freshly 1.0 M ascorbic acid solution. Pipette 50.0 cm^3 of this solution into a container provided with gas inlet and outlet, the former tube ending in a sintered disc. Purge the solution with nitrogen after adding 5.0 cm^3 conc. HCl. Add slowly MnO_2 until a slight excess remains after most of it has dissolved. Remove the excess by adding a minimum of solid ascorbic acid. Continue bubbling oxygen-free nitrogen until a solid separates out. Filter under suction. Wash on the filter with 20 cm^3 aliquots of water, then ethanol and finally ether. Dry by continued suction while pressing between filter paper.

Add syrupy phosphoric acid to a little of your product and heat with diphenylamine. Heat carefully and observe any colour changes.

Run an infrared spectrum of your product and compare it with that of reagent manganese (II) oxalate dihydrate.

Submit a sample of your product to elemental analysis and obtain a mass spectrum.

12.7.2.9 Kinetics of the MnO_2-catalysed decomposition of aqueous H_2O_2

Although the decomposition of hydrogen peroxide to water and oxygen, is thermodynamically feasible, its solution can be kept without decomposition at low temperature and in absence of catalysts. One of the efficient catalysts is manganese dioxide. The kinetics of the catalysed decomposition can be studied by following the volume of oxygen liberated.

Preparation and determination of $[H_2O_2]$

Dilute 10.0 cm^3 of 50 volume H_2O_2 to a 100 cm^3. Dilute an aliquot of this solution 10-fold. Pipette 25.0 cm^3 of the final solution, freshly prepared, into a conical flask. Add a few drops of ferroin indicator and titrate against 0.1 M standardised cerium (IV), sulphate. Repeat and calculate from the average titre the concentration of hydrogen peroxide.

Kinetic runs

Use the method described above for the reduction by hydrazine, replacing hydrazine solution by 20.0 cm^3 of H_2O_2 solution, prepared by 4-fold dilution of 20-volume H_2O_2. Check the chart speed compatible with the faster gas evolution in this case. Repeat using different samples and choose one sample of battery-active dioxide and prepared doped powders and study the effect of doping on the kinetics.

12.7.2.10 The exchange between water in battery active MnO_2 and D_2O

Water plays an important role in the depolarising activity of battery-active MnO_2. The exchange between water in the solid and water in the surroundings can be studied by using isotopic D_2O.

Determination of the percentage D_2O in aqueous solution
(Anal. Chem. **22** (1950) 690).
Prepare a series of aqueous solutions containing 1-5% (w/v) of heavy water and measure the transmission of each solution at 3.98 μm using a cell with fluorite windows. Plot the transmissions against % D_2O.

Rate of exchange with MnO_2
Use a battery-active sample eg I.C.S.5 and determine the loss in weight on heating at 120°C and on heating at 450°C. Weight out accurately 0.50 g portions of the powder in a tube provided with a standard joint. Add 3.0 cm^3 water, 0.06 cm^3 0.01 M HCl and 2.0 cm^3 D_2O. Shake in a thermostat at 35°C for a given period. Centrifuge, discard the liquid and wash the solid with water. Connect the tube via the joint to a vacuum line, cool with liquid nitrogen and evacuate for some time (1-2 hours). Connect the tube to an isolated section of the vacuum line containing a calibrated bulb cooled with liquid nitrogen. Heat the solid in the original tube to 450°C using a heating coil and collect the water liberated from it in the cooled bulb until no more is evolved.

Seal off above the calibration mark, break the sealed top, make up to the mark with water and measure as above to determine the percentage of D_2O and hence calculate the percentage of combined water in the solid exchanged with heavy water. Repeat using increasing shaking times and plot the % water exchanged against the square root of time and comment on the plot.

12.8 STUDIES OF PERMANGANATES

Potassium permanganate solutions are common oxidants. Due to the strong colour of the solution, it acts as a self indicator. The titrations with permanganate are conducted in liberally acidified solutions, when permanganate is reduced to Mn(II). If [acid] is insufficient, reduction to colloidal dioxide is observed and can be overcome by adding acid to dissolve it. Permanganate solutions are usually standardised against oxalate. Although the reaction is catalysed by Mn(II) ions initially formed, the titrations should be carried out at 70°-80°C.

In presence of semiconductor powders, suspended in permanganate solution, uv irradiation was found to lead to reduction by electrons promoted to the conduction band of the catalyst. Presumably reduction produces manganate (VI). This however disproportionates to permanganate and manganese dioxide.

12.8.1 The role of the Catalyst in the Permanganate/Oxalate Titration

The catalytic effect of Mn(II) ions in the reaction was found to be related to oxalato-manganese complexes involved in the catalytic cycle. Since, V also forms oxalato-complexes in the +2, +3 and +4 oxidation states, it was thought that vanadium ions may also catalyse the reaction.

Prepare ~0.02 M permanganate solution as usual. To 25.0 cm^3 of standard 0.05 M oxalate, add a few drops of the permanganate from a burette. Heat to 80°C and continue to titrate to the usual end point. Repeat but add a drop of V(II) or V(III) sulphate solution (Sec.10.2.3) to the oxalate solution and add from a burette the permanganate solution without heating. After each drop shake well and allow time for the permanganate colour to disappear before adding the next drop. When only a faint colour remains after standing record the volume used and compare it with the volume used in the initial titration. Comment on your results.

12.8.2 The Photocatalysed Decomposition of Aqueous Potassium Permanganate

Weigh out accurately two 0.300 g of anatase into two petri dishes (7 cm diameter). Pipette 50.0 cm^3 of 0.002 M $KMnO_4$ solution into each petri dish. Prepare this solution by 10-fold dilution from 0.02 M $KMnO_4$ (filtered through glass wool and standardised). Stir magnetically the suspensions, at a constant speed and irradiate under a low pressure mercury lamp for 30 minutes in marked reproducible positions. Measure the pH of the 0.002 M $KMnO_4$ solution before irradiation.

After irradiation, filter the suspensions quantitatively through a weighed G4 sintered glass crucible (previously dried to constant weight at 120°C). Collect the filtrate in a clean dry Buchner flask and measure its pH without discarding any liquid (ie the volume used for pH measurement should be returned to the Buchmer flask. Then complete the quantitative transfer of the precipitate to the crucible and quantitatively make up the filtrate and washings to 200 cm^3 in a volumetric flask. To a 50.0 cm^3 aliquot of the final solution, add a known excess of standard $Na_2C_2O_4$ solution (50.0 cm^3 of 0.005 mol dm^{-3}, made up by 10-fold dilution of a standard 0.05 M solution, used to standardise $KMnO_4$ solution). Titrate with 0.002 M $KMnO_4$ solution, after acidifying with dilute H_2SO_4 (50 cm^3) and heating to 80°C (the temperature should be > 70°C at the end-point).

Carry out duplicate titrations. Calculate the amount (ie mols) of $KmnO_4$ decomposed.

Wash the precipitate on the crucible until the washings are not coloured and then dry the crucible to constant weight at 105°C. Compare the mass of MnO_2 obtained in the reaction (ie mass of residue on crucible - 0.600) with the amount of $KMnO_4$ decomposed and the change in pH observed.

Carry out a blank experiment by repeating the procedure without using a solid. After irradiation, filter through filter paper. The result of the titration gives the uncatalysed reaction and should be subtracted from the result obtained previously.

Repeat using other photocatalysts eg ZnO, rutile and compare the efficiency of the different catalysts.

To study the kinetics of the reaction, using purest ZnO as above but irradiate for different periods eg 10, 20, 40 and 60 minutes. Plot log $[MnO_4^-]$ decomposed against time and comment on the results.

Repeat keeping all the conditions constant but varying the amount of catalyst and plot the mols MnO_4^- decomposed hr^{-1} against mass of ZnO.

Repeat one experiment adjusting the initial pH of the $KMnO_4$ to 2.0 and observe the effect of pH. Comment on your results.

13

Iron

13.1 INTRODUCTION

The chemistry of iron is less extensive than that of manganese. After group 7, transition metals become reluctant to achieve high oxidation states. The common oxidation states of iron are +2, +3 and +6. The latter is only stable as the tetrahedral $[FeO_4]^{2-}$ in alkaline solution and quickly liberate O_2 at lower pH values. Iron (II) is represented by the non-stoichiometric oxide and numerous salts and complexes. Although it has a d^6 configuration, most of its complexes are high spin. Only strong ligands such as cyanide, bipyridyl and phenanthroline give low spin diamagnetic octahedral complexes. Iron (II) chloride or sulphate solutions are slowly oxidised in air. On the other hand, iron (III) solutions are mild oxidants unlike their neighbours Mn(III) and Co(III) which are powerful oxidants. This contrast may be associated with the d^5 configuration, exactly ½ filled t_{2g} and e_g levels in high spin octahedral environment or in tetrahedral complexes. Ligands with strong ligand fields cause spin-pairing. Complexation also affects the Fe(III)/Fe(II) reduction potential. Generally iron (III) complexes are more stable than iron (II) complexes but the reverse is the case for complexes such as those with bipyridyl and phenanthroline, where π bonding is involved. The diamagnetic ferrocene is a clear example of organometallic compounds. Of the oxides of iron, α- and γ- Fe_2O_3 and their hydrated forms are the most important besides the mixed valence magnetic oxide Fe_3O_4. Ligands capable of π bonding stabilise oxidation states lower than 2.

13.2 QUALITATIVE TESTS

13.2.1 Iron(II) compounds

(a) Heat in a dry test tube a few crystals of $FeSO_4.7H_2O$ and expose to any gases: a blue litmus paper and an acidified dichromate paper.

(b) Heat in a dry test tube a little Fe(II) carbonate and test for any gas.

(c) Repeat using Fe(II) oxalate and test for any gas(es) with lime water and palladium (II) chloride.

(d) To separate portions of a solution of iron (II) sulphate or chloride, add:
   (i) a solution of NaOH, check the solubility of any precipitate in excess of the reagent and then add a little hydrogen peroxide;
   (ii) acidified persulphate solution, allow to stand for minutes and then add thiocyanate solution;
   (iii) a solution of hexacyanoferrate (III);
   (iv) a solution of hexacyanoferrate (II);
   (v) a solution of a thiocyanate;
   (vi) acidified dichromate.

13.2.2 Iron (III) compounds

(a) Heat in a dry test tube a few crystals of iron (III) sulphate and test with blue litmus;

(b) Heat a little iron (III) nitrate with a glass wool plug near the top and test with a glowing splint and with blue litmus;

(c) To separate portions of an acidified solution of iron (III) chloride or sulphate, add the reagents as in (i), (iii)-(v) above.

(vi) Kl solution and test with a starch paper;
(vii) Sn(II) chloride solution;
(viii)neutralise before adding an acetate solution.

13.2.3 Hexacyano-complexes

(a) Heat iron (II) complex crystals carefully after adding a little conc. sulphuric acid, test for any gas(es) with palladium (II) chloride and acidified dichromate:*

(b) Add to separate portions of the solution of the complex:
  (i) silver nitrate solution and then a little conc. nitric acid and carefully heat;
  (ii) copper sulphate solution;

(c) Repeat all the above using the iron (III) complex.

13.3 ANALYTICAL CHEMISTRY OF IRON

The standard reduction potential of iron (III) /(II) in acid solution is:

$$Fe^{3+} + e \leftrightharpoons Fe^{2+} \qquad E^{o} = 0.77\ (pH = 0) \qquad (13.1)$$

For any redox couple whose E^{o} is appreciably more positive, the oxidant will oxidise Fe(II) to Fe(III) and for couples whose E^{o} is less positive, or negative, the reductant of the couple will reduce Fe(III) to Fe(II). However, E^{o} for Fe(III)/Fe(II) changes when the ions are complexed or when the solutions have higher pH values. Thus for the hexacyano-complexes, E^{o} is given by:

$$[Fe(CN)_6]^{3-} + e \leftrightharpoons [Fe(CN)_6]^{4-} \qquad E^{o} = 0.36V(pH=0) \qquad (13.2)$$

The simple titrations of iron (II) or (III) ions use redox titrations but because of their redox nature, potentiometric or other electrochemical methods may be as useful.

When complexed with bipyridine or phenanthroline, strongly coloured complexes of Fe(II) or Fe(III) are formed. These are the basis of spectrophotometric methods of their determination.

Gravimetric analysis is usually carried out by precipitating Fe(III) in alkaline media and weighing the precipitate after heating to form iron (III) oxide. Precipitation is preceded by oxidation when the original solution is that of iron (II).

13.3.1 Titrimetry of iron (II)

Solutions of iron (II) salts are slowly oxidised in air. Hence solutions should be freshly prepared in boiled-out water and stored in an inert atmosphere (Sec.9.2.3). However, hexacyanoferrate (II) solutions are more stable.

Determination of Fe(II) using standard dichromate

E^{o} for dichromate/Cr(III) is given by:

$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \leftrightharpoons 2Cr^{3+} + 7H_2O \qquad E^{o} = 1.33V(pH = 0) \qquad (13.3)$$

Hence iron (II) solutions can be titrated against standard potassium dichromate solution. Because of the high purity of the purest solid, it can be considered as a primary standard. Solutions are made up by weighing the finely ground solid and making up in a volumetric flask. A redox indicator is necessary for dichronate titrations.

Pipette 25.00 cm^3 of the ~ 0.1 M iron (II) solution, add 5 cm^3 of 1:1 H_3PO_4 solution and 0.5 cm^3 of diphenylamine sulphonate indicator solution. Titrate with standard M/60 dichromate solution until the colour changes sharply from green to dark violet. Repeat to obtain concordant results and calculate from the average titre the concentration of Fe(II) in g dm^{-3} of solution.

Determination of Fe(II) by titration against standardised Ce(IV) sulphate solution
The standard reduction potential for Ce(IV)/Ce(III) is given by:

$$Ce(IV)+e \rightleftharpoons Ce(III) \qquad E^{o}=1.44V(pH=0) \qquad (13.4)$$

This shows that Ce(IV) will oxidise Fe(II) but unlike dichromate, Ce(IV) compounds are not usually available as highly pure solids. However, technical grade ammonium cerium (IV) nitrate can be recrystallised and the purified crystals dissolved to give a solution. This, however, has to be standardised by titration against $K_4[Fe(CN)_6]$. The purest salt can be considered as a primary standard. The value of E^0 depends on the nature of the anion.

Recrystallisation of technical ammonium cerium(IV) nitrate
Recrystallise 25 g of the solid by warming with 20 cm^3 of HNO_3 (1:3 by volume) and 8 g NH_4NO_3 until dissolved, filtering the boiling solution if necessary through glass fibre GF paper in a Buchner funnel and cooling the filtrate in ice. Filter the solid which separates through GF paper at the pump and continue suction for 1-2 hours to remove HNO_3. Dry at 80°-85°C in an oven. Weigh your product to the nearest cg and note your % recovery.

Preparation of 0.1 M cerium(IV) sulphate
Dissolve about 14 g of dry recrystallised cerium(IV) ammonium nitrate in 50 cm^3 water in a 400 cm^3 beaker, add dil. ammonia solution slowly and with stirring until a slight excess is present (~ 30 cm^3 of 2.5 M NH_3 solution are required). Filter the precipitated cerium(IV) hydroxide with suction through GF paper and wash with five 25 cm^3 portions of water to remove ammonium nitrate; leave the precipitate under suction for 30 minutes. Transfer the precipitate back to the original beaker as far as possible and remove the residual cerium(IV) hydroxide on the filter by washing with four 25 cm^3 portions of 2 M H_2SO_4 previously warmed to 60°C. Add the washings to the precipitate in the beaker and warm until the precipitate dissolves completely. Allow to cool, transfer the solutions to a 250 cm^3 volumetric flask and make up to the mark with distilled H_2O. The solution should be ~ 0.1 M $Ce(SO_4)_2$.

13.3.1.1 Standardisation of 0.1 M $Ce(SO_4)_2$ solution with potassium hexacyanoferrate(II)

Pipette, using a safety pipettor, 25.00 cm^3 of standard 0.1 M solution of $K_4[Fe(CN)_6]$ into a conical flask. Add 75 cm^3 dil. H_2SO_4 and 0.5 cm^3 N-phenylanthranilic acid indicator. Titrate with the $Ce(SO_4)_2$ solution to the first sharp colour change from colourless to violet/red. Repeat the titration to obtain concordant results. Calculate from the average titre the molarity of $Ce(SO_4)_2$.

13.3.1.2 Determination of Fe(II) in solution

Pipette 25.00 cm^3 of the Fe(II) solution, previously prepared as described above, into a conical flask. Add 20 cm^3 dil. H_2SO_4, 15 cm^3 H_2O and 2 drops ferroin indicator. Titrate with the standardised $Ce(SO_4)_2$ solution until the colour changes sharply from orange red to a pale blue. Repeat the titration to obtain concordant results. Calculate, from the average titre, the concentration of Fe^{2+} in g dm^{-3}.

13.3.2 Titrimetric determination of Fe(III)

The reduction potential of the Sn(IV)/Sn(II) couple in acid solution, although not know precisely, shows that Sn(II) is likely to reduce Fe(III) to Fe(II) but $SnCl_2$ solutions are not very stable and are kept in contact with Sn. However, when an excess of $SnCl_2$ solution is added to an Fe(III) solution, it reduces it to Fe(II). Before this is titrated eg against dichromate, the excess Sn(II) has to be removed by reaction with $HgCl_2$ solution carefully when the excess Sn(II) is removed as can be seen by the formation of Hg(I) chloride precipitate.

$$2HgCl_2+SnCl_2 \rightarrow SnCl_4+Hg_2Cl_2(s) \qquad (13.5)$$

Weigh out 8 g purest iron(III) chloride hexahydrate, into a 400 cm^3 beaker. Add water containing a few cm^3 conc. HCl and dissolve by stirring. Transfer to a volumetric flask and make up to 250 cm^3. Pipette a 25.0 cm^3 aliquot into a 250 cm^3 conical flask, add 3 cm^3 conc. HCl and then add, dropwise 0.25 M tin(II) chloride solution until the yellow colour just disappears and then gradually add a saturated mercury(II) chloride solution to remove the excess tin(II) when a slight silky mercury(I) chloride is formed. Allow to stand for a minute, add 5 cm^3 of orthophosphoric acid, a few drops of N-methyldiphenylamine indicator and titrate with standard M/60 dichromate solution as above.

13.3.2.1 Titrimetric determination of Fe(II) together with Fe(III)

When the solution of the mixture is titrated against standard dichromate solution, only Fe(II) reacts, being oxidised to Fe(III). However, when an identical aliquot is treated with $SnCl_2$ solution as above and then titrated against the same dichromate solution, the titre gives the combined Fe(II) and Fe(III). The latter can be calculated from the difference between the two titres.

Using purest solids, weigh out accurately ~ 9.80 g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ and ~ 6.03 g $(NH_4)Fe(SO_4)_2.12H_2O$, acidify with dil. sulphuric acid and make up to 250 cm^3 in a volumetric flask.

Prepare a standard dichromate solution by weighing accurately between 0.9 and 1.1 g of the dried purest potassium dichromate and making up to 250 cm^3 with water.

Pipette 25.00 cm^3 of the iron solution, add 5 cm^3 of orthophosphoric acid, 50 cm^3 of water and a few drops of sodium N-methyldiphenylamine sulphonate indicator solution and titrate with the dichromate solution until the end-point is marked by the appearance of a blue-violet colour. Repeat to obtain concordant results.

To another 25.00 cm^3 of solution, add 3 cm^3 of concentrated hydrochloric acid, then heat to boiling. Add 0.25 M aqueous tin(II) chloride solution dropwise until the yellow colour of the iron(III) is just discharged. Cool the solution rapidly under the tap and add immediately 5 cm^3 of a saturated solution of mercury(II) chloride, to remove the excess of tin(II). A slight, silky, precipitate of mercury(I) chloride should have formed: if the precipitate is dense grey, or black, reject the sample and commence again. Otherwise allow the mixture to stand for one minute, then add 5 cm^3 of the orthophosphoric acid, 50 cm^3 of water, the indicator solution, and titrate with the standard dichromate. Repeat to obtain concordant results. Calculate the concentrations of Fe(II) and Fe(III) in mol dm^{-3}.

13.3.2.2 Titrimetric determination of hexacyanoferrate(III)

Although the reaction of hexacyanoferrate(III) and iodide is reversible, it proceeds quantitatively in presence of slightly acidified Zn(II) solution due to the formation of the sparingly soluble $K_2Zn_3[Fe(CN)_6]_2$.

Weigh out accurately ~ 8.2 g purest $K_3[Fe(CN)_6]$ into a beaker, dissolve in water and transfer quantitatively to a volumetric flask and make up to 250 cm^3. Pipette 25.0 cm^3 of the solution into a 250 cm^3 conical flask. Add ~ 2 g KI dissolved in 20 cm^3 water and 15 cm^3 of a solution containing 2 g $ZnSO_4.7H_2O$. Note the liberation of iodine. Titrate immediately with standardised 0.05 M thiosulphate solution until the colour is pale yellow. Then add 2 cm^3 of freshly prepared starch solution and continue titration until the blue colour has just disappeared. Repeat to obtain concordant results. Calculate from the average titre the concentration of hexacyanoferrate(III) in mol dm^{-3}.

13.3.3 Spectrophotometric determination of Fe(II) and Fe(III)

Iron(II) forms a red complex with 1,10-phenanthroline (phen) in slightly acidic solution, according to:

$$Fe^{2+} + 3\ \text{phen} \rightleftharpoons [Fe(\text{phen})_3]^{2+} \qquad (13.6)$$

Use purest ammonium iron(II) sulphate and prepare a stock 10^{-2} M solution freshly using boiled-out water (slightly acidified). Prepare acetic acid/acetate buffer of pH~ 4.5 (65% 0.1 M acid: 35% by volume 0.1 M acetate). Prepare by successive dilution, using the buffer solution for dilution, a series of Fe(II) solutions in the range: 2×10^{-5} - 2×10^{-4} M. Run the spectrum of the latter solution after adding 0.25% solution of the monohydrate of purest phenanthroline dissolved in the buffer solution. Use 10 cm^3 of the Fe(II) solution and add 5 cm^3 of the buffer solution + 2 cm^3 of phenanthroline solution and make up to 20 cm^3. Locate the wavelength of maximum absorption and measure the absorbance at 396 nm. Repeat using three or four more dilute solutions and check the applicability of Beer's law (Sec.2.4.1).

Choose one of the above solutions and dissolve in it a weight of purest ammonium iron(III) sulphate to give an equal concentration to the iron(II) and react it with phenanthroline as above and measure the absorbance at 396 nm. Draw your conclusions.

13.3.4 Gravimetric determination of iron

Weigh out accurately ~ 5 g of purest ammonium iron(II) sulphate, dissolve in some water, add 50 cm^3 conc. HCl and make up to 500 cm^3. Pipette 50.0 cm^3 of the solution into a beaker and heat to boiling. Add 2 cm^3 conc. nitric acid and boil for a few minutes. After diluting to ~ 300 cm^3 boil again and add slowly, with constant stirring, 1:3 ammonia solution until excess has been added, indicated by mercury(I) nitrate paper.

Boil for a few minutes to coagulate the precipitate. Discontinue heating and allow the precipitate to settle. Decant the supernatant through No.54 Whatman paper. Wash by decantation with hot 1% solution of ammonium nitrate three times. Transfer the precipitate quantitatively to the filter paper, using a "policeman" and a hot water wash bottle. Wash with hot water until the washings indicate that all chlorides have been removed. After thorough drainage, fold over the edges of the filter paper and transfer to a weighed clean silica crucible with a cover. Dry the paper by placing the crucible several cm's above a small flame. Gradually increase the heat until the paper chars. Then raise the temperature to dull redness and burn off by displacing the cover and keeping the crucible slightly inclined. Ignite for 10 minutes when all the carbon should be burnt off. Final ignition may be carried out in a muffle furnace at 550°C until constant weight is attained. Duplicate determinations are required. Calculate from each result, the concentration of Fe(II) in the original solution in g dm^{-3}.

Modification for Fe(III) solutions
Weigh out accurately ~ 6 g of purest ammonium iron(III) sulphate and dissolve in water, acidify with dil. HCl to prevent hydrolysis and make up to 500 cm^3. Pipette 50.0 cm^3 of the solution into a beaker, add 20 cm^3 1:1 HCl, dilute to 200 cm^3 and heat to boiling. Add slowly the ammonia solution and continue as above. Repeat using another aliquot of the solution. Calculate the concentration of Fe(III) in g dm^{-3}.

13.4 SPECTRAL AND MAGNETIC STUDIES

13.4.1 Fe(II) compounds

Fe(II) complexes have a d^6 configuration and may be of high spin in octahedral ligand field. This will be reflected in their d-d absorption spectra and in their magnetic moment. The latter indicates 4 unpaired electrons. The d-d spectrum is expected to exhibit one band, whose position depends on the ligand's position in the spectrochemical series. However with strong ligands eg in hexacyanoferrate(II), the absorption spectrum shows 3 bands and the compound is diamagnetic.

Grind purest ammonium iron(II) sulphate into a fine powder and measure its magnetic moment by the Evans method (Sec.2.1.3).

Prepare a solution of iron(II) perchlorate by dissolving purest barium perchlorate in 1 M perchloric acid, warm gently to remove carbon dioxide bubbles. Add slowly with stirring 0.1 M solution of $(NH_4)_2SO_4.FeSO_4.6H_2O$ until precipitation is complete. Filter through G4 sinter and collect the filtrate in a clean conical flask. As soon as possible fill a 1 cm spectrophotometer cell with the solution, stopper the cell and record the spectrum over the range 800-350 nm.

Grind purest potassium hexacyanoferrate(II) and measure its magnetic moment by the Gouy method (Sec.2.1.3).

Prepare 0.03 M solution of potassium hexacyanoferrate(II) and dilute 25.0 cm^3 to 250 cm^3. Record the spectrum in a 2 cm cell between 800 and 300 nm. Dilute 10 cm^3 of the solution to 100 cm^3 and record the spectrum between 300 and 250 nm. Dilute an aliquot of the latter solution 10-fold and record the spectrum at the shorter wavelengths. Compare these spectra with the previous spectrum.

13.4.2 Fe(III) compounds

High spin octahedral iron(III) complexes have a $(t_{2g})^3(e_g)^2$ configuration and their magnetic moment shows 5 unpaired electrons. Their d-d spectra, like those of Mn(II) have very weak bands. However, low spin complexes eg hexacyanoferrate(III) have one unpaired electron. Its absorption spectrum shows that its d-d bands are superimposed on charge transfer bands.

Grind purest ammonium iron(III) sulphate to a fine powder and measure its magnetic moment. Repeat using potassium hexacyanoferrate(III).

Prepare a concentrated acidified solution of iron(III) nitrate or ammonium iron(III) sulphate and record the absorption spectrum in a 4 cm or 10 cm cell over the range 350-850 nm.

Prepare a 0.05 M solution of potassium hexacyanoferrate(III) and dilute 10 fold after acidifying slightly. Record the absorption spectrum over the range 350-650 nm. Dilute 5 fold and record the spectrum over the range 200-350 nm. Comment on your results.

13.5 SURFACE CHEMISTRY OF α-IRON(III) OXIDE

13.5.1 Preparation and characterisation of α-iron(III) oxide

This oxide is the best characterised oxide of iron and can be readily prepared from iron(III) chloride solution by precipitation with ammonia when the hydrous oxide or hydroxide is formed. This can be converted to α-iron(III) oxide by roasting. It can be characterised by one or more of the techniques described in Sec.2.1.

Prepare a 0.1 M solution of iron(III) chloride acidified with nitric acid. By the slow addition of ammonia to the boiling solution, as in Sec.13.3.4, precipitate the hydroxide or hydrous oxide, wash thoroughly and dry at 110°C. Then roast at 550°C in a muffle furnace. Grind a portion to a very fine powder and submit to XRD and compare the pattern with that of α-Fe_2O_3. Obtain a thermogravimetric curve for the 110°C dried powder. Carry out a BET surface area determination on the final product.

Determination of PZZ of α-Fe_2O_3

Measure the electrophoretic mobility of a very dilute suspension of the very fine particles suspended in 10^{-3} or 10^{-3} M sodium chloride solution over the pH range 2 to 10 and hence find PZZ. Refer to sec.2.1.4 for details.

Effect of phosphate on PZZ

Using a supporting electrolyte of 10^{-2} M in sodium chloride and in *ortho*-phosphate, measure the mobility of the particles over a pH range 5.5-10. Comment on the plot mobility/pH in this case, compared to the plot obtained without phosphate.

Adsorption of phosphate on α-iron(III) oxide

Prepare a stock solution of 0.05 M K_2HPO_4 in 0.1 M sodium perchlorate. By successive dilution using the perchlorate for dilution, prepare 2.5, 1.0, 0.5, 0.25 and 0.125 x 10^{-4} M solutions of phosphate. Adjust the pH of each solution to 6.0 using a pH meter. Equilibrate 1.00 g of your iron oxide with 25.0 cm^3 of 0.1 M perchlorate in a round bottom centrifuge tube for a few hours. Centrifuge and carefully withdraw 20.0 cm^3 of the clear supernatant replacing it by 25.0 cm^3 of one of the phosphate solutions. Equilibrate in a shaking thermostat for 4 hours, maintaining the temperature at 35°C. Repeat using the other phosphate solutions. In each case, centrifuge and determine [phosphate] by the vanadomolybdate method (Sec.6.10.3). Calculate the amount adsorbed g^{-1} and plot against the equilibrium concentration. Repeat all the above, adjusting the pH to 7.0,8.0,9.0 or 10.0.

Compare the adsorption isotherms by plotting them together for the different pH values. Comment on these results with reference to the electrophoretic mobility at different pH values.

13.6 OXALATE COMPOUNDS

13.6.1 Preparation and analysis of iron(II) oxalate

This compound is precipitated when an iron(II) salt solution is mixed with oxalic acid. When dissolved in acid and titrated with permanganate, the latter oxidises both iron(II) and oxalate. If then the titrated solution is reduced by zinc amalgam to regenerate Fe(II), the latter is then determined by titration with the same permanganate solution.

13.6.1.1 Preparation.

Dissolve 15 g of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in 50 cm^3 of warm distilled water, add 1 cm^3 dil. H_2SO_4. To the well stirred solution, add 75 cm^3 of a solution containing 7.5 g $H_2C_2O_4.2H_2O$. Cautiously heat the mixture to the boiling temperature, avoiding shaking and then allow the precipitate to settle. Decant the clear liquid (without transferring the solid) through a filter. Stir the precipitate with 50 cm^3 hot distilled water and again decant the clear supernatant liquid. Then filter the precipitate on a Buchner funnel by suction. Wash the precipitate with hot water thoroughly and then with acetone (No flames!). Dry by continued suction and pressing between filter paper while applying suction. Record the weight of your product. Calculate the percentage yield based on iron.

13.6.1.2 Analysis

Dissolve 0.2 g of your product in 25 cm^3 of dil. H_2SO_4 and warm slightly. Add standardised ~ 0.02 M $KMnO_4$ solution from a burette until the liquid assumes a brown colour. Then heat to 80°C and continue titration to the first faint permanent pink colour (the temperature should be ~ 70°C at the end point). The titre is due to the oxidation of both Fe(II) and $C_2O_4^{2-}$. Repeat and, from the average, calculate the percentage purity of your product.

Amalgamate ~ 100 g of zinc shot by covering with 2% mercury(II) chloride solution and stirring for 10 minutes. Decant the solution from the zinc and wash three times with water by decantation until Cl^--free. Add the solid to the titrated solution obtained above and heat on a water bath for half an hour until a drop of the solution, when mixed with a drop of thiocyanate solution, produces only a faint pink colour. Then cool the mixture, filter through glass wool and wash with dilute sulphuric acid by decantation, collecting the filtrate and washings in a conical flask. Then titrate with the same permanganate solution. Repeat and calculate the percentage of iron in your preparation and hence its percentage purity and compare the results with those obtained above.

13.6.2 Preparation and analysis of $K_3[Fe(C_2O_4)_3].3H_2O$

Many metal ions form complexes with oxalate ions. These are generally anionic complexes, in which the oxalate is coordinated to the metal by its two oxygens ie it acts as a bidentate or chelate ligand. Thus the complexes are stabilised by the chelate effect.

Iron(III) forms a trisoxalato-complex which can be precipitated as the potassium salt, by mixing $FeCl_3$ solution with $K_2C_2O_4$ solution:

$$Fe^{3+}+3C_2O_4^{2-}\rightarrow[Fe(C_2O_4)_3]^{3-} \text{ (molar ratio 1:3)} \quad (13.7)$$

The complex is high spin and is expected to exhibit optical isomerism.

13.6.2.1 Preparation.

Mix, with constant stirring, 45 cm^3 of the 1.5 M solution of potassium oxalate with 15 cm^3 of 1.5 M $FeCl_3$ solution. Scratch the sides of the container while cooling in an ice bath, when green crystals of $K_3[Fe(C_2O_4)_3].3H_2O$ separate. When crystallisation appears complete, filter through a Buchner funnel. Wash with an equivolume mixture of water and ethanol and finally with acetone. Dry by continued suction while pressing between filter paper.

Weigh your product and calculate the percentage yield based on oxalate. The solid and its solution are sensitive to light; and should be stored in dark glass.

Oxalato-complexes of metals, when heated with H_2SO_4, generally react with $KMnO_4$ solution and can be titrated with standardised $KMnO_4$:

$$2MnO_4^-+5C_2O_4^{2-}+16H^+\rightarrow 10\,CO_2+2Mn^{2+}+8H_2O \quad (13.8),$$

$KMnO_4$ acts as a self indicator.

13.6.2.2 Analysis.

Weigh out accurately about 0.2 g of your product and dissolve it in 50 cm^3 dil. H_2SO_4. Heat the solution nearly to boiling (80°C) and titrate with standardised 0.02 M $KMnO_4$ solution to the first permanent faint pink colour. The temperature should be 70°-80°C during the titration. Repeat and calculate from each result the percentage $C_2O_4^{2-}$ in your sample and hence its average percentage purity.

Add to the titrated solution after heating to boiling, Zn dust in small amounts until the colour is discharged. Continue heating for two minutes. Filter and wash the filter paper, collecting the filtrate and washings in a conical flask. Cool the solution and immediately titrate with the permanganate solution. Repeat to obtain concordant results. Calculate the percentage iron in your product and hence its percentage purity.

13.6.2.3 Qualitative tests

(a) Heat a little solid gently in a dry tests tube and expose a blue cobalt paper.
(b) Then heat more strongly, test for any gaseous products. Cool the residue, add a little dilute sulphuric acid. Note any changes and test for any products.
(c) Add 2 cm^3 conc. sulphuric acid carefully to a little solid, warm and test for products.*
(d) Dissolve a little solid in dil. HCl and then add $SnCl_2$ solution.
(e) Dissolve a little solid in dil. sulphuric acid and then add thiocyanate solution.
(f) Dissolve the solid in a minimum of acetic acid then add calcium chloride solution.

13.6.3 Photolysis of the complex salt solution

Trisoxalatoferrate(III) solutions, like other analogous complexes of the 3d transition metal series, undergo photoreduction, when irradiated over a range of wavelengths. The system has been studied as a useful actinometer especially when low intensity sources are used. The Fe(II) yield can be easily determined spectrophotometrically as the highly coloured phenanthroline complex.

Weigh out ~ 0.74 g of your preparation, add 10 cm^3 dilute sulphuric acid and make up to 250 cm^3 with water. Irradiate an aliquot of your solution using a low pressure mercury lamp. Pipette 10 cm^3 of the irradiated solution, add 5.0 cm^3 of the acetate buffer solution used above and 2.0 cm^3 of 0.1% phenanthroline solution, shake well and measure the absorbance at the wavelength of maximum absorption determined in Sec.13.4.1. Repeat using uranyl oxalate solution described in Sec.2.10.2 but irradiate for a longer period. From Φ of the latter actinometer, determine Φ for the trisoxalatoferrate(III) actinometer.

13.7 STUDIES OF $[Fe(phen)_2(CN)_2]$

This is a commercially available low spin complex of Fe(II) which has a low solubility in water but dissolves readily in organic solvents due to the bulky aromatic ligands and the fact that it is not charged. The colours and absorption spectra of these solutions show interesting trends related to the solvent parameters. Due to its inert character, the kinetics of its oxidation by various oxidants and in various solvents offers an insight into the energetics and mechanisms of these reactions.

13.7.1 Solvent effects on the colour and electronic spectra of the complex

*(J.Chem.Educ.*62(1985)459; *Spectrochim.Acta,*26A(1970)1369).

Dissolve a little of the solid complex in a few cm^3 of solvents of varying donor numbers or acceptor numbers and note the gradual change in colour.

Prepare ~ 10^{-4} M solution in each of the following solvents: nitrobenzene, ethanol, acetic anhydride, water and formic acid. Record the spectra of the solutions over the range 300-700 nm. Correlate the long wavelengths absorption of the bands and the acceptor numbers of the solvent or the E_T solvent parameter.

13.7.2 Effect of oxidant on the rate of oxidation of $[Fe(phen)_2(CN)_2]$

Use the apparatus in Fig.2.12. Prepare a stock 3 x 10^{-4} M solution of the complex in water and a stock 6 x 10^{-3} M solution of potassium persulphate. Place a volume of the former solution in flask A and an equal volume of the latter solution in flask B. Allow to reach thermal equilibrium at 50° in a thermostat for at least 20 minutes. Then mix the solutions thoroughly as you start a stopwatch. Collect aliquots of the reaction mixture in flask C cooled in ice/salt mixture. This is done at 5, 10,15, 20, 30, 40, 60, 90 minutes. The reaction mixture is then left for more than a day to reach "completion". Measure the absorbance at the wavelength of maximum absorption of a solution whose composition is identical to the initial mixture. Determine the absorbance at the same wavelengths of all the aliquots after allowing them to warm so that the spectrophotometer cell does not mist up. Plot log absorbance against time and find the rate constant. Repeat at least at three other temperatures and calculate from the results the activation parameters.

Repeat using purest cerium(IV) sulphate. Comment on the effect of oxidant on the kinetics.

13.7.3 Solvent effects on the energetics of reactions *(Coord.Chem.Rev.*31(1980)93)

When the kinetics of a reaction is studied in water and this is compared to the situation where water is partially or completely replaced by another (usually organic) solvent, the energetics of the reaction change depending on the effect of the solvents on the stabilisation of the reactants ie initial state (i.s.) and the stabilisation of the transition state, t.s. The change from solvent A to solvent B may increase or decrease the free energy of activation, ΔG_{act}. The magnitude of the change, $\delta\Delta G_{act}$ depends on the relative magnitude of the stabilisation or destabilisation of the initial and transition states. The change in the free energy of reactants depends on their solubility in the two solvents: S(A) and S(B). This is equal to the free energy of transfer from A to B or ΔG_{tr}, given by:

$$\Delta G_{tr}=nRT\ln[S(A)/S(B)] \qquad (13.9),$$

where n is the number of particles in a molecule and R and T are the usual symbols. The free energy of transfer of the transition state, ΔG(t.s.) is obtained from the relation:

$$\Delta G(t.s.)=\delta\Delta G_{act}+\Sigma\Delta G_{tr} \qquad (13.10)$$

where the summation Σ applies to the reactants.

13.7.4 Energetics of the persulphate oxidation of the complex in water/ethanol mixtures

Repeat the runs in Sec.13.7.2 using at least two ethanol/water mixtures eg 25% and 50% ethanol (v/v). Calculate in each case ΔG_{act} and hence work out $\delta\Delta G_{act}$ for the solvent mixtures.

Determination of the solubility of potassium persulphate

Prepare a saturated solution of the salt in the alcohol/water mixtures used. Gradually add crystals while magnetically stirring keeping the temperature at 25°C until a little solid remains undissolved. Pipette an aliquot of the supernatant into a weighed evaporating basin. Weigh the basin and contents and heat on an electric water bath until all the solvent has been removed. After cooling, reweigh and determine the solubility. Calculate ΔG_{tr} from the known solubility in water and in the solvent mixture. Estimate ΔG_{tr} for K^+ ions and hence work out ΔG_{tr} for the persulphate.

Alternatively record the u.v. spectrum of a 5×10^{-3} M solution of the salt in the ethanol/water mixture and determine the wavelength of maximum absorption. Prepare at least three other solutions of various concentrations. Plot absorbance at the determined wavelength against concentration. Use the plot to calculate the concentration of the saturated solution.

Determination of the solubility of the complex

Prepare a stock solution of 5×10^{-5} M in the complex in water. By dilution, prepare at least three solutions with other concentrations. Measure the absorbance at the wavelength of maximum absorption for the solutions. Plot absorbance against concentration and work out ε in $m^2\ mol^{-1}$. Prepare a saturated solution of the complex in water by sonicating a concentrated solution for 30 minutes after adding more solid until a residue remains undissolved at 25°C. Measure the absorbance of the supernatant at the same wavelength and hence calculate the solubility at 25°C.

Repeat using the alcohol/water mixtures. In these cases, start with 1.5×10^{-4} M solution in 25% ethanol/water solution and 5×10^{-4} M solution in 50% ethanol/water solution. Calculate ΔG_{tr} for the mixed solvents used, and hence calculate ΔG_{tr}(i.s.) and ΔG_{tr}(t.s.). Plot these as well as $\delta\ \Delta G_{act}$ against percentage alcohol and comment on your results.

13.8 STUDIES OF FERROCENE

Ferrocene or $(\eta^5\text{-}C_5H_5)_2$ Fe is one of the more stable organometallic compounds. It is a representative of the sandwich compounds where a metal is located between two organic ligands below and above the metal ion. The two rings of ferrocene retain most of their aromatic character and hence the extensive range of reactions of ferrocene which resemble organic reactions.

13.8.1 Preparation and characterisation of ferrocene

The common laboratory method is to react freshly prepared anhydrous iron(II) chloride with cyclopentadiene (obtained from the dimer) dissolved in diethylamine. The reaction is represented by:

$$2C_5H_6+FeCl_2+2(C_2H_5)_2NH\rightarrow(C_5H_5)_2Fe+2C_2H_5NH_2Cl \qquad (13.11)$$

The product of the reaction is characterised by its melting point, and its infrared and electronic spectra.

13.8.1.1 Preparation of anhydrous iron(II) chloride

Use a 250 cm^3 3 necked flask provided with a mechanical stirrer and a reflux condenser at the top of which fit a trap containing 200 cm^3 concentrated sodium hydroxide. Weigh into the flask 20.0 g anhydrous iron(III) chloride. Pipette 30 cm^3 of chlorobenzene into the flask. Heat the mixture and reflux with stirring for 2 hours. Allow to cool and filter the iron(II) chloride produced at the pump and wash with portions of CH_2Cl_2 (CARE!)

Meanwhile, heat 25 cm^3 of dicyclopentadiene to reflux using a short Vigreux fractionating column. Collect in an ice-cooled receiver the fraction which boils at 41°C, which is cyclopentadiene. Use for the preparation of ferrocene immediately after preparation.

13.8.1.2 Preparation of ferrocene

Weigh out in a 250 cm^3 conical flask 9.6 g of the iron(II) chloride obtained above and add 10 g of cyclopentadiene dissolved in 40 cm^3 of diethylamine (dispensed and used in a fume cupboard) and a magnetic follower. Stopper the flask and allow to stir fir 90 minutes. Then add 75 cm^3 of 20% HCl and stir thoroughly. Filter the residue under vacuum. This is heated with three 50 cm^3aliquots of hot petroleum ether. Filter under suction. Combine the filtrates and evaporate to leave a residue of ferrocene. Recrystallise from cyclohexane. Weigh your product and calculate the percentage yield based on iron. Determine its melting point and its magnetic susceptibility by a suitable method (Sec.2.1.3).

13.8.1.3 Spectral study

Run the infrared spectrum of your preparation in a Nujol mull and note the bands of ferrocene.

Prepare a 10^{-4} M solution of ferrocene in methanol and in cyclohexane and run an electronic spectrum over the range 500-200 nm.

13.8.2 Acetylation of ferrocene and characterisation of the product

Either one or two of the aromatic rings of ferrocene can be involved in the acetylation, depending on the reagents and conditions used. The product of acetylation is characterised by its melting point and its infrared and electronic spectra. When acetic anhydride in methylene chloride is used, the monoacetyl derivative is obtained.

Dissolve 5.0 g of ferrocene in 80 cm^3 of methylene chloride and add 10 g of acetic anhydride. Fit a round bottom flask with a stirrer, a dropping funnel and a drying tube. Add dropwise, with stirring, 25 cm^3 of boron trifluoride etherate over 30 minutes, and stir the solution for 3 hours. Transfer to a separating funnel, add excess sodium acetate solution and shake vigorously. Separate the organic layer and dry it over anhydrous sodium sulphate. Filter, remove the solvent and recrystallise the product twice from toluene/ 60°/80°C petroleum ether. Record the yield, determine the m.p. and compare it with that of ferrocene. Calculate the % yield.

Characterisation of the product

Record the infrared spectrum of your product in Nujol mull or KBr disc. Assign the bands and compare with the spectrum of ferrocene.

Prepare ~ 10^{-3} M solution in methanol and a similar solution in cyclohexane. Record the absorption spectra in the range 400-700 nm. Dilute each solution 10-fold in the respective solvent and record the spectra over the range 200-400 nm.

13.9 HIGHEST OXIDATION STATE OF IRON : FERRATES (VI)

Like other 3d transition metals, the highest oxidation state is more stable in alkaline media. However, these oxidation states become less stable beyond Mn. The highest state available for iron is +6, attainable in alkaline solution when iron(III) species are oxidised by a strong oxidant. The tetrahedral ferrate(VI) is like the tetrahedral $\{MO_4]^{n-}$ ions of the earlier 3d metals.

Preparation of barium ferrate(VI)

Prepare 0.5 M iron(III) nitrate solution acidified to prevent hydrolysis. Prepare 2 M solution of NaOCl in water. Dissolve 2 g NaOH in 50 cm^3 of the solution. Heat to boiling and add, dropwise, the iron solution until there is no change in colour. Boil the mixture for 2 minutes. Filter the suspension through a glass wool plug and collect the filtrate in a conical flask. Add slowly to the filtrate barium chloride solution while stirring. Filter the precipitate under suction, wash with a little water and dry by pressing between filter paper under suction.

Qualitative tests

Add dil. HCl to part of the solid, quickly insert a glass wool plug in the test tube and test with a glowing splint. When completely dissolved, add to separate portions

(i) potassium thiocyanate solution;
(ii) potassium hexacyanoferrate(II) solution;
(iii) sodium hydroxide solution.

Account for the reactions in the preparation and in the tests

14

Cobalt

14.1 INTRODUCTION

The chemistry of cobalt is simpler than that of iron. The +6 oxidation state is hardly represented. Although the two common oxidation states of +2 and +3 are known, Co^{3+} is not stable in aqueous solution, liberating oxygen from water. The solid fluoride is stabilised by the high lattice energy. On the other hand, cobalt(II) salts are known as solids and the pink $[Co(H_2O)_6]^{2+}$ ion is stable in solution. However, Co(II) complexes are generally less stable than those of Co(III) complexes. Cobalt(II) has a special tendency to form tetrahedral complexes such as the blue tetrachlorocobaltate(II) which is a high spin species like other tetrahedral complexes and like many Co(II) octahedral complexes. Only strong ligands cause spin-pairing of the latter complexes eg the hexanitrocobaltate(II). The vast majority of the stable cobalt(III) complexes are octahedral and diamagnetic. The d^6 configuration and the relatively high pairing energy lead to the stable $(t_{2g})^6$ configuration. Because these complexes are kinetically inert, the kinetics of ligand substitution has been extensively studied. The inertness is related to the very high ligand field stabilisation energy. Cobalt resembles iron in forming the mixed valence spinel tricobalt tetroxide.

14.2 QUALITATIVE TESTS ON COBALT(II)

Prepare a solution of cobalt(II) chloride or sulphate and separately add to portions each of the following reagents.

(a) Dilute NaOH gradually and then in excess, allow to stand in air.
(b) Dilute NaOH, centrifuge, discard the supernatant, add to the residue an excess of ammonia solution followed by 10 volume hydrogen peroxide.
(c) Conc. HCl in excess.
(d) Dilute acetic acid to a concentrated solution, followed by concentrated potassium nitrite solution.
(e) Solid ammonium thiocyanate, shake to dissolve and then add amyl alcohol; shake carefully.
(f) Solid sodium bicarbonate until the solution is saturated, then add hydrogen peroxide.
(g) Ammonia solution dropwise, shake and then add excess reagent,
(h) A solution of hexacyanoferrate(II).
(i) A solution of hexacyanoferrate(III).
(j) Concentrated solution of sodium thiosulphate dropwise after neutralising the cobalt(II) solution.
(k) A solution of potassium chromate.
(l) Oxalic acid solution added gradually, allow to stand.
(m) Ammonium sulphide solution.

14.3 STUDIES OF COBALT(II) COMPOUNDS

The cobalt salts available are those of Co(II) which are pink in colour. On the other hand, Co(II) complexes are fewer and generally less stable than those of Co(III). In fact, in presence of numerous ligands, Co(II) is readily oxidised to the inert Co(III) complexes. Cobalt(II) has a tendency to form intensely coloured tetrahedral complexes, generally with anionic ligands.

14.3.1 Analytical chemistry of Co(II)

There are fewer analytical methods for Co(II) compared to other 3d metals.

14.3.1.1 Determination of Co(II) by atomic absorption

This is the simplest method when high concentrations of other elements are absent.

Prepare 10^{-3} M solution of purest ammonium cobalt(II) sulphate slightly acidified to prevent hydrolysis. By successive dilution, prepare a series of solutions in the range 10^{-4}-10^{-5} M. Use an atomic absorption spectrometer, setting the wavelength to 240.7 nm. Use an air-acetylene flame with flow rates of 8.0 and 3.0 dm^3 min^{-1} respectively, adjusting the slit width and burner height according to instructions supplied by the manufacturers. Plot absorbance against concentration and use this calibration plot to determine [Co(II)] in solutions of unknown [Co(II)].

14.3.1.2 Complexometric titration of cobalt(II) with EDTA

Cobalt(II), like other transition metal ions, forms a stable complex with EDTA. The suitable pH for the titration, adjusted by hexamine, is pH6.0 and the indicator is xylenol orange.

Weigh accurately about 5.0 g of purest ammonium cobalt(II) sulphate and make up to 250 cm^3 in water. Prepare a 0.05 M solution of purest disodium salt of EDTA. Pipette a 25.0 cm^3 aliquot of the cobalt solution into a conical flask, add 25 cm^3 water, 3 drops of xylenol orange indicator and dilute sulphuric acid slowly until the colour changes from red to yellow. Add powdered hexamine while shaking until the red colour is restored. Check with narrow range pH stick that the pH is 6. Titrate with the EDTA solution after warming the cobalt solution to about 40°C. Near the end point, add the EDTA solution slowly until the colour changes to yellow. Repeat and calculate from the average titre, [Co(II)] in mol dm^{-3}

14.3.1.3 High frequency titration of Co(II) against EDTA (Sec.2.5.2)

Because the end-point is not easy to locate in the above titration, high frequency titration offers an advantage. Prepare 0.01 M Co(II) solution and 0.1 M EDTA solution. Dilute each solution five-fold ie 50 cm^3 of each diluted to 250 cm^3. A measured volume of the Co(II) solution is pipetted in the titration vessel and the EDTA solution is added from a microburette. The titration curve obtained shows a minimum at the end-point.

14.3.1.4 Gravimetric determination of cobalt

In neutral solution, cobalt(II) salt solutions react with mercury(II) chloride and ammonium thiocyanate to produce a blue precipitate: $Co[Hg(SCN)_4]$ which is soluble in acids and in excess of the precipitating solution. Hence it is necessary to control the conditions carefully for quantitative analysis.

Weigh out accurately about 2.5 g of purest ammonium cobalt(II) sulphate, dissolve it in water and make up to 250 cm^3. If during dissolution a precipitate appears, add dropwise dilute HCl to dissolve it. To a 25.0 cm^3 aliquot of the solution, safely pipette 4.8 cm^3 of 5.4% w/v mercury(II) chloride solution and then 5.2 cm^3 of 6.0% w/v of ammonium thiocyanate solution, while stirring the solution. Continue stirring for a couple of minutes and leave the beaker, after covering with a watch glass, for 2 hours to allow for crystal growth. Collect the blue precipitate in a prepared and weighed G4 sintered glass crucible, wash with 3 cm^3 solution of 1% w/v of each of the precipitants in water, then with 5 cm^3 iced distilled water. Dry at 100°C to constant weight. Calculate from duplicate determinations the concentration of the original solution in mol Co(II) dm^{-3}.

14.3.2 Preparation of cobalt(II) complexes

Cobalt(II) forms more tetrahedral complexes than any other 3d transition metal ion. Similar to all other tetrahedral complexes, Co(II) complexes are high spin and so are most of its octahedral complexes. However the octahedral complexes are readily oxidised to the more stable Co(III) complexes. Few octahedral Co(II) complexes are low spin, similar in that respect to the few known square planar complexes.

14.3.2.1 Preparation of dianilinedichlorocobalt(II)

This compound is an example of a tetrahedral complex; such geometry is particularly favoured by Co(II) especially in combination with weak field ligands such as chloride. The presence of the large organic ligand renders it easier to isolate a solid complex from solution. This preparation is an example of the preparation of a complex in a non-aqueous solution.

Dissolve 1.8 g of $CoCl_2.6H_2O$ in 10 cm^3 of methanol. Add 1 cm^3 aniline, stir, filter off the product and dry at the pump while pressing between filter paper. Weigh your product and calculate the percentage yield based on cobalt. Treat a little of the product with water until no further change is observed. Account for the change.

14.3.2.2 Preparation of mercury tetrathiocyanatocobaltate(II)

Dissolve 14 g of cobalt(II) sulphate heptahydrate and 15 g ammonium thiocyanate in 25 cm^3 water by boiling. Dissolve 13.5 g mercury(II) chloride in 150 cm^3 water by boiling. Add to this solution the other boiling solution with continuous stirring and continue for a few minutes to precipitate the complex compound. Weigh your product and calculate the % yield based on cobalt.

14.3.2.3 Preparation of bisethylenediaminecobalt(II) diiodoargentate

Prepare the following solutions in deaerated water (by bubbling nitrogen for 10 minutes); (a) 1.44 g cobalt(II) chloride hexahydrate in 50 cm^3 water to which 0.51 g diaminoethane has been added; (b) 2.9 g silver nitrate in 25 cm^3 water, to which a solution of 5 g LiI in 25 cm^3 water was added so that the precipitated AgI redissolves. Place the freshly prepared deaerated solutions in a glove box (Sec.2.9.1). Add solution (a) to solution (b) with stirring until precipitation seems complete. Filter under suction, wash with small volumes of aqueous LiI then with small volumes of acetone. Dry by continued suction. Weigh your product and calculate the % yield based on Co.

14.3.3 Electronic spectra and magnetic moments of Co(II) complexes

Most Co(II) complexes are high spin. On the basis of its d^7 configuration and from a generalised Orgel diagram (Fig.14.1), three d-d spin-allowed bands are expected.

However, for $[Co(H_2O)_6]^{2+}$, the longest wavelength band is in the near ir and the third band is not observed. The observed band is ascribed to the $^4T_{1g}$ (F)→$^4T_{1g}$(P) transition.

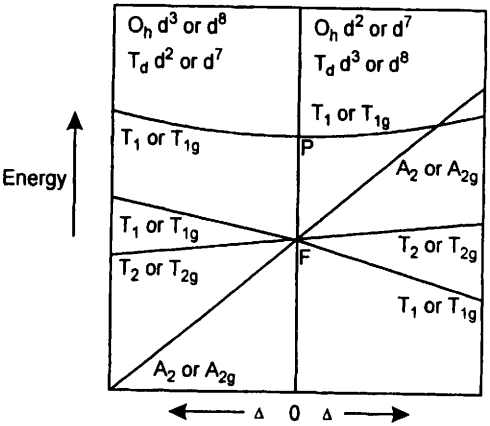


Figure 14.1 A generalised Orgel diagram for octahedral complexes with 2, 3, 7 (high spin) or 8 d electrons.

The more intensely coloured tetrahedral complexes owe their intensity to the relaxation of the Laporte rule since they have no inversion centre. Again three d-d spin-allowed transitions are expected but one band is observed in the visible region due to the $^4A_2$→$^4T_1$(P) transition and the fine structure is due to spin-orbit coupling. For the two geometries, 3 unpaired electrons lead to large spin-only magnetic moments, augmented by orbital contributions even for tetrahedral complexes. In this case, spin-orbital coupling allows an increase in the spin-only moment by an amount proportional to the coupling constant. However, the square planar complexes are expected to have one unpaired electron since they are low spin.

Prepare 0.1 M solution of cobalt(II) nitrate or chloride in water and run its spectrum in a 10 mm cell over the range 400-800 nm. To a portion of the solution add conc. HCl, shake well to attain maximum colour and run the spectrum over the same range. Comment on the spectra, comparing their appearance and intensity.

Alternatively dissolve an alkali metal chloride in 0.1 M cobalt(II) chloride hexahydrate for the second spectrum. Run a reflectance spectrum on the last complex prepared above. If an instrument is available, obtain an e.s.r. spectrum. Measure the magnetic susceptibility of a purest Co(II) salt and of the two complexes last prepared and work out the number of unpaired electrons from the effective magnetic moment. Alternatively use the Hg(II) complex to calculate the constant C (equation 2.6) from the result of the Gouy balance.

14.4 STUDIES OF COBALT(III) COMPLEXES

Cobalt(III) chemistry is dominated by Co(III) complexes. A large number of these have been prepared and studied during this century and their structure and bonding have been elucidated with the advance in instrumentation. Since most of these complexes are octahedral, low spin, diamagnetic and kinetically inert, their reactions can be conveniently studied. They undergo numerous reactions: acid and base hydrolysis, ligand exchange, reduction and, where applicable, isomerisation.

14.4.1 Electronic Spectra

The electronic spectra of these complexes resemble the spectra of the spin-free diamagnetic Fe(II) complexes and can be interpreted using a simplified Tanabe-Sugano diagram (Fig.14.2). Prepare a 5x10^{-3} M solution of the purest $K_3[Co(CN)_6]$ and run its spectrum in a 1 cm quartz cell over the range 200-400 nm. Prepare a solution of $[Co(NH_3)_3Cl]Cl$ (Sec.14.7.1) of the same concentration and run its spectrum similarly over the range 300-600 nm. Dilute 100 fold and run the spectrum over the range 200-300 nm.

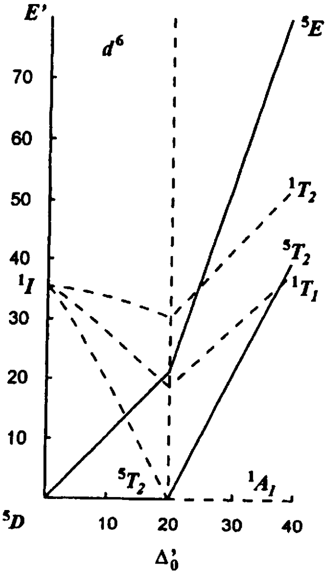


Figure 14.2 A simplified Tanaba-Sugano diagram for d^6 configuration in an octahedral ligand field.

14.5 STUDIES OF POTASSIUM TRISOXALATO COBALTATE(III) TRIHYDRATE

This compound is easily prepared by oxidation of cobalt(II) carbonate, with lead dioxide in presence of oxalic acid and potassium oxalate. It can be analysed for oxalate by permanganate titration and for cobalt by titrating iodine liberated on adding Kl to the acidified solution, after precipitating cobalt(III) oxide.

14.5.1 Preparation and analysis

14.5.1.1 Preparation

To 100 cm^3 H_2O in a 400-600 cm^3 beaker, add 5.04 of $H_2C_2O_4.2H_2O$ and 14.74 g of $K_2C_2O_4.H_2O$ (both finely ground). Heat until a clear solution is obtained, and then gradually add 4.76 g of powdered $CoCO_3$ and stir to dissolve it. When the solution has cooled to 40°C, while it is vigorously stirred, add slowly 4.78 g of PbO_2 (this should be finely powdered), followed by 5.0 cm^3 glacial acetic acid added dropwise. Continue stirring for 1 hour, during which time the colour changes from red to deep green. Decant the liquid through No.42 filter paper collecting the filtrate in a 500-600 cm^3 beaker. Transfer the unused PbO_2 to a Pb residues bottle. Cool the filtrate in ice and gradually add to it 100 cm^3 alcohol while stirring, when the green crystalline solid separates.

Allow to crystallise and then filter the product under suction. Wash twice with a little alcohol and dry by continued suction while pressing between filter paper. Weigh the product to the nearest cg and calculate the percentage yield. Store in the dark in a fridge.

14.5.1.2 Analysis

Weigh out accurately about 0.8 g of the product in about 50 cm^3 H_2O; add 3 cm^3 10% NaOH solution to decompose the complex rapidly, warm if necessary. Filter through GF paper and wash the residue of Co_2O_3 with hot H_2O. Combine the filtrate and washings, cool and make up to 100 cm^3 in a volumetric flask. Titrate 25.0 cm^3 aliquots with standardised 0.02 M $KMnO_4$, after acidifying with 50 cm^3 dil. H_2SO_4 and heating to 80°C. The temperature at the end-point should be >70°C. Repeat and calculate from the average titre the percentage oxalate in your product and hence its % purity.

14.5.1.3 Determination of Cobalt

Transfer the filter paper carefully and quantitatively to a conical flask acidify liberally with dilute HCl after adding 1.5 g KI. Cover with a watch glass and allow to stand until all the black Co_2O_3 dissolves. Titrate the liberated iodine against standardised 0.05 M thiosulphate, adding 2 cm^3 freshly prepared starch solution when the colour is straw yellow. Calculate the % Co in your preparation and hence its % purity.

14.5.2 Kinetics of the acid hydrolysis of the complex ions

The hydrolysis or aquation of the complex ion can be studied by the change in the colour of the solution from deep green to the pink Co(II) formed by the accompanying electron transfer. The time T at which the colour changes from green to grey represents a constant [complex]/[Co(II)] ratio. When acidified solutions of different [complex]'s are heated, if τ is independent of the concentration of the complex, first order kinetics is indicated. When the experiment of a given [complex] and acidity is heated at different temperatures and τ is determined, a linear plot of log τ *vs* 1/T(K) confirms first order kinetics and is used to calculate the activation energy. When a run is carried in absence of acid, the slow rate shows the catalytic role of the acid.

Prepare 0.16 M solution of the complex by weighing the crystals and making up the solution to 500 cm^3 using ice-cold dil. H_2SO_4 to dissolve the solid and to make up the solution. Keep the dil. H_2SO_4 used and the solution made up in an ice/water bath to avoid decomposition. All solutions should be well shaken on preparation. Prepare from the stock solution, 25.0 cm^3 solution aliquots with concentrations in the range 0.16-0.08 M (eg 0.12, 0.10 and 0.08 M), using ice-cold dil. H_2SO_4 for the dilution. Pipette 20.0 cm^3 of each solution into a boiling tube and suspend in a 2 dm^3 beaker containing water at 70°-80°C kept constant within 0.5°C. The tubes will warm up at the same rate. Note the time τ on a stopwatch when each solution turns grey. The stopwatch should be started when the solutions are suspended in the hot water.

To help you judge the colour, you can heat 20 cm^3 of the most concentrated and the most dilute solutions until the colour changes clearly to pink with no further change. Then add, from a graduated pipette, the original solution dropwise with stirring until a grey colour can be clearly observed. Store the solutions in ice-cold water as a reference colour.

Since τ is proportional to $1/a^{n-1}$, where τ is the time required to complete a certain fraction of the reaction, a is the initial concentration and n is the order of the reaction. Use your results to find out the order of reaction.

To determine the activation energy, weigh out accurately 0.800 g of the solid (4-5 separate portions), place each in a boiling tube and pipette 20 cm^3 dil. H_2SO_4 in another boiling tube. Keep all tubes suspended in an ice/water bath until required. Suspend a tube containing the solid and another containing the acid in a thermostat or alternatively in a 2 dm^3 beaker containing water at a temperature in the range 70°-90°C. When the acid and solid (in the separate tubes) attain thermal equilibrium, read the temperature of the water and mix the solid and acid thoroughly as you start a stop watch. Keep stirring until the colour changes to grey. Repeat at 3-4 other temperatures. Since τ is proportional to 1/k, assuming first order kinetics, calculate the activation energy from the variation of ln k with the reciprocal of the absolute temperature.

To demonstrate the catalytic role of H^+, repeat one of the experiments where τ was highest but using water instead of the acid and compare with the run in presence of the acid.

14.5.3 Kinetics and mechanism of the reduction of the solution of the complex ion

The reduction potential E^o for $[CoOx_3]^{3-}/[CoOx_3]^{4-}$ was estimated to be 0.57 V and that of $[CoOx_2(H_2O)_2]^-/[CoOx_2(H_2O)_2]^{2-}$ to be 0.78 V (Ox stands for C_2O_4). Hence the complex ion may oxidise the reduced form of any redox couple whose E^o is appreciably lower than these values.

14.5.3.1 The reduction with sulphite

Since sulphite and sulphate solutions are colourless and the complex ion solution is strongly coloured and the colour of the reduced form is less intense but pink, the kinetics can be followed by measuring the absorbance at the wavelength of maximum absorption of the reactant.

Prepare a 0.01 M solution of the complex in water and run its absorption spectrum in a 10 mm cell over the range 360-800 nm. Locate the wavelengths of maximum absorption.

Use the apparatus in Fig.2.12. Pipette a suitable volume of the complex solution into flask A and an equal volume of 0.2 M solution of sodium sulphite into flask B. Place the set up in a thermostat at 55°C. Ensure that coolant water is running in the condenser. After thermal equilibration, mix the two solutions thoroughly as you start a stopwatch. Withdraw a sample into flask C after 5, 10 and 15 minutes, cooling in ice-salt. Continue withdrawing samples at 20, 30, 40 and 50 minutes. Increase the times between withdrawals and finally withdraw a sample after a long time say 2-3 hours. When convenient warm the collected aliquots to 15°C and fill a 10 mm cell and to avoid misting the cell immediately measure the absorbance at the wavelength of maximum absorption. Run the spectrum of the final sample as above. Work out the difference (A_t-A_f) where A_t is the absorbance at time t and A_f is the final absorbance. Plot log (A_t-A_f) against time. If the plot is linear, calculate the rate constant from the slope.

Repeat at at least 3 other higher temperatures. For the run at the highest temperature, measure an aliquot of the final solution, add to it gradually, with stirring, a solution of barium chloride in 2.5 M HCl. Allow the precipitate to settle and determine its [sulphate] as in Sec.7.3.4.

14.5.3.2 Reduction with hydrazinium salt

Repeat the series of experiments above replacing sulphite by a solution of hydrazinium chloride or sulphate.

14.5.3.3 Solid state photolysis of the complex compound

The photoreduction of the complex compound has been studied in solution and in the solid state. In either case, the photoreaction can be represented by:

$$2[Co(C_2O_4)_3]^{3-} \rightarrow 2Co^{2+} + 5C_2O_4^{2-} + 2CO_2 \qquad (14.1)$$

The Co(II) produced, on reacting with iron(III) chloride in presence of phenanthroline, produces the intense colour of $[Fe(phen)_3]^{2+}$.

Weigh out about 0.2 g of your preparation and dissolve in 5 cm^3 water. Pour the solution, with stirring into 25 cm^3 ethanol. Wash the precipitate by decantation with two successive portions of ethanol. Discard the supernatant leaving a few drops of liquid in the slurry. Gradually add the slurry to a weighed glass slide, drying each drop of slurry until an area of 1-2 cm^2 is covered. Then place under a low pressure mercury lamp and irradiate for an hour. Carefully wash the film produced into a beaker containing a few drops of iron(III) chloride, in 10 cm^3 water. Add 2 cm^3 of the acetate buffer (as in Sec.13.6.3) and ½ cm^3 of 1% phenanthroline solution. Mix thoroughly and measure the absorbance at 510 nm and calculate the mole % of the complex reduced to Co(II).

14.5.4 Preparation of Durrant's salt $K_4[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2].3H_2O$

Although first described in 1905, some controversy arose about its structure. The common preparative method is by oxidising Co(II) carbonate or oxalate with hydrogen peroxide in presence of potassium oxalate and oxalic acid.

It can be analysed for oxalate and for cobalt as described previously. However, the salt decomposes at 100°C, accompanied by evolution of CO_2 and change of colour.

Dissolve 25.0 g of potassium oxalate monohydrate and 7.5 g of powdered oxalic acid dihydrate in 80 cm^3 of boiling water. Add, in portions, 7.0 g of cobalt(II) carbonate. Boil this solution for a short time and filter the hot solution into a 250 cm^3 beaker. Dissolve 9.0 g of potassium oxalate monohydrate in the boiling filtrate and adjust the temperature to within the range 58-60°C. Add 35 cm^3 of '20-volume' hydrogen peroxide slowly from a burette fitted with an extension to the jet so that the peroxide solution enters at the bottom of the solution in the beaker. The addition should take not less than 10 min, the temperature being kept within 58-60°C, and the mixture stirred gently with a 'policeman' to minimise adherence of the small dark green crystals of the product to the walls of the beaker. When all the hydrogen peroxide has been added, cool the mixture in a bath of tap water, stirring occasionally. Filter and wash the residue twice with cold water, then with an equivolume mixture of ethanol and water and finally with ethanol. Dry the product in a stream of air by continued suction while pressing between filter paper. Weigh your product to the nearest cg and calculate the % yield.

Infrared spectra

Prepare a KBr disc of your preparation and of the trisoxalato-complex prepared earlier and run the infrared spectra. Compare the spectra of the two preparations.

14.6 STUDIES OF HEXAMMINECOBALT(III) CHLORIDE

14.6.1 Preparation and analysis of the complex

Cobalt(II) chloride is readily oxidised to Co(III) in presence of ammonia as a complexing agent and an oxidant such as hydrogen peroxide. The stability of the octahedral diamagnetic complex is related to its $(t_{2g})^6$ configuration. The addition of charcoal during the reaction catalyses the formation of the required product. The complex can be analysed for the outer sphere chloride either volumetrically or gravimetrically. Cobalt can be determined in a similar way as for the trisoxalato-complex. Ammonia can be liberated from the complex by an alkali and determined by acid/base titration.

14.6.1.1 Preparation

Dissolve 6.0 g of cobalt(II) chloride in a boiling solution of 6.0 g of ammonium chloride in 12 $cm^3$of water in a 100 cm^3 beaker. Add the hot solution to 0.5 g of active charcoal placed in a dry flask and cool the mixture. Rinse the beaker with 20 cm^3 of conc. ammonia (d=0.880) in the fume cupboard carefully and add to the flask. Cool the flask in ice to less than 10°C and then slowly add 18 cm^3 of "20 volume" hydrogen peroxide, in portions, with brisk shaking. Slowly warm the mixture to 60°C and maintain at 50°-60°C with frequent shaking until the pink colour of Co(II) is removed (in about 20 minutes). When crystals begin to separate, cool the mixture first by running water and then in an ice bath. Filter off the crystals and, without washing, transfer to a beaker containing a boiling mixture of 75 cm^3 of water and 3 cm^3 of concentrated HCl. When all the solid except the black charcoal has dissolved, filter the hot solution using a fluted filter paper. Add 20 cm^3 of conc. hydrochloric acid and allow it to crystallise in an ice-bath. Then filter through a Buchner funnel, press the crystals between filter paper while applying suction and allow to dry by continued suction. Weigh the product and calculate the % yield based on Co.

14.6.1.2 Analysis

Weigh out accurately about 0.2 g of your dried preparation, which had been finely ground, into a conical flask and dissolve it in 170 cm^3 water, then add 10 drops of K_2CrO_4 indicator. Titrate with 0.100 M $AgNO_3$ solution until 1 drop produces a permanent faint red colour or precipitate. Note the colour of $[Co(NH_3)_6]^{3+}$ ions persist throughout the titration. Duplicates are required. Calculate from your results the percentage Cl^- in your preparation and hence the percentage purity of your product.

14.6.1.3 Determination of ammonia

Assemble a round bottom flask provided, through a multiple adapter, with a 50 cm^3 separating funnel and a still head. Connect the latter to a condenser whose outlet is joined to an inverted L tube ending in an inverted funnel dipping in 50.0 cm^3 0.5 M HCl. Weigh out accurately about 0.5 g of your preparation into the flask. Check that the system is gas tight ie it has no leaks, then add 50 cm^3 of 5% NaOH solution. Heat the flask, which should contain antibumping granules, gently and bring gradually to the boil. Continue until the volume in the flask is about 10 cm^3. Ensure that the level of the acid in the beaker is never below its level in the funnel. Eventually cool the flask and disconnect the assembly. Rinse the funnel into the acid in the beaker and titrate it against standard 0.5 M NaOH solution. Calculate the mols of acid neutralised by the liberated ammonia from the complex and hence the mass of this ammonia and the percentage purity of your preparation. Use the residue in the flask to determine the percentage Co in your preparation. Calculate the molar ratio $Co:NH_3:Cl$ and comment on your results.

Complexes of the hexammine cobalt(III) with trisoxalato-complexes

It is known that large anions tend to precipitate large cations whereas small anions form insoluble salts with small cations. Trisoxalato-complexes of the metals from Ti to Co are known and the more stable ones can be readily prepared. The reaction between the cationic and anionic complexes can be easily carried out and the products analysed. For this study 4 to 5 times the quantities described in the above preparation should be used.

14.6.2 The product of the reaction between hexamminecobalt(III) and trisoxalatovanadate(III)

If a 1:1 molar ratio of a solution of the chloride of the cobalt complex anion and a solution of the potassium salt of the vanadium complex are mixed, a precipitate is formed and it can be analysed for combined (V+ oxalate) and for cobalt. This can be carried out to verify its formula.

Weigh out about 2.67 g of the cobalt complex and dissolve in 60 cm^3 water. Weigh out about 4.77 g of the vanadium complex (Sec.10.3.2) and dissolve it in 100 cm^3 water and add the solution slowly with stirring to the cobalt complex solution. Allow to stand in an ice bath until precipitation seems complete. Filter under suction and wash on the filter with small volumes of ethanol. Dry by continued suction while pressing between filter paper. Analyse for (V+ oxalate) using standardised permanganate (Sec.10.3.2) and for cobalt as above in trisoxalatocobaltate(III). Assign a formula to the product.

14.6.3 The reaction of the cobalt complex ion with trisoxalatochromate(III)

Dissolve 2.44 g of prepared $K_3[Cr(C_2O_4)_3].3H_2O$ (Sec.11.4.3) in a minimum of hot water. Dissolve 1.34 g of your prepared cobalt complex in a minimum of hot water and add the solution slowly and with stirring to the Cr complex solution. Allow to cool under the tap and then in an ice bath until crystallisation seems complete. Filter under suction, wash with a little acetone and dry under suction as described above.

High frequency titration (Sec.2.5.2)

Pipette a large volume of 3-5 x 10^{-3} M solution of the Cr complex into a high frequency titration vessel. Add, with stirring, 5 x 10^{-2} M solution of the cobalt complex in a microburette. Plot the reading against volume of the latter solution and calculate the molar ratio of the reactants.

14.6.4 The reaction between the cobalt complex and trisoxalatocobaltate(III)

This reaction is similar to the above-mentioned reactions. The product can be analysed as above.

Prepare a solution of 2.67 g $[Co(NH_3)_6]Cl_3$ in water. Dissolve 5.0 g of $K_3[Co(C_2O_4)_3].3H_2O$ in 100 cm^3 of water. Warm the solution and add to it, dropwise and with constant stirring the cobalt complex solution. Allow to stand in an ice/salt bath with occasional stirring until crystallisation seems to be complete. Filter under suction, wash on the filter with small volumes of water (test the washings with $AgNO_3$). Dry by continued suction while pressing between filter paper. Weigh your product.

Weigh out accurately about 0.45 - 0.5 g of your preparation, add a solution of NaOH (5.0 g of NaOH in 50 cm^3 water). Heat until no more black Co_2O_3 separates. Filter through GF/C paper in a funnel, wash the residual Co_2O_3 with hot water. Combine the filtrate and washings and make up to 100 cm^3 in a volumetric flask.

Pipette 25.00 cm^3 of the solution obtained into a 250 cm^3 conical flask, add about 50 cm^3 dil. H_2SO_4 and heat to about 80°C. Titrate with standardised 0.02 M $KMnO_4$ to the first permanent faint colour. The temperature at the end-point should be 70°-80°C. Repeat the titration and calculate, from the average titre, the C_2O_4 content.

Transfer quantitatively the filter paper containing Co_2O_3 to a 250 cm^3 conical flask, add about 1.5 g KI and acidify freely with dil. HCl. Cover with a watch glass and allow to stand until all the black particles have dissolved. Titrate the liberated I_2 with standardised 0.05 M $Na_2S_2O_3$ solution until the colour fades to straw yellow. Dilute to about 200 cm^3 and add 2 cm^3 of freshly prepared starch solution. Continue titration until the dark blue starch/I_2 adsorption complex disappears for 1 minute. At the end point the pale pink colour of Co(II) remains in solution. Calculate the percentage Co in your compound and the molar ratio: Co/oxalate.

Spectral study
Run the infrared spectra of the prepared complexes and compare them with the spectra of the trisoxalato-complexes used. Prepare KBr discs for running the spectra and assign the bands.

14.7 STUDIES OF COMPLEXES CONTAINING AMMONIA AND OTHER LIGANDS

Under various experimental conditions, mixed ligand complexes containing ammonia and other ligands, have been prepared. The general method involves the oxidation of a Co(II) salt in presence of ammonia, ammonium chloride and another ligand. Like the other Co(III) complexes so far studied, they are low spin, diamagnetic and kinetically inert. They exhibit interesting characteristics.

14.7.1 Preparation and analysis of chloropentaamminecobalt(III) chloride

Dissolve 5.0 g of cobalt(II) carbonate in a solution of 15 cm^3 conc. HCl + 35 cm^3 water. Once all gas evolution seems to cease even after warming, filter off any undissolved residue from the technical grade carbonate. Add to the filtrate 5.0 g of ammonium chloride dissolved in 50 cm^3 conc. ammonia in the fume cupboard and then add, slowly and with stirring, 80 cm^3 of 6% hydrogen peroxide. When no more effervescence is observed, draw a stream of air through the solution for an hour. Then add conc. HCl to neutralise the solution (use a dip pH strip) when the complex salt precipitates. Then add 20 cm^3 conc. HCl and heat on a water bath for 2 hours. Wash the precipitate with water by decantation to get rid of any aqua complex and filter at the pump. Wash with small volumes of ethanol and dry by continued suction while pressing between filter paper and eventually heat at 110°C to constant weight.

Determine the % ammonia and % cobalt as in Sec.14.6.1.

14.7.2 Preparation of carbonatotetraamminecobalt(III) nitrate

Dissolve 20 g ammonium carbonate in 60 cm^3 water and add 60 cm^3 conc. ammonia. Dissolve 15 g cobalt(II) nitrate in 30 cm^3 water and add to this solution, with stirring, the carbonate solution. Then add slowly 8 cm^3 of 30% hydrogen peroxide. Pour into an evaporating basin and heat in the fume cupboard (without allowing to boil) until the volume is reduced to 90 cm^3, adding gradually during this time 5 g ammonium carbonate. Filter the hot solution under suction, cooling the filtrate in an ice bath, when red crystals are formed. Collect these by filtration under suction, washing on the filter with a small volume of iced water and then a small volume of ethanol. Dry by continued suction while pressing between filter paper. Weigh your product to the nearest cg and calculate % yield.

14.7.2.1 Conversion to the chloropentaamminecobalt(III) chloride

Dissolve 5.0 g of your preparation in 50 cm^3 water and add conc. HCl gradually until no more gas is evolved. Add conc. ammonia to neutralise any excess acid (test with pH paper) and add 5 cm^3 of ammonia. Heat, without boiling, for 20 minutes. Cool and add 75 cm^3 conc. HCl and reheat for 30 minutes until the colour changes to purple-red. Cool to room temperature and allow to stand to complete the crystallisation. Wash by decantation with iced water and then filter under suction. Wash on the filter with a little ethanol and suck dry. Complete drying in an oven at 110°C. Weigh as above and compare with the product obtained in the earlier experiment.

14.7.3 Study of linkage isomers

A few ligands may have two different coordinating atoms and when either of the two is coordinated to the metal, two linkage isomers are obtained. An example of such a ligand is NO_2 which may coordinate to the metal via the N giving a *nitro*-complex or it may coordinate via the O giving a *nitrito*-complex. Two linkage isomers can be prepared from the chloro-complex prepared above using a nitrite to exchange with the chloride ligand.

14.7.4 Preparation pentaamminenitritocobalt(III) chloride

Dissolve 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ in 30 cm^3 solution (25 cm^3 H_2O to 5 cm^3 conc. NH_3) warming gently to dissolve the solid. Filter and neutralise the filtrate to litmus with 4 M HCl and cool. Add 2.5 g $NaNO_2$ and allow to stand and then add 1.5 cm^3 1:1 HCl. Cool in ice, filter off the salmon-pink product, wash with a few cm^3 ice-cold H_2O and a little alcohol. Dry by continued suction while pressing between filter paper. Record your yield and calculate the percentage yield based on Co.

14.7.5 Preparation of pentaamminenitrocobalt(III) chloride

Dissolve 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ in 20 cm^3 of 2 M NH_3 solution. Heat in a water bath until the salt dissolves. Cool and acidify to pH4 with 4M HCl. Add 2g $NaNO_2$ and heat gently until the red precipitate first formed has dissolved. (The precipitate may only appear transiently). Cool and add carefully 20 cm^3 conc. HCl. Cool in ice and filter off the yellow brown crystals and wash with alcohol. Dry by continued suction while pressing between filter paper. Record your yield and calculate the % yield.

Analysis of the two isomers

The percentage of cobalt in either isomer or in the previously prepared mixed ligand complexes can be determined as before.

Weigh out accurately about 0.5 g of any of your preparations in a conical flask. Add 20 cm^3 of dil. NaOH and heat on a sand bath in the fume cupboard to distil off the NH_3 liberated. A suspension of black Co_2O_3 remains in the flask. Cool under the tap and filter through GF/C filter and wash well with H_2O. Transfer the filter quantitatively to a clean conical flask, add ~ 1.5 g KI and acidify freely with dil. HCl. Cover with a watch glass and allow to stand until all the black particles have dissolved. Titrate the liberated I_2 with standardised 0.1 M $Na_2S_2O_3$ solution until the colour fades to straw yellow. Dilute with H_2O to ~ 200 cm^3 and add 2 cm^3 freshly prepared starch solution. Continue the titration carefully until the dark blue starch/I_2 adsorption complex disappears for 1 minute. At the end-point the pale pink colour of Co(II) remains in solution. Repeat and calculate from each result the % Co in your preparation and hence its % purity.

14.7.6 Preparation of trinitrotriamminecobalt(III)

When cobalt is simultaneously coordinated to three ammonia ligands and three nitro groups, a neutral complex is formed which would not give an electrically conducting solution and is likely to be more soluble in organic solvents than the other complexes prepared earlier. Such a complex can be prepared from chemicals similar to the ones used in the other mixed ligand complexes but under different conditions.

Dissolve 7.0 g cobalt(II) carbonate in a hot mixture of 40 cm^3 of water and 20 cm^3 of glacial acetic acid. Filter if necessary. Cool the solution to room temperature and add 70 cm^3 of concentrated ammonia (d = 0.88) containing 15 g of sodium nitrite. Cool the mixture in ice and, when the solution is at a temperature of 10°C or less, add slowly with stirring 20 cm^3 of '20 volume' hydrogen peroxide solution. Keep the mixture in ice for 20 minutes and then add 0.5 g of charcoal. Heat the mixture at a temperature just below boiling point for 45 to 60 minutes, keeping the volume of solution constant by the addition of distilled water. Cool the mixture in ice and filter off the crude product. Wash with ice cold water, then with ethanol and finally with ether. Dry in a stream of air. Dissolve in a volume of hot water equivalent to 30 times the weight of crude dry product, acidified with a few drops of glacial acetic acid. Filter the hot solution and allow to crystallize. Wash the crystals successively with ice cold water, ethanol and ether and dry in a stream of air. Weigh your product and calculate the % yield.

14.7.7 Characterisation of the mixed ligand complexes

The usual spectroscopic techniques: ir, visible/uv and reflectance spectroscopy can be used for characterisation. Measurement of the molar electrical conductivity of solutions and comparing with solutions of simple salts can be used to establish the charges in the ionic components of the complexes. In the case of the chloro-, nitrito- and carbonato-complexes, measurements of conductivity and recording of spectra should be done on freshly prepared solutions. KBr discs are preferably used for recording infrared spectra.

Nitrito-to nitro-solid state isomerisation

Place a suitable sample of the freshly prepared nitrito-complex in an oven at 150°C. At intervals say, 20, 40, 70, 110 minutes, take a small amount and run an ir spectrum and quickly prepare a 0.01 M solution and run the visible electronic spectrum between 400-750 nm. Compare these with the freshly prepared compound and with the spectra of the nitro-compound. Draw your conclusions.

14.8 STUDY OF POLYAMMINO-COMPLEXES

Chelating diamines eg diaminoethane (en) or diaminopropane (pn) form complexes when mixed with cobalt(II) salts in presence of an oxidant. Mixed ligand complexes may be also prepared in presence of a second ligand.

14.8.1 Preparation and analysis of *trans*-dichlorobis (diaminoethane) cobalt(III) chloride

Mix 12 cm^3 of 1,2-diaminoethane with 120 cm^3 of water and add this to a solution of 32 g of cobalt(II) chloride hexahydrate in 100 cm^3 of water. Cautiously add 40 cm^3 of freshly dispensed 50 volume hydrogen peroxide. Then add 40 cm^3 of 1:1 conc. HCl/water and evaporate until a surface crust forms. Cool the container and filter off the crystals under suction. Wash on the filter with ethanol and then with ether (no flames!).

Continue suction while pressing between filter paper. Heat at 110°C to remove any HCl gas. Recrystallise from a minimum of hot water at 35°C.

Analysis of the complex

Determination of ionisable Cl^- is the simplest way but the usual titrimetry described previously is unsuitable for the strongly coloured complex solution. Two alternative titrations using mercury(II) nitrate are suitable. Alternatively passing a solution through a cation exchange resin removes the coloured cation, the colourless solution can be then titrated using chromate as indicator.

Prepare an approximately 0.005 M solution of the complex in 0.1 M nitric acid (the latter is used to suppress further aquation), add sodium nitroprusside indicator and titrate immediately with 0.0099 M mercury(II) nitrate prepared from recrystallised purest monohydrate. The appearance of a turbidity of mercury(II) nitroprusside indicates the end-point. This can be detected visually or instrumentally.

Weigh out accurately about 0.1 g of your preparation, dissolve in 30 cm^3 of 0.1 M nitric acid. Heat until the solution changes colour to pink and no further colour change is observed. Add 1 cm^3 of diphenylcarbazone/bromophenol blue indicator and titrate with 0.01 M mercury(II) nitrate solution until the first tinge of blue purple does not disappear. Repeat to get concordant results. Calculate from the average results the % chloride and hence the percentage purity of your sample. (The chloride corresponds to the ionisable chloride + the chloride replaced by water on aquation (see below).

14.8.2 Kinetics of the aquation of the complex ion

On heating a solution of the complex in slightly acidified aqueous solution, one coordinated chloride is replaced by a water molecule to produce the pink ion $[Coen_2Cl(H_2O)]^{2+}$. The half time of reaction, $t_{0.5}$, is indicated by the appearance of a grey colour. The first order kinetics and the activation parameters can be studied in a similar way to the acid hydrolysis of the trisoxalatocobaltate (Sec.14.5.2), replacing dilute sulphuric acid by 0.1 M nitric acid and carrying out runs at temperatures between 50°-75°C.

14.8.3 Kinetics of the reduction of the complex ion

When a solution of the complex compound is warmed with a solution of a suitable reductant, the Co(II) complex formed will be pink similar to other octahedral Co(II) complexes and the kinetics of reduction can be followed by the same simple method of timing the appearance of the grey colour which corresponds to a given ratio of [oxidised complex]/[reduced Co(II) complex].

Prepare a series of solutions of the complex compound in the concentration range of 0.02-0.04 M using boiled-out ice-cold water and store in an ice bath. Freshly prepare a series of purest ascorbic acid solution in the concentration range of 0.4-0.8 M using boiled-out ice-cold water and store in an ice bath. Pipette 10 cm^3 of 0.02 M complex solution into a boiling tube and pipette 10 cm^3 of 0.4 M ascorbic acid solution in another tube. Place the two tubes in a thermostat or a 2 dm^3 beaker containing water at 10°C. Place the two tubes in the water and allow them to reach its temperature. Then mix the two solutions vigorously while you start a stopwatch and note the time τ of the appearance of the grey colour. Repeat using other concentrations in the same molar ratio of complex: ascorbic acid. If the times for the appearance of the grey colour for the different concentrations are nearly equal (within experimental error) it can be assumed that the reaction is pseudo first order. Using a 0.04 M solution in the complex and 0.8 M in ascorbic acid, note the times of the appearance of the grey colour at temperatures in the range 5°-20°C and calculate the activation energy. As an extra precaution against the oxidation of ascorbic acid in air, the solutions may be initially purged with nitrogen and stoppered throughout the runs. If the times τ are independent of initial [complex], this indicates first-order kinetics. Then log τ *vs* I/T can be used to calculate the activation energy. Compare the results with those obtained for the acid hydrolysis/aquation reaction.

Repeat using hydrazinium chloride or sulphate solution instead of ascorbic acid. Note the difference between the two reductants.

14.9 SOLVENT EFFECTS ON *TRANS*-$[Co(en)_2Cl_2]^+$ REACTIONS

The isomerisation and solvolysis reactions of the *trans*-complex have been extensively studied in various protic and aprotic solvents by various groups. However, the reduction of the complex cation has not been properly investigated.

14.9.1 Kinetics of the solvolysis of the complex in DMF/H_2O mixtures

The reaction may be followed in a similar way to that described for the aquation of the complex described earlier ie timing the appearance of the grey colour from the green solution before it changes to purple. The spectrum of this final solution should be run over the range 400-700 nm to be compared with the spectrum of the initial solution. Locate the suitable wavelengths to follow the reaction spectrophotometrically.

For this procedure, place a suitable mass of the complex compound in flask A (Fig.2.12) and a suitable volume of 50% v/v of DMF/water in flask B so that the [complex] in solution is 0.01-0.02 M. Place in a thermostat at 40°C and after thermal equilibration, pour the solvent to the solid and shake vigorously as you start a stopwatch. At suitable intervals withdraw small aliquots into flask C, cooled in ice/salt. When convenient quickly fill a spectrophotometer cell with an aliquot, warm in water to stop the misting of the cell surface and measure the absorbance at one or two suitable wavelengths. Plot ln absorbance against time and calculate the rate constant. Repeat at 2 or 3 other temperatures >40°C and calculate from the results the activation parameters. Draw your conclusions, comparing the results with those obtained in aqueous solution.

14.9.2 Solvent effect on the reduction of the complex ion by ascorbic acid

14.9.2.1 The reduction in DMF solution

When a solution of the complex in DMF is mixed with a solution of ascorbic acid in DMF and the mixture warmed, the colour of the mixture does not change to grey and then pink as in aqueous solution but the colour darkens and becomes purple/green, indicative of formation of a more strongly absorbing reduction product. Hence the study of this reaction in this solvent is of particular interest.

Mix equal volumes of ~ 0.001 M in the complex in DMF and 0.002 M in ascorbic acid in a flask provided with an upright condenser with running water through it. Warm in a water bath at ~ 40°C for 1-2 hours. Run the spectra of the initial reaction mixture and the solution after warming. Locate the suitable wavelengths to follow the reaction spectrophotometrically. Run the spectra over the range 450-750 nm and in the range 250-450 after dilution with an equal volume of DMF.

flask B. Place the apparatus in a thermostat at 50°C while passing nitrogen through the system. After thermal equilibration, mix the solutions thoroughly while you start a stopwatch. At suitable intervals, withdraw aliquots in flask C, cooled in an ice/salt mixture. Collect a final sample after 2-3 hours. Measure the absorbance at suitable wavelengths as explained above. Determine the order of reaction and comment on your results.

14.9.2.2 Effect of methanol cosolvent on the energetics of the activated complex in the reduction of the complex by ascorbic acid in methanol/aqueous solution

As discussed in Sec.13.7.3, $\Delta G_{t.s.}$ can be calculated from energetics of a reaction in 2 solvents and from ΔG_{tr}, for the reactants from one solvent to another. When a series of mixed solvents are used, the trend in the stabilisation/destabilisation of the transition state compared to the reactants can be determined. This may shed some light on the transition state.

The kinetics of the reactions in methanol/water mixtures can be followed in the same way as the reduction in water discussed above. Prepare solutions of the complex and of ascorbic acid in the following solvents: 25% v/v methanol in water, 40% v/v methanol in water, 50% v/v methanol in water and 40% v/v ethanol in water. Use a temperature range of 10°C-20°C and calculate the free energy of activation in each case and compare it with the corresponding value in water.

Determination of the solubility of ascorbic acid in the above solvents

Since Mn(III) sulphate solutions react rapidly with ascorbic acid solution (Sec.12.4.1), the solubility of ascorbic acid can be determined by titrating a known volume of the saturated solution at 298 K.

Pipette a suitable volume of any of the solvents used in the kinetic runs into a stoppered conical flask, flush with nitrogen and equilibrate thermally at 298 K. Quickly add purest ascorbic acid while stirring magnetically until a little solid remains, flush with nitrogen again and, after covering with the stopper, leave for 20 minutes. Quickly and carefully withdraw a suitable volume with a pipette, without being close to the undissolved solid. Add a few drops of ferroin indicator and titrate against freshly prepared and standardised Mn(III) sulphate solution (Sec.12.4.1). Calculate ΔG_{tr} for ascorbic acid from water to each solution. Since stable Mn(III) solutions are <0.02 M, the aliquot of the saturated ascorbic acid solution has to be small and an aliquot is titrated after dilution with nitrogen-purged solvent. The dilutions and titrations should be carried out rapidly. Titration under reduced pressure (Sec.10.3.2) is advisable. Calculate from the solubility ΔG_{tr} for ascorbic acid. Use the data for the *trans*-complex in MeOH/water solutions (*Transition Met.Chem.*9(1984)193, Fig.1) to estimate (by both interpolation and extrapolation) ΔG_{tr} of the complex from water to the MeOH/water solutions used and hence find ΔG_{tr} (initial state) ie reactants (complex cation and ascorbic acid) and hence, work out ΔG_{tr} (activated complex) and plot all the values against % MeOH for the solutions used. Comment on your results.

14.10 OTHER AMMINE COMPLEXES

Numerous complexes of Co(III) containing en as the only ligand or with other ligands have been prepared and studied. Similarly other diamines form complexes with Co(III), the nearest to en is pn (1,2-propanediamine).

14.10.1 Preparation of [Co(pn)$_3$]Br$_3$ *(Inorg.Synth.,*14(1959)58).

Dissolve 2.38 g of Co(II) carbonate in 6.7 cm^3 conc. HBr in a dm^3 flask provided with a magnetic stirrer and 3 necks, joined to a reflux condenser, a separating funnel and a thermometer. When the salt has dissolved, add 500 cm^3 ethanol, and allow to reflux for 10-15 minutes over an electric heating appliance, while being mechanically or magnetically stirred. Add to the solution 6.8 cm^3 of redistilled reagent grade 1,2-diaminopropane. Then add to the refluxing solution, dropwise, 1.6 g reagent grade bromine dissolved in 100 cm^3 absolute ethanol. Filter the hot solution through a sintered crucible and wash the crystals obtained with small volumes of absolute ethanol then acetone. Dry by continued suction and then in an oven at 50°C. Weigh your product and calculate the % yield based on Co(II) carbonate. Characterise the product by elemental analysis (C,H,N,Br). Prepare a ~ 0.01 M solution in water or MeOH/water solution and run its spectrum over the range 400-700 nm.

14.10.2 Preparation of [Co(en)$_3$]Br$_3$

Use the same procedure as for the above complex but the volume of diaminoethane to be used is 5.5 cm^3. The compound can be characterised as above.

14.10.3 Preparation of *trans*-[Co(pn)$_2$Cl$_2$]Cl

Follow the same procedure as with the complex with diaminoethane (Sec.14.8.1) but use 4.76 g Co(II) chloride hexahydrate, 3.8 cm^3 of diaminopropane. Calculate the % yield based on Co(II) chloride. Analyse for ionised Cl$^-$ by titration as before. Prepare a KBr disc and run the ir spectrum and compare it with that of the en complex.

15

Nickel

15.1 INTRODUCTION

Nickel is the top metal in Group 10. Its electronic configuration is [Ar]$3d^8 4s^2$. Similar to other 3d transition metals, its two 4s electrons are readily lost, forming Ni^{2+} ions. The +2 oxidation state dominates the chemistry of nickel. Hence its oxide, NiO, its sulphide, NiS, its halides, NiX_2 and its oxosalts contain Ni^{2+} ions. In aqueous solutions of its salts, $[Ni(H_2O)_6]^{2+}$ ions are stable at pH values <7. Although octahedral complexes of nickel are known, the d^8 configuration of Ni^{2+} has a tendency to adopt a square planar arrangement in the diamagnetic complexes using hybridised $d_{x^2-y^2}$,s,p_x and p_y orbitals. Lower oxidation states are stabilised by π-bonding ligands.

Few Ni(III) complexes can be easily prepared when strong oxidants oxidise Ni(II) in alkaline media in presence of chelating ligands. These complexes have a d^7 configuration whereas Ni(IV) complexes have d^6 configuration and thus resemble Co(III) complexes in being low spin diamagnetic octahedral and kinetically inert. Of particular interest are the complexes in which a macrocyclic ligand encapsulates Ni(IV) which is at the centre of an octahedron. The stability of these complexes is ascribed to the macrocyclic effect: the extra stability compared to complexes in which the number of rings is one less than in the macrocyclic complex.

15.2 QUALITATIVE TESTS OF NICKEL SALTS

(a) Heat a little NiO in a Pyrex tube strongly and note any changes.

(b) Dissolve $NiCl_2.6H_2O$ or $NiSO_4.6H_2O$ in water and add to separate portions:

  (i) NaOH solution: test the solubility of any precipitate in excess of the reagent;

  (ii) $(NH_4)_2S$ solution: test the solubility of any precipitate in dil. HCl and in hot conc. HNO_3* (this should be done carefully);

  (iii) aqueous NH_3: test the solubility of any precipitate in excess of the reagent;

  (iv) potassium hexacyanoferrate(II) solution; test the solubility of any precipitate in ammonia;

  (v) potassium hexacyanoferrate(III) solution; test the solubility of any precipiate in ammonia;

  (vi) disodium hydrogen orthophosphate solution; test the solubility of any precipitate in acetic acid;

  (vii) sodium dithionite to a boiling solution.

15.3 DETERMINATION OF NICKEL (II)

The complexometric determination of Ni^{2+} ions is a rapid titrimetric method. On the other hand, the gravimetric determination of Ni^{2+} ions by precipitation with dimethylglyoxime is a lengthy method. Compare the results of the two methods for the determination of nickel, described below. Some instrumental methods are also suitable.

15.3.1 Complexometric titration of nickel

Since a suitable indicator is not always available for the direct titration against EDTA, a back titration is recommended (Sec.2.2.4) where a known excess of standard EDTA solution is added to an aliquot of the nickel solution, back titrating the excess against standard $ZnSO_4$ solution. To 25.00 cm^3 of 0.1M Ni(II) solution, add a known excess (50.00 cm^3) of the standardised O.1.M. EDTA solution in a 400 cm^3 conical flask. Dilute the solution to about 200 cm^3 and add 4 cm^3 of the buffer solution (pH = 10) and 1 - 2 drops of Eriochrome Black T indicator. Titrate the excess of EDTA with standard 0.1 M zinc sulphate solution until the colour changes sharply from blue to greenish red. Repeat to obtain concordant results. Calculate, from the average titre, the concentration of nickel(II) in g dm^{-3}.

15.3.2 Gravimetric determination of nickel

A solution of dimethylglyoxime in ethanol precipitat3es Ni^{2+} ions from hot faintly acidic solution. If the disodium salt of the reagent is available, a 2% solution is used to precipitate the red square planar diamaquatic complex (Fig.15.1).

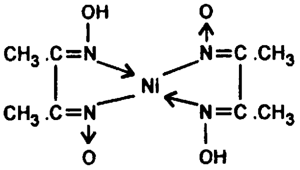


Figure 15.1

Weigh out accurately 0.25 to 0.26 g of purest $(NH_4)_2SO_4.NiSO_4.6H_2O$, dissolve it in water, add 14 cm^3 of dilute hydrochloric acid (2.5 M) and dilute to about 200 cm^3 with water. Heat the solution to 70-80°C, then add 20 cm^3 of the 1% dimethylglyoxime in ethanol solution. Add dropwise, with stirring, dilute purest ammonia solution until precipitation occurs, then add 2 cm^3 in excess. Allow the precipitate to settle and, after testing for complete precipitation, digest for 1 hour before filtering through a No.4 sintered-glass crucible, previously dried to constant weight. Wash the precipitate with cold water until free from chloride, then dry to constant weight at 120°C. Duplicate determinations are required. Calculate the percentage nickel in the salt used.

15.3.3 Instrumental analysis of nickel (II) in solution

Nickel salt solutions can be readily analysed by atomic absorption or polarographically (Secs.2.4.3; 2.5.4).

Prepare a stock solution of 0.01 M solution of purest nickel sulphate or chloride. By successive dilution, prepare 5 or more solutions in the concentration range of 2×10^{-4}-10^{-5} M. Follow the instructions of the manufacturer of the spectrometer, use an air/acetylene flame with a flow rate of 8.0 dm^3 min^{-1} and 3.0 dm^3 min^{-1} for the two gases respectively. Suitable wavelengths are: 232.0 nm (major) and 234.6 or 351.5 nm. Very low concentrations of Ni in presence of cobalt have been determined by cathodic stripping voltametry, using standard additions *(J.Chem.Educ.* ***74*** (1997)1444).

15.4 Ni(II) COMPLEXES

Nickel (II) complexes are generally either octahedral or square planar. The octahedral complexes like the hexaaqua ion are blue or green and paramagnetic. The square planar complexes, on the other hand, are diamagnetic and are red or yellow. A few complexes are tetrahedral which cannot be prepared in aqueous solution. They are also paramagnetic.

15.4.1 Octahedral complexes

Preparation of hexamminenickel(II) tetrafluoroborate(III)

When ammonia is added to aqueous Ni(II) salt solutions, water is replaced by ammonia in the coordination sphere of Ni(II). The $[Ni(NH_3)_6]^{2+}$ ion can be precipitated by large anions eg tetrafluoroborate.

Dissolve 6 g nickel chloride ($NiCl_2.6H_2O$) in 10 cm^3 warm water and add slowly, with stirring 10-12 cm^3 0.880 ammonia in a fume cupboard (CARE) until all the initial green precipitate of nickel hydroxide has redissolved. Add carefully, with stirring, 15 cm^3 cold water to redissolve the violet crystals of hexamminenickel(II) chloride. The addition of too much water will dissociate the complex with the reformation of nickel hydroxide. Filter the solution from any undissolved residue and add to the filtrate a warm solution of 5 g ammonium tetrafluoroborate in 50 cm^3 2 M aqueous ammonia. The crystalline hexamminenickel (II) fluoroborate is immediately deposited but remains almost invisible in the solution as its refractive index is almost the same as that of the solution. Filter off the crystals and wash with 1 M aqueous ammonia until the filtrate is colourless; then wash with acetone and dry in air at room temperature. Weigh your product to the nearest centigram and calculate the percentage yield.

15.4.2 Square planar Ni(II) complexes

When two diamine chelating ligands replace four water molecules in $[Ni(H_2O)_6]^{2+}$, a square planar complex is formed. The following two preparations are based on the precipitation of large cations by large anions and on the chelate effect.

15.4.2.1 Preparation and analysis of $[Ni(H_2N.CH(CH_3).CH_2.NH_2)_2][CuI_2]_2$

Add 1.2 g of 1,2 diaminopropane to 3.0 g $Ni(CH_3COO)_2.4H_2O$ dissolved in 100 cm^3 H_2O. Dissolve 6.6 g of CuI in saturated KI solution by heating or boiling. Heat the Nickel(II) complex solution to 90°C before adding 10.0 g of KI and then add the solution to the hot copper(I) complex solution. Cool the mixture and allow to stand in ice. When precipitation seems complete, wash the crystals by decantation several times with hot saturated KI solution. Then wash by decantation with 90% ethanol (100 cm^3 in small volumes) and then with acetone (100 cm^3 in small volumes). Dry by continued suction while pressing between filter paper and then in a vacuum desiccator.

Weigh your product to the nearest centigram and calculate the percentage yield based on the mass of CuI.

Analysis

The compound can be characterised by elemental analysis. Heating with nitric acid oxidises the anion to copper (II) nitrate with the removal of some I_2 leaving CuI. Cu(II) is then determined by reaction with excess iodide librating I_2 which is titrated with thiosulphate.

Obtain %C, %N and %H in your product by elemental analysis (Sec.2.1.7).

Weigh out accurately about 0.5 g of your preparation, add 14 cm^3 dil.HNO_3 and warm gently in the fume cupboard. Remove the flame when I_2 starts to sublime vigorously. When the vigorous reaction has subsided, heat gently and then strongly until all the I_2 has been expelled. (The operation may be carried out in a small flask). Then add to the clear blue/green solution saturated $(NH_4)_2CO_3$ solution dropwise until a faint permanent precipitate remains. Remove the precipitate by a drop or two of acetic acisd (the pH should be 4 - 5.5, as indicated by narrow range pH paper). Transfer quantitatively to a conical flask, the volume of the final solution could be 25 - 30 cm^3. Then add 5 cm^3 of 10% KI solution, when I_2 is liberated and a precipitate of CuI forms. Run in from a burette standardised 0.05 M $Na_2S_2O_3$ solution until the brown colour of I_2 fades. Dilute to 100 cm^3 and add 1 cm^3 of freshly prepared starch solution and continue the titration carefully until the blue colour fades. Then add 10 cm^3 of a 10% solution of purest NH_4SCN and complete the titration quickly until the blue colour disappears. At the end point, the flesh coloured CuI (darkened by the colour of Ni^{2+}) will remain in solution. Duplicates are required.

Calculate from each result the percentage of Cu in your preparation and hence its percentage purity. The titration may be carried out potentiometrically (Sec.2.5.1).

15.4.2.2 Preparation of $[Ni(H_2NCH(CH_3)CH_2NH_2)_2][AgI_2]_2$

Follow the above procedure but using 5.8 g $AgNO_3$ dissolved in 100 cm^3 saturated KI (instead of CuI). Add this solution is to the hot Ni(II) complex solution and continue as above. Weigh the final product and calculate the percentage yield on the basis of $AgNO_3$.

Compare the appearance of the three prepared complexes and comment on their structure.

15.5 NICKEL (III) COMPLEXES

Like other 3d metals, Ni(III) is more stable in alkaline media. Hence NI(III) complexes are prepared by oxidising Ni(II) salts in alkaline solution with a strong oxidant in presence of a chelating ligand. Biuret is an example of a chelating ligand which forms a Ni(III) complex when Ni(II) salt solution is oxidised by persulphate in an alkaline medium forming the chelate complex.

15.5.1 Preparation of potassium bis(biureto)nickelate (III)

Dissolve 3.3 g biuret ($NH_2CONHCONH_2$) in a solution of 4.5 g KOH in 23 cm^3 water. Add to this solution, dropwise and with constant stirring, a solution of 3.95 g $NiSO_4.6H_2O$ in 23 cm^3 water. Then add, with stirring, a solution of 8.25 g $K_2S_2O_8$ in 450 cm^3 water. Filter the blue-black precipitate formed at the pump, wash with 2 M H_2SO_4(3 x 15 cm^3) and water at 70°C (5 x 15 cm^3) and dry at 110°C.

Weigh the product $K[Ni(NHCONHCONH)_2]$ and calculate the percentage yield based on $NiSO_4.6H_2O$.

15.5.2 Analysis

Ascorbic acid solution, freshly prepared and standardised, will reduce Ni(III) to Ni(II), the excess ascorbic acid can be back titrated with any suitable oxidant eg Mn(III) sulphate.

Weigh out accurately about 0.4 g of your preparation, previously finely ground. Add a known excess of standard ascorbic acid solution (50 cm^3 of 0.028 M solution, freshly prepared in boiled-out distilled water). The solid should dissolve completely, when Ni(II) is formed in solution. Titrate the excess ascorbic acid against standardised $Mn_2(SO_4)_3$ solution (Sec.12.4.1) using N-phenylanthranilic acid as indicator. The end point is indicated by a sudden change to violet colour. Repeat the determination and calculate the percentage Ni in your sample and hence the percentage purity of your preparation.

15.6 Ni(IV) COMPLEXES

Interest in Ni(IV) complexes arises from their d^6 configuration like Co(III) complexes. Hence Ni(IV) complexes are expected to be octahedral diamagnetic and kinetically inert. This facilitates their preparation and characterisation.

15.6.1 Preparation and analysis of potassium tris-dimethylglyoximatonickelate (IV) hexahydrate *(J.Chem.Soc.Dalton Trans.* (1983) 1225).

When a nickel (II) chloride solution is made alkaline and the resulting hydroxide is oxidised with chlorine and treated with an alkaline solution of dimethylglyoxime, the Ni(IV) complex is formed. This is taken up in an anion exchange resin and when eluted, the solution produced can be vacuum dried to get the crystalline complex.

Dissolve 2.38 g nickel (II) chloride in 10 cm^3 water and add 10 cm^3 of 2.0 M solution of KOH. Stir the suspension well and pass a stream of chlorine at the rate of 1 cm^3 min^{-1} until a permanent shiny grey/black mass is formed. Bubble nitrogen through the suspension for 30 minutes and then add an alkaline solution of dimethylglyoxime (made up of 0.22 g KOH and 1.5 g dimethylglyoxime in 20 cm^3 water) while stirring the mixture vigorously. Continue stirring for 60 minutes and filter. Wash the filtrate repeatedly with ether. Pass the aqueous solution through an anion exchange column (1.5 x 12.5 cm resin, 200-400 mesh in the hydroxide form) at the rate of ½ cm^3 min^{-1} keeping the temperature in the range 0 - 5°C by circulating ice-cold water jacket round the column. Use 0.02 M KCl solution whose pH had been adjusted to 11.6 for eluting the middle portion of the coloured band on the resin. Dry the eluted solution by evacuation. Weigh out your product and calculate the % yield based on Ni.

The complex can be analysed by decomposing it using 1 M HCl acid and determining Ni(II) titrimetrically as in Sec.15.3.1.

15.7 SPECTRAL AND MAGNETIC STUDIES

15.7.1 Ni(II) compounds

Ni(II) salt solutions contain $[Ni(H_2O)_6]^{2+}$ ions which have a d^8 configuration. In an octahedral field, the simplified Orgel diagram is qualitatively similar to that of Cr(III) (Fig.14.1) except that the terms are triplets rather than the quartet terms of Cr(III). Accordingly the d-d spectra of octahedral Ni(II) complexes are expected to exhibit three spin-allowed d-d bands. But because Δ_0 for the divalent ion is small and because water is not a strong ligand, the first band in the spectra of aqueous Ni(II) solutions is in the near ir. When a stronger ligand replaces water, the band shifts to shorter wavelengths.

Prepare ~ 0.2 M solution of $Ni(CH_3CO_2)_2.4H_2O$ and add gradually $NH_2(CH_2)_2NH_2$ with shaking, until the maximum change in colour is achieved. Record the visible/u.v. spectrum of the solution in a 1 cm quartz cell, using water as a blank.

Prepare ~ 0.2 M solution of $NiCl_2.6H_2O$ and add gradually, with shaking, ammonia solution until the initial precipitate redissolves and maximum colour change is produced. Measure the spectrum as above. If available, use a spectrophotometer whose wavelength range extends to 1000 nm.

Comment on the two spectra. What quantitative conclusions can be drawn from the first spectrum?

Prepare concentrated solutions of the two diammino-Ni(II) complexes in dimethylformamide and in acetonitrile and run their u.v./visible spectra.

The magnetic susceptibility of Ni(II) compounds and complexes depends on their structure and the ligands strengths. Determine the magnetic susceptibility of the precipitated complex in Sec.15.3.2 and of the other prepared complexes.

Prepare KBr discs of the prepared complexes and record their ir spectra and compare them with the published spectra of the ligands.

15.7.2 Ni(III) complexes

The prepared Ni(III) complex, like other Ni(III) complexes, has a coorination number of 4. Its structure could be either square planar or tetrahedral. Its d^7 configuration indicates that it will have 1 unpaired electron if it is planar but 3 if it is high spin tetrahedral. Magnetic measurements are important for establishing its structure. Tetrahedral d^7 complexes may have 3 spin-allowed d-d transitions though some may be in the near ir region. The ir spectrum is likely to be ascribed to the ligand.

Grind your prepared complex into a fine dry powder and pack it into the tube of a Gouy or Evans balance and measure its magnetic susceptibility and hence its effective magnetic moment and suggest its structure.

Prepare 0.2 M solution of your complex in 0.1 M KOH and run its spectrum over the range 700-400 nm. Dilute in stages using KOH solution to obtain 10^{-4} M solution and run its u.v. spectrum. Draw your conclusions.

Make a KBr disc of biuret and of your preparation and run their ir spectra. Assign the bands and compare the two spectra.

15.7.3 Ni(IV) complexes

Ni(IV) complexes have a d^6 configuration and the favourite geometry is octahedral with low spin $(t_{2g})^6$ electron arrangement, indicating that they are likely to be diamagnetic like Co(III) complexes.

Grind your preparation to a fine powder. Use the powder for measuring the effective magnetic moment and recording its ir spectrum. Compare with the precipitated complex in Sec.15.3.2.

Use ice cold KOH solution to dissolve the prepared complex to give 3 x 10^{-4} M solution at pH12 and run its spectrum in 1 cm cell over the range 200-750 nm. Comment on the spectrum.

16

The Coinage Metals

16.1 INTRODUCTION

Group 11 of the Periodic Table contains the three coinage metals: Cu, Ag and Au. Gold compounds are not generally available because of their price and are not considered in this book. A comparison of the first ionisation energy, I_1, of the three metals, I_1+I_2 and $I_1+I_2+I_3$,(where the subscripts 1, 2 and 3 refer to the first, second and third ionisation energies respectively) shows that the lowest I_1+I_2 is that of Cu, in agreement with the prominence of the +2 state in the chemistry of copper. These compounds and complexes have a d^9 configuration. Hence they are coloured and paramagnetic. The blue or green solutions show an absorption band near the red end of the spectrum. The broadness of these bands indicate the operation of a Jahn-Teller distortion, expected for $(t_{2g})^6(e_g)^3$ configuration in octahedral environments. On the other hand, the few Cu(1) compounds are diamagnetic. They are either insoluble binary compounds or stabilised by complex formation with soft base ligands. Because the positive reduction potential ($Cu^{2+}+2e \rightarrow Cu$) in acid solution, Cu does not displace H_2 from acids but may be attacked by oxidising acids. On the other hand, silver has the lowest I_1, in agreement with the prominence of Ag(I) compounds. Because of their d^{10} configuration, the solutions are colourless and have no visible absorption bands and they are diamagnetic. Silver (II) complexes are known and because of their d^9 configuration, they are coloured and paramagnetic. The positive reduction potential ($Ag^{+}+e \rightarrow Ag$) indicates the stability of the metal in solutions of non-oxidising acids. Together with Cu and Au and some heavier transition metals, they are described as noble metals.

16.2 QUALITATIVE TESTS ON COPPER AND ITS COMPOUNDS

16.2.1 Copper and Cu(II) salts

(a) To a little piece of copper turning, add 1-2 cm^3 of each of the following acids, warm gently if necessary and test for any gaseous products:
  (i) conc. HCl, heat and allow to stand;
  (ii) conc. sulphuric acid, heat and expose a paper strip soaked in acidified dichromate;
  (iii) dilute nitric acid, expose a moist blue litmus paper;
  (iv) conc. nitric acid and test as in (iii).

(b) To a solution of a copper salt e.g. the sulphate, add separately:
  (i) dilute HCl and then H_2S solution (in the fume cupboard); after centrifuging, test the solubility of any precipitate in hot dil HNO_3;
  (ii) dilute NaOH solution; check the solubility of any precipitate in excess NaOH, then carefully boil any suspension remaining;

(iii) dilute NH_3 dropwise; note changes in colour, then add EDTA solution;
(iv) $K_4[Fe(CN)_6]$ solution; check the solubility of any precipitate in dil NH_3;
(v) KI solution slowly; centrifuge any precipitate formed and wash with H_2O; test the filtrate with starch paper and test the solubility of the residue in boiling conc. KI solution;
(vi) NH_4SCN solution, then add a little H_2SO_3 solution (in the fume cupboard);
(vii) a clean iron wire or nail; adjust the pH to about 4 and add 1,10 phenanthroline solution;
(viii) α-benzoin oxime reagent; to a drop of weakly acidified $CuSO_4$ solution on a test paper; expose this paper to ammonia fumes from conc. NH_3 (in the fume cupboard).

(c) Acidify $CuSO_4$ solution with conc. HCl and carry out a flame test.
(d) Heat solid $CuSO_4.5H_2O$ strongly, then cool and add a drop of H_2O.

16.2.2 Cu(I) salts

(a) Add separately to a solution of CuCl in dil. HCl:
(i) sodium hydroxide solution, heat any precipitate and note any colour changes;
(ii) ammonia solution, shake and allow to stand;
(iii) KI solution;
(b) Heat a little CuCl in a dry test tube.
(c) Add to a little CuCl 1,2-diaminoethane and note any changes.

16.3 STUDIES OF COPPER(I) COMPOUNDS

16.3.1 Preparation and disproportionatio of copper (I) oxide

Copper (I) compounds are generally obtained by the reduction of copper (II) compounds. $CuSO_4$ will be reduced by SO_3^{2-} in presence of Cl^- ions to form a soluble $Na_2[CuCl_3]$ complex.

$$2Cu^{2+}+SO_3^{2-}+H_2O \rightarrow 2Cu^{+}+2H^{+} + SO_4^{2-} \qquad (16.1);$$

$$Cu^{+}+3Cl^{-} \rightarrow [CuCl_3]^{2-} \qquad (16.2).$$

On hydrolysis, Cu(I) eventually separates as Cu_2O.

Dissolve 6g $Na_2SO_3.7H_2O$ and 5g NaCl in 50 cm^3 H_2O. Prepare a solution containing 2.5g $CuSO_4.5H_2O$ in 25 cm^3 H_2O. Boil the SO_3^{2-}/Cl^- solution and add to it slowly, preferably from a pipette, the Cu^{2+} solution. As the latter enters the hot liquid, a green precipitate momentarily forms but quickly redissolves to a colourless liquid containing $Na_2[CuCl_3]$. Cool the solution, transfer to a tap funnel and run it slowly into a well-stirred solution of 10g borax in 200 cm^3 H_2O. A light yellow finely divided precipitate first forms but it darkens rapidly. Continue boiling for about 30 minutes; the precipitate becomes crystalline and brick red in colour. Allow the solid to settle, wash by decantation with H_2O, filter and then wash with H_2O on the filter and then wash with acetone and dry in warm air. (No flames should be left near the acetone). Weigh your product and calculate the % yield.

Cu_2O, like other Cu(I) compounds, tends to disproportionate in acid solutions. Cu(II) solutions are formed because of the highly negative enthalpy of hydration of Cu^{2+} which compensates the extra ionisation energy.

To an accurately weighed amount of your preparation (0.1 - 0.15 g) add 10 cm^3 of 1.5M sulphuric acid in a boiling tube. Warm, if necessary, until the colour of the solution does not change. Filter through a prepared weighed sintered glass crucible, collecting the filtrate in a clean Buchner flask. Wash the residue with water, dry the crucible at 105°C and work out the weight of the residue. Transfer the filtrate quantitatively to a volumetric flask, make up to 25 cm^3 and determine [Cu^{2+}] by one of the methods in Sec.16.4.1. Calculate the molar ratio of the 2 products.

16.3.2 Copper(I) complexes

Cu(I) complexes preferentially coordinate with ligands which are soft bases. The complexes precipitate under appropriate conditions.

16.3.2.1 Preparation and analysis of the diodocuprates(I)

CuI dissolves in concentrated KI on heating. The $[CuI_2]^-$ anions formed can be precipitated by large cations e.g. $[Me_4N]^+$ or the larger alkali metal ions. The complexes are not stable in water but can be dissolved in some organic solvents. Complexes which contain other halide ligands or a different Cu:I ratio are known but are less stable.

Prepare a solution of 15.0 g KI in 10 cm^3 and add to it 2.5 g CuI. Then dissolve 2.5 g tetramethylammonium iodide in 50 cm^3 saturated KI solution. Heat in each case to ensure dissolution and heat each solution to boiling and mix the two solutions while stirring. Then cool carefully under running water and place in an ice/salt bath to complete the precipitation of $[(CH_3)_4N][CuI_2]$. Filter under suction, wash with a little ethanol and then a little acetone. Dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on CuI.

Place an accurately weighed portion (about 0.2 g) in a round bottom flask fitted with an upright condenser, add 25 cm^3 dilute nitric acid. Heat gently until all the iodine is liberated. Then cool and add enough chloroform to dissolve the iodine down the condenser into the flask. Filter through a prepared G4 sintered crucible. Wash CuI on the crucible until the filtrate is colourless. Dry at 110°C to constant weight. Add to the original filtrate 20 cm^3 conc. HCl in a reagent bottle with a stopper and titrate with 0.01M potassium iodate shaking well between the additions until the organic layer is just decolorised.

16.3.2.2 *Preparation, analysis and photolysis of $Na[Cu_2I_3]$*

Dissolve 2.5 g CuI in acetone and add 1.0 g NaI, adding more acetone to ensure dissolution. Evaporate to dryness and collect and weigh the crystals formed. Analyse as above and calculate the % purity of your preparation.

Weigh out 2 g of your preparation and dissolve in 10 cm^3 saturated KI solution. Irradiate using a low pressure mercury lamp for 3 hours. Transfer quantitatively to a conical flask and titrate the liberated iodine with freshly prepared standardised 0.002 M sodium thiosulphate. Carry out a blank experiment. To measure the quantum yield, irradiate a uranyl oxalate solution under identical conditions for 10 minutes. (Sec.2.10.2). Record the reflectance spectra of the original product before irradiation and a portion of the irradiated product after washing and drying.

16.3.2.3 Preparation of trithioureacopper (I) chloride

Thiourea is a soft base ligand and can stabilise Cu(I).

Dissolve 5.0 g of thiourea in 25 cm^3 hot water, add 1.0 g copper turnings and 5 cm^3 conc. HCl. Heat on a steam bath until copper dissolves. Filter while hot and allow the filtrate to cool until crystallisation seems complete. Filter under suction, wash with acetone and dry under suction. Weigh the product to the nearest cg. Recrystallise from acidified 5% thiourea solution and filter the recrystallised product and weigh it after washing and drying as above.

16.4 STUDIES OF COPPER (II) COMPOUNDS

16.4.1 Analytical chemistry of Cu(II)

16.4.1.1 Gravimetric determination of Cu^{2+} as CuSCN

H_2SO_3 (sulphurous acid) reduces Cu^{2+} to Cu^+ which can be precipitated as CuSCN by adding ammonium thiocyanate solution. The essential experimental conditions are: slight acidity of the solution since copper(I) thiocyanate dissolves on decreasing the pH; the presence of a reductant to reduce Cu^{2+} to Cu^+, a slight excess of the precipitant, since a large excess increases the solubility of Cu thiocyanate.

Pipette 25.0 cm^3 of the copper (II) solution (~0.064 M) into a 400 cm^3 beaker, dilute to about 50 cm^3 and add a few drops of dilute hydrochloric acid followed by 30 cm^3 of the saturated sulphurous acid solution. Dilute to about 150 cm^3, heat nearly to boiling and add from a pipette 10% ammonium thiocyanate solution until present in slight excess. Set aside to cool, ensure that precipitation is complete and allow to stand for two hours. Filter through a No.4 sintered glass crucible previously dried at 120°C. Wash the precipitate 10 times with a cold solution prepared by adding to every 100 cm^3 of water, 1 cm^3 of 10% ammonium thiocyanate solution and 5 drops of saturated sulphurous acid. Finally wash several times with 20% alcohol until free from thiocyanate and dry to constant weight at 120°C. Weigh as copper (I) thiocyanate, Cu(SCN). Duplicate determinations are required. Calculate the concentration of Cu^{2+} in the original solution in g dm^{-3}.

16.4.1.2 Titrimetric determination of Cu^{2+} solution

In weakly acidic solution, Cu^{2+} reacts with iodides according to:

$$2\,Cu^{2+}+4I^{-}\rightarrow 2CuI+I_2 \qquad (16.3)$$

The liberated iodine is titrated against standardised sodium thiosulphate solution

$$2\,Cu^{2+}\equiv I_2\equiv 2S_2O_3^{2-} \qquad (16.4)$$

At a high pH, the reaction is slow and at a low pH, I^- is likely to be oxidised in air. A moderate excess of iodide ensures complete reaction.

The precipitated CuI and the adsorption of iodine by the CuI make the end-point difficult to detect. This is mitigated by adding KSCN just before the end-point

Pipette 25.0 cm^3 of ~0.1 M Cu^{2+} solution into a conical flask and add 10 cm^3 of 10% KI solution. Titrate the liberated iodine with a standardised 0.05 M sodium thiosulphate solution until the iodine colour fades to a straw colour. Then add 2 cm^3 of freshly prepared starch solution indicator and continue titration until the blue colour just fades. Then add 10 cm^3 of 10% thiocyanate solution when the blue colour becomes more intense. Complete the titration quickly until the blue colour does not reappear within a minutes. The flesh-coloured precipitate CuI remains at the end-point.

16.4.1.3 Instrumental analysis of Cu(II) solution

Either atomic absorption spectrometry (Sec.2.4.3) or polarography (Sec.2.5.4) can be used to determine the concentration of Cu^{2+} in dilute solutions. Prepare a series of solutions of Cu^{2+} in the range 10^{-4}-10^{-5} M. Use an AA spectrometer, setting the wavelength at 324.7 nm an air flow of 5.0 dm^3 min^{-1} and acetylene flow of 2.0 dm^3

min^{-1}. Set burner height and slit setting according to the instructions of the manufacturers and measure the absorbance of each solution prepared. Plot absorbance against $[Cu^{2+}]$ and use the plot to determine the concentration of the above solutions after appropriate successive dilutions.

16.4.2 The kinetics and mechanism of the solubility of CuO in ascorbic acid solution

When acidified ascorbic acid solution is added to the black CuO, the solid starts to dissolve on heating giving a coloured solution. To follow the reaction, the absorbance of the solution at a suitable wavelength is measured at intervals. Since ascorbic acid solutions are oxidised in air, it is necessary to exclude air during the runs.

Pipette 50.0 cm^3 of 0.1 M freshly prepared ascorbic acid and 4.0 cm^3 2.5 M HCl into a 100 cm^3 conical flask fitted with a rubber bung with 2 holes: one for a tube used for purging with nitrogen and the other carrying a Bunsen valve. Place in a shaking thermostat (or better an orbital incubator) at a constant temperature between 20° and 35°C. Purge the solution with nitrogen for at least 20 minutes. Weigh out accurately 1.50 g purest CuO and equilibrate at the same temperature. Then add it quickly to the flask, purge with nitrogen while starting the shaking at a constant rate say 250 rpm for a given time. A series of such flasks are necessary for a kinetic run, using a suitable range of times between 10 and 100 minutes. Remove each flask from the thermostat at the chosen time. Quench in an ice/salt bath and quickly filter through a weighed sintered crucible, collecting the filtrate in a clean flask. Determine the concentration of copper(II) by one of the analytical methods discussed above. Wash the residue until the filtrate is colourless. Dry at constant weight at 120°C. Compare the loss in mass and the mass of Cu(II) found in the filtrate. Run an electronic spectrum of an aliquot of the filtrate and compare it with that of the filtrate from a blank experiment in which ascorbic acid solution is replaced by water. Repeat at 3 or 4 other temperatures. Plot $[Cu^{2+}]$ against time to check the order of the reaction. Calculate an activation energy and attempt to explain the results.

16.4.3 Copper(II) complexes

Copper(II) forms numerous complexes with N- and/or O- coordinating ligands. Because of Jahn-Teller distortion, coordination number 4 is often encountered. An interesting class of complexes contain a cationic Cu(II) complex with an anionic cu(I) complex.

16.4.3.1 Preparation and analysis of $[Cu(NH_3)_4]SO_4.H_2O$

This can be readily prepared from copper sulphate and ammonia. Dissolve 2.5 g copper sulphate pentahydrate in 10 cm^3 water. Add 5 cm^3 of conc. ammonia and then add, dropwise, 5 cm^3 of ethanol while stirring. Filter the fine precipitate under suction and dry by continued suction as usual. Weigh the product to the nearest cg and calculate % yield.

The product is readily analysed by determining the loss in mass when heated followed by the determination of Cu(II) in the residue.

Weigh out accurately about 0.5 g of your preparation in a weighed clean crucible and heat gently on a sand bath and then in an oven at 150°C to constant weight. Calculate the % loss in weight. Dissolve the residue and determine [copper(II)] by one of the methods in 16.4.1.

16.4.3.2 Preparation and analysis of bis-1,2-diaminopropanecopper(II) diiodocuprate(I)

Add 0.9 g of 1,2-diaminopropane to 1.1 g $CuCl_2.2H_2O$ in 25 cm^3 H_2O. Heat to 90°C and then dissolve 5 g KI in the solution. Dissolve 2.3 g CuI in 10 cm^3 H_2O by adding KI to the boiling solution. Then add to the solution the hot Cu(II) complex while stirring. Cool to allow for precipitation and filter under suction. Wash with small portions of EtOH (50 cm^3) and acetone (50 cm^3). Dry by continued suction and store in a vacuum desiccator. Weigh your product and calculate the % yield.

Heating with nitric acid oxidises Cu(I) to Cu(II) and removes all the iodine. Cu(II) is then determined titrimetrically or by instrumental analysis.

Weigh out accurately about 0.5 g of your preparation, add 14 cm^3 dil. HNO_3 and warm gently in the fume cupboard. Remove the flame when I_2 has been expelled. Then add to the clear solution $(NH_4)_2CO_3$ solution dropwise until a faint permanent precipitate remains. Remove this by a drop or two of acetic acid (the pH should be 4.0-5.5, as indicated by narrow range indicator paper). Transfer quantitatively to a conical flask and add 8 cm^3 of 10% KI, when I_2 is liberated and a precipitate of CuI forms. Titrate with standardised 0.05 M thiosulphate solution as in Sec.7.5.1. Calculate the % copper in your preparation from duplicate runs and hence calculate the % purity of your preparation.

16.4.4 Spectral and magnetic studies of Cu(II) (Sec.2.1.3 and 2.4.2)

Since Cu(I) has d^{10} configuration, its compounds are diamagnetic and do not exhibit d-d bands but Cu(II) compounds have a d^9 configuration and they are paramagnetic and their very broad d-d absorption band illustrates the Jahn Teller effect.

Measure the room temperature magnetic susceptibility of the prepared complexes and work out the effective magnetic moment and the number of unpaired electrons. Make KBr discs of the prepared complexes and compare the spectra with those of the ligands. Dissolve the last prepared complex in the minimum of dimethyformanide and record its absorption spectrum in a 10 mm quartz cell over the range 250-300 nm.

To study the effect on the electronic spectrum of replacing water as a ligand by ammonia, prepare a 1 M solution of Cu(II) nitrate in water. Dilute 1 cm^3 of the solution with either water or conc. ammonia make up to 100 cm^3 and record the spectra in a 1 cm cell over the range 400-800 nm. Mix an equal volume of the nitrate solution with conc. ammonia and record the spectrum as above. Calculate the ligand field splitting parameter from the wavelengths of maximum absorption. Comment on your results.

16.5 COPPER (III) COMPLEXES

The higher oxidation states of transition metals are more stable in alkaline solutions. Strong oxidants are needed in presence of suitable ligands preferably chelate-forming ligands.

Preparation, analysis and characterisation of potassium bis-(biureto)cuprate(III)

Cu(II) sulphate is oxidised by persulphate in presence of biuret dissolved in alkali.

Dissolve 1.1 g biuret in 8 cm^3 of water in which 1.5 g KOH had been dissolved. Dissolve 1.25 g copper sulphate pentahydrate in 5 cm^3 water. Add the solution to the biuret solution and heat to 70°C and add the solution to theCu(II) solution at 70°C, with constant stirring. Dissolve 2.75 g potassium persulphate in 5 cm^3 water and heat to 70°C.

Cool and allow to stand for complete precipitation. Filter the precipitate under suction. Wash on the filter with three 5 cm^3 2 M sulphuric acid and then with five 5 cm^3 water at 70°C. Dry at 110°C and weigh. Calculate the percentage yield.

The complex can be analysed by adding a slight excess iron(II) chloride solution in HCl. This will be oxidised to iron(III) chloride and copper(III) will be reduced to copper(II) chloride. Since the two chlorides absorb at different parts of the spectrum, they can be determined spectrophotometrically.

Prepare a solution of 5×10^{-3} M iron(III) chloride in 1 M HCl. Standardise the solution by reduction to Fe(II) using $SnCl_2$ and titrating iron(II) with standard dichromate as in Sec.13.3.2. Using 1 M HCl for dilution, prepare a series of solutions in the range 10^{-4}-8×10^{-4} M. Record the spectrum of the latter solution in a 10 mm cell over the range 300-800 nm and locate a wavelength of maximum absorption. Measure the absorbance at this wavelength for the series of solutions and plot absorbance against [Fe(III)]. Carry out a similar process for purest copper(II) chloride in 1 M HCl and for purest iron(II) chloride in 1 M HCl. For the latter, all solutions and the acid used for dilution, should be purged with nitrogen for 20 minutes before being freshly made for further steps. Spectra should be run in stoppered or vacuum cells and spectral measurements carried out immediately after preparation.

Weigh out accurately about 0.20 g of your preparation into a Buchner flask, with a bung carrying a separating funnel. Prepare 0.05 M iron(II) chloride in 1 M HCl and place immediately in the funnel. Apply suction to the flask, and allow about 20 cm^3 of the solution to be added to the solid. Ensure that the solid has dissolved and that maximum colour has developed. Transfer the contents of the flask quantitatively to a measuring flask and make up to 1000 cm^3 using 1 M HCl. Measure the absorbance in a 10 mm stoppered or vacuum cell at the wavelengths chosen above. Calculate the % Cu in your preparation and hence work out its % purity.

16.6 QUALITATIVE TESTS ON SILVER COMPOUNDS

The majority of silver salts are insoluble and generally precipitate as white solids. Among the few soluble salts, the most important are the nitrate, the fluoride and the oxochloro-compounds. In the tests for anions in earlier chapters 3-8, tests with silver nitrate were mentioned. The following summarises these tests. To a neutral solution of each of the following salts, add silver nitrate solution dropwise and shake to check the possibility of solubility in excess. Test the solubility of any precipitate separately in dilute or conc. ammonia or in dilute nitric acid. Use sodium or potassium salts of the anions:

(i) chloride, (ii) bromide, (iii) iodide, (iv) sulphite, (v) sulphate, (vi) thiosulphate, (vii) bromate, (viii) iodate, (ix) nitrite, (x) orthophosphate, (xi) pyrophosphate, (xii) metaphosphate, (xiii) carbonate, (xiv) silicate, (xv) borax, (xvi) ammonium sulphide, (xvii) sodium hydroxide, (xviii) ammonia.

16.6.1 Spot test

To a drop of the silver salt solution on a watch glass add a drop of potassium chromate solution.

16.6.2 Reduction of Ag^+ to Ag

(a) Dip in separate portions of silver nitrate solution: (i) an iron nail; (ii) piece of Zn foil; (iii) a drop of Hg;

(b) Add ascorbic acid solution to acidified silver nitrate solution.

16.6.3 Catalytic effect of Ag^+

(a) To a solution of a manganese(II) salt in dilute sulphuric acid, add a few drops of silver nitrate solution and some solid persulphate. Boil gently for a few minutes and notice the changes taking place.

(b) Repeat using a solution of chromium(III) sulphate instead of the manganese salt.

(c) Add sodium chloride solution to a Ce(IV) salt solution and shake well. Then add a few drops of silver nitrate.

16.7 ANALYTICAL CHEMISTRY OF SILVER

Both gravimetric and volumetric analyses can be carried out based on the same principles used for the determination of chlorides. In the gravimetric method 0.2 M HCl is used for precipitating silver ions from dilute ~0.005 M solution acidified with 1% nitric acid by volume.

The precipitant is added slowly, with stirring, to the silver solution. After allowing the precipitate to settle by warming and setting aside in the dark (to allow for crystal growth), the precipitate is filtered in a prepared G4 sintered crucible and dried at 100°C to constant weight.

Among the instrumental methods, electrogravimetry (Sec.2.3.2) can be used but the best results are obtained from the silver cyano-complex. But because of the high toxicity of cyanides, the method cannot be recommended.

16.7.1 Determination of silver by atomic absorption

Prepare a stock solution of 0.01 M silver nitrate, acidified to pH5-6. Using a very dilute nitric acid solution (pH5), prepare a series of solutions from the stock solution in the range: 10^{-5}-5×10^{-5} M. Measure the absorbance of each solution at 328.1 nm in an atomic absorption spectrometer using an air/acetylene flame (flow ratio 8.0 and 3.1 dm^3 min^{-1} respectively) using the slit setting and burner height recommended by the manufacturer. Plot absorbance against concentration and use the calibration plot for [Ag(I)] determination of any dilute silver solution.

16.8 THE PHOTOCATALYSED DEPOSITION OF SILVER

When anatase pigment eg P25, suspended in silver nitrate solution, is irradiated by a uv source, the electrons are promoted from the valence band of the semiconductor to the conduction band. On reaching the surface, these electrons reduce Ag^+ to Ag. This can be used as a method of removing silver from aqueous solution.

Prepare a solution of silver nitrate by dissolving 1.0 g of the purest salt in water slightly acidified with nitric acid and make up to 1 dm^3 in a volumetric flask. Suspend anatase pigment into the solution such that the concentration of the suspension is 1% w/v. Disperse by sonication and irradiate with a low pressure mercury lamp, with stirring, for 30 minutes. Filter the suspension through a G4 sintered glass disc, preferably after centrifuging, and wash on the filter with water until the filtrate is silver-free (check by adding dil. HCl to a little). Dry at 120°C, weigh and find the % silver deposited.

Recovery of silver from the photocatalyst

Since titanium dioxide is not affected by acids even when they are hot, whereas silver dissolves in hot dilute nitric acid, it is possible to recover silver from the catalyst.

While keeping the crucible connected to a clean Buchner flask, add small volumes of hot dilute nitric acid, allow it to react and then apply suction. Repeat until all the dark silver particles have dissolved. Wash on the filter with small volumes of acid. Collect the filtrate and washings into a high frequency cell and titrate against standard 0.01 M NaCl. Locate the end-point by the point of the intersection of the two linear parts (Sec.2.5.2).

16.9 ADSORPTION OF SILVER IONS ON SILICA

Precipitated silica is an efficient adsorbent for metal ions. However, the pH should be adjusted so that no hydrolysis products are formed.

Prepare a set of silver nitrate solutions in the range 10^{-3}-10^{-5} M in 0.1 M pot-assium nitrate. Prepare a stock solution of 0.1 M potassium nitrate. Shake a 4% suspension of the silica in the latter solution for 6-12 hours in a centrifuge tube placed in an orbital incubator set at 25°C. After centrifuging withdraw from the suspension a fifth of the supernatant replacing it by one of the silver solutions. Adjust the pH to 5.0 using dilute nitric acid and shake in the thermostatted incubator whose temperature is set to 25°C for 4-5 hours. Centrifuge and filter the supernatant through G4 sinter or GF/F paper. Analyse the filtrate for $[Ag^+]$ by atomic absorption. Calculate the amount adsorbed g^{-1} of silica and check whether Langmuir's isotherm (Sec.2.1.6) is applicable or not.

16.10 SILVER(I) COMPLEXES

Ag(I) tends to form complexes with a number of ligands. Of particular interest are those formed with iodide and the copper(II) cationic/silver(I) anionic complexes.

16.10.1 Preparation and analysis of $(Me_4N)[Ag_2I_3]$

Iodo complexes of Ag(I) are formed when AgI is dissolved in I^- solution, the formula of the anionic complex depends on the conditions of the reaction. It is often possible to obtain crystalline products using salts containing a large cation. Tetraalkylammonium salts are characterised by their stability in water. Some of the complexes have high ionic conductivities. Although AgI is available commercially, it is easy to prepare it and use it for preparing the complex.

Weigh out 1.66 g KI into a large beaker and dissolve it in about 300 cm^3 H_2O and add 1 cm^3 of conc. HNO_3. Dissolve 1.70 g $AgNO_3$ in 100 cm^3 distilled water. Add the $AgNO_3$ solution slowly and with constant stirring to the iodide solution. Heat nearly to boiling while stirring continuously until the supernatant liquid is nearly clear. Filter through a Buchner funnel using acid-washed filter paper. Dry by continued suction and pressing between filter paper. Weigh your product and calculate the percentage yield based on Ag.

Dissolve 2.3 g the prepared AgI in 10 cm^3 of boiling dimethylformamide. Dissolve 1 g of $(CH_3)_4$ NI in the minimum amount of water, and add the solution to the boiling AgI solution, gradually. On cooling, crystals of the complex precipitate. Filter through a Buchner funnel, wash with CH_3OH, acetone and dry by pressing between filter paper and by continued suction. Weigh your product and calculate the percentage yield based on AgI.

The complex can be analysed by titrimetric determination of iodine and/or gravimetric determination of Ag as AgI.

Weigh out accurately about 0.4 g of your preparation into a round bottom flask fitted with a joint. Fit an upright condenser and add 40 cm^3 of dilute nitric acid. Warm the flask gently until iodine is liberated and then heat to complete the liberation of iodine. When the reaction seems complete, cool the apparatus and pour down the condenser 5 cm^3 of CCl_4 or $CHCl_3$ to dissolve and extract the iodine liberated and then filter through a weighed sintered glass crucible to retain AgI. Collect the filtrate in a bottle provided with a ground stopper. Wash with two 1 cm^3 portions of the organic solvent and collect the washings in the bottle. Add in the following order: ~10 cm^3 H_2O, 60 cm^3 conc. HCl and titrate the iodine with 0.01 M KIO_3 solution until the organic layer is no longer violet.

Wash the precipitated AgI on the sintered glass crucible with very dilute HNO_3 (½ cm^3 conc. + 200 cm^3 H_2O) and dry to a constant weight at 140°C. Calculate the percentage of AgI in your preparation.

16.10.2 Preparation, analysis and photolysis of $Cs[Ag_2I_3]$

Dissolve 1.0 g CsI and 1.81 g AgI in 60 cm^3 acetone. Filter if this seems necessary and evaporate on a hot plate to yield the product. Analyse as above.

Spread a thin layer of the dried preparation on a Petri dish and expose to a low pressure mercury lamp until a noticeable colour change is seen. Mix the irradiated powder, after grinding well, with KBr and run the reflectance spectrum over the range 400-750 nm, using KBr as a blank. Carry out identical procedure with the original preparation and compare the two spectra.

16.10.3 Preparation, analysis and photolysis of $[Cu(NH_3)_4][AgI_2]_2$

The cation of the previously prepared Cu(II) complex is precipitated as the iodoargenate by mixing the solutions of the reactants. The product can be easily analysed gravimetrically as AgI after heating with nitric acid.

Dissolve 1.44 g of $AgNO_3$ in the minimum quantity of water. Prepare a hot saturated KI solution (~40 cm^3) and add it to the $AgNO_3$ solution until the precipitated AgI just redissolves. Dissolve 2.8 g of your product $[Cu(NH_3)_4]SO_4.H_2O$ in 60 cm^3 H_2O. Heat to boiling and add to the solution the boiling solution of the Ag iodo-complex slowly with stirring. Allow to cool under the tap and then in an ice bath until no more crystals separate. Filter under suction and wash with 50 cm^3 C_2H_5OH (in small portions) and dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield.

Weigh out accurately about 0.3 g of your product in a beaker and add to it about 20 cm^3 dilute HNO_3 and 100 cm^3 H_2O. Heat gently until all the iodine has been lost (this should be carried out in the fume cupboard). Cool and filter through a prepared sintered glass crucible (heated to constant weight at 130°C). Wash well with small volumes of CCl_4 and then heat to constant weight at 130°C. Duplicates are required. Calculate from each result the percentage Ag in your preparation and hence its % purity.

16.10.3.1 Photolysis and pyrolysis

Irradiate a thin layer of your preparation as above for the Cs $[Ag_2I_3]$ complex. Irradiate separately thin layers of CuI and of AgI.

Pyrolysis of the complex.

Weigh out accurately about 0.2 g of your preparation. Heat gently at first on sand bath in the fume cupboard and then in an oven at 105°C to constant weight. Note the colour change and calculate the % loss in mass. Compare the appearance of the heated and irradiated products.

16.11 PREPARATION AND ANALYSIS OF A SILVER(II) COMPLEX

The persulphate oxidation of Ag(I) is indicated by the black colour seen when silver ions catalyse the persulphate oxidation of Cr(III) or Mn(II). The presence of a chelating ligand is expected to stabilise silver(II). Dipyridyl forms complexes with silver nitrate readily. Persulphate oxidises Ag(I) in the complex to Ag(II) replacing the nitrate as a counter ion.

16.11.1 Preparation of $[Ag(bipy)_2]S_2O_8$

The first step in the preparation is to prepare the Ag(I) complex which is then oxidised by persulphate.

16.11.1.1Preparation of $[Ag(bipy)_2](NO_3)$

Weigh out 4.2 g silver nitrate and 7.8 g bipyridyl. Dissolve each in hot aqueous ethanol and mix the two hot solutions. Allow to cool and to crystallise. Collect the crystals by filtration under suction. Recrystallise from hot alcohol. Filter under suction while pressing between filter paper. Weigh your preparation and calculate the % yield based on Ag.

16.11.1.2 Preparation of the Ag(II) Complex

Prepare a cold saturated solution of potassium persulphate and add an excess of the persulphate. Stir the silver(I) complex prepared above with the cold persulphate solution until the crystalline yellow needles are replaced by a red brown microcrystalline solid (this may take 1-2 hours). Wash thoroughly with cold water. Filter under suction as above. Store in a vacuum desiccator.

16.11.1.3 Analysis

The product can be analysed by titrating the iodine liberated when excess KI solution is added.

Weigh out accurately about 0.2 g of your preparation, add excess of 10% KI solution and shake well until maximum colour of iodine is formed. Titrate using standardised 0.05 M thiosulphate solution as in Sec.7.3.3. Characterise the freshly prepared product by ir spectroscopy and by measuring its magnetic susceptibility (Sec.2.1.3).

17

The Zinc Group

17.1 INTRODUCTION

The zinc group or group 12 of the Periodic Table comprises the metals: Zn, Cd and Hg. By losing the two s electrons, the elements form the M^{2+} ions which have a completed^{10} sub-shell. This stable configuration explains the prominence of the +2 oxidation state in binary and complex compounds. This configuration also accounts for the diamagnetism of the compounds and the absence of d-d bands in their electronic spectra. The +1 oxidation state is significant for Hg but becomes much less significant in Cd and is hardly observed in Zn. In this state, no M^{+} ions are formed, rather the ions $(M\text{-}M)^{2+}$ which contain a covalent metal-metal bond. Some mercury compounds contain covalent bonds to non-metals, especially N. This is consistent with the high electronegativity of Hg, the electronegativity increasing down the group. Mercury is also unique in having a positive reduction potential ($E^{o}Hg^{2+}/Hg$) whereas the potential is negative for Cd and more negative for Zn. These two metals are reactive and can displace hydrogen from acids unlike mercury which is a noble metal.

Hg^{2+} and, to a less extent, Cd^{2+} are soft acids and prefer to coordinate with soft base ligands. The three M^{2+} ions are more polarising than those of group 2. Hence their compounds deviate more from ionic character than those of group 2. Parallel to this, group 12 metals form more numerous and more stable complexes than those of group 2. However, $Cd(OH)_2$ is more basic than the amphoteric $Zn(OH)_2$ whereas $Hg(OH)_2$ is only a very weak base. The chalcogenides, especially those of Zn and Cd are semiconductors and may act as photocatalysts.

17.2 QUALITATIVE TESTS

Use solutions of the nitrates of either Zn, Cd or Hg(II) acidified with a little nitric acid. Add to each solution separately:

(a) NaOH solution, check the effect of excess reagent;
(b) ammonia solution, check the effect of excess reagent;
(c) ammonium sulphide solution, check the effect of nitric acid;
(d) hydrogen sulphide gas in the fume cupboard, check the effect of nitric acid;
(e) disodium hydrogen phosphate solution in presence of ammonium salts;
(f) potassium hexacyanoferrate(II); solution.

17.2.1 Special tests for zinc

(a) Heat ZnO and then allow to cool;
(b) Add to a solution of the nitrate, chloride or sulphate separately;
    (i) potassium sulphite solution;

(ii) potassium hexacyanoferrate(III) solution;
(iii) magnesium ribbon.

17.2.2 Special tests for Cd

Add to a solution of the nitrate or sulphate separately:

(a) potassium chromate solution;
(b) potassium thiocyanate solution;
(c) zinc granules.

17.2.3 Special tests for Hg(II)

Use a solution of the nitrate. Add separately to a solution slightly acidified with nitric acid:

(a) sodium thiocyanate solution;
(b) potassium iodide solution;
(c) tin(II) chloride solution;
(d) a piece of copper metal.

17.2.4 Special tests for Hg(I)

To a solution of the nitrate acidified with dilute nitric acid, add separately:

(a) dil. HCl; then add ammonia solution;
(b) NaOH solution;
(c) ammonia solution;
(d) KI solution;
(e) potassium chromate solution;
(f) tin(II) chloride solution;
(g) sodium nitrite solution.

17.3 ANALYTICAL CHEMISTRY OF ZINC

The easiest method for the determination of zinc ions in aqueous solution is by complexometric titration. A suitable instrumental method is by atomic absorption. Gravimetrically, zinc can be precipitated with 8-hydroxyquinoline (or oxine) and weighed as the oxinate.

17.3.1 Complexometric determination of zinc

Zinc forms a stable complex with EDTA and can be determined by direct titration.

Prepare a zinc ion solution by dissolving 0.66 g of purest zinc sulphate heptahydrate in water, slightly acidified and made up to 250 cm^3 in a volumetric flask. Pipette 25.0 cm^3 of the solution into a conical flask, add 5-6 drops of Solochrome T indicator and 10 cm^3 of buffer solution (pH10). Titrate with standardised 0.01 M EDTA solution until the purple red colour loses any trace of red and changes to blue. Repeat to obtain concordant results and calculate the concentration of Zn^{2+} in mol.dm^{-3}. (Prepare the indicator solution by adding 0.2 g of the pure indicator to 15 cm^3 of triethanolamine and 5 cm^3 of ethanol).

17.3.2 Titration with $K_4[Fe(CN)_6]$ solution (Sec.13.3)

Pipette 25.0 cm^3 of the Zn^{2+} ion solution, which is ~0.1 M, into a 250 cm^3 conical flask. Add 50 cm^3 of dil. H_2SO_4 (2 M), 1.0 g of $(NH_4)_2SO_4$ and 4 drops of diphenylbenzidine indicator. Titrate slowly and with vigorous shaking with the standard 0.05 M $K_4[Fe(CN)_6]$/0.001 M $K_3[Fe(CN)_6]$ solution to the first permanent colour change from purple to yellow green. A false end-point may be observed when the purple colour prematurely fades, but if the solution stands for a few minutes the purple colour returns.

The end-point is eventually observed when the purple colour changes permanently to yellow green.

Repeat the titration to obtain concordant results and calculate the concentration of Zn^{2+} ions in the original solution in mol. dm^{-3} and in g dm^{-3}.

17.3.3 Determination of zinc by atomic absorption (Sec.2.4.3)

Using purest zinc sulphate heptahydrate, prepare a 0.01 M solution. By successive dilution, prepare a series of solutions in the range 5×10^{-4}-10^{-5} M, slightly acidified to avoid hydrolysis. Set the wavelength of the instrument at 213.9 nm (a secondary wavelength is 307.6 nm). Use an oxygen-acetylene flame, with the rates of flow of 8.0 dm^3 min^{-1} and 3.0 dm^3 min^{-1} respectively. Refer to the instrument manual for the recommended slit width and burner height. Plot the absorbance against zinc ion concentration and use the calibration plot for finding the concentration in an unknown solution.

17.3.4 Gravimetric determination of zinc

Zinc ions, like many other di-and trivalent ions, are precipitated by 8-hydroxyquinoline (oxine) forming the oxinates [M(oxinate)$_n$] where n is the valence of the metal ion and the number of chelate rings formed. Precipitation starts at a characteristic pH value and is complete with in a range of higher pH's, these being pH 3.3 and >4.4 respectively for zinc oxinate.

Pipette 25.0 cm^3 of 0.09 M zinc sulphate solution, dilute to 100 cm^3 with water and dissolve in the solution 5 g purest potassium acetate and 4 g glacial acetic acid. Warm the solution to 60°C and add with stirring a 2% solution of oxine in 2 M acetic acid. Boil for a few minutes to coagulate the precipitate. Check for complete precipitation, adding a slight excess of the oxine solution. Filter in a prepared G4 sinter, wash with hot water and dry at 130^{oC} to constant weight. Calculate from duplicate determinations, the average [Zn(II)] in mol dm^{-3}.

17.3.5 Fluorometric determination of zinc

Like Al and Cd, zinc oxinate fluoresces when irradiated with a medium pressure mercury lamp. The intensity of the fluorescence can be used for the determination of zinc ions in solution. The formation of the oxinate is similar to the above method. The addition of gum arabic solution stabilises the suspension.

Prepare a 2% solution of gum arabic by grinding the solid to a fine powder before dissolving in water and (if necessary) filtering and then making up to 100 cm^3 in a volumetric flask. Prepare a 0.06 M solution of purest zinc sulphate acidified with dil. HCl. Dilute in stages 100-fold. Prepare a solution of 5% oxine w/v in 12% w/v glacial acetic acid using the purest grade. Using a burette, deliver volumes of the zinc solution in the range 5-25 cm^3 into separate 100 cm^3 volumetric flasks. To each flask add 10 cm^3 of 2 M ammonium acetate, 4 cm^3 of the gum solution and 0.40 cm^3 of the oxine solution using a calibrated micropipette. Make up to the mark with water, shake and immediately record the fluorescence spectrum of the most concentrated solution. Locate the wavelength maximum and use this wavelength for the other solutions which are made up immediately before use. A reference cell may contain a suitable fluorescent solution. Plot the intensity of the emitted light against [Zn^{2+}] and use the standardisation plot to determine the concentration of any unknown dilute zinc salt solution.

17.4 STUDIES OF ZINC COMPLEXES

Zinc forms a number of complexes but they are not as numerous as those of the 3d transition metals. They are generally less stable than those of the preceding metals. The complexes may be cationic, anionic or neutral e.g. the complex with 8-hydroxyquinoline encountered above.

17.4.1 Preparation and analysis of $[Zn(NH_3)_4][BF_4]_2$

The tetrahedral tetraamminezinc(II) ion can be precipitated by the large tetrafluoroborate(III) anion. The complex can be analysed by dissolving in a known excess of HCl, back titrating the excess with standard alkali.

Recrystallise 3 g of NH_4BF_4 (Sec.4.4.1). Dissolve 2 g of zinc sulphate heptahydrate in the minimum volume of water. Add conc. ammonia until the precipitate initially formed has completely dissolved. Add a solution of the recrystallised fluoroborate to the zinc salt solution with stirring. Allow the precipitate to stand until crystallisation seems complete. Filter the complex precipitated under suction. Wash on the filter with small volumes of acetone. Dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on zinc.

Weigh out accurately about 0.25 g of your preparation into a conical flask. Add 50.0 cm^3 of 0.1 M HCl from a burette followed by a few drops of methyl red indicator. Titrate with standard 0.1 M NaOH until the colour changes to yellow. Repeat to obtain concordant results. Calculate the average % purity of your preparation.

17.4.2 Preparation and ir spectrum of $[Zn(acac)_2].H_2O$ (acac=2_y4-pentanedioate)

(Inorg. Synth. **10** (1967)74)

Dissolve 10 g 2,4-pentanedione and 4 g NaOH in 50 cm^3 water. Add the solution slowly and with stirring, to a solution of 14.4 g zinc sulphate hepthydrate in 50 cm^3 water. Allow to stand for one hour, filter under suction, wash with water and dry by continued suction while pressing between filter paper. Weigh your product and calculate the % yield based on Zn.

Prepare a KBr disc and run the infrared spectrum over the range 4000-400 cm^{-1} (Sec.2.4.2). Obtain elemental analysis data (%C, %H).

17.5 ANALYTICAL CHEMISTRY OF CADMIUM

Like zinc ions, cadmium ions can be titrated in buffered solutions with EDTA but the end-point is more easily located by high frequency titration than by an indicator. Among the instrumental methods suitable for the determination of cadmium in dilute solutions, atomic absorption is ideal and polarography is also suitable. Gravimetrically, cadmium can be precipitated as the oxinate similar to zinc. In addition, it can be precipitated as molybdate.

17.5.1 Complexometric titration of cadmium

The cadmium complex with EDTA is nearly as stable as that of zinc. In the direct titration, xylenol orange is a suitable indicator and hexamine is used to buffer the solution.

Prepare 0.05 M solution of purest cadmium sulphate or nitrate. Pipette 25.0 cm^3, dilute with 50 cm^3 of water and add 3 drops of xylenol orange indicator and then one drop of dilute sulphuric acid to turn the colour to yellow. Then introduce powdered hexamine with agitation until the colour is clearly red. Alternatively add a 15% solution of hexamine. Check with a pH stick that the pH is 5. Then titrate with standard 0.05 M EDTA solution until the solution turns yellow. Repeat to obtain concordant results and calculate from the average titre, the concentration of Cd(II) in mols dm^{-3}.

The end-point is more easily detected by high frequency titration. Use 0.01 M solution of cadmium salt and 0.01 M solution EDTA. Plot the instrument reading against the volume of EDTA. The inverted V shaped plot has a maximum at the end-point.

17.5.2 Determination of cadmium ions by atomic absorption (Sec.2.4.3)

Prepare a stock solution of 0.05 M cadmium sulphate or nitrate. By successive dilution prepare a series of solutions in the concentration range of 5 x 10^{-4} to 10^{-5} M. Set the wavelength of the spectrometer to 228.0 nm (326.1 nm is a secondary wavelength). Adjust the air flow at 8.0 dm^3 min^{-1} and C_2H_2 flow at 3.0 dm^3 min^{-1}. Then measure the absorbance of each solution and plot against concentration. Use the calibration plot to determine the concentration of an unknown solution.

17.5.3 Gravimetric determination of cadmium

Precipitation as oxinate

Follow the same procedure as for zinc. Prepare a stock solution by weighing 3.4 g of the sulphate or 4.1 g of the nitrate and make up to 250 cm^3 in a volumetric flask. Pipette 25.0 cm^3 into a 400 cm^3 beaker. Add 75 cm^3 water and then gradually add 1 M sodium carbonate solution until there is a faint cloudiness. Remove this by the dropwise addition of dilute acetic acid. Warm to 60°C and dissolve in the solution 5 g purest sodium acetate. Then add 2% solution of 8-hydroxyquinoline in ethanol with stirring until a slight excess has been added. Heat the suspension to the boiling point and allow the precipitate to settle. Check for complete precipitation and filter after 10 minutes in a prepared G4 sintered crucible. Wash on the sinter with hot water and dry to constant weigh at 130°C. Calculate from the average of duplicates the concentration of cadmium in mol dm^{-3}.

17.6 COMPLEX COMPOUNDS OF CADMIUM

Cadmium, like zinc, forms cationic, anionic and neutral complexes which generally resemble the zinc complexes.

17.6.1 Preparation and analysis of $[Cu(en)_2][CdBr_4]$

*(G.Spacu; P.Spacu, Bull.Soc.Sriite Clug.*5(1930)387).

$CdBr_2$ dissolves in KBr solution forming a tetrahedral tetrabromocadmiate(II) anions which can be precipitated by large cations.

Prepare a solution of 2.72 g cadmium bromide and dissolve in this solution 2.38 g KBr and heat to dissolve the solids. Prepare a solution 2.42 g copper(II) nitrate trihydrate to which 1.2 g diaminoethane has been added and heat the solution. Add the hot solution slowly and, with constant stirring, to the hot cadmium complex solution. Allow to cool and filter the dark violet crystals under suction. Wash on the filter with water to remove any unreacted compounds then with small volumes of alcohol and ether . Dry by continued suction while pressing between filter paper.

17.7 ANALYTICAL CHEMISTRY OF MERCURY

Hg(II) can be precipitated from solution in nitric acid by periodates. The precipitated $Hg_5(IO_6)_2$ is the basis of a gravimetric method. It can also be used for iodometric titration by adding excess iodide in acidic solution and titrating the liberated iodine. A spectrophotometric method is based on the formation of a coloured complex with dithizone.

17.7.1 Titrimetric determination of Hg(II)

Weigh out accurately 3.4 g purest mercury(II) nitrate. Dissolve in 0.15 M nitric acid and make up to 250 cm^3 in a volumetric flask using the acid for dilution. Pipette 25.0 cm^3 aliquot of the solution into a beaker. Add about 125 cm^3 0.15 M nitric acid. Dissolve 2 g purest sodium or potassium periodate in 50 cm^3 water and add the solution slowly with stirring to the boiling mercury(II) solution. Cool and check for complete precipitation. Filter through a GF paper and wash on the filter with small volumes of water. Transfer the paper carefully to a conical flask and acidify freely with dilute HCl followed by 20% KI solution until all the precipitate dissolves leaving a clear solution. Titrate the solution with standardised 0.05 M thiosulphate using starch as indicator (Sec.7.3.3) or potentiometrically using a bright platinum electrode coupled with a calomel electrode (Sec.2.5.1). Repeat and calculate from the average titre the concentration of Hg(II) in mol dm^{-3}.

17.7.2 Spectrophotometric determination of Hg(II)

Dithizone forms an orange complex with Hg(II) ions and the complex is soluble in chloroform.

Prepare a 0.05 M solution of purest mercury(II) nitrate in 0.5 M sulphuric acid. By successive dilution, prepare 4 or 5 solutions in the range 0.0075-0.0005 M using sulphuric acid for dilution. Pipette 20.0 cm^3 of each solution into a graduated separating funnel and add 20 cm^3 of 0.5 M acetic acid and 5.0 cm^3 of chloroform. Shake well until the top aqueous layer is saturated. Run off and discard the lower chloroform layer. Pipette into the funnel 5.0 cm^3 of 0.001 M dithizone in chloroform and shake well to extract the orange complex into the lower layer, leaving a colourless top layer. Run off the bottom layer into a 10 mm spectrophotometer cell. Use the extract from a 0.01 M solution to run the spectrum over the range 400-600 nm and locate the wavelength of maximum absorption and record the absorbance at this wavelength. Using 20.0 cm^3 aliquots of the other Hg(II) solutions, measure the absorbance of the orange complex at the wavelength found from the spectrum. Plot absorbance against [Hg(II)]. Repeat using solutions of Hg(II) chloride. Use the calibration plots to find [Hg(II)] of solutions of unknown concentration.

17.7.3 Gravimetric determination of Hg(II)

Follow the same steps as in 17.7.1 but filter the precipitate in a prepared sintered glass crucible. After washing the precipitate with water, dry to constant weight at 100°C. Calculate from duplicates, the concentration of Hg(II) in mol dm^{-3}.

17.8 COMPLEX COMPOUNDS OF MERCURY(II)

Hg(II) is a soft acid and tends to coordinate to soft bases e.g. I^- and SCN^-.

17.8.1 Preparation of Ag(I) and Cu(I) tetraiodomercurate(II)

These are readily obtained by precipitating $[HgI_4]^{2-}$ by either of the two coinage metals. In the case of Cu, Cu(II) sulphate is reduced to Cu(I) prior to the precipitation. These two complexes are said to be **thermochromic** i.e. undergo reversible colour change at a characteristic temperature (*J.Chem.Educ.*75(1998)57).

(a) To a boiling solution of 3.25 g mercury(II) nitrate, add a 10% KI solution until the precipitate initially formed just redissolves to produce a clear solution. Then add 50 cm^3 of a solution of 3.4 g silver nitrate. Boil to achieve complete precipitation. Allow to cool and filter at the pump. Wash with a small volume of acetone and dry by continued suction. Place a small amount in a micro-tube. Immerse in a heated water bath and record the temperature at which the colour changes from yellow to orange. Then remove from the bath and allow to cool and again note the temperature at which a colour change takes place.

(b) To prepare the Cu(I) complex, weigh out 2.5 g copper(II) sulphate pentahydrate and dissolve in 25 cm^3 water. Dissolve 6 g sodium sulphite heptahydrate and 5g NaCl in 50 cm^3 water. Boil the solution and add to it the copper(II) solution. Stir to obtain a clear solution after initial precipitation. Use half the quantities of the tetraiodomercurate(II) prepared above and add to this solution the copper(I) solution prepared, with constant stirring, to obtain a precipitate. Allow to cool, filter, wash and dry as above. Check the temperature at which the colour changes from red to purple as above, and the reverse change on cooling.

17.8.1.1 Qualitative tests

Carry out the following sequence of reactions on a small quantity (0.02-0.025 g) of the prepared solid. Record and interpret your observations.

(a) Suspend the solid in water. Heat to boiling and cool. Add an excess of potassium iodide solution, boil until the reaction is complete and cool. Separate the precipitate (A) from the solution (B). Thoroughly wash A with water.

(c) Suspend A in water. Add an excess of potassium thiocyanate solution, warm, shake and and cool. Separate the precipitate (C) from the solution (D).

(d) Wash C with water and add concentrated nitric acid.

(e) Acidify D with dilute hydrochloric acid and add several drops of potassium chromate solution followed by carbon tetrachloride. Shake and allow to stand.

(f) To separate portions of B:
  (i) immerse a piece of copper wire (freshly cleaned in concentrated nitric acid and washed with water), warm and allow to stand:
  (ii) acidify with dilute hydrochloric acid, pass in hydrogen sulphide and warm.

17.8.2 Preparation of $[Cu(en)_2][HgI_3(SCN)]$ (Ref. as in Sec.17.6.1)

Prepare the nitrate of the copper complex as in Sec.17.6.1. Dissolve 2.7 g mercury(II) chloride in 35 cm^3 and add to the solution 3.3 g KI and 3.4 g NH_4 SCN. After dissolving the solids, add 15 cm^3 ethanol and carefully bring to the boil on an electric water bath. Using the copper complex prepared as above (Sec.17.6.1), add the concentrated solution to the mercury complex solution with vigorous stirring until precipitation seems complete. Cool in an ice/water bath to complete the precipitation and continue as in 17.6.1.

Analytical methods for this complex and the cadmium complex are given in the reference.

17.9 THE NATURE OF MERCURY (I)

Physicochemical measurements are used to establish whether Hg(I) in its salts is represented by Hg^+ or by the $(Hg\text{-}Hg)^{2+}$ ion. If X-ray diffraction measurements are available, a comparison of the d spacings of the chlorides of Hg(I) and Hg(II) would clarify the situation. The Raman spectrum of Hg(I) chloride could reveal a band due to Hg-Hg vibration.

An easy experiment to establish the nature of the Hg(I) ion is to compare the molar conductivity of Hg(I) nitrate to that of KNO_3 and $Ba(NO_3)_2$ since the latter is uni-divalent electrolyte whereas potassium nitrate is a uni-univalent electrolyte.

Weigh out accurately 7.02 g of purest mercury(I) nitrate dihydrate, 1.26 g of purest potassium nitrate and 3.27 of purest barium nitrate. Dissolve each solid separately in conductivity water and make up to 250 cm^3 in a volumetric flask. Use a conductivity cell with platinised electrodes, some centimetres apart which had been cleaned and stored filled with conductivity water. Rinse the cell with the mercury(I) solution several times, place in a thermostat at 298 K, allow to equilibrate thermally and measure its resistance (Sec.2.5.2). Repeat the same steps using the other two solutions and compare the data from the three solutions. What conclusions can be drawn from your results?

Grind mercury(I) chloride to a fine powder. Measure its magnetic susceptibility (Sec.2.1.3). How does the result help to elucidate the nature of Hg(I) ions?

17.10 PHOTOCATALYSIS EXPERIMENTS

The chalcogenides of the three metals are semiconductors and generally act as photocatalysts in oxidations and/or reductions induced by radiation. On the other hand, Hg(II) and Cd(II) can be photocatalytically reduced under suitable conditions. Care has to be taken to allow for the adsorption of the ions by the powdered catalyst.

17.10.1 Photocatalysed reduction of Ag(I) by ZnO

Weigh out accurately 0.20 g purest ZnO. Suspend in 20 cm^3 of saturated silver sulphate solution. Stirring the suspension magnetically, irradiate in a reproducible position under a low pressure mercury lamp for 30 minutes. Filter through a prepared sintered crucible, wash till the filtrate is Ag^+-free. Heat at 100°C for one hour and reweigh.

Repeat using 0.20 g of either anatase or rutile. In a repeat experiment, instead of heating the product, add 20 volume H_2O_2 to achieve maximum colour change.

17.10.2 The photocatalysed removal of Hg(II) from aqueous solution

The electrons promoted from the catalyst's valence band to its conduction band, when a suspension is uv-irradiated, will reduce Hg^{2+} in solution to Hg which will deposit on the catalyst particles.

Weigh out accurately 0.20 g of purest ZnO, anatase or tungsten trioxide into suitable containers. Pipette 25.0 cm^3 of 0.05 M or 0.005 M mercury(II) nitrate or chloride. Irradiate in a reproducible position under a low pressure mercury lamp for say 30 minutes, while the suspension is magnetically stirred. After irradiation, filter (after centrifuging if necessary). Withdraw with a pipette 20.0 cm^3 of the filtrate into a 50 cm^3 separating funnel. Use the procedure in Sec.17.7.2 to determine [Hg(II)] in the filtrate and hence calculate the % Hg(II) removed from solution. It is advisable to have 3 or 4 suspensions irradiated simultaneously, combining the filtrates and determining [Hg(II)] as before. The suspensions should be kept in reproducible positions under the lamp and stirred at a constant speed. A blank determination for a suspension shaken in the dark for the same period, gives the % of Hg(II) ions adsorbed by the particles. This should be subtracted from the total decrease in [Hg(II)]. Compare the results from the different catalysts and for the two concentrations used. Compare the behaviour of the nitrate and chloride of Hg(II).

17.10.3 The photocatalysed removal of Cd^{2+} ions from aqueous solution

Cd(II) ions are more difficult to reduce than Hg(II). For their photocatalysed reduction, purging the suspension with nitrogen, removes oxygen which would compete with Cd^{2+} ions for the photopromoted electrons. In addition, a hole scavenger e.g. methanol will minimise holeelectron recombination which would reduce the efficiency of the process.

Use a medium or a high pressure mercury lamp and place the catalyst/solution suspension in a vessel surrounding the lamp's quartz thimble. Arrange for stirring the suspension magnetically and for bubbling nitrogen through the suspension throughout the run. The lamp should be cooled by water or nitrogen, according to the recommendation of the manufacturer. Place a suitable volume of 0.1% w/v(w being the weight of purest 3 $CdSO_4.8H_2O$) in the irradiation vessel. Ensure that the level of the suspension is above the lamp's arc. Irradiate a suspension of 0.4% w/v of anatase catalyst, the solution containing say 5% v/v of methanol. After 3 hours irradiation, centrifuge and then collect by filtration an aliquot for [Cd(II)] by atomic absorption or a suitable instrumental method. Carry out a blank by stirring a similar suspension for 3 hours in the dark and determining [Cd(II)] in the filtrate which would give the amount adsorbed. Use this as a correction for the amount reduced. Study some of the variables such as the irradiation time, the catalyst concentration and [MeOH]. Draw your conclusions.

17.10.4 The photocatalysed reduction of chromate using ZnTe or CdSe

Use a 10^{-2} M potassium chromate solution whose pH has been adjusted to 7.0. Suspend the catalyst in the solution with the catalyst concentration of 0.8% w/v. Irradiate the magnetically stirred suspension for 2 hours using a xenon lamp (if available) where the lamp output is focused on the optical glass window of the irradiation vessel. If a medium pressure mercury lamp is used, place the suspension in a vessel surrounding the Pyrex thimble of the lamp. After irradiation, centrifuge and collect by filtration, an aliquot for absorbance measurement. Run the spectrum of the original solution over the range 300-600 nm in a 1 cm cell and locate the wavelength of maximum absorption and record the absorbance at this wavelength. Measure the absorbance at this wavelength of the filtrate after irradiation. Prepare a calibration plot for absorbance against [chromate] using a range of 4×10^{-4}-4×10^{-5} M solutions (as in Sec.12.4.4 for dichromate) and use it to find out [chromate] in the filtrate and hence calculate the % chromate reduced by irradiation

These photocatalysed reactions are environmentally important since they remove toxic metal pollutants from waters.

18

Nuclear, Radiochemical and other Experiments

18.1 INTRODUCTION

This concluding chapter contains a number of interesting experiments which did not fit into the previous chapters. Various nuclear and radiochemical experiments are described because certain physico-chemical processes can be only demonstrated using radioisotopes as tracers, and because the stringent safety rules for using open radioactive sources trains students in safety and careful planning of experiments. The other experiments described complement the previous chapters increasing yet further the wide range of experimental techniques covered in this book.

18.2 SEPARATION OF PROTOACTINIUM FROM URANIUM BY SOLVENT EXTRACTION

The nuclide ${}^{238}_{92}U$ decays according to the following scheme:

$$ {}^{238}U \xrightarrow[4.5 \times 10^9\ yr]{\alpha(4.18)} {}^{234}Th \xrightarrow[24d]{\beta\,(0.19)} {}^{234}Pa \xrightarrow[725]{\beta^-(2.31)} {}^{234}U \xrightarrow[2.5 \times 10^9\ yr]{\alpha\,(4.77)} {}^{230}Th \qquad (18.1) $$

(All the energies are in MeV units: the β^- energies are the maximum energies E_{max}. γ radiation is emitted in all these disintegrations). Protoactinium forms a chloro-complex in presence of high concentrations of hydrochloric acid. Uranium also forms a chloro-complex (coloured yellow) but thorium does not. About 95% of the proto-actinium complex is extracted by organic solvents such as *iso*-butylmethyl ketone or amyl acetate but only a third of the uranium complex is extracted. After the extraction, when the organic layer is counted in a liquid Geiger-Müller (G-M) counter, the α particles from ${}^{238}U$ will not penetrate its glass wall and will not be detected. The count rate of the organic layer is due to the energetic β^- particles from the short-lived ${}^{234m}Pa$. ${}^{234}Th$ is not extracted in the organic layer and its low energy β^- particles are less penetrating than those of ${}^{234m}Pa$.

When a solution of uranyl nitrate, $UO_2(NO_3)_2$, in hydrochloric acid is shaken with the organic solvent, the bottom aqueous layer will contain ${}^{234}Th$, and most of the ${}^{238}U$. In this layer, ${}^{238}U/{}^{234}Th$ will produce the daughter ${}^{234m}Pa$. On counting in a liquid G-M. counter, the growth of the activity of ${}^{234}Pa$ can be followed. After the solvent extraction, the top organic layer will contain the chloro-complex of ^{234m}Pa, with some ^{238}U but only the particles of ^{234m}Pa will be counted in a liquid G-M counter. By following the count rate with time, the characteristic half-life, $t_{½}$, of ^{234m}Pa may be determined.

Objects of the experiment

1 The procedure involves the determination of the half-life of the short-lived ^{234m}Pa. This determination of $t_{½}$ is useful for the identification and characterisation of radioisotopes.

2 The liquid G-M counter is used for measuring the activity due to the more energetic β^- particles of ^{234m}Pa separated from U and Th.

Pour carefully, through a funnel, 3.0 cm^3 of a 33% w/v solution of $UO_2(NO_3)_2$ into a 10 cm^3 cylinder and add 7.0 cm^3 of concentrated hydrochloric acid and transfer to a 50 cm^3 separating funnel. Add 9.5 cm^3 of isobutylmethyl ketone from a measuring cylinder into the funnel and shake vigorously for half a minute. As soon as the two liquids start to separate, run off the heavier aqueous layer into a 50 cm^3 beaker and start a stopwatch. When all the aqueous layer has been separated, pour the organic layer carefully into a liquid G-M counter. The counter should be clean, dry and ready for use before the experiment is started. The organic solvent layer will cover the G-M counter but no liquid should reach the outer glass surface. This surface is carefully wiped before introducing the counter into the lead castle to avoid its contamination.

The liquid sample is counted, as soon as possible, for 10 second intervals. Record the count rate and continue counting, increasing the time to 20, 40 and 60 seconds gradually as the count rate drops. After about 10 minutes, the count rate is found to be nearly constant. About 20 minutes after starting the counting, a final count for 600 seconds is made to determine the background due to any activity which passed to the organic layer other than that of ^{234m}Pa. Each count rate is corrected for the resolving time of the counter (obtained from tables) and for the experimentally determined background.

A plot of $\log_{10}$ (corrected count rate) as ordinate against time, as abscissa, is constructed. The half-life, $t_{½}$, is calculated from the slope of the linear plot:

$$t_{½}=0.693/(2.30\text{x}slope)=\sim 0.301/slope \qquad (18.2)$$

The count rate may be extrapolated to zero time when the stopwatch was started and the half-life could be estimated from the time during which the count rate falls from A c.p.s. to A/2 c.p.s. Log -linear graph paper may be used to construct the linear plots of the decay of the activity of ^{234m}Pa.

If necessary the organic layer is mixed with the aqueous layer in the separating funnel, which is shaken vigorously for ½ minute. The aqueous layer is then run into a beaker as before and the organic layer is counted as soon as possible in the same way as described above. The experiment may be repeated using amyl acetate for extraction.

The counter is cleaned by washing with small amounts of conc. HCl several times and then with water discharging the washings into the bottle labelled Radioactive Aqueous Residues. At the end of the experiment, pour the liquids into the respective labelled bottles: Radioactive Organic Residues and Aqueous Residues. The activity of the solutions are very low but it is advisable to use disposable gloves, to be discharged in a special pedal bin. At the end, dry your hands after washing them thoroughly.

18.3 BACKSCATTERING OF β^- PARTICLES

β^- particles passing through a medium undergo collisions with its nuclei and electrons. As a result of these scattering collisions, a particle may reverse its path when it is said to be back-scattered. The number of back-scattered particles increases as the thickness of the medium increases up to a maximum or plateau when saturation back-scattering is reached. Thicknesses above a certain value (about 1/3 of the range of the β^- particles in the medium) will not give an increased number of back-scattered particles. The back-scattering intensity depends on the angle of scatter (i.e. the geometry of the set up), the atomic number of the scattering medium.

Stick with sellotape a piece of ^{90}Sr (pure β^- emitter) (^{90}Sr) foil to a thick aluminium plate (Al) (~5 mm thick) and hold it in position (with thick tape) to a thin aluminium plate which fits just under the end-window of a Geiger-Müller (G-M) counter inside its lead castle. The Sr foil will be separated from the counter by thick aluminium which absorbs its β^- particles. Both aluminium plates have a circular hole opposite the end window of the counter. (See Fig.18.1)

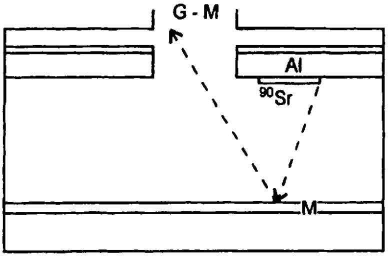


Figure 18.1 A sketch of the arrangement for studying the hack-scattering.

Place an aluminium absorber (say 21.0 mg cm^{-2}) (M) on the second shelf of the counter's lead castle and count for 200 seconds. Repeat this after replacing the aluminium absorber by thicker absorbers in turn (e.g. 55, 82, 240, 712 and 1335 mg cm^{-2}).

Replace the aluminium absorber (1335 mg cm^{-2}) by a copper absorber of the same thickness on the second shelf and count for 200 seconds. Repeat using instead of copper, lead absorbers of the same thickness. Repeat using an iron absorber instead.

Change the position of the ^{90}Sr source by moving it to alter the angle of scatter and place the lead absorber used previously and count for 200 seconds.

To determine the background stick the ^{90}Sr source at the bottom of aluminium absorber (1335 mg cm^{-2}) and count for 600 seconds. Calculate the count rate and subtract it from all count rates determined.

Plot the corrected count rate against the thickness of the aluminium absorbers. Plot the corrected count rate, against the atomic number of the absorber used. Comment on your results.

18.4 INVESTIGATION OF THE EXCHANGE OF AgI(s) and Ag^+(aq.) USING ^{110m}Ag

The dynamic nature of the equilibrium between a sparingly soluble ionic solid and its ions in aqueous solution can be only demonstrated by using radiotracers, e.g. ^{110m}Ag.

Using labelled Ag nitrate solution, AgI is prepared by precipitation. When equal masses of the labelled solid are shaken with inactive silver nitrate, the activity acquired by the solution is due to the exchange between the active solid and silver ions in solution. The very low solubility of AgI could not account for the observed activity. ^{110m}Ag has a half-life of 253 days and emits β^- particles as well as γ rays. The decay scheme is represented in Fig.18.2. Although the β^- particles are not very energetic, the solid AgI may be counted under an end-window G-M counter whereas the Ag^+ solution could be counted in a liquid G-M counter. Alternatively the γ rays from the solid or the solution may be counted in a scintillation counter.

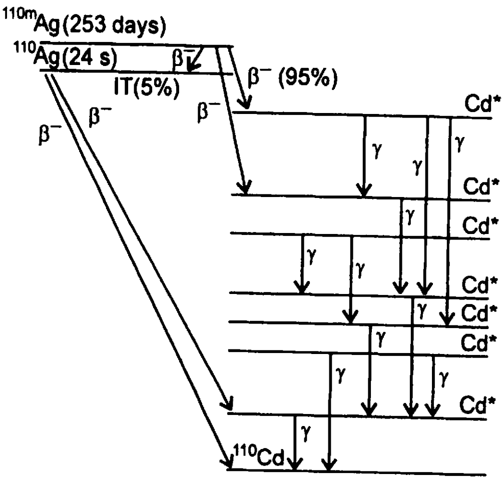


Figure 18.2 The decay scheme of ^{110m}Ag.

Dissolve a 10μCi(370 kBq) labelled silver tablet in a beaker by adding dilute nitric acid, add a solution of 18.2 g inactive silver nitrate in water and make up the combined solution to 1 dm^3 in a volumetric flask. Make up a solution of 2.96 g KI dm^{-3} (to which a few cm^3 of conc. nitric acid have been added) and add to this solution, the labelled silver nitrate solution, dropwise with constant stirring. Heat to ~80°C for 10 minutes. Filter under suction, wash thoroughly with very dilute nitric acid and dry at 120°C. Weigh accurately 5.0 g of your preparation and place it in the inner beaker of Fig.2.1, add to it 100 cm^3 of 0.002 M inactive silver nitrate and keep magnetically stirred at 25°C as you start a stopwatch. At intervals, apply suction to withdraw an aliquot of the solution through the filter. Pipette a 1 cm^3 aliquot (after 3 minutes) into 10 cm^3 of water in a counting vial and count the γ activity in a NaI (Tl-activated) scintillation counter using integral counting with a suitable H.V. and an appropriate level of pulse gate (to exclude most of the thermal noise and background counts). Count for at least 1000s. Repeat at suitable times up to 30 minutes. Repeat using a lower temperature, say 15°C by circulating cold water in the jacket of the beaker. Plot the corrected count rate against time and comment on your results. Use the safety instructions in Sec.18.9.1.

18.5 SELF ABSORPTION AND BACKSCATTERING OF LOW ENERGY β^- PARTICLES

When a β^- emitter is counted as a solid on a planchet, some of the β^- particles hit the planchet and bounce back. The back-scattering increases as the atomic number of the planchet material increases. The solid β^- emitter will also reflect some of the β^- particles. This self-scattering depends on the presence of heavy atoms in the sample and on the shape and size of the sample crystals. When the layer of the β^- emitter is relatively thick, some of the β^- particles are absorbed by the sample. When the sample is very thin, the self-absorption is negligible and it is said to be infinitely thin. When the thickness of the sample is such that the β^- particles from the bottom cannot reach the top, the sample is described as infinitely thick. Self-absorption depends on the weight of the sample. The count rate can be kept fairly constant when the sample is infinitely thin or infinitely thick.

In this experiment the weak β^- emitter ^{35}S is used to demonstrate the phenomena of back-scattering and self-absorption. An infinitely thin layer of $Na_2{}^{35}SO_4$ is deposited on two aluminium planchets and on a steel planchet. A constant activity is used for the three $Na_2{}^{35}SO_4$ samples. Comparing the count rates of the two aluminium planchets shows the reproducibility. Comparing the count rates of the aluminium and of the steel planchet demonstrates the effect of atomic number on the back scattering. Two $Ba^{35}SO_4$ precipitates, of different thickness are counted. Comparing their count rates demonstrates the phenomenon of self-absorption.

I Wash two aluminium planchets and a steel planchet with alcohol and dry by vigorous wiping with tissue paper. The planchets should be very clean to ensure that the solution to be evaporated is evenly spread on them. This is essential to produce infinitely thin deposits of uniform size and thickness.

With a thin cotton swab apply a well-defined ring of silicone grease (this keeps the liquid from spreading into the corners of the planchet which would draw most of the sample into the corners, leading to poor reproducibility and low counting efficiency), on the outer 1/8in of each planchet. Use a toothpick to add a bit (<1 mg) alkaline solid detergent, e.g. Alconox to the inner part of each planchet. Then pipette 0.1 cm^3 of $Na_2{}^{35}SO_4$ solution. The pipette tip should be moved around to speed dissolving the detergent but should be kept away from the grease. The pipette is rinsed with a drop of H_2O, which is discharged into the planchet. Evaporate off the water under an infrared lamp, kept 9 inches above the planchet. The solution should be spread as evenly as possible during the evaporation, e.g. by tilting the planchet. The dried samples are counted in the top shelf of the lead castle of an end-window G-M counter. 10,000 counts are collected and the count rate is corrected for the background and for the resolving time of the counter.

II To a 4.5 cm^3 aliquot of the radiosulphate solution, add 243 mg of anhydrous Na_2SO_4, weighed to the nearest mg and swirl carefully to dissolve the solid in the solution. Transfer 3.0 cm^3 of the solution to a 250 cm^3 flask, using a serological pipette. Add 50 cm^3 of H_2O and 1 cm^3 of 0.05 M HCl. Clamp the flask, bring the solution to a boil and then add 10 cm^3 of a 10% solution of barium chloride, in small portions, using a Pasteur pipette. Allow the suspension to cool slowly and store the pipette in the cooling flask, ejecting any liquid that may rise in the pipette. To the cool suspension, add a drop of a nonionic detergent. Apply suction to the Buchner flask of the filtering assembly, Fig.18.3, which is fitted with a fibre-glass disc. Transfer about 5 portions of the sulphate suspension to the filtering assembly with a Pasteur pipette, moving its tip around the funnel walls. Using the pipette as a pouring rod, pour as much of the suspension as possible into the filtering assembly. Repeat with rinse boiling water. Before the deposit becomes dry, rinse the chimney and filter cake with 10 cm^3 of boiling water, using a clean Pasteur pipette. Keep the suction for a minute, remove the upper part of the funnel carefully and then turn off the suction. Transfer the filter paper and deposit to a planchet and dry for 20 minutes under an infrared lamp. Measure the activity, placing the planchet on the top shelf of the lead castle. Transfer the remainder of the radiosulphate solution (i.e. 1.5 cm^3) to a 100 cm^3 flask. Add 25 cm^3 of H_2O and 0.5 cm^3 of 0.05 M HCl, bring to the boil and then add 5 cm^3 of the 10% barium chloride solution as described above. Follow the detailed procedure as given above and compare the corrected count rates of the two $Ba^{35}SO_4$ deposits.

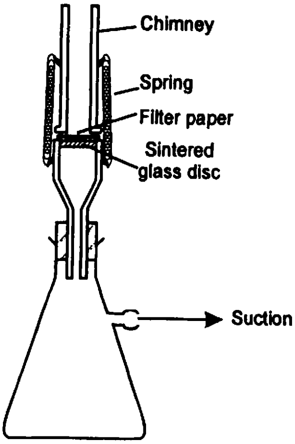


Figure 18.3 A sketch of the filter assembly.

The solid planchets used in the first part of the experiment are discarded in a special beaker. The solid $Ba^{35}SO_4$ precipitates and the filter paper are discarded in a second labelled container. Soak contaminated glassware in Decon 90 overnight after rinsing with water and storing the water in a bottle labelled ^{35}S residues.

18.6 THE NEUTRON SOURCE AND NEUTRON ACTIVATION

Although a number of radioisotopes are commercially available, we found that using our neutron source, allowed the activation of several elements. The activated species were used for many experiments to be described later.

18.6.1 The laboratory neutron source

In our Radiations Laboratories, a 1 Ci ^{241}Am/ ^{9}Be source produced neutrons by the nuclear reaction between α particles, from Am, and Be nuclei according to:

$$^{9}Be(\alpha,n)^{12}C \tag{18.3}$$

The advantages of this source are the long half-life of Am($t_{½}$=458 years) and the low energy of its γ rays (0.06 MeV). The high energy neutrons (E_n up to about 12 MeV) produced by reaction (18.3) are thermalised by paraffin wax, to render them more effective in inducing nuclear reactions. A thickness >0.05 m of wax is considered adequate for moderating neutrons.

Fig.18.4a depicts the source, with its lead container, placed in a perspex tube embedded in paraffin wax in a mobile steel drum (0.3 m radius, 0.65 m high). Embedded at the same level as the source were five perspex tubes at 45 mm, five at 105 mm and two at 130 mm from the source. The thermal neutron flux or fluence is a maximum at about 50 mm from the source, in the innermost channels; the fluence decreasing sharply as the distance increases beyond 50 mm.

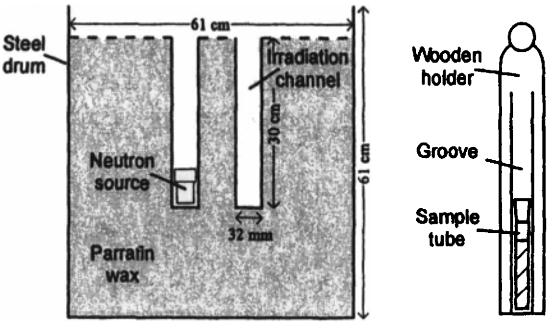


Figure 18.4 A sketch of thecross-section of the drum (a) enclosing the neutron source. The wooden holder (b) is shown on the right.

Using the laboratory neutron source, we could demonstrate:

(i) the exponential decay and hence the half-life of induced β-activity;
(ii) the form of the growth of activity with irradiation time;
(iii) the high neutron absorption by cadmium leading to a product of low activity;
(iv) the resolution of a composite decay curve arising from a mixture of sources with two different half-lives;
(v) simple neutron activation analysis;
(vi) the attenuation of neutron fluence in a target.

18.6.2 Thermal neutron reactions

When a target nucleus, ${}^{A}{}_{Z}X$, is irradiated by thermal neutrons, the reaction induced, known as radiative capture, is represented by:

$$ {}^{A}{}_{Z}X(n,\gamma){}^{A+1}{}_{Z}X \qquad (18.4)$$

where the product nucleus is a radioactive isotope of the target and it usually decays according to:

$$ {}^{A+1}{}_{Z}X \rightarrow {}^{A+1}{}_{Z+1}Y + \beta^{-} + \bar{\nu} + Q \qquad (18.5)$$

The capture of the neutron raises the neutron/proton ratio in the compound nucleus formed, favouring β^{-} emission. Reaction (18.5) is usually accompanied by γ emission from the excited states of ${}^{A+1}{}_{Z+1}Y$.

When a target of mass m is irradiated for time t by thermal neutrons, the activity induced, A_o, will be given by:

$$A_o=(\Phi m f\sigma L/M)[1-\exp(-t\ \ln 2/t_{0.5})] \qquad (18.6),$$

where Φ is the neutron fluence, L is the Avogadro constant, f is the fractional abundance of the target isotope whose relative atomic mass is M and whose activation cross section is σ and $t_{½}$ is the half-life of the radioactive product. When a sample is irradiated for 6 $t_{½}$, the activity is equal to $(1-(½)^6)$, i.e. (63/64), of the maximum or saturation value (Φ mfσL/M). For most experiments there is, therefore, no point in irradiating samples for longer than about 7 times the half-life of the product of interest. The probability of a nuclear process is expressed in terms of a cross section, σ, usually quoted in barns (1 barn=10^{-28}m^2).

18.7 COMPARATIVE NEUTRON ACTIVATION ANALYSIS

In comparative activation analysis, an analysed standard is irradiated with thermalised neutrons under identical conditions to those of the sample to be analysed and they are counted after activation under the same conditions. The mass of element X to be determined is calculated from the relation:

Mass of X in sample
=mass of X in standard x count rate of sample/count rate of standard (18.7)

The standard should be as close as possible to the sample in composition, consistency etc. to minimise self shielding i.e. attenuation of the neutron flux in a target during irradiation, and the self absorption of β^- particles during counting.

18.7.1 Neutron activation analysis of VO(acac)$_2$ and V(acac)$_3$

Since $K_3[V(C_2O_4)_3].3H_2O$ can be easily prepared in a high degree of purity and can be easily analysed (Sec.10.3.2), it can be used as a standard for the determination of V in the two neutral complexes, ^{51}V has an abundance of 99.8%. In spite of its low cross-section of 4.5 barns, the convenient $t_{½}$ of the product of activation, ^{52}V, 3.77 min, and especially the energies of its decay products. β^-:2.47 MeV and γ:1.44 MeV, neutron activation analysis is a quick non-destructive method.

Weigh out accurately in a soda glass tube a mass of each of the three complexes so that they pack to the same height in the identical tubes. Place one sample in a wooden holder (Fig.18.4b)and place it in an irradiation channel and leave it for 27 minutes. Quickly start a stopwatch as you withdraw a tube from the source and note the time when you start counting it in a NaI(Tl) solid scintillation counter using integral counting setting the H.V, to 860 V and E to 2.5 V. Count initially for 20 second intervals, increasing the time gradually as the count rate decreases. Calculate in each case the count rate as c.p.s. after subtracting the previously determined background (including thermal noise) by counting an empty tube for a long time (4000-6000 seconds) under the same conditions. Plot the corrected count rate against time, taken as the time between start and finish of a counting period. Use semilog paper and extrapolate the best line to time=0 i.e. when the sample was withdrawn from the source. Taking the mass of V in the standard from previous analysis (Sec.10.3.2), calculate the mass of V in each of the two other complexes and compare with the chemical analytical data.

18.8 RADIOMETRIC TITRATION

In radiometric titration, the titrant and/or titrand is labelled. After the reaction and separation of the products e.g. by filtering a precipitate, either or both products are counted. A plot of the count rate against the volume of titrant shows a sudden change of slope at the end-point. An example of a reaction accompanied by precipitation is the titration of La^{3+} against $[Fe(C_2O_4)_3]^{3+}$ solution. When a solution of $La(NO_3)_3$ is bombarded with thermal neutrons in the neutron source, the nuclide ^{139}La (99.9% abundant) undergoes an (n,γ) reaction producing the radioactive ^{140}La. Its half life is 40.2 hours and its maximum β^- energy 1.34 MeV and its γ energy is 1.60 MeV ∴ it can be conveniently counted in ∴ a G-M end window, a G-M liquid or scintillation counter. Since $La(NO_3)_3.6H_2O$ is hygroscopic, the experiment could be adapted to determine its water of crystallisation.

Weigh out 4.3 g of the solid, dissolve in 100 cm^3 water. Place 25 cm^3 aliquots in large soda glass tubes and irradiate with thermalised neutrons in the neutron source for one week. Prepare 100 cm^3 of 0.4 M solution of $K_3[Fe(C_2O_4)_3].3H_2O$ (Sec.13.6.2). After withdrawing the nitrate solutions from the source, combine the solutions in a beaker on a tissue paper-lined tray. Wear disposable gloves throughout.

Pipette a volume V_1 cm^3 of the active solution (with a safety pipette) into a 25 cm^3 beaker. Heat nearly to boiling on a water bath and add V_2 cm^3 of 0.4 M iron complex solution dropwise and with stirring. Allow the suspension to settle and filter under suction through GF/F paper in a filter assembly, Fig.18.2, collecting the filtrate in a clean dry receiver. Pipette 9 cm^3 of the filtrate (safety pipette) into a liquid G-M counter. Transfer it to the lead castle and count for an adequate time (>60 min) setting the H.V.of the counter at 420 V.

V_1/cm^3	10	10	9	8	7	6	6	5
V_2/cm^3	2	3	4	5	4	5	6	7

Calculate the count rate in each case after subtracting the background. To obtain comparable results, multiply the count rate by $(V_1+V_2)/9$. Plot the count rate against the volume of titrant $V_2 x 10/V_1$. Taking the concentration of iron(III) complex as 0.40 mol dm^{-3}, calculate the concentration of $La(NO_3)_3$ in mol dm^{-3}. Hence work out the number of molecules of water of crystallisation in the solid.

18.9 THE SZILARD-CHALMERS PROCESS IN SOLID SODIUM IODATE

The Szilard Chalmers process

This involves breaking of a covalent chemical bond when a radioactive atom, formed by neutron activation, recoils as a γ ray is emitted. When the active hot atom formed is separated from the large excess of inactive target nuclei, its formation is demonstrated by its radioactivity. Separation is possible since the hot and the inactive nuclei are in different oxidation states.

^{127}I has a natural abundance of 100% and a medium activation cross-section. When activated by thermal neutrons, ^{128}I is formed and its β^- particles emitted are energetic (Fig.18.5) and its $t_{½}$ is not too short. When solid sodium iodate is activated by thermal neutrons, the I-O bond is broken as iodine recoils. NaI thus formed can be separated because it can be precipitated as AgI which can be separated from silver iodate which is soluble in conc. ammonia.

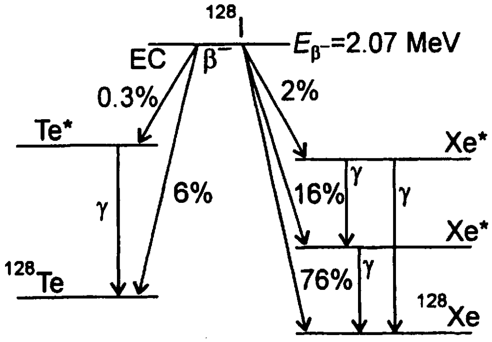


Figure 18.5 The decay scheme of ^{128}I.

Pack 1.2 g sodium iodate accurately weighed, into a soda glass tube and leave in the neutron source for 2½ hours. Start a stopwatch as you withdraw the tube from the source. Spread a portion of the active solid evenly on a weighed planchet, cover with sellotape and count under the window of a G-M counter using short counting times, increasing this as the count rate decreases. Quickly dissolve the remainder of the active solid in warm water in a beaker on a lined tray, add carrier powdered NaI and then silver nitrate solution, dropwise with stirring, to precipitate silver iodide and silver iodate. Then add ammonia solution and stir. Filter the suspension in a filter assembly using GF paper. Dry by suction and carefully transfer the paper to a planchet and cover with sellotape and count as above, noting the time on the stopwatch when you start either counter. Plot the count rate, corrected for background, against the mid-time of a counting period, taking the time when you started the stopwatch as zero. Use semilog paper and extrapolate to zero time to find the initial activity. After 2½ hours weigh the planchet with the iodate and find the mass of iodate dissolved and hence the mass of I in the precipitated AgI. Calculate the initial count rate g^{-1} of iodine, referring to the whole sample. Calculate the same for the iodate and estimate the % of I-O bonds broken by the recoil process.

Special precautions when using open radioactive sources

The dangers associated with the use of radionuclides can be divided into two main types of hazard, i.e. radiation and contamination. In elementary work, radiation hazard is a minimum as the amount of activity is small. Hence contamination is by far the greater hazard. The following rules have been drawn up to give a guide to those using radiation materials:

1 Laboratory coats must be worn.
2 Nothing should be removed from the radiation laboratory without permission.
3 Only properly prepared samples can be taken into the Counting Room. Carry these on a tray and in a suitable container.
4 A background count should be taken before and after counting a sample in order to check if the counting chamber has been contaminated or not.
5 Wear rubber gloves when using open sources and wash these thoroughly before removed. (Monitor if necessary). Or wear disposable polythene gloves which, after use, must be placed in the bins provided.

6 Never pipette a solution or a liquid by mouth. Use the appropriate safety pipettes and keep these in a beaker.
7 A tray, lined with disposable paper, should be used for all manipulations, e.g. transfer of solutions, dilutions, etc.
8 Evaporate all liquids and solutions in the fume cupboard.
9 Keep all contaminated glassware on a tray so that each flask, pipette, etc. can be accounted for at the end of the experiment.
10 Report any accidents or spillage immediately, ensuring that all other workers are aware of the contaminated area.
11 Before leaving the laboratory, wash your hands thoroughly and monitor them in the hand monitor.

18.10 STUDIES OF SURFACTANT SOLUTIONS

Except for non-ionic surfactants, other surfactants contain an organic carbon chain ending in a polar group which may be cationic or anionic. Solutions of surfactants have numerous applications and their aqueous solutions exhibit some interesting behaviour.

18.10.1 Aqueous solutions of sodium oleate

Sodium oleate is best prepared from oleic acid, which is commercially available in a pure state by saponification. Weigh out 28.25 g purest oleic acid, place in a 150 cm^3 beaker and heat on a water bath. Prepare 10% w/v solution of NaOH. Add the solution, slowly and with stirring, to the hot oleic acid until the acid is saponified (~40 cm^3 will be required). Separate the solid soap formed by filtration under suction. Recrystallise from ethanol. Prepare solutions from the solid using dilute NaOH to keep the pH at 10 to stop hydrolysis.

18.10.1.1 Analysis of sodium oleate solutions

Solutions of sodium oleate can be titrated against the cationic surfactant cetyltrimethyl ammonium bromide CTAB. The purest solid is kept in a vacuum a desiccator over P_2O_5 to dry it.

Prepare a series of oleate solutions in the range 0.01-0.10 mM and a 0.05 mM CTAB solution. Pipette a suitable volume of the oleate solution (10-25 cm^3) into a flask or bottle with a stopper, dilute to ~100 cm^3. Add 2-3 drops of bromophenol blue, a few drops of M sodium carbonate to adjust the pH to 10.0 and 50 cm^3 chloroform. Titrate with the CTAB solution, shaking vigorously after each addition, until the blue colour shifts to the organic layer. Repeat to obtain concordant results and calculate, from the average titre, [oleate] in m mol dm^{-3}. Repeat using other concentrations of oleate using larger volumes for the more dilute solution.

18.10.1.2 Determination of the critical micellar concentration (c.m.c.) of sodium oleate

Use a suitable available method for determining the surface tension of the oleate solutions already prepared. Some modern instruments have facilities for the determination of surface tension, interfacial tension and c.m.c. Plot the surface tension against molar oleate concentration and locate the concentration beyond which the surface tension does not change significantly.

18.10.2 Surfactant mixtures

Some surfactants which have a relatively long carbon chain produce a marked lowering of the surface tension of water when dispersed in it, their c.m.c. is comparatively high. Oleic acid is an example and is used for upgrading minerals by froth flotation. The surfactant molecule is attached to a mineral particle by its polar group. These compounds are termed collectors. Another group of surfactants also used in flotation are called frothers. Their molecules are comparatively smaller and they cause a small lowering of the surface tension of water and their c.m.c.'s are low. It is interesting to investigate the behaviour of a mixture of a collector and a frother.

Weigh out accurately ~0.35 g of purest oleic acid and disperse in 1 dm^3 of deionised water. Using this for dilution, prepare a series of solutions with decreasing concentration down to 0.01 g $dm^{-3.}$ Measure the surface tension of each solution and plot it against [oleic acid] and locate its c.m.c. Weigh out accurately ~0.04 g of purest *iso*-amyl alcohol (3-methylbutan-l-ol) and disperse in 1 dm^3 of water. By successive dilution, prepare solutions of lower concentration down to 0.005 g dm^{-3}. Carry out measurements as above for oleic acid.

Prepare a series of oleic acid solutions in which [amylalcohol] is 0.01 g dm^{-3} and measure their surface tension and plot this against [oleic acid] on the same graph paper as above. Comment on the two plots.

Prepare two or three oleic acid/amyl alcohol mixtures where the concentration of each is on the lower end of the previous plots and compare the values of $\Delta\gamma=\gamma_w-\gamma_f$ and $\Delta\gamma^1=\gamma_o-\gamma_m$ where γ's are the surface tensions of water (w), alcohol (f), oleic acid (o) or the mixture (m). Comment on your results.

18.10.3 Surface tension of aliphatic alcohols

Traube's rule

In a series of homologous compounds e.g. aliphatic alcohols, Traube noticed that for each additional CH_2 group, the concentration to give a certain surface tension is reduced by a factor of 3. Langmuir gave an interpretation of this empirical rule by considering the work required to transfer 1 mol of solute from the solvent to the surface.

Prepare stock solutions of the normal primary alcohols $C_nH_{2n+1}OH$ (n=3-5) in which the mole fraction, n, of the alcohol is 0.01. By successive dilution, prepare 4 or more solutions with decreasing mole fraction down to 0.001. Measure the surface tension of each solution by a suitable method and plot it against log n. Using *sec*-or *tert.* butanol (butan-2 ol and 2-methyl-propan-2 ol) prepare solutions similar to those used above and carry out similar runs and comment on your results.

18.11 CdS COLLOIDS *(J.Am.Chem.Soc.*109(1987)5649)

When colloidal particles of very small diameter are prepared by carefully regulating the conditions, it was found that their electronic structure changes with size (size quantisation). CdS colloids of very small particle size were found to fluoresce, the colour depending on the particle size.

Prepare a 2×10^{-4} M solution of cadmium perchlorate. Dissolve, in a 500 cm^3 aliquot, in a 1 dm^3 flask, $(NaPO_3)_6$ to give 2×10^{-4} M solution, bubble nitrogen (or Ar if available) for 15 minutes. Adjust the pH to 8.0-8.3 using NaOH. Inject in the gas phase the calculated amount of H_2S gas to obtain a yellow suspension. Repeat using the same concentrations of reagents in a 200 cm^3 solution. Insert a combined glass electrode and inject a 1 M borax solution to adjust the pH to 7-8. If a fluorimeter is available, record the fluorescence spectra of the two colloids prepared. Even without an instrument, it can be shown that when the colloids are activated at various starting pH values the colour of their fluorescence changes with the starting pH.

Activate the prepared sols by the addition of 1 M NaOH to give a pH of 10.5. Then add 1 M cadmium perchlorate solution dropwise until the intensity of fluorescence reaches a maximum, when the excess [Cd^{2+}] is ~$6x10^{-4}$ M. Record the fluorescence spectra when different pH values are used.

18.12 STUDIES OF THE SUPERCONDUCTOR YBCO

The observed disappearance of electrical resistance when mercury and a few other alloys were cooled at liquid He temperature, led to the term superconductors. Only in 1986 did an oxide exhibit superconductivity and at higher transition temperatures, T_c. The following year the ceramic oxide $YB_2Cu_3O_{7-\chi}$ (or YBCO) was found to become superconductor at a temperature >77 K (the boiling point of nitrogen). The ease of its preparation and its study makes it an interesting material.

18.12.1 Preparation and characterisation of YBCO ($YBa_2Cu_3O_{7-x}$)

Provided the temperature of heating Y_2O_3, $BaCO_3$ and CuO is kept at ~930°C for a long time, the resulting compound exhibits superconductivity at -196°C.

Grind to a fine powder the three above compounds separately in an agate mortar. Weigh out accurately amounts of the three compounds so that the atomic ratio Y:Ba:Cu=1:2:3 (hence the name 123). Mix the ground weights well and ensure that they are dry. Place the mixture in one or more clean porcelain boats and heat in a silica tube placed in an electric tube furnace. Heat the furnace making sure that the temperature is kept within the range 920°-950°C for at least 20 hours. Switch off and allow to cool slowly in air. When cold, break the lumps, place in an insulating container, cover with liquid nitrogen and move a small strong magnet ($SmCo_6$ or $Nd_2Fe_{14}B$) close to the lumps. If they move away, indicating they are being repelled by the magnet, this proves that the compound is the required superconductor. Even if a powder is obtained, it could be sprinkled round the magnet immersed in liquid nitrogen, a clear gap round the magnet confirms the superconductivity. This magnetic behaviour is referred to as the Meissner effect. To demonstrate this more vividly, grind your product to a fine powder e.g. to pass through a 45 μm sieve. Obtain a pellet in the hydraulic press used for preparing KBr discs. A pressure of 50000 lb m^{-2} is adequate to produce a pellet. Cool the pellet in liquid nitrogen in a shallow polystyrene container, place the magnet above it and notice that the magnet levitates above the pellet. Measure the electric resistance of the pellet by an ordinary Avometer. Pour liquid nitrogen to cover the pellet and note the sharp drop in resistance to zero as the pellet cools. If a sample had not been carefully prepared by adjusting the temperature it will be very dark green and its resistance will increase on cooling showing it to be semiconducting and not superconducting.

18.12.2 Analysis of YBCO

The most important parameter is the value of χ in the formula which gives the hole concentration. For simplicity this is represented as the Cu(III) content. The simplest analytical method is iodometric. A weight of the sample is dissolved in 1 M HCl in air, when Cu(III) is reduced by water to Cu(II). Then the Cu^{2+} originally present and Cu^{2+} so formed liberate iodine when treated with KI solution. The iodine is then titrated with thiosulphate. Hence 1 mol of YBCO is equivalent to 1 mol of thiosulphate. In a separate experiment, the same mass of YBCO is treated under vacuum with 1 M KI/0.7 M HCl solution when Cu(III) reacts with iodide according to:

$$Cu^{3+}(aq)+3I^{-}(aq)\rightarrow CuI(s)+I_2(aq) \qquad (18.8)$$

whereas Cu(II) reacts as usual liberating ½ mol of iodine. The liberated iodine is equivalent to $Cu^{2+}+2Cu^{3+}$. The difference between the two titres gives the hole concentration. The main disadvantage of the method is that it relies on a small difference between two larger titres.

The combined determination of total Cu, Ba and Y is possible by dissolving a weight of powder in 1 M HCl. On treatment with sulphuric acid, barium sulphate precipitates and weighed. The filtrate containing Cu^{2+} and Y^{3+} is then treated with SO_2/SCN^- solution when Cu is precipitated as thiocyanate and weighed. The filtrate contains Y which is determined by EDTA titration or assayed spectrophotometrically.

Determination of barium

Weigh out accurately ~0.25-0.30 g of your powdered preparation, add 25 cm^3 I M HCl and boil gently for 10 minutes to dissolve the powder. Dilute to 200 cm^3 heat to just below boiling and add, slowly with stirring, 3 cm^3 0.5 M sulphuric acid. Heat until the precipitated barium sulphate settles and test for complete precipitation by drops of sulphuric acid. Filter through 540 filter paper, collecting the filtrate in a clean beaker. Determine barium sulphate gravimetrically as in Sec.7.3.4. Alternatively, filter through a prepared sintered glass crucible and treat as in Sec.7.3.4.

Determination of total copper

Add to the filtrate 30 cm^3 of freshly prepared saturated sulphur dioxide solution in the fume cupboard. Heat to near boiling and add 2.5 cm^3 of 10% potassium or ammonium thiocyanate solution, slowly with constant stirring. Allow to cool and stand, preferably overnight. Filter, wash and dry as in Sec.16.4.1, collecting the filtrate in a clean evaporating basin.

18.12.3 Determination of Y

Although Y^{3+} in aqueous solution can be determined by EDTA titration, Cu^{2+} ions have to be removed by a lengthy procedure. However, the organic dye arsenazo (6-phenylazo-3-arsonophenylazochromotropic acid) forms a violet complex with Y(III).

Study of the Y^{3+}/arsenazo complexes

Prepare a standard Y^{3+} solution by dissolving 0.5 g of purest yttrium oxide in conc. HCl by warming and making up to 50 cm^3 in a volumetric flask. Using conc. HCl for dilution prepare a series of solutions in the range of 0.005-0.05 M. Pipette 5.0 cm^3 of each solution into a 10 cm^3 volumetric flask, add 0.3 cm^3 of 0.02% arsenazo solution and make up to the mark. Run the spectrum of each solution over the range 500-700 nm, using a blank of 0.3 cm^{3}dye solution, 5 cm^3 conc. HCl made up to 10 cm^3. Locate the wavelength of maximum absorption and plot it against [Y(III)] to verify the applicability of Beer's law.

Spectrophotometric determination of Y in YBCO

Evaporate the filtrate from the previous operation (after precipitating Cu) to dryness, pipette 5.0 cm^3 conc. HCl, to the residue, warm to dissolve. After cooling, add 0.3 cm^3

of the dye and make up to 10 cm^3 and measure the absorbance at the wavelength used above. Determine the [Y] from the calibration curve and find the % Y in your preparation. If the residue is small, halve the volumes used.

18.12.4 Spectrophotometric determination of the hole concentration

Consider Cu^{3+} as the hole in the sample, which is usually ~1/3 of the total Cu. When a slight excess of iron(II) chloride solution is added to the powder dissolved in HCl, Fe(III) chloride and copper(II) chloride are formed. The latter represents the total Cu and the former is equivalent to Cu^{3+} or hole concentration. Since the spectra of the two cations have well separated absorption maxima, the spectrophotometric method gives Cu(III) and total Cu in the same spectrum (see Sec.16.5).

Using purest solids and nitrogen purged 1 M HCl, prepare a solution which is 2.7×10^{-3} M in iron(III), 4.7×10^{-4} M in Cu(II) and 1.4×10^{-3} M in iron(II). As soon as possible record the spectrum of the solution in a 10 mm vacuum uv cell over the range 250-900 nm. Locate the absorption maxima and compare them with those obtained in Sec.16.5. Dilute 10-fold with the same acid solution and locate the maxima and measure the absorbance at these maxima. Into a tube provided with a side arm and a ground glass stopper (Fig.18.6), weigh out accurately ~0.02 g of the powdered semiconductor and ~0.005 g of iron(II) chloride tetrahydrate (from the purest solid stored in a vacuum desiccator in the dark). Add quickly 10 cm^3 1 M HCl from a pipette, after connecting the side arm by Tygon to the side arm of a vacuum uv cell. By turning its stopper (which is provided with a side arm and stopcock) evacuate the system for a few minutes. Allow the sample to dissolve under vacuum, shaking if necessary. Transfer the solution to the cell by careful manipulation with the system kept under vacuum, and measure the absorbance near the wavelengths previously located. To fit the cell with its stopper in the spectrophotometer cell compartment, a box is made to fit the compartment and to allow for the system to be measured. The box should be blackened and covered completely with a black cloth to stop any stray light entering the cell compartment. Calculate from the absorbances measured [Cu total) and [hole] in your solution and hence the formula of the superconductor. Check that the absorbance corresponding to [hole] does not change with time. This indicates that the excess Fe(II) was not oxidised by oxygen during the experiment. Repeat using a different mass of the powder and a corresponding mass of iron(II) salt (slightly >required to react with ~1/3 of the total Cu).

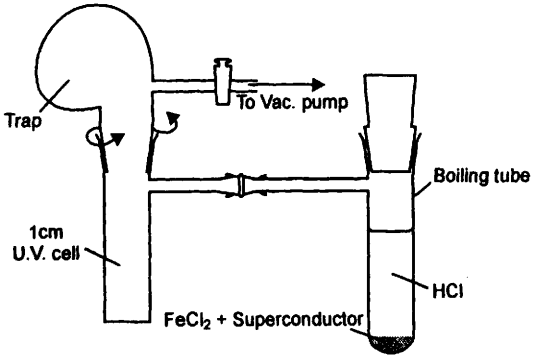


Figure 18.6 A sketch of the set-up for the spectrophotometric determination of the hole concentration in YBCO.

18.12.5 YBCO-catalysed decomposition of hydrogen peroxide

Since YBCO contains Cu in two oxidation states, it was thought that it may be a suitable catalyst for the decomposition of hydrogen peroxide. You can use the apparatus depicted in Fig.2.13 for the catalysed reaction. Weigh out a suitable mass of the powdered superconductor, say 0.2 g, in vessel B and pipette 10 cm^3 of water into B. Pipette 10.0 cm^3 of hydrogen peroxide solution say ~0.2 M into the funnel A. Allow time for thermal equilibrium by circulating water from the thermostat around A and B. Then run the hydrogen peroxide solution to the powder, as you start a stopwatch, while agitating preferably magnetically at a constant speed. At intervals, measure the volume of oxygen collected in the burette C, noting the atmospheric pressure and the water vapour pressure at the temperature recorded by an accurate (0-100°C) thermometer placed adjacent to the burette between C and D. Repeat measuring the volumes at suitable increasing times and plot volume against time. Repeat using a range of $[H_2O_2]$ down to 0.03 M, plotting the results as above. Plot initial (H_2O_2) against log initial slope and hence work out the order of reaction. Using a chosen concentration of hydrogen peroxide, repeat a run at 3 or more other temperatures. Using the Eyring equation (2.77), calculate the activation parameters.

18.13 STUDIES USING ASCORBIC ACID

18.13.1 Stability of ascorbic acid solutions

(F.J.Kakis, C.J.Rossi,*J.College Sci.Teaching,* 3(1974)No.3)

When exposed to air, ascorbic acid solutions are oxidised to dehydroxy ascorbic acid (Fig.18.7). This may hydrolyse to diketogulonic acid. The ene-diol of ascorbic acid gives a uv absorption maximum.

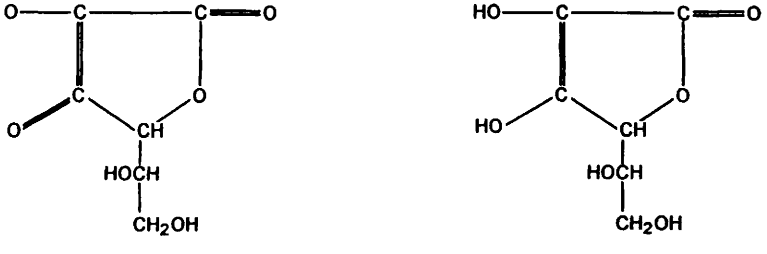


Figure 18.7 The structural formulae of ascorbic acid (left) and dehydroxoascorbic acid (right).

Weigh out accurately 17.61 mg purest ascorbic acid, dissolve in boiled-out deionised water and quickly make up to 1 dm^3 in a volumetric flask. Start a stopwatch as you keep an aliquot of the solution in a beaker exposed to air in a thermostat at say 20°C. As soon as possible run the spectrum in a uv cell in the range 200-300 nm and locate the wavelength of maximum absorption and note the absorbance at this wavelength and the time on the watch. At intervals, measure the absorbance of an aliquot of the solution at the same wavelength (for up to 3-4 hours). Plot log absorbance against time and find the order of the reaction. Repeat using solutions thermostatted at 3 other temperatures (say between 15° and 30°C). Find the rate constant at each temperature and hence calculate the activation parameters.

18.13.2 Analytical chemistry of ascorbic acid solution

Since ascorbic acid is a strong reductant, many oxidants have been used to determine it in solution or even in Vitamin C tablets using redox indicators or other instrumental methods.

The oxidation of ascorbic acid by iodine

When an excess of standardised iodine solution is added to an aliquot of ascorbic acid solution, the excess can be back-titrated against standardised thiosulphate.

Prepare freshly 0.05 M ascorbic acid (using the purest solid and boiled-out deionised water) and a 0.05 M iodine solution. Pipette 25.0 cm^3 of the ascorbic acid solution in a conical flask (or preferably a Buchner flask). Titrate with the iodine solution until the colour remains brown after shaking. Then add ~15 cm^3 and note the volume used. In the case of using the Buchner, place the burette in a hole in the bung of the flask and evacuate before starting titration. Stir magnetically as you add the iodine solution. Replace the burette by another containing standardised 0.05 M thiosulphate solution and titrate the excess iodine as in Sec.7.3.2). Repeat and calculate from average results the concentration of ascorbic acid in the original solution or the purity of the solid acid used. A titrimetric method using Mn(III) has been described in Sec.12.4.1. The kinetics and mechanism of the oxidation of ascorbic acid in solution by Ce(IV) or permanganate have been studied as well as various methods of determination of ascorbic acid. However, the reaction with hexacyanoferrate(III) has been more fully studied.

18.13.3 Kinetics and mechanism of the oxidation of ascorbic acid by hexacyanoferrate (III) *(J.Phys.Chem.*73(1969)1996)

Freshly prepare 0.02 M ascorbic acid solution using the purest solid and nitrogen-purged deionised water. Prepare a stock solution of 0.02 M purest potassium hexacyanoferrate(III). By successive dilution prepare a series of solutions of the latter in the concentration range 0.001-0.0001 M. Run the spectrum of the 0.001 M solution in a 1 cm cell over the range 370-500 nm and locate the wavelength of maximum absorption. Record the absorbance at this wavelength for all the prepared solutions and plot against [complex].

Use an apparatus similar to Fig.2.12. Pipette a suitable volume of 0.002 M iron complex in flask A and an equal volume of 0.02 M ascorbic acid in 1 M HCl in flask B. Equilibrate thermally at say 20°C while purging with nitrogen. Start a stopwatch as you mix thoroughly the two solutions. At intervals, transfer a small volume of the mixture to flask C cooled in ice/salt. When suitable, warm an aliquot to ~15°C to stop misting the cell and fill a 10 mm cell with an aliquot, stopper the cell and determine the absorbance, A_t, at the wavelength previously found. Take a final reading after a conveniently chosen long time. Plot log $(A_t\text{-}A_f)$ against time t where A_f is the final measured absorbance. Find the order of reaction with respect to the iron(III) complex. Alternatively, use a range of concentrations of ascorbic acid, keeping the [complex] and $[H^+]$ constant and show how the rate constant obtained as above varies with [ascorbic acid]. Keeping all conditions constant except temperature, carry out runs at 3 or more other temperatures and determine the activation parameters. Choose suitable concentrations of reactants and temperature, carry out runs at different $[H^+]$ using HCl of different concentrations to dissolve ascorbic acid. Plot the rate constant against $1/[H^+]$. Suggest a mechanism for the reaction.

General References

The following textbooks are useful for this chapter and the earlier chapters 3-17.

1 A.I.Vogel, *Macro and Semimicro Qualitative Inorganic Analysis*, 4th Ed., Longmans, 1959.
2 D.T.Burns, A Townshend and A.H.Carter, *Inorganic Reaction Chemistry*, Vol.2, Parts A and B, Ellis Horwood, 1981.
3 *Inorganic Synthesis*, series with various editors.
4 W.G.Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, 1962.
5 *Chemical Principles in Practice*, Ed.J.A.Bell, Addison Wesley, 1967.
6 D.A.Cooke, *Inorganic Reaction Mechanisms*, The Chemical Society, 1979.
7 J.W.McMillan, *Radiochemical Methods of Analysis*, Plenum, 1975.

References at the end of Chapter 2 are also useful for Chapters 3-18.

APPENDIX 1

A1.1 Fire Extinguishers

The Fisher Scientific U.K. has included in their Chemicals Catalogue, codes for fire extinguishers used in different situations. The following codes are shown below, produced with permission of Fisher Scientific U.K.

Code	**Meaning**
C	Carbon dioxide.
P	Dry chemical powder.
W	Water spray.
F	Alcohol or polymer foam.
D	Class D fire extinguishing material only ± metal fires.
H	Halons/BCF.
Not P	**Do not** use dry chemical powder extinguisher on this material.
Not C	**Do not** use carbon dioxide extinguisher on this material.
Not W	**Do not** use water.

Examples: Acetic acid: C,P,W,H.
Diethyl ether(ether): C,P,F.H.
Sodium: D, Not W, Not C.

A1.2 Spillage treatment

The Fisher Scientific U.K. has also published a coded list for spillage treatment. The list codes are given below, published with permission from Fisher Scientific U.K.

Code	**Meaning**
A	Shut off ignition sources.
B	Evacuate area.
C	Wear face shield or goggles, gloves and protective clothing, including rubber boots
D	Wear breathing apparatus, gloves and protective clothing, including rubber boots.
E	Wear dust mask, face shield or goggles, gloves and protective clothing including rubber boots.
F	Flush to drain with copious amounts of water.
G	Apply non-flammable dispersing agent and work to an emulsion with brush and water ± run to waste with copious amounts of water. If dispersant not available, absorb on dry sand, vermiculite or other suitable inert absorbent. Sweep up, transfer to closable salvage container and arrange for disposal by burial on a safe approved site or evaporation in a safe open area.
H	Wash spillage site with water and soap/detergent. Iodine stains can be cleared by mopping with sodium thiosulphate or metabisulphite solution.
I	Ventilate area to evaporate solvent and dispel vapour.
J	A leaking cylinder (lecture bottle) or ampoule can be vented slowly to air in a safe open area.
K	Sweep up carefully, avoiding formation of dust cloud, transfer to closable salvage container and arrange for disposal by the appropriate method or retain for recovery
L	Spread soda ash liberally over the spillage and mop up cautiously with water ± run this to waste, diluting greatly with running water.
M	Special procedure for mercury spillage: (a) Use Mercury Clean-up Kit, (obtainable from Fisher Scientific UK, Catalogue No.M/3754), full instructions are supplied with each kit. (b) Recover as thoroughly as possible with shovel and transfer to another container with close fitting lid. This container should be plastic, glass, earthenware or iron. If in confined space ± try to contain spillage and clean up as far as possible by mechanical

means, e.g. vacuum probe. Treat whole area with a wash composed of equal parts of slaked lime and flowers of sulphur mixed with sufficient water to make a thin paste. Apply liberally over affected area. After 24 hours wash off with water, and dispose of washings via authorised toxic waste service if sizeable volume involved.

N Site of spillage should be washed thoroughly to remove all oxidant ± paying particular attention to any organic matter such as wood, paper or textiles which may become dangerously combustible when dry. Contaminated clothing should be removed and thoroughly washed.

P Cover with DRY Sand. Sweep up and transfer to closable salvage container and arrange for disposal by appropriate method.

Q Shut off cylinder if without risk.

R Ensure area is safe before permitting re-entry of personnel.

Examples: Sulphuric acid: B,D,L
Ammonia: B,C,F
Hydrofluoric acid: B,D,L (Risk: 26/27/28,35; Safety: 7/9,36/37,45)

A1.3 Waste disposal

The Fisher Scientific U.K. has also included as an Appendix to their Chemicals Catalogue, codes for waste disposal recommendations. Tutors are advised to display the codes in the laboratories, after seeking permission or at least, students should be urged to look up for the codes when they use the coded chemicals. This is even more important for laboratory technicians.

A1.4 First aid

The same company has also included a list of recommended first aid procedures. The same remarks as above apply here.

APPENDIX 2

A2.1 Concentrated acids and concentrated ammonia.

The molar concentration of these acids and ammonia as supplied are compiled in table A2.1 which includes the volume required to dilute to 1 dm^3 to obtain 1 M solution.

Table A2.1

Acid	Formula	[acid]/mol dm^{-3}	Volume in cm^3 to give 1 dm^3 of 1 M solution
Sulphuric (98%)	H_2SO_4	36.8	54.3
Hydrochloric	HCl	11.65	85.8
Nitric HNO_3	15.8	63.3	
Perchloric (60%)	$HClO_4$	9.2	108.7
Orthophosphoric	H_3PO_4	15.2	65.8
Acetic CH_3CO_2H	17.4	57.5	
Hydrofluoric	HF	22.6	44.2
Ammonia	NH_3	18.1	55.3

A2.2 Concentration of common reagents in the laboratory

Dilute hydrochloric, nitric, perchloric or acetic acid are usually 2.5 M but dilute sulphuric acid is 1.25 M.

Solutions of the following salts are usually 0.5 M with respect to the hydrated salt: ammonium thiocyanate, copper sulphate, iron(III) chloride, iron(II) sulphate, potassium iodide, potassium thiocyanate. Solutions of the following salts are usually 0.25 M: barium chloride, calcium chloride, lead acetate, potassium chromate, potassium hexacyanoferrate(II), tin(II) chloride (with few pieces of Sn to stop aerial oxidation), zinc nitrate.

Solutions with other molarites are collected in Table A2.2.

Table A2.2 Molar concentration of common reagents

Reagent	**ammonium acetate**	**ammonium carbonate**	**ammonium chloride**	
Concentration/M	3	2	5	
Reagent	**ammonium nitrate**	**ammonium sulphate**	**ammonium sulphide**	
Concentration/M	1	1	3	
Reagent	**calcium sulphate**	**cobalt nitrate**	**iodine in KI**	**Mercury(II) chloride**
Concentration/M	0.017	0.15	0.05 in 0.12 KI	0.099
Reagent	**potassium hexacyanoferrate(III)**	**potassium permanganate**		
Concentration/M	0.167	0.02		
Reagent	**silver nitrate**	**silver sulphate**	**sodium acetate**	**sodium carbonate**
Concentration/M	0.1	0.025	3	1.5
Reagent	**disodium hydrogen phosphate**			
Concentration/M	0.335			

A2.3 Special reagents and indicator solutions

The concentrations usually used or special conditions of preparation will be described in the following appendices, when these solutions are used in the corresponding main chapters.

A2.4 Simple calculations

If the relative molar mass RMM of a chemical is M, to prepare a solution of concentration M mol dm^{-3} (or usually denoted as 1 M), M g of the chemical are dissolved and made up to 1000 cm^3 (i.e. 1 dm^3). The concentration is 1 M mol cm^3.To prepare 250 cm^3 of this solution (M x 250/1000)g are used. To prepare an χM solution, χ x M g are made up to 1 dm^3.

If a volume of V cm^3 is used in titrimetry for a solution which is χ.M, the number of mols of chemical = Vχ/1000.

When m mols of a substance are found to be in a volume V cm^3, the molar concentration =mx1000/V mol dm^{-3}.

If in a reaction a molecules of a reactant A whose RMM is M (a) completely react with b molecules of another B whose RMM is M (b), the number of mols of B reacting with m_1 mols of A= ($m_1$xb/a).

If B is a product of a preparation resulting from a reaction with A in a similar stoichiometry, if the mass of A used is m_1, the expected mass of B is

$$m_1[bM(B)/a.M(A)]=m_2$$

If the actual mass produced is m_3

∴ The percentage recovery =m_3x100/m_2

A2.5 Nomenclature

Since manufacturers of laboratory chemicals use the traditional names, these names are usually used in the text. IUPAC recommended a system of nomenclature, the details of which are found in e.g. in *Nomenclature of Inorganic Chemistry: Recommendations 1990:* G.J.Leigh, Ed., Blackwell Scientific, Oxford. Certain old names are still permissible e.g. perchloric $HClO_4$, chloric $HClO_3$, chlorous $HClO_2$ and hypochlorous HOCl acids. The salts have the *ic* changed to *ate* or *ous* changed to *ite*. Alternatively $HClO_4$ is named tetraoxochloric (VII) acid. Although potassium persulphate $K_2S_2O_8$ is sold under this name, it is preferable to name it peroxodisulphate since peroxomonosulphates are known though not usually available commercially. Potassium permanganate $KMnO_4$ does not contain a peroxo-group but it is commonly called permanganate. Alternatively tetraoxomanganate(VII) is a clearer description.

The nomenclature of organic compounds is only relevant to this book in connection with the simpler organic acids and their salts or their derivatives. Naming of the smaller molecules is based on the name of the saturated hydrocarbons: the alkanes. Methane CH_4, ethane C_2H_6, propane C_3H_8 and butane C_4H_{10} are used but the higher alkanes are named using the Greek prefix: *penta-*, *hexa-* etc. The acids, alcohols, aldehydes etc. are named using the stem name of the alkane. Thus: C_2H_5OH is ethanol (normally just called alcohol), CH_3CHO is ethanal, CH_3COOH is ethanoic acid and so on. The common names eg. CH_3COONa, sodium acetate, is still in use. Another commonly accepted name is $H_2C_2O_4$ (oxalic acid) although an alternative is ethanedioic acid. In the text a number of organic ligands are used with the old and/or recommended name. However, the formulae are always given which identify the chemical.

Coordination compounds are mentioned in the text with the formula given with or without the name. A few examples are given below to illustrate the rules of nomenclature.

Trans $[Co(en)_2Cl_2]Cl$ is *trans*-[bis,(1,2-diaminoethane)dichlorocobalt(III) chloride
$[Co(NH_3)_6][Cr(C_2O_4)_3].3H_2O$ is

Hexaamminecobalt(III) tris(ethanedioato)chromate(III) trihydrate

From the practical point of view, the formula and the structure are more important than the name for characterising a compound.

APPENDIX 3

A3.2.1

(a) Hardness increases in the series: Na<Li<Ba<Ca

(b) Na_2O_2 and the oxides of Li,Mg,Ca or Ba are formed (with some nitride for the latter four)
(i) All are soluble except MgO ($Ca(OH)_2$ is slightly soluble).
(ii) Nitrides give ammonia (g) with NaOH (gas blackens the paper).

(c) $MOH(aq)+H_2(g)$ are formed. Hydroxide $+Cu^{2+}\rightarrow Cu(OH)_2(s)$ blue.

(d) $M(OH)_2+H_2(g)$ are produced.

(e) $2M+2C_2H_5OH\rightarrow 2C_2H_5OM+H_2(g)$

(f) $M+2HCl\rightarrow MCl_2+H_2(g)$ (M=Mg or Ca which reacts more vigorously);
Mg not reactive with water.

A3.2.2

(a) Solids become moist, absorb water and carbon dioxide.

(b) Only MgO is insoluble, its suspension is alkaline, other solutions are also alkaline.

(c) (i) $OH^-+Fe^{3+}\rightarrow Fe(OH)_3(s)$ red brown;
(ii) $OH^-+NH_4Cl\rightarrow NH_3(g)+H_2O+Cl^-$ (gas blackens the paper).

(d) Hydrogen peroxide formed, reduces and decolourises permanganate.

(e) Hydrogen peroxide decomposes to water and oxygen (rekindles the splint).

(f) Yellow CrO_4^{2-} is formed.

(g) $CaO(s)+H_2O\rightarrow Ca(OH)_2+$ heat. Solution is lime water.

A3.2.3

(a) Except Na and K carbonates, the others decompose $\rightarrow$oxide$+CO_2(g)$, (turns lime water turbid).

(b) $2NaHCO_3\rightarrow Na_2CO_3+CO_2+H_2O$.

(c) $2MNO_3\rightarrow 2MNO_2+O_2$(M=K,Na); Other nitrates give oxide $+NO_2+O_2$
(NO_2 is acidic with water, the residual oxide is alkaline).

(d) $MNO_2(aq)$ (M=K,Na) form brown $[Fe(H_2O)_5(NO)]^{2+}$

A3.2.4

(1) Li^+ precipitated as
(a) Li_3PO_4, (b) LiF, (c) Li_2CO_3.

(2) Na^+ precipitated as $NaM(UO_2)_3(CH_3COO)_9$ yellow (M=Zn or Mg)

(3) K^+ precipitated as (a) $K_2Na[Co(NO_2)_6]$(yellow), (b) $KClO_4$, (c) $K_2[PtCl_6]$ (yellow).

(4) (*J.Chem.Educ.*75(1998)55).

Ion	Li	Na	K	Ca	Sr	Ba
Colour	carmine red	yellow	lilac	brick red	crimson	apple green

(5) Mg^{2+} precipitated as: (a) $Mg(OH)_2$; (b) $MgCO_3$; (c) $Mg(NH_4)PO_4$; (d) no ppt [carbonate] reduced; (e) yellow $Mg(C_9H_6NO)_2.4H_2O$.

(6) (a) $MCO_3(s)$ (M=Ca,Sr,Ba) is formed; (b) $MC_2O_4(s)$ (all three) is obtained;
(c) MSO_4 (all three; Ca^{2+} in conc. solutions is precipitated; (d) $MSO_4(s)$ (M=Sr,Ba) is produced; (e) $MCrO_4$ precipitates (M=Sr,Ba) Ca^{2+} in conc. solution.

A3.2.5

(a) $LiH+H_2O\rightarrow LiOH(aq)+H_2$

(b) $CaH_2+2H_2O\rightarrow Ca(OH)_2+2H_2$

A3.3

Students should be reminded about the care in using and storing ion selective electrodes for any cation or anion. Presence of other ions e.g. H^+ influence the reading on the mV meter (or ion meter if available).

A3.4.1 (Sec.2.2.4)

Buffer pH10: Dissolve 7 g ammonium chloride in 60 cm^3 conc. ammonia and make up to 100 cm^3.

Eriochrome black T: Dissolve 0.2 g in 15 cm^3triethanolamine ($N(CH_2CH_2OH)_3$)+5 cm^3 ethanol.

Purest disodium salt of EDTA, dried at 80°C, can be weighed to give a standard solution, provided deionised water is used.

Magnesium complexonate: Mix equal volumes of 0.2 M EDTA and 0.2 M magnesium sulphate. Adjust the pH to 8-9. You can use 0.1 M Mg EDTA (commercially available).

A3.4.1.1

Calculation

Molar ratio M^{2+}: EDTA=1:1

If volume of EDTA is V cm^3

$\therefore$Mols EDTA=Vx0.1/1000 =mols of Ba in 25.0 cm^3(m)

$\therefore$[Ba]=mx1000/25 (mol dm^{-3})

A3.4.1.2

Similarly for EDTA standardisation

If volume of EDTA used =V cm^3

Mols of Ca^{2+} used =25x0.1/1000=mols EDTA in V cm^3

$\therefore$[EDTA]=2.5x10^{-3}x1000/V (mols dm^{-3})

If $CaCO_3$ is used: mols of Ca=0.2/RMM (100.09)

A3.4.2

Methyl red indicator. Dissolve 1 g of the acid in 600 cm^3 ethanol and make up to 1 dm^3

A3.4.2.1

$Mg(NH_4)PO_4.6H_2O$ %Mg=9.909

$Mg_2P_2O_7$ %Mg=21.85

If mass of the latter precipitate is m g

$\therefore$Mass of Mg in 25 cm^3=0.2185xm

$\therefore$[Mg]=0.2185xmx1000/25 mol dm^{-3}

A3.4.2.2

$CaC_2O_4.H_2O$ %Ca=27.43

On heating to 500°C, $CaCO_3$ is formed, %Ca=40.04.

A3.4.2.3

Standardisation of 0.02 M permanganate (Sec.12.8.1)

$5C_2O_4^{2-}+2MnO_4^-+8H^+\rightarrow 2Mn^{2+}+4H_2O+10\,CO_2$

5 mols $C_2O_4^{2-}\equiv$2 mols MnO_4^-

If the volume of 0.02 M permanganate used is V cm^3

$\therefore$Mols of permanganate = Vx0.02/1000

$\therefore$Mols of oxalate = 2.5xVx0.02/1000=mols Ca^{2+}

$\therefore$Mass of Ca=2.5xVx0.02x40.08/1000 g

If the volume of the calcium solution is 25 cm^3 [Ca]=2.5xVx0.02/25 mol dm^{-3}

A3.4.2.4

% Ba in $BaCrO_4$=54.21

Other calculations are as above.

A3.4.2.5

Precipitation of barium sulphate from homogeneous solution

Sulphamic acid solution liberates sulphate ions slowly on boiling. When mixed with the barium solution, barium sulphate precipitates slowly giving a more easily filtrable precipitate.

$NH_2SO_3H+H_2O \rightarrow NH_4^{+}+SO_4^{2-}+H^{+}$

About 0.2 g purest barium chloride in ~100 cm^3 water with 1.0 g of the acid is heated at ~98°C for 38 minutes is recommended. See Sec.7.3.2.2.

A3.4.3.1

The precipitated $CaC_2O_4.H_2O$ can be subjected to TGA and DTA (*Anal.Chim.Acta,* **1**(1947)345).

High frequency titration of Ca^{2+} against oxalate (*Z.anorg.allgem.Chem.*319(1962)94) also used for orthophosphate with magnesia mixture (Sec.6.10.1) and $[Cr(C_2O_4)_3]^{3+}$ with $[Co(NH_3)_6]^{3+}$ (Sec.14.6.3).

A3.5.2

*Powder Technol.*9(1974)107 reports the results using, ^{22}Na and ^{137}Cs with solid scintillation counting.

A3.5.3

*Chim.Ind.*103(1970)1347 reports the results of adsorption on quartz of labelled $^{45}Ca^{2+}$, $^{89}Sr^{2+}$ and $^{140}Ba^{2+}$ solutions using radioisotope dilution analysis. A discussion of the trend when quartz or TiO_2 are used as adsorbents appears in *Chem. & Ind.* (1975)704.

A3.5.4

The results are given in *Chem.Ind.*(1977)229.

A3.6 Additional study and references.

Measure the electrokinetic potential of quartz in 10^{-3}-10^{-4}M in each of the chlorides of the three alkaline-earth metals at pH10.5 or pH7.0. (*Disc.Faraday Soc.*52(1971)377).

Titration of monoprotic acids with NaOH contaminated with carbonate (*J.Chem. Educ.*65(1988)181).

Analysis of Sr in marine aquariums by atomic absorption *ibid.*74(1997)1192.

Electrokinetic potential of magnesium carbonate at different pH's (*J.Colloid Interface Sci.*45(1973)449).

*J.Chem.Educ.*75(1998)1013 reports on recording the sodium emission spectrum using a sodium lamp, a uv/visible spectrophotometer and an optical fibre guide.

The solubility of calcium sulphate in potassium nitrate solution is reported in *J.Chem.Educ.*33(1956)610, to show the effect of ionic strength. The article shows how solubility studies of lead sulphate in sulphuric acid solutions of different concentration can be used to estimate the second dissociation constant of the acid.

Another solubility study of calcium sulphate in various salt solutions is reported (*ibid,* 39(1962)622) which includes solubility data in ammonium perchlorate.

APPENDIX 4

A4.2.1

(a) Acid soluble in water, pH5-6,

(b) Acid soluble in ethanol,

(c) $H_3BO_3 \rightarrow HBO_2 \rightarrow B_2O_3$,

(d) Soluble in water and slowly hydrolysed. With 85% phosphoric acid hydrogen and B_2H_6 are produced,

(e) (i) On heating white fumes of H_3BO_3 are observed;
(ii) H_3BO_3 precipitates from conc. solution;
(iii) $H_3BO_3+3CH_3OH \rightarrow B(OCH_3)_3(g)$ (green flame)$+3H_2O$;
(iv) red brown colour;
(v) white $AgBO_2(s)$;
(vi) white $Ba(BO_2)_2(s)$.

(f) Metal Cr Mn Fe Cl Ni Cu
colour yellow(green) violet yellow(green) blue(blue) red brown(grey) green colour in reducing flame between brackets (if colourless in this flame, it is left out).

(g) $4NaBO_3+5H_2O \rightarrow 4H_2O_2+Na_2B_4O_7+2NaOH$; H_2O_2 reduces MnO_4^- and gives O_2 on heating.

A4.2.2.1

(a) (i) $H_2(g)$ on scratched surface; (ii) more H_2, surface oxide layer broken.

(b) Devarda's alloy (45% Al) + $2Al+2OH^-+ 6H_2O \rightarrow 2[Al(OH)_4]^-+3H_2(g)$.

(c) $8Al+3NaNO_3+5NaOH+18H_2O \rightarrow 3NH_3+8Na[Al(OH)_4]$.

(d) NO_2^- reduced to NH_3 (fumes of NH_4Cl with HCl)

A4.2.2.2

(a) Al_2Cl_6 sublimes, with H_2O gives HCl.

(b) $[Al(H_2O)_6]Cl_3$ loses water on heating and some HCl(g).

(c) $Al_2Cl_6+12H_2O \rightarrow 2(Al(H_2O)_6]Cl_3$+heat.

(d) Hydrolysis to HCl

A4.2.2.3

(a) (i) $Al^{3+}+3OH^- \rightarrow Al(OH)_3(s) \rightarrow [Al(OH)_4]^-(aq)$ (*J.Chem.Educ.*75(1998)60),
(ii) $Al(OH)_3(s)$ slightly soluble in excess,
(iii) $Al_2(SO_4)_3+4Na_2HPO_4 \rightarrow 2Na_2SO_4+H_2SO_4+2AlPO_4(s)$ soluble in HCl and in NaOH,

(b) Blue $Co(AlO_2)_2$ is obtained.

(c) $LiOH(aq)+H_2(g)+Al(OH)_3(s)$ (soluble in NaOH) are obtained.

A4.3

Phenolphthalein indicator: Dissolve 0.1 g in 150 cm^3 ethanol and make up to 250 cm^3 (pH range 8.3-10.0).
H_3BO_3 forms complex with polyhydroxy organic molecules which are stronger acids.
1 mol boric acid ≡1 mol NaOH
If volume of 0.1 M NaOH is V cm^3, mols boric acid =Vx0.1/1000 in 25 cm^3
∴[Boric acid]=(Vx0.1/1000)x(1000/25) mol dm^{-3}

A4.4.1

NH_4F gives $NH_4[BF_4]$ (*Inorg.Synth.*2(1946)23).
37.0 g give 104.8 g for 100% yield. 15 g give 42.5 g
If the mass of product is m g. % yield=mx100/42.5

A4.5.1

$Al(NH_4)(SO_4)_2.12H_2O$ RMM 453.33

1 mol Al reacts with 1 mol EDTA ≡ 1 mol of Zn.

If the volume of Zn = V cm^3, mols Zn = Vx0.01/1000=mols EDTA

Since both EDTA and Zn are 0.01 M

∴Volume of EDTA reacting with Al^{3+}=(40-V) cm^3

∴mols Al^{3+}=(40-V)x0.01/1000 in 25 cm^3

∴$[Al^{3+}]$=(40-V)x0.01/25 (mol dm^{-3})

Aluminium oxinate contains 5.87% Al

If the precipitate weighs m g, its Al weighs 0.0587xm g in 75 cm^3

∴[Al]=0.0587xmx1000/(75x26.98) mol dm^{-3}

A4.6.1

1 mol Al gives 1 mols $K_3[Al(C_2O_4)_3].3H_2O$ *(Inorg.Synth.*1(1939)36)

27 g Al gives 462 g complex

∴1 g Al gives=462/27=17.11 g

If mass of product is m g ∴% yield=mx100/17.11 (usual yield 65%)

1 mol complex has 3 oxalate ligands i.e. 3 mols

∵Mols of oxalate ≡ 2.5 mols permanganate

∴Mols of oxalate =2.5xVx0.02/1000 mols=m

V is the volume of 0.02 M permanganate

Mass of oxalate in complex =mx88.08g

If mass used in analysis is w g, % oxalate =mx88.08x100/w

Theoretical % for pure sample = 57.16 % purity = % found x 100/57.16

A4.6.2

$Al(NO_3)_3.9H_2O$ gives $Al(C_5H_7O_2)_3$ *(Inorg.Synth.*2(1946)25)

∴375.1 g produce 324.3 g complex

Theoretical yield =8x324.3/375.1=6.92 g,

When the actual yield is m g, % yield =mx100/6.92

Unlike the oxalato-complex, this complex is insoluble in water but it is soluble in organic solvents. This contrast is due to the organic ligands surrounding Al which makes the complex hydrophobic. On the other hand, the polar oxalate ligands surrounding Al in the oxalato-complex explain the hydrophilic nature of the solid.

% C =55.6 % H =6.5 in the $[Al(acac)_3]$ complex. Its m.p. is 194.6°C.

A4.6.3 (See Sec.2.4.2)

Expected bands are listed in K.Nakamato, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. Pp.244-7 for 4.6.1 and pp.259-263for 4.6.2, Wiley Interscience, 1986. The reference also contains data for the other coordination compounds prepared in the later chapters.

APPENDIX 5

A5.2

(a) Charcoal (or graphite) conduct electricity.
(b) Silicon is only a semiconductor.
(c) $C+2H_2SO_4 \rightarrow 2H_2O+CO_2+2SO_2(g)$ reduces dichromate.
(d) Tetrachloromethane is kinetically inert to hydrolysis.
(e) $SiCl_4+2H_2O \rightarrow SiO_2(s)+4HCl$+heat (rapid hydrolysis)
(f) $2HCOONa \rightarrow Na_2C_2O_4+H_2(g)$ (reduces $PdCl_2$ to Pd(s) (dark).
(g) $2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2(g)$.
(h) Lime water $Ca(OH)_2+CO_2 \rightarrow CaCO_3(s)+H_2O$.
$CaCO_3+H_2O+CO_2 \rightarrow Ca(HCO_3)_2(aq)$.
(i) (i) white $BaCO_3(s)$ soluble in $HCl \rightarrow BaCl_2(aq)$;
(ii) as in (i); (iii) as in (i);
(iv) white Ag_2CO_3; soluble in HNO_3, silver nitrate is formed; soluble in NH_3 $[Ag(NH_3)_2]^+$ is formed;
(v) basic Hg(II) carbonate(s) precipitates, eventually turns red brown;
(j) (i) $Mg(HCO_3)_2$ is soluble; on heating, the carbonate precipitates;
(ii) no precipitate;
(iii)alkaline pH;
(k) Hydrolysis gives $CO_2+NH_4^+$ (produces ammonia with NaOH)
(l) (i) Ag(OCN)(s) white soluble in ammonia and in nitric acid;
(ii) $[Co(OCN)_4]^{2-}$ (aq) blue, more intense in alcohol;
(iii)lilac blue precipitate soluble in $CHCl_3$;
(m) Yellow colour produced, with sulphuric acid, SO_2 is formed (turns paper green).
(n) (i) Ag(SCN)(s) white$\rightarrow[Ag(SCN)_2]^-$ soluble, also soluble in NH_3;
(ii) black $Cu(SCN)_2(s)$ slowly$\rightarrow$Cu(SCN) grey white;
(iii)blood red colour complexes where the anion replaces water as a ligand, extracted in ether;
(iv) blue $[Co(SCN)_4]^{2-}(aq)$ facilitated by acetone;
(v) $SCN^-+3Zn+8H^+ \rightarrow 3Zn^{2+}+CH_3NH_3^++H_2S(g)$ (gives black PbS);
(vi) $4H_2O_2+SCN^-+3OH^- \rightarrow SO_4^{2-}+4H_2O+NH_3(g)+CO_3^{2-}$ (the latter liberates CO_2 with HCl), $BaCl_2(aq)$ precipitates sulphate;
(o) (i) Hydrated silica precipitates especially on boiling;
(ii) as in (i), NH_4^+ acts as a weak acid;
(iii)yellow silver silicate with some oxide, dissolves in acid or ammonia;
(iv) $BaSiO_3(s)$ white soluble in nitric acid;
(v) yellow soluble molybdosilicate polyanions.
(p) $SiF_4(g)$ liberated, with water hydrated silica is formed (makes water turbid)
$3SiF_4+2H_2O \rightarrow 2SiF_6^{2-}+4H^++SiO_2$.

A5.3.1

Any adsorbed water is lost at 105°C. Dried pure carbonate loses 45.97% of its mass at 1200°C. Residue CaO combines with water gives hydroxide and heat.

A5.3.2

Thymol blue indicator: Weigh 0.5 g of the indicator neutralise with 0.1 M NaOH by grinding in a glass mortar and make up to 500 cm^3. The pH range is 8.0-9.6.
Bromophenol blue: as above. pH range 3.0-4.6.

The titres (average of duplicates), with the two indicators, are expected to be in 1:2 ratio within the experimental error.

A5.3.4

If the volume in the first titration is V_1 cm^3

Mols HCl=V_1x0.2/1000 ∴Mols of carbonate =2V_1x0.2/1000.

If the volume of the second titration is V_2 cm^3.

Volume equivalent to bicarbonate =(V_2-2V_1) cm^3

Mols bicarbonate =(V_2-2V_1)x0.2/1000

∴[bicarbonate] =(V_2-2V_1)x0.2/25 mol dm^{-3}.

A5.3.5

If the first titre is V_1 cm^3 and the second is V_2 cm^3, [OH^-]=V_2x0.2/25 mol dm^{-3}

(V_1-V_2)is equivalent to the carbonate: $CO_3^{2-}+2H^+ \rightarrow CO_2+H_2O$

∴[carbonate] =2(V_1-V_2)x0.2/25 mol dm^{-3}

A5.3.6

$(NH_4)Fe(SO_4)_2 \cdot 12H_2O$ is the usual source of Fe(III) 1 mol Ag^+≡1mol SCN^-

[SCN^-]=25x0.1/V mol dm^{-3}

(Volume of thiocyanate solution=V cm^3)

A5.3.7

%SCN in CuSCN=47.76

If mass of the precipitate is m g

∴mass of SCN=0.4776xm g ≡0.4776xm/58.07 mols

[SCN^-]=0.4776xmx1000/(58.07x25) mol dm^{-3}

A5.4

The results of these experiments and the experimental details are found in K.Haywood, M.A.Malati in *Proceedings of 4th Greenhouse Gas Technology Conference*, Eds. B.Eliasson *et al*, Elsevier Science, Oxford, 1999, p1011. This has references to earlier work in this area. The reason for expressing the results in KW hour^{-1} is to appreciate the energy consumption; KWhr is the usual unit for electrical energy consumption. This topic is environmentally important since carbon dioxide is the major Greenhouse gas.

Alternative determinations of methanol are described in M.H.Rayner, *International Labmate* 19(Oct.1994)14.

A5.5

A sample of Portland cement OPC gave the following results:

Oxide	SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	TiO_2	Mn_2O_3
%w/w	19.4	64.0	5.2	3.1	3.4	1.2	0.7	0.3	0.3	0.1

A5.6.1

For results of analysis and P.Z.C. of a B.D.H. sample see *J.Chem.Tech.Biotechnol.*32(1982)781.

A5.6.2

See *J.Chem.Soc.,Faraday Trans.I*,79(1983)2311. This also includes the adsorption of Cd^{2+} ions by the same silica.

A5.7.1

(a) Medium hardness, malleable.

(b) $Sn+2HCl \rightarrow SnCl_2(aq.)+H_2(g)$.

(c) Sn dissolves to form Sn(II) and Sn(IV) nitrates and NH_4^+ (gives $NH_3(g)$ with alkalis) is formed.

(d) Sn dissolves in alkali liberating $H_2(g)$.

A5.7.2

(i) Initial white SnO precipitates, it dissolves in excess forming $[Sn(OH)_3]^-$ and $[Sn(OH)_4]^{2-}$;
(ii) white SnO precipitates, insoluble in excess;
(iii) dark brown SnS(s) is formed, soluble in conc.HCl and in $(NH_4)_2S_2$ giving SnS_3^{2-} (or $[Sn(SH)_6]^{2-}$);
(iv) white Hg_2Cl_2(s) precipitates changing to dark Hg(s) in excess;
(v) Zn displaces Sn(s) (spongy);
(vi) red solution changes to pale green Fe(II);
(vii) dark Ag(s) deposited;
(viii) permanganate decolourised by Sn(II) which reduces it to Mn^{2+}.

A5.7.3

(i) White $SnO_2.2H_2O$ precipitates which is soluble in excess giving $[Sn(OH)_6]^{2-}$;
(ii) gelatinous hydrated oxide precipitates, insoluble in excess;
(iii) yellow SnS_2 precipitates which is soluble in conc.HCl and in $(NH_4)_2S_2$ forming $[Sn(SH)_6]^{2-}$
(iv) Fe reduces Sn(IV) to $SnCl_2$ (see A5.7.2 above);
(v) Zn reduces Sn(IV) to metallic Sn(s).

A5.8.1

If the volume of iodine is V cm^3, the number of mols of iodine=number of mols Sn(II)=Vx0.05/1000 in 25 cm^3 ($Sn(II)+I_2 \rightarrow Sn(IV)+2I^-$)
$\therefore$[Sn(II)]=Vx0.05/25 mol dm^{-3}.

A5.9.1

118.7 g Sn give 372.5 g SnI_2.$\because$Expected mass of SnI_2=0.5x372.5/118.7
% yield=mass obtained x118.7x100/(0.5x372.5)
If a melting point apparatus can be adapted for measurement under nitrogen, the melting point of the product can be determined.

A5.9.2

118.7 g Sn give 626.3 g SnI_4 % purity=mass obtained x118.7x100/(0.5x626.3).
The reference in Sec.5.9 gives preparation of SnI_4 from SnI_2 and of $Na_2[SnI_6]$.
Expected m.p. of SnI_4 is 145°C.
Expected reaction in the first gravimetric method is the oxidation of SnI_4 to SnO_2
% Purity =mass obtained x626.3x100/(0.5xRMM of SnO_2).
In the alternative determination, the iodide from SnI_4 is oxidised by iodate to ICl (Andrews titration conditions, Sec.8.3.3).
$SnI_4+2IO_3^-+12H^++10Cl^- \rightarrow 6\ ICl+SnCl_4+6H_2O$.
Mols iodate used =Vx0.025/1000, where V cm^3 is the volume used.
Mols SnI_4=Vx0.025/2000
Mass SnI_4=Vx0.025x626.3/2000 g
% Purity=Vx0.025x626.3/(20xmass used)

A510.1

Calculation of % yield as above
Titration of chloride as in Sec.8.3.1.

A5.10.2

%Yield as above.

A5.11.1

(a) Oxide and carbonate layer are removed. The metal is very soft (it marks paper). It dissolves in nitric acid giving Pb(II) nitrate.
(b) Pb forms $[Pb(OH)_3]^-$ and hydrogen is evolved.
(c) $6PbO+O_2 \rightarrow 2Pb_3O_4$(red). Temperature must be <400°C. Increase in mass depends on the extent of reaction.
(d) PbO dissolves to give the nitrate, which precipitates $PbCl_2$ with HCl.
(e) PbO_2 is insoluble in the acid ∴No effect of adding HCl.
(f) $PbO_2+4HCl \rightarrow PbCl_2+2H_2O+Cl_2(g)$ (bleaches litmus). $PbCl_2$ dissolves in conc. HCl as $[PbCl_4]^{2-}$.
(g) $Pb_3O_4+4HNO_3 \rightarrow 2H_2O+Pb(NO_3)_2+PbO_2(s)$.
(h) $Pb_3O_4+8HCl \rightarrow 3PbCl_2+Cl_2+4H_2O$.
(i) Colourless $Pb(CH_3COO)_4$ is formed but it is sensitive to moisture, hydrolysing to brown PbO_2 but is soluble in organic solvents.

A5.11.2

(i) $PbCl_2(s)$ precipitates, soluble in excess hot water depositing crystals on cooling; soluble in conc. HCl giving $[PbCl_4]^{2-}$ and $[PbCl_3]^-$;
(ii) PbI_2 yellow solid, soluble in boiling water and behaves like the chloride; soluble in excess giving $[PbI_4]^{2-}$;
(iii) white $PbSO_4$ precipitates, soluble in ammonium acetate due to the formation of lead acetate; solubility in NaOH due to $[Pb(OH)_3]^-(aq)$;
(iv) $Pb(OH)_2(s)$ white, soluble in excess giving $[Pb(OH)_3]^-$;
(v) $PbBr_2(s)$ similar to $PbCl_2(s)$ as above;
(vi) white $PbF_2(s)$;
(vii yellow $PbCrO_4(s)$ soluble in NaOH and in nitric acid;
(viii)white $Pb(SO_3)(s)$;
(ix) white $Pb(C_2O_4)(s)$;
(x) white $Pb(IO_3)_2(s)$;
(xi) white $Pb_3[H_2IO_6]_2(s)$;
(xii) black PbS(s), oxidised to white lead sulphate.

A5.12.1

Xylenol orange indicator: dissolve 0.5 g in 100 cm^3 water
Pb(II) reacts with EDTA in a 1:1 molar ratio
If volume of EDTA is V cm^3, number of mols EDTA=
Vx0.05/1000=number of mols of Pb(II)
∴[Pb(II)]=Vx0.05/25 mol dm^{-3}

A5.12.2

Mass of Pb in $PbCrO_4$=mass of precipitate x0.6411=m g
% Pb in the salt=mx100/mass of salt

A5.12.3

$2PbCrO_4+2H^+ \rightarrow 2Pb^{2+}+Cr_2O_7^{2-}+H_2O$
$Cr_2O_7^{2-}+14H^++6I^- \rightarrow 3I_2+2Cr^{3+}+7H_2O$
Mols of I_2=½Vx0.05/1000 (V=volume of thiosulphate used)
Mols of dichromate=Vx0.05/6000
Mass of Pb=2Vx0.05x207.2/6000=m g
%Pb=mx100/mass of lead nitrate
Alternative titration of $Cr_2O_7^{2-}$ against standardised Fe(II) (Sec.13.3.1).

A5.12.4

It facilitates the calculation if the EDTA and the Pb(II) solutions are of the exact molarity. Hence, the third titre will be 50.0 cm^3 and in the first two titres: V_1 and V_2, the volume is multiplied by 2 to obtain the EDTA equivalent since the EDTA solution is twice as concentrated as the Pb(II) solution.

The total mols of EDTA added/aliquot=25.0x0.2/(1000x10)=m_1

The number equivalent of EDTA mols in excess=2xV_1x0.01/1000=m_2

$\therefore$ The number of mols of EDTA reacting with the solder (Pb+Sn)=m_1-m_2

The number of mols of EDTA liberated from the Sn complex=2xV_2x0.01/1000 =mols of Sn=m_3

$\therefore$ The number of mols of Pb=(m_1-m_2)-m_3

When each number of mols of Sn or Pb is multiplied by the respective RAM, the mass of each metal is obtained and the % of each metal is calculated from the mass of solder used. If this is taken as m g, the % Sn=m_3x118.7x100/(0.1xm)

A5.12.5

Number of mols of dichromate=Vx0.05/1000=number of mols of Pb

$\therefore$[Pb(II)]=Vx0.05/25 (V=volume of dichromate used).

For a spectrophotometric method see *J.Chem.Educ.*67(1990)608 (also relevant for Sec.17.7.2); *Anal.Chem.*68(1996)727 (also refers to other instrumental techniques).

*J.Chem.Educ.*75(1998)1018 describes an ir study of the Pb/EDTA bonding.

A5.13.2

278.1 g lead chloride give 580.1 g of the complex

% Yield=(m_2x278.1x100)/(m_1x580.1)

(m_1=mass of elad chloride used, m_2=mass of complex obtained)

580.1 g $(C_5H_6N)_2[PbCl_6]$ gives 239.2 g PbO_2.

If mass of lead dioxide obtained is m g, the mass of complex =mx580.1/239.2=m_1

% Purity=m_1x100/mass used

A5.14

0.35 g of the catalyst suspended in 70 cm^3 0.0496 M lead acetate solution was irradiated for 120 minutes using the medium pressure mercury lamp (as in A5.4). The concentration of lead, determined at intervals is depicted in Fig.A5.1. Preliminary results indicated that a fair % of acetate was oxidised to CO_2, as indicated by titrating the NaOH solution in the exit bubblers. Initial investigation showed that the percentage of lead ions adsorbed by the powder was <10%. The results suggested that some metallic lead and/or its oxide were formed as a result of the photocatalytic reactions. This area is environmentally important because of the toxicity of lead salts.

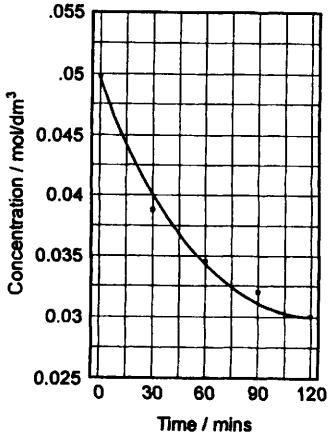


Fig. A5.1 The concentration of lead (II) left in solution as a function of irradiation time.

A5.15 Additional references

Cyanides have been excluded from the experiments because of their high toxicity. However cyano-complexes may be inert and are safer. They represent an important class of complexes and have been extensively studied. Analysis for cyanide in waste water is described by P.A.Bruttel, *International Labmate* **21**(6)(1996)9. The article indicates the advantage of using titrodes (combined glass electrode and a noble metal electrode) for potentiometric indication. Other titrations tried: sulphide, sulphite or thiosulphate and oxalate in non-aqueous solution. *J.Chem.Educ.*​**41**(1964)610 gives an example of a double clock reactions involving the hydration of carbon dioxide.

The preparation of cationic complexes of Si with acetylacetone are reported in *Inorg.Synth.*7(1962)31. In the same series, details of the preparation and properties of $Pb(CH_3COO)_4$ are given (*ibid.*​**1**(1943)47).

APPENDIX 6

A6.2.1

(a) $Mg_3N_2+6H_2O \rightarrow 3Mg(OH)_2+2NH_3$ (turns the paper black).
(b) $NH_4Cl(s) \leftrightarrows NH_3(g)+HCl(g)$, reformed solid deposited.
(c) Lighter $NH_3(g)$ detected.
(d) Heavier $HCl(g)$ detected.
(e) $(NH_4)_2CO_3 \rightarrow 2NH_3(g)+H_2O+CO_2(g)$ (heavier).
(f) $3(NH_4)_2SO_4 \rightarrow 4NH_3(g)+6H_2O+N_2+3SO_2(g)$ (heavier).
(g) SO_2 reduces acidified dichromate to green Cr(III).
(h) Evolved ammonia (i) turns litmus blue; (ii) forms white NH_4Cl fumes; (iii) turns paper black; (iv) turns paper yellow-brown; (v) pH>7.
    Reaction in (iii):$2Hg_2^{2+}+4NH_3+NO_3^- \rightarrow 3NH_4^++Hg_2N(NO_3)+2Hg(s)$ (black).
(i) (i) yellow ammonium salt precipitates.
    (ii) yellow ammonium salt precipitates.
    (iii) yellow to brown colour:$NH_3+2[HgI_4]^{2-}+3OH^- \rightarrow 7I^-+3H_2O+Hg_2NI$.

A6.2.2

(a) $2Cu^{2+}+2NH_2OH \rightarrow 4H^++N_2+H_2O+Cu_2O$(red).
(b) $4Fe^{3+}+2NH_2OH \rightarrow N_2O+H_2O+4H^++4Fe^{2+}$(light green).
(c) Dark Hg precipitates and N_2 evolved.
(d) as (c) with Ag(s) precipitate.
(e) $2Fe(OH)_2+NH_2OH+H_2O \rightarrow NH_3(g)+2Fe(OH)_3(s)$red.
(f) $Zn+3H^++NH_2OH \rightarrow Zn^{2+}+H_2O+NH_4^+(aq)$, this liberates $NH_3(g)$.
(g) yellow brown Hg_2NI less intense than in Sec.6.2.1 (i)-(iii) above.

A6.2.3

(a) Nitrogen evolved and Mn(IV) is reduced to +3 state.
(b) (i) Cu(s) precipitates;
    (ii) $4MnO_4^-+5N_2H_4+12H^+ \rightarrow 5N_2+16H_2O+4Mn^{2+}$ (practically colourless);
    (iii) molybdenum blue formed;
    (iv) dark Ag(s) is formed;
    (v) $2I_2(ag)+N_2H_4 \rightarrow N_2+4HI$ (colour discharged);
    (vi) Fe(III) is reduced to Fe(II) (pale green) and $N_2+NH_3(g)$ are formed, the latter turns paper black;
    (vii) $N_2H_4+Zn+4H^+ \rightarrow Zn^{2+}+2NH_4^+$ (yields ammonia with alkali).

A6.2.4

(a) HCl displaces HNO_2; on warming the latter decomposes:
    $3HNO_2 \rightarrow H_2O+HNO_3+2NO(g)$ (turns to brown NO_2 in air).
(b) (i) Brown $[Fe(H_2O)_5(NO)]^{2+}(aq)$ is formed; it decomposes and evolves NO on warming;
    (ii) $AgNO_2(s)$ from conc. solutions is precipitated;
    (iii) $NO_2^-+I^-$ (acidified) liberate $I_2(aq)$ (brown) turns starch blue;
    (iv) MnO_4^- is reduced to Mn(II) (hardly coloured) and NO_2^- oxidised to $NO_3^-(aq)$;
    (v) $CO(NH_2)_2+2HNO_2 \rightarrow 2N_2+3H_2O+CO_2(g)$;
    (vi) $NH_4NO_2 \rightarrow 2H_2O+N_2(g)$;
    (vii) nitrite is reduced to $NH_3(g)$;
    (viii) yellow $K_2Na[Co(NO_2)_6](s)$ is formed.

A6.2.5

(a) Sulphuric acid displaces nitric acid, which fumes in air and decomposes:
    $4HNO_3 \rightarrow 2H_2O+O_2+4NO_2(g)$(brown).
(b) Nitric acid is formed which dissolves Cu to give $Cu(NO_3)_2$ as (blue) and gaseous nitrogen oxides evolved.

(c) Brown ring $[Fe(H_2O)_5(NO)]^{2+}$ is formed following reduction of HNO_3:
$6FeSO_4+2HNO_3+3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3+4H_2O+2NO$.

(d) (i) $3H_2S+2H^++2NO_3^- \rightarrow 4H_2O+3S(s)+2NO(g)$, the latter gives NO_2 in air, followed by: $2NO_2+H_2O \rightarrow HNO_2+HNO_3$;
(ii) $4Zn+NO_3^-+7OH^-+6H_2O \rightarrow 4[Zn(OH)_4]^{2-}+NH_3(g)$.

A6.3.1.1

If volume of 0.1 M NaOH is 50 cm^3, number of mols=50x0.1/1000(=m_1)
If volume of 0.1 M HCl used is V cm^3
The number of mols HCl=Vx0.1/1000 mols (m_2)
∴Number of mols NaOH reacting with ammonium chloride solution
=(m_1-m_2) reacting with 25 cm^3 ammonium solution
∴$[NH_4^+]=(m_1-m_2)$x1000/25 mol dm^{-3}
Methyl orange indicator: dissolve 0.5 g of the sodium salt in 1 dm^3 water add 15.2 cm^3 0.1 M HCl. Available solution is 0.04%.
The reaction between ammonium ions and methanal liberates hydrogen ions according to:
$4NH_4^++6HCHO \rightarrow 6H_2O+C_6H_{12}N_4+4H^+$
The liberated acid can be titrated against standardised NaOH.

A6.3.1.2

Prepare Nessler's solution by dissolving 50 g of mercury(II) iodide and 35 g KI in water (see text). Cool and add, slowly with stirring, 80 g NaOH in 350 cm^3 water and make up to 500 cm^3. Allow to stand in the dark for 3-4 days and use the supernatant. Commercially available solution can be used.

Beer's law is applicable over the range of concentrations of ammonium salts given.

A6.3.1.3

When using an ammonia sensitive electrode, care should be taken in handling and storage as well as the effect of other ions in solution.

A6.3.2

Number of mols of hydrazinium salt=0.1xm/130.12 (m g is the mass used).
If the volume of M/60 iodate solution used is V cm^3, the number of mols used =V/60000
The molar ratio expected is 1:1
Reaction $IO_3^-+\underline{N_2}H_5^++H\underline{Cl}=I\underline{Cl}+\underline{N_2}+3H_2O$
Ox.no. -2 -1 +1 0

J.Chem.Soc., Dalton Trans.(1984)919 reports on the kinetics and mechanism of the oxidation of hydrazine by periodate, using gas volumetric analysis for nitrogen. $[I^-]$ and $[IO_3^-]$ were also monitored.

A6.3.3

Alternatively use accurately weighed portions of ~0.09 g, dissolve in 175 cm^3 water and proceed as in the text.
MgO is added to avoid an acidic solution.
Starch indicator solution: Mix 1.0 g of soluble starch with a little water and add to 100 cm^3 of boiling water with continuous stirring, boil for a little and cool. Then add 1 g KI and drops of chloroform or 5 mg mercury(II) iodide. Freshly made solution is added only when the colour of iodine fades to straw yellow.
If the volume of 0.05 M iodine solution is V cm^3, the number of mols iodine used =Vx0.05/1000 mols.
If the mass of the salt used is m g in 250 cm^3, the mass in 25 cm^3 is 0.1 m
∴Number of mols of hydroxylammonium chloride is 0.1 m/69.49
Ratio mols I_2:mols NH_2OH:HCl is expected to be 1:1

$2\underline{N}H_2OH+2I_2 \rightarrow \underline{N}_2O+4I^-+4H^++H_2O$

Ox.no. -1 $+1$

To prepare I_2 solution dissolve 12.7 g resublimed I_2 in 1 dm^3 water in which 20 g KI had been dissolved. The iodine solution should be standardised (Sec.7.3.3).

The suggested titration with BrO_3^- solutions gave erratic results. This oxidant is involved in oscillatory reactions. This behaviour may explain the erratic results.

A6.3.4.1

Mols permanganate used $=30\times0.02/1000\ (=m_1)$

Since Fe(II) and permanganate react according to:

$MnO_4^-+5Fe^{2+}+8H^+ \rightarrow Mn^{2+}+5Fe^{3+}+4H_2O$

0.02 M permanganate is equivalent to 0.1 M Fe(II) and if the solution used have these exact molarities, the calculation would be easier.

If the total volume of Fe(II) used $=V_1$ cm^3

and the volume of permanganate equivalent to excess Fe(II) $=V_2$ cm^3

$\therefore$Volume of Fe(II) reacting with excess permanganate $=(V_1-V_2)$ cm^3

$\therefore$Mols permanganate remaining after reacting with nitrite

$=[30-(V_1-V_2]\times0.02/1000\ (=m_2)$

$\therefore$Mols permanganate reacting with nitrite $=(m_1-m_2)$

$\therefore$Mols nitrite $=2.5(m_1-m_2)$ in 25 cm^3 aliquot

[Nitrite] $=2.5(m_1-m_2)\times1000/25$ mol dm^{-3}

$2MnO_4^- +5NO_2^-+6H^+ \rightarrow 2Mn^{2+}+5NO_3^-+3H_2O$

A6.3.4.2

See DOE Standing Committee of Analysts

Methods for the Examination of Water and Associated Materials, "Oxidised Nitrogen in Waters", 1981, p.148.

A 4 cm cell is more suitable for dilute solutions. A linear calibration plot of absorbance against concentration was found in the range 2.5×10^{-7}-1.5×10^{-6} M.

An initial study of the adsorption of nitrite by Degussa P25 anatase showed that the pH should be higher than 3. The study should be done under nitrogen.

*Ind.Engng.Chem.Anal.Ed.*14(1942)420 describes a method for determination of a low concentration of $NaNO_3$ in $NaNO_2$.

A6.3.6

*J.Chem.Educ.*74(1997)1459 describes spectral studies of NO_2 and N_2O_4 and other atmospheric pollutants.

A6.4

Results and further details are found in *J.Photochem.Photobiol A Chem.*89(1995)215.

A6.5.1

See *Inorg.Synth.*5(1957)87 for an alternative preparation.

$N_2O_4+H_2O \rightarrow HNO_2+HNO_3$+heat (acidic pH)

$2HNO_2 \leftrightharpoons H_2O+N_2O_3$(blue)

$FeSO_4$ gives the brown $[Fe(H_2O)_5(NO)]^{2+}$

$3HNO_2 \rightarrow HNO_3+2NO+H_2O$

A6.5.2

See *Preparative Inorganic Reactions,* Vol.1(1964)Ed.W.L.Jolly,p.141.

A6.6

Expected ratio of permanganate: reductant is 0.30:1 for $N_2H_5^+$ and 1.68:1 for NH_3OH^+. These stoichiometries indicate competition for a free radical intermediate.

A6.7

The red colour of the complex in which ammonia replaces chloride, and the yellow colour in which NO_2 replaces chloride appear very quickly, indicating the original complex is labile in these reactions. For other reactions of the cobalt complex see Sec.14.8.2.

A6.8

A solution of the prepared complex, acidified with nitric acid would precipitate $[Cr(NH_3)_6][Co(C_2O_4)]$ when mixed with a solution of the Co complex. This is isomeric with $[Co(NH_3)_6][Cr(C_2O_4)_3]$ (Sec.14.6.2) see also *J.Amer.Chem.Soc.*65(1943)250; *Inorg.Synth.*3(1950) 153.

A6.9.1

(a) White P glows in the dark when exposed to air due to oxidation. It dissolves in carbon disulphide but not in water.

(b) $P_4(s)+3OH^-+3H_2O \rightarrow 3H_2PO_2^-(aq)+PH_3(g)$ (burns in air due to P_2H_4 impurity); with silver nitrate, a white precipitate is formed which darkens by Ag(s) produced.

A6.9.2

(a) $Ca_3P_2+H_2O \rightarrow Ca(OH)_2(aq)$ alkaline+$PH_3(g)$ see (b) above.

(b) PH_3 reduces silver nitrate to finely divided Ag(dark). Initially $Ag_3P.3AgNO_3$ precipitates.

(c) $PCl_3+3H_2O \rightarrow 3HCl+H_3PO_3(aq)$, the latter gives $Ag_2HPO_3(s)$ white precipitate, then it darkens; permanganate decolourised (reduction to Mn(II)). Heat evolved.

(d) $PCl_5+4H_2O \rightarrow 5HCl+H_3PO_4$+heat; the latter gives $Ag_3PO_4(s)$ (yellow).

(e) $P_4O_{10}+6H_2O \rightarrow 4H_3PO_4(aq.)$, which reacts with Mg liberating hydrogen.

A6.9.3(a)

	Na_2HPO_4	$Na_4P_2O_7$	$NaPO_3$
(i) precipitate	yellow	white	white (slowly)
in dil.NH_3	soluble	soluble	soluble
in dil.acid	soluble	not in dil.acetic	soluble
(ii) precipitate	pale blue	very pale blue	none
(iii) precipitate	white	white	none
excess reagent	insoluble	soluble	
(iv) precipitate	white	white	white on warming
in acetic acid	soluble	insoluble	soluble

(b) (i) yellow$(NH_4)_3PMo_{12}O_{40}.2HNO_3.H_2O(s)$ soluble in ammonia or in NaOH;
(ii) yellow white $FePO_4(s)$;
(iii) white zirconyl phosphate precipitates.

A6.9.4

(a) $8Na_2HPO_3 \rightarrow 2PH_3(g)+4Na_3PO_4+Na_4P_2O_7+H_2O$
$4NaH_2PO_2 \rightarrow Na_4P_2O_7+H_2O+2PH_3(g)$

(b)

	NaH_2PO_2	Na_2HPO_3
(i) decolourisation	slow in cold	on warming
(ii) precipitate	white slowly darkens	white darkens on warming
(iii) precipitate	red due to reduction	blue
	warm	excess
(iv) precipitate	white $Hg_2Cl_2 \rightarrow Hg$ dark	white→Hg (black)
(v) Precipitate	none	white $BaHPO_3$

(c) The acid is reduced by either solid to $SO_2(g)$ (turns paper green).

(d) Zinc and acid reduce either solid to $PH_3(g)$ (darkens paper:Ag(s)).

(e) With NaOH, $H_2(g)$ is formed (burns in air with a pop).

A6.10.1
See reference in A3.4.3.1

A6.10.2
%PO_4 in $Mg(NH_4)PO_4.6H_2O$=38.68
%PO_4 in $Mg_2P_2O_7$=85.34.

A6.10.3
Perchloric acid media are more suitable for analysing phosphate in iron minerals. Data and other references in M.A.Malati *et al*, *Bul.Inst.Egypte*(1962)127.

A6.10.4
*Anal.Chim.Acta.*27(1962)31 gives details and results.

A6.10.5
See Sec.2.5.1. The two inflection points in the titration curve are seen. Derivative curves give sharper location of the respective pH values.

A6.11
Although two equivalents of alkali neutralise the acid, the third H in the formula is not acidic, the P-H bond in the neutralised acid accounts for the disproportionation of Ag_2HPO_3 precipitate to Ag and $H_2PO_4^-$.

A6.12.1
(a) (i) Sb(III) gives orange Sb_2S_3 soluble in $(NH_4)_2S_2$ to give $(NH_4)_3SbS_4$ and in KOH forming soluble oxoanions. Sb(V) gives with H_2S, orange red Sb_2S_5 soluble in $(NH_4)_2S_2$ to give $(NH_4)_3SbS_4$ and in alkali to give oxosalts;
(ii) Zn or Fe displace black Sb(s) from either solution (Sb(V) should be acidified with HCl);
(iii) Sb(III) salt solutions are hydrolysed: $SbCl_3+H_2O=2HCl+SbOCl(s)$ white; whereas Sb(V) precipitates a basic salt;
(iv) Sb(III) gives a yellow $[SbI_4]^-$ solution; whereas Sb(V) is reduced to Sb(III) liberating brown iodine;
(b) (i) NaOH precipitates white Sb_4O_6 aq, soluble in excess to give $[Sb(OH)_6]^{3-}$;
(ii) Sb_4O_6 aq. precipitates (insoluble in excess ammonia);
(iii) thiosulphate precipitates Sb_2S_3 with $HSO_4^-(aq)$;
(iv) yellow $[Sb(C_9H_6NO)_3]$ oxinate precipitates. Reagent is 2% in 2 M acetic acid to which ammonia is added until a precipitate is formed which dissolves on warming.

A6.12.2
(a) (i) Brown Bi_2S_3 precipitates (also obtained by using H_2S); soluble in acids; e.g. to give $[BiCl_4]^-$ with HCl or $Bi^{3+}(aq)$ in nitric acid;
(ii) white $Bi(OH)_3$ precipitates; slightly soluble in excess, turns to yellow BiO(OH) on boiling;
(iii) white $(BiO)_2CO_3$ precipitates;
(iv) White $BiO(NO_3)$ precipitates, soluble in acids;
(v) dark brown BiI_3 precipitates, with warm water gives BiOI(s); excess KI gives yellow solution of BiI_4^- (extracted by the alcohol);
(vi) white $BiPO_4$ precipitates;
(vii) brick red $Bi[Cr(SCN)_6]$ precipitates (Sec.11.6.1 for preparing the Cr complex);
(viii)in the reagent, SnO(aq) first precipitates but dissolves to $Sn(OH)_6^{2-}$, the reagent precipites black Bi(Sn(II) is an effective reductant);
(ix) yellow $Bi_2C_4H_6N_2O_4$ precipitates;
(x) yellow $[Bi(C_9H_6N.O)_3]$ precipitates;
(xi) $3Fe+2Bi^{3+}\rightarrow 3Fe^{2+}+2Bi(s)$ black;

(b) $5NaBiO_3+2MnSO_4+16HNO_3 \rightarrow 5Bi(NO_3)_3+NaNO_3+2Na_2SO_4+7H_2O+2HMnO_4$ (purple solution).

A6.13.1.1

$K(SbO)C_4H_4O_6+I_2+4NaHCO_3 \rightarrow KNa(C_4H_4O_6)+2NaI+NaH_2SbO_4+H_2O+4CO_2$

If the volume of iodine solution is V cm^3, the number of mols used =Vx0.05/1000

=number of mols of Sb in 50 cm^3

$\therefore$[Sb]=Vx0.05/50 mol dm^{-3}

A6.13.1.2

In the titration of Sb(V), when the medium is acidic, iodide is oxidised

$Sb(V)+2I^- \rightarrow Sb(III)+I_2$

If the volume of thiosulphate used is V cm^3, the number of mols of I_2=½xnumber of mols of thiosulphate=½xVx0.05/1000

$\therefore$[Sb(V)]=½xVx0.05/50 mol dm^3

A6.13.2.1

Pyrocatechnol violet indicator: dissolve 1 g in water and make up to 100 cm^3

Bi(III) and EDTA react in 1:1 molar ratio

If the volume of EDTA is V cm^3, its number of mols=Vx0.05/1000

=mols of Bi in 25 cm^3

$\therefore$[Bi]=Vx0.05/25 mol dm^{-3}

A6.13.2.2

%Bi in the precipitate ($BiPO_4$)is 68.76%. Mass of Bi=0.6876xm (m=mass of precipitate)

If the mass of the Bi salt is m_1

%Bi=0.6876xmx100/m_1

A6.13.2.3

The yellow complex has an absorption maximum at 460 nm. The use of phosphinic acid is to reduce interfering ions e.g. Fe(III) but if none is expected, this acid could be left out.

A6.14

The glove box should have containers with phosphorus(V) oxide spread in thin layers to absorb any moisture and moisture-free nitrogen used.

Tests (a) The solid quickly absorbs moisture from air

(b) (i) white AgCl is the main precipitate together with some silver salts of P;

(ii) white precipitate of basic Sb salt.

Further details about the compound and related compounds are found in *Chem.Rev.***66**(1966)87. The compound has been also obtained and characterised in solution (*J.Chem.Soc.*(1963)38). $[FPCl_3][SbCl_6]$ was studied in *Inorg.Chem.***2**(1963)813.

A6.15

The preparation, characterisation and analysis of the Cr(III) EDTA complex are described in *Educ.Chem.***12**(1975)12. The observed retarding effect of Bi(III) suggests that it ties up some of the free EDTA in the Cr complex which may be related to the high stability of its EDTA complex.

A6.15 Additional experiments and references

Arsenic compounds have not been used in teaching laboratories for at least two decades because of their notorious toxicity. However, arsenic(III) and As(V) compounds resemble those of Sb, although the latter exhibits what is called "middle row anomaly". An interesting kinetic experiment of the oxidation of As(III) by Ce(IV) is described in *J.Chem.Educ.***39**(1962)635.

For the kinetics of oxidation of hydrazine by periodate see *J.Chem.Soc.Dalton Trans.*(1984)919. For the heterogeneous oxidation of hydrazine by barium chromate see *J.Chem.Soc.Faraday Trans.***81**(1985)1113.

Hexahydroxylamminecobalt(III) halides are reported in *Inorg.Chem.*3(1964)1320.

The liquid complexes of triethylammonium and triethylphosphonium chlorides with Cu(I) chloroanions can be used to study fused salts (*Educ.Chem.* **12**(1975)84).

The preparation of a number of phosphates is given in *Inorg.Synth.*3(1950)98-105.

APPENDIX 7

A7.2.1

(a) Sulphur melts to a yellow liquid, which darkens and becomes more viscous at higher temperatures but becomes more fluid before boiling. The mobile liquid, when quenched in water, gives "plastic" S.

(b) S+Fe→FeS(black) not attracted by a magnet, with HCl gives H_2S(g). The acetate paper blackened by PbS formation.

(c) S is soluble in pyridine but not in water.

(d) $S+2H_2SO_4 \rightarrow 3SO_2+2H_2O$ (some white SO_3 vapour).

(e) $S+4HNO_3 \rightarrow 4NO_2+2H_2O+SO_2(g)(SO_2\ (aq.) \rightarrow BaSO_3(s))$.

(f) As in (d), but no SO_3 is formed. SO_2 turns dichromate green due to Cr(III) formation.

(g) S+Hg→HgS(s) black.

(h) $S+Na_2SO_3 \rightarrow Na_2S_2O_3(s)$ see later for thiosulphate Sec.7.2.5.

(i) $4S+6NaOH \rightarrow 3H_2O+2Na_2S+Na_2S_2O_3$, black Ag_2S precipitates; (ii) red violet Fe complex is formed $+S_2O_3^{2-}$(aq.) for reaction with silver nitrate see Sec.7.2.5.

(j) black HgS(s) precipitates.

(k) $S_2Cl_2+2H_2O \rightarrow 2HCl(aq.)+SO_2+H_2S$, the latter two would give some S(s).

A7.2.2

(a) $FeS+2HCl \rightarrow FeCl_2(aq)+H_2S(g)$ (forms black PbS or yellow CdS).

(b) (i) $Na_2S(aq.)+2AgNO_3 \rightarrow 2NaNO_3+Ag_2S(s)$ black, soluble in hot acid;

  (ii) $Na_2S(aq.)+Pb(CH_3CO_2)_2 \rightarrow 2Na(CH_3CO_2)(aq.)+PbS(s)$ black soluble in hot acid;

  (iii) red violet colour $[Fe(CN)_5NOS]_2^{8-}$(aq.);

  (iv) black brown stain of Ag_2S.

A7.2.3

(a) $SO_3^{2-}+2HCl \rightarrow H_2O+2Cl^-+SO_2(g)$ (causes dichromate to turn green).

(b) SO_2(g) forms $CaSO_3$(s) white.

(c) (i) $BaCl_2+Na_2SO_3 \rightarrow 2NaCl+BaSO_3(s)$ white, soluble in HCl;

  (ii) $2AgNO_3+Na_2SO_3 \rightarrow 2NaNO_3+Ag_2SO_3(s)$ white, soluble in excess forming $[Ag(SO_3)_2]^{3-}$ and in ammonia forming $[Ag(NH_3)_2]^+$;

  (iii) hydrogen peroxide oxidises $BaSO_3$ to $BaSO_4$ insoluble in acids;

  (iv) permanganate decolourised (reduction to Mn^{2+});

  (v) dichromate turns green (reduction to Cr(III));

  (vi) white $PbSO_3$(s) soluble in cold acid; oxidised on boiling to $PbSO_4$ which is insoluble in acids;

  (vii) I_2 is reduced to I^- and hence decolourised;

  (viii)sulphite reduced to H_2S(g) which blackens the lead acetate paper.

A7.2.4.1

(a) $2S_2O_4^{2-}+4H^+ \rightarrow S(s)+2H_2O+3SO_2(g)$ (paper turns green); orange colour which fades with the deposition of yellow S.

(b) immediate reaction as (a).

(c) (i) Black Ag (from ammoniacal solution); otherwise black Ag_2S(s) is formed;

  (ii) Cu_2S(s) precipitates from acid solution; in neutral solution Cu(s) forms;

  (iii) dark Hg(s) or black HgS(s) precipitate;

  (iv) grey Hg(s) precipitates and SO_2(g) evolved;

  (v) permanganate decolourised (reduction to Mn(II); $2MnO_4^-+2S_2O_4^{2-}+4H^+ \rightarrow 2Mn^{2+}+S_2O_6^{2-}+2SO_4^{2-}+2H_2O$;

  (vi) reagent reduced to hexacyanoferrate(II);

  (vii) black NiS(s) precipitates on heating;

  (viii)CrO_4^{2-} reduced to Cr(III); $S_2O_4^{2-}$ oxidised to SO_4^{2-} (precipitated as white $BaSO_4$);

  (ix) SO_2(g) evolved and Fe(III) reduced to Fe(II) (nearly colourless in dilute solution).

A7.2.5

(a) Crystals initially melt, on further heating decompose to Na_2S_5, S and Na_2SO_4; adding dil.HCl liberates $H_2S(g)$.
(b) (i) iodine decolourised: $I_2+2S_2O_3^{2-}\rightarrow S_4O_6^{2-}+2I^-$;
  (ii) white $Ag_2S_2O_3$ precipitates, soluble to give $[Ag(S_2O_3)_2]^{3-}$ in excess; darkens on warming (due to Ag(s));
  (iii) white $PbS_2O_3(s)$ precipitates, soluble in excess, darkened on boiling (PbS formed);
  (iv) a blue ring is formed at the surface between the two liquids (molybdenum blue);
  (v) violet colour of $[Fe(S_2O_3)_2]^-$ rapidly fades, thiosulphate oxidised to $S_4O_6^{2-}$ and Fe(III) reduced to Fe(II):
  (vi) permanganate reduced to nearly colourless Mn(II);
  (vii) dichromate reduced to green Cr(III);
  (viii)CuS (black precipitate formed on boiling).
(c) Dilute HCl displaces $H_2S_2O_3$ which is unstable and decomposes to S and $SO_2(g)$ (turns paper green).

A7.2.6

(a) $Na_2S_2O_6\rightarrow SO_2(g)$ (paper turns green)+Na_2SO_4 (gives white $BaSO_4(s)$).
(b) Conc. acid reacts similarly on heating: $Na_2S_2O_6+2HCl\rightarrow 2NaCl+H_2SO_4+SO_2$.
(c) (i) No precipitate, the barium salt is soluble;
  (ii) $S_2O_6^{2-}+I_2+2H_2O\rightarrow 2SO_4^{2-}+-4H^++2I^-$ (iodine decolourised);
  (iii) $[Fe(S_2O_6)_3]^{3-}(aq)$ (red) is formed;
  (iv) $S_2O_6^{2-}+2OH^-\rightarrow H_2O+SO_4^{2-}$ (precipitates white barium sulphate)+SO_3^{2-} (turns dichromate green);
  (v) white $PbS_2O_6(s)$ precipitates;
  (vi) brown MnO_2.aq.(s) precipitates;
  (vii) purple $[Ni(en)_3]S_2O_6(s)$ precipitates.

A7.2.7

(a) (i) $BaSO_4(s)$ white precipitates, fairly soluble in conc.HCl, soluble in EDTA(aq.);
  (ii) PbSO(s) white precipitates (soluble in EDTA and in ammonium acetate);
  (iii) $Ag_2SO_4(s)$ crystalline precipitates from concentrated solution.
(b) Sulphate reduced to sulphide, (with acid gives $H_2S(g)$).

A7.2.8

(a) The acid extracts O and H (the elements of water) leaving black C.
(b) $2H_2NSO_3^-+3Br_2+2H_2O\rightarrow N_2+2HSO_4^-+6H^++6Br^-$ (bromine decolourised).
(c) Nitrogen evolved and sulphate formed (precipitates white barium sulphate).

A7.2.9

(a) Sulphate and oxygen (rekindles splint) are formed, decomposition initially gives peroxommonosulphate (K_2SO_5).
(b) $2K_2S_2O_8\rightarrow 2K_2SO_4+2SO_3+O_2$ (rekindles the splint).
(c) $2Mn^{2+}+5S_2O_8^{2-}+8H_2O\rightarrow 2MnO_4^-10HSO_4^-$ + $6H^+$ (red violet colour of permanganate observed, Ag^+ catalyse the reaction).
(d) $2Cr^{3+}+3S_2O_8^{2-}+8H_2O\rightarrow 6SO_4^{2-}+16H^++2CrO_4^{2-}(aq.)$ yellow colour (or orange $Cr_2O_7^{2-}$ in acid solution) catalysed by Ag^+.
(e) (i) Black silver oxide is formed;
  (ii) on boiling, sulphate is produced which precipitates white $BaSO_4$;
  (iii) iodide oxidised to iodine (dark blue starch paper);
  (iv) nickel(II) hydroxide oxidised to black NiO_2.

A7.3.1

$S^{2-}+I_2\rightarrow S+2I^-$

Mols of iodine added $=35\times0.01/1000=m_1$

Mols of thiosulphate $=V\times0.01/1000=m_2$ (V volume used)

Mols of excess iodine $=m_1-\frac{1}{2}m_2=$mols of sulphide in 25 cm^3

$[S^{2-}]=(m_1-\frac{1}{2}m_2)\times1000/25$ mol dm^{-3}

The concentration in the original solution is 10 times this concentration.

A7.3.2.1

Calculation for titrimetry is the same as above A7.3.1

$SO_3^{2-}+I_2+H_2O\rightarrow SO_4^{2-}+2I^-+2H^+$

A7.3.2.2

Mass of sulphite in precipitate $=m\times0.3430$ g in the solid (m=mass of precipitate)

Mass of sodium sulphite found $=m\times0.3430\times126.05/80.07$

%Purity =(mass found/mass taken)x100

A7.3.2.3

Details of the spectrophotometric method are found in *Talanta*,**16**(1969)144 which includes determination of sulphur dioxide in air. The wavelength of maximum absorption was 387 nm.

A7.3.3

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

$IO_3^-+5I^-+6H^+\rightarrow 3I_2+3H_2O$

$\therefore IO_3^-\equiv 6S_2O_3^{2-}$

$[IO_3^-]=$mass used/214=M

Mols of iodate solution used =25xM/1000

Mols of thiosulphate =25xM/6000 in V cm^3 (V=volume used)

$[S_2O_3^{2-}]=25\times M/6\times V$ mol dm^{-3}

A7.3.4.1

If the EDTA and Mg salt solution have the same molar concentration, the number of excess mols of EDTA$=V\times0.05/1000=m_1$ (V=volume used)

Total number of mols EDTA $=35\times0.05/1000=m_2$

Mols EDTA complexed with barium $=m_2-m_1=$mols Ba sulphate in 25 cm^3

$[\text{Sulphate}]=(m_2-m_1)\times1000/25$ mol dm^{-3}

A7.3.4.3

At the recommended potential, Pb^{2+} give a diffusion current. The titration curve resembles an obtuse angle, with a slightly rounded end-point

Mols of Pb nitrate used =Vx0.01/1000 (V is the volume used)

=mols of sulphate in 25 cm^3

[Sulphate]=Vx0.01/25 mol dm^{-3}

A7.3.5.1

Mols Fe(II) solution used $=25\times0.1/1000=m_1$

Mols permanganate ≡excess Fe(II)=Vx0.02/1000 (V cm^3 used)

Mols Fe(II) in excess $=5\times V\times0.02/1000=m_2$

Mols Fe(II) reacting $=m_1-m_2=\frac{1}{2}$ mols persulphate in 25 cm^2

$[S_2O_8^{2-}]=\frac{1}{2}(m_1-m_2)\times1000/25$ mol dm^{-3}

A7.3.5.2

1 mol permanganate ≡2.5 mols oxalate (or oxalic acid)
$S_2O_8^{2-}+C_2O_4^{2-}+2H^+\rightarrow 2CO_2+2HSO_4^-$
Mols oxalic acid added =50x0.05/1000=m_1
Mols of excess oxalic acid =2.5xVx0.02/1000=m_2 (V volume of permanganate)
Mols acid reacting =m_1-m_2=mols $K_2S_2O_8$
Mass of persulphate =(m_1-m_2)x270.3 g =m_3 g
%Purity =m_3x100/mass weighed.

A7.3.6

If the volume of the iron(III) complex used in the first titration is
V_1cm^3, the number of mols =V_1x0.1/1000
∵1 mol of Fe complex =½ mol of $S_2O_4^{2-}$ (Equation 7.9)
∴The number of mols of dithionite =½xV_1x0.1/1000 in 50 cm^3 solution
[$S_2O_4^{2-}$]=½xV_1x0.1/50 mol dm^{-3}
In the last titration, if the volume of the Fe(III) complex used =V_3
The number of mols of Fe complex ≡thiosulphate=8xV_3x0.1/7000
∴The number of mols of thiosulphate=V_3x0.1/7000 (equation 7.8)
∴Mass of solid thiosulphate=V_3x0.1x248.2/7000=m g
∴%Purity of thiosulphate= mx100/mass weighed
If the volume used in the second titration is V_2 cm^3,
the number of mols Fe(III) complex =V_2x0.1/1000
The volume of Fe(III) complex ≡sulphite =V_2-2V_1-(8V_3/7)=V_4
[SO_3^{2-}]=½V_4x0.1/50 mol dm^{-3} (equation 7.7)

A7.4.1

The reference gives the refractive indices of the barium salt $BaS_2O_6.2H_2O$ as 1.594 and the method of its measurement as well as values for the alkali metal salts. See also *Inorg.Synth.*2(1946)167-199.
222.3 $K_2S_2O_5$ gives 238.9 g $K_2S_2O_6$
Expected mass = mx238.9/222.3=m_1(m=mass of reactant used).
If the mass of product is m_2 ∴% yield=m_2x100/m_1
The refrective index reported in the reference is 1.456.

A7.4.2

65.38 g Zn give 193.5 g Zn S_2O_4
Expected mass of product =mx193.5/65.38 (m=mass of Zn used)
% Yield =(mass of product x65.38x100/(mx193.5)
$S_2O_4^{2-}+2Ag^++2H_2O\rightarrow 2Ag+2HSO_3^-+2H^+$
$Ag^++SCN^-\rightarrow Ag((SCN)(s)$
Fe^{3+}(aq.) forms red brown coloured complexes with SCN^- (aq.)
If the volume of thiocyanate used is V cm^3
Number of mols of titrant =Vx0.5/1000=mols of excess Ag^+(aq.)=m_2
Mols of Ag^+(aq.) added =25x0.1/1000=m_1
∴Mols of Ag^+ reacting =(m_1-m_2)=½ mols of ZnS_2O_4
Mols of ZnS_2O_4=½(m_1-m_2)=m_3 mols
∴Mass of ZnS_2O_4=m_3x193.5=m_4
% Purity =m_4x100/mass weighed.

A7.5.1

6x249.68 g $CuSO_4.5H_2O$ give 1142 g $3Cu_2S_2O_3.2Na_2S_2O_3.6H_2O$
Expected mass of product =m_1x1142/(6x249,68) =m_2 (m_1=mass of Cu salt)

% Yield =m_3x100/m_2 (m_3=mass of product)
$3Cu_2S_2O_3.2Na_2S_2O_3.6H_2O$ contain 5 thiosulphate ions
If the volume of iodine solution is V_1 cm^3
$\therefore$Total mols of iodine =V_1x0.05/1000=m_1
If the volume of thiosulphate reacting with the excess iodine is V_2 cm^3
$\therefore$Mols of thiosulphate used =V_2x0.02/1000
Mols of excess iodine =½xV_2x0.01/1000=m_2
$\therefore$Mols of iodine reacting =m_1-m_2
$\therefore$Mols of $S_2O_3^{2-}$ consumed =2(m_1-m_2)
$\therefore$Mass of $S_2O_3^{2-}$=2(m_1-m_2)x112.12 g (=m_3)
If mass weighed =m g, it contains 0.5114xm_4 g $S_2O_3^{2-}$
$\therefore$Percentage purity =m_3x100/(0.5114xm_4)
For calculating the % Cu in the complex use Sec.16.4.1.2, taking into account that all the Cu(I) is oxidised to Cu(II) which reacts with iodide:
$Cu^{2+}+2I^- \rightarrow CuI(s)+I_2$
Ratio Cu:$S_2O_3^{2-}$=6:5

A7.6.1
The reference contains results and further details.

A7.6.2
See *J.Chem.Educ.***63**(1976)197 for details.

A7.6.3
A linear plot is expected. The second-order rate constant is ~4x10^{-3} dm^3 mol^{-1} s^{-1} at ~25°C. See *Educ.Chem.***35**(1998)132 for second-order reactions including the reaction in 7.6.4.

A7.6.4
$5H_2O_2+2MnO_4^-+6H^+ \rightarrow 2Mn^{2+}+8H_2O+5O_2$
If volume of permanganate used is V cm^3,
the number of permanganate mols =Vx0.02/1000
$\therefore$Mols of H_2O_2 present =2.5xVx0.02/1000 in 50 cm^3
[H_2O_2]=2.5xVx0.02/50 mol dm^{-3}
Molybdates catalyse the H_2O_2/I^- reaction.

A7.9.1
(a) (i) yellow mixture of Se and S are produced from selenites; brown TeS_2 or TeS is produced from tellurite;
(ii) $BaSeO_3$(s) white precipitates, soluble in acids or $BaTeO_3$(s) white precipitates, also soluble in acids;
(iii) Ag_2SeO_3(s) white is formed; yellow Ag_2TeO_3(a) precipitates;
(iv) $HgSeO_3$(s) white is obtained;
(v) Se(s) red precipitates on boiling; black Te(s) is formed;
(vi) I^- oxidised to I_2 (turns starch blue) decolourised by thiosulphate; or black TeI_4(s) precipitates which dissolves in excess, giving $[TeI_6]^{2-}$;
(vii) oxidation to SeO_4^{2-} by either oxidant;
(viii)red Se(s) is given by either reagent; black Te(s) is formed on boiling with hydrazinium chloride;
(ix) reduction to red Se(s) or to black Te(s);
(x) same as in (ix);
(xi) yellow $[Se(S_2O_3)_2]^{2-}$(aq.) is obtained or yellow solution (similar to Se complex) is formed;
(xii) red Se(s) or yellow Te(II) thiourea complex is product.

(b) reduction to red Se(s).
(c) Te(s) is formed on heating.

A7.9.2

- (a) (i) Se(s) separates only on boiling; Te(s) separates on boiling;
  - (ii) $BaSeO_4$(s) white, precipitates (soluble in boiling conc.HCl), or white BaH_4TeO_6(s) separates.
- (b) (i) Reduction to selenite and oxidation of the acid to chlorine (bleaches the paper);
  - (ii) on warming Se(s) is formed; (yellow turns to red).
- (c) (i) black Te(s) is obtained;
  - (ii) Te(s) is formed on prolonged boiling;
  - (iii) Te(s) precipitates;
  - (iv) TeI_6^{2-}(aq.) red brown is obtained;
  - (v) white Ag_6TeO_6 is obtained from neutral solution or white CaH_4TeO_6(s) precipitates.

A7.10 Additional references and experiments

An article in *J.Chem.Educ.*54(1977)582 describes a DTA system and a thermogram of sodium thiosulphate pentahydrate.

The clock reaction involving methanal and sodium hydrogen sulphite is discussed in *J.Chem.Educ.*53(1976)197.

APPENDIX 8

A8.2.1

(a) $HF(g)$ evolved, reacts with moisture and glass giving hydrated silica (turbidity in the tube).

(b) (i) white $CaF_2(s)$ precipitates;
  (ii) solution decolourised due to formation of $FeF_6^{3-}(aq.)$;
  (iii) white ThF_4 precipitates;
  (iv) white LaF_3 precipitates;
  (v) no precipitate (NaF is soluble).

(c) $Cl^-(s)$ +conc.$H_2SO_4 \rightarrow HCl(g)$:fumes of NH_4Cl with ammonia; Br^-+ conc.sulphuric$\rightarrow HBr(g)$ (tested as HCl)+$Br_2(g)$ (fluorescein turns pink)+SO_2 (dichromate paper turns green), I^-+ sulphuric acid$\rightarrow$some $HI(g)$+$I_2(g)$ (turns starch blue)+$H_2S(g)$ (turns lead paper black).

(d) $Br^-+H_3PO_4 \rightarrow HBr$ (tested like HCl), I^- gives $HI(g)$ (tested as HCl, some decomposition gives $I_2(g)$.

(e) (i) $Ag^+ + Cl^- \rightarrow AgCl(s)$ white (dissolves in ammonia to give $[Ag(NH_3)_2]Cl$), $Br^- + Ag^+ \rightarrow AgBr(s)$ (pale yellow, dissolves in conc. ammonia, Ag + $I^- \rightarrow AgI(s)$ yellow insoluble in ammonia; all precipitates dissolve in conc.KI.
  (ii) $Pb^{2+}+2X^- \rightarrow PbX_2(s)$ white for X=Cl or Br; yellow for X=I; all dissolve in excess of boiling water, precipitating as crystals on cooling.

(f) $X^-+MnO_2+H_2SO_4 \rightarrow X_2(g)$; Cl_2 bleaches litmus, bromine turns fluorescein red or iodine turns starch blue.

(g) Chloride gives $CrO_2Cl_2(g)$ red (hydrolysed by water to orange dichromate becomes yellow chromate in NaOH); bromide gives $Br_2(g)$ (soluble in water to a yellow solution, decolourised by NaOH).

(h) $Cl_2(aq.)+2X^- \rightarrow X_2(aq.)+2Cl^-$ (no reaction with chloride), bromine or iodine extracted by chloroform to give respectively a red brown or violet solution.

(i) (i) $2Cu^{2+}+4I^- \rightarrow 2CuI(s)+I_2$ (decolourised by thiosulphate);
  (ii) iodide oxidised to iodine (paper turns blue), nitrite reduced to NO;
  (iii) $Hg^{2+}+2I^- \rightarrow HgI_2(s)$ (scarlet) soluble in excess forming $[HgI_4]^{2-}(aq.)$;
  (iv) $PdCl_2(aq.)+2KI \rightarrow 2KCl+PdI_2(s)$ brown red.

A8.2.2

(a) MnO_4^- oxidises HCl to chlorine (bleaches litmus and turns KI/starch blue).

(b) Chlorine water reacts with KI as in (h) above.

(c) $Cl_2(aq.)+2Hg(l) \rightarrow Hg_2Cl_2(s)$ white.

(d) Bromine is soluble in water, more soluble in chloroform.

(e) (i) $KI+Br_2 \rightarrow 2KBr+I_2(aq.)$;
  (ii) $S_2O_3^{2-}+4Br_2+5H_2O \rightarrow 2SO_4^{2-}+8Br^-+10H^+$ (all colourless);
  (iii) $2Ag^++Br_2+H_2O \rightarrow AgBr(s)+AgOBr(aq.)+2H^+$, on warming AgBr+ another solid $AgBrO_3$ are formed;
  (iv) red violet bromophenol blue at pH5;
  (v) litmus turns red at first but slowly bleached;
  (vi) $3Br_2+6\,OH^- \rightarrow 5Br^-+BrO_3^-+3H_2O$ (all colourless).

(f) Iodine slightly soluble in water, soluble in ethanol (brown solution) and in CCl_4 (violet solution).

(g) (i) $I_2+2S_2O_3^{2-} \rightarrow S_4O_6^{2-}+2I^-$ (all colourless);
  (ii) blue adsorption complex is obtained;
  (iii) $6\,OH^-+3I_2 \rightarrow IO_3^-+5I^-+3H_2O$ (all colourless).

A8.2.3

(a) (i) $NaOCl+H_2SO_4 \rightarrow NaHSO_4+HOCl$; HOCl oxidises Fe(II) to Fe(III), which is precipitated to rust coloured Fe_2O_3 aq.;
  (ii) I^- oxidised to iodine (turns starch blue);

(iii) $H_2O_2+OCl^-\rightarrow Cl^-+H_2O+O_2(g)$ (rekindles splint);

(iv) $Mn^{2+}+2OH^-\rightarrow Mn(OH)_2(s)$; $2Mn(OH)_2+OCl^-\rightarrow 2MnOOH(s)+Cl^-+H_2O$ (buff precipitate is formed which slowly darkens);

(v) $2Cr^{3+}+3OCl^-+10\ OH^-\rightarrow 3Cl^-+5H_2O+2CrO_4^{2-}$ (yellow solution);

(vi) $2Co^{2+}+OCl^-+2OH^-\rightarrow Cl^-+2H^++Co_2O_3(s)$ (black, catalyses decomposition of 2 $OCl^-\rightarrow 2Cl^-+O_2(g)$ (rekindles splint);

(vii) $Pb^{2+}+OCl^-+H_2O\rightarrow Cl^-+2H^++PbO_2(s)$ (dark).

(c) $OCl^-+H^+\rightarrow HOCl$; $HOCl+Cl^-+H^+\rightarrow H_2O+Cl_2(g)$ (bleaches litmus).

A8.2.4

(a) $2KXO_3\rightarrow 3O_2(g)$ (rekindles splint)+2KX (gives AgX with Ag^+, AgX tested as in A8.2.1(e)(i) above).

(b) $3KClO_3+3H_2SO_4\rightarrow H_2O+3KHSO_4+HClO_4+2ClO_2$ (yellow); $KBrO_3+H_2SO_4\rightarrow KHSO_4+HBrO_3$ (which decomposes to $O_2(g)+H_2O+Br_2(g)$ which turns fluorescein pink); $KIO_3+H_2SO_4\rightarrow KHSO_4+HIO_3$, with $FeSO_4$, this acid is reduced to HI.

(c) (i) Chlorate does not give a precipitate; bromate gives white $AgBrO_3(s)$ soluble in dilute ammonia; iodate gives white $AgIO_3(s)$ also soluble in dil.ammonia;

(ii) $XO_3^-+6Fe^{2+}+6H^+\rightarrow 3H_2O+X^-+6Te^{3+}$ (forms red complex with SCN^-);

(iii) $XO_3^-+3NO_2^-\rightarrow 3NO_3^-+X^-$ (give AgX(s) tested in A8.2(e)(i) above);

(iv) $XO_3^-+3H_2S\rightarrow 3S(s)$ (colloidal yellow S)$+3H_2O+X^-$.

(d) $2KClO_3+4HCl\rightarrow 2KCl+2H_2O+Cl_2(g)+2ClO_2$ (yellow).

(e) $6Mn^{2+}+12PO_4^{3-}+6H^++ClO_3^-\rightarrow Cl^-+3H_2O+6\ [Mn(PO_4)_2]^{3-}$ violet $6Mn^{2+}+6H^++BrO_3^-\rightarrow Br^-+3H_2O+6Mn^{3+}$ (transient wine colour); further liberation of bromine and oxidation of Mn to $MnO_2(s)$ (brown).

(f) $BrO_3^-+5Br^-+6H^+\rightarrow 3H_2O+3Br_2$ (brown red); $IO_3^-+5I^-+6H^+\rightarrow 3H_2O+3I_2$ (dark brown).

(g) (i) white $Ba(IO_3)_2(s)$;

(ii) white $Pb(IO_3)_2$ precipitates;

(iii) white $Hg(IO_3)_2$ is formed;

(iv) $6IO_3^-+5SCN^-+6H^++2H_2O\rightarrow 5HSO_4^-+5HCN+3I_2$

A8.2.5

(a) $KXO_4\rightarrow KX+2O_2(g)$ (rekindles splint); KX gives AgX (for X=Cl, precipitate soluble in dilute ammonia but AgI is insoluble even in conc. ammonia).

(b) (i) $KClO_4$ is sparingly soluble; precipitates from conc. solution;

(ii) NH_4ClO_4 is also sparingly soluble;

(iii) $Cd^{2+}+4NH_3\rightarrow [Cd(NH_3)_4]^{2+}$(aq.) gives white $[Cd(NH_3)_4](ClO_4)_2(s)$.

(c) (i) Yellow $Ag_2H_3IO_6(s)$ precipitates but quickly changes to Ag_5IO_6 which is soluble in ammonia or in 1:1 nitric acid;

(ii) orange $Hg_5(IO_6)_2(s)$ precipitates;

(iii) white precipitate of $Ba_5(IO_6)_2$ is obtained;

(iv) yellow $CeHIO_6.6H_2O(s)$;

(v) brown iodine liberated (reduction by ascorbic acid);

(vi) $IO_4^-+2I^-+2H^+\rightarrow IO_3^-+H_2O+I_2$(aq.) (brown);

(vii) Mn^{2+} is oxidised to MnO_4^-(aq.) (purple).

A8.3.1.1

Fluorescein indicator: dissolve 0.2 g in 100 cm^3 70% ethanol.
Diiododimethylfluorescein: dissolve 1.0 g in 100 cm^3 70% ethanol.
If the volume of $AgNO_3$ in the first titration is V_1 cm^3.
Number of mols of $Ag^+=V_1x0.1/1000$=mols of Cl^- and $I^-=m_1$
If the volume of silver solution in the second titration is V_2,
the number of mols of $Ag^+=V_2x0.1/1000$=mols of iodide$=m_2$
$\therefore$The number of mols of chloride$=(m_1-m_2)$ in 25 cm^3

$\therefore$[Cl$^-$]=(V$_1$-V$_2$)x0.1/25 mol dm^3
[I$^-$]=V$_2$x0.1/25 mol dm^{-3}

A8.3.1.2

Mass of fluoride in PbClF=mx0.07261 g (m=mass of precipitate)
[F$^-$]=mx0.07261x1000/(50x19.00) mol dm^{-3}

A8.3.2

$\mathrm{OCl^-+2I^-+2H^+\rightarrow Cl^-+H_2O+I_2}$
If the volume of thiosulphate used is V cm^3,
the number of mols of iodine =½Vx0.05/1000=mols of OCl$^-$
[OCl$^-$]=½Vx0.05/25 in the titrated solution
[OCl$^-$] in the original solution =½Vx0.5/25 mol dm^{-3}.

A8.3.3.1

If the volume of thiosulphate used is V cm^3,
the number of mols of thiosulphate =Vx0.05/1000
The number of mols of iodine =½Vx0.05/1000
$\therefore\mathrm{ClO_3^-+6I^-+6H^+\rightarrow Cl^-+3H_2O+3I_2}$
$\therefore$The number of mols of chlorate =$^1/_3$Vx0.05/2000 in 25 cm^3
$\therefore$[ClO$_3^-$]=$^1/_3$xVx0.05/(2x25) mol dm^{-3}

A8.3.3.2

If the volume of HCl used is V cm^3,
the number of mols of HCl=Vx0.1/1000
The number of mols iodate =Vx0.1/6000 in 25 cm^3
$\therefore$[IO$_3^-$]=Vx0.1/(6x25) mol dm^{-3}
If methyl red indicator is used, the colour changes at the end-point from yellow to red. The indicator solution is prepared by dissolving 0.25 g in 250 cm^3 hot water.

A8.3.3.4

Mass of chloride in AgCl=mx0.2474 g (m=mass of precipitate)
$\therefore$[ClO3$^-$]=mx0.2474x1000/(35.45x50) mol dm^{-3}

A8.3.3.5

If the volume of iodate used is V cm^3,
the number of mols of iodate =Vx0.025/1000
$\therefore$The number of mols of iodide =2Vx0.025/1000 in 25 cm^3
$\therefore$[I$^-$]=2VX0.025/25 mol dm^{-3}

A8.3.4

If the volume of thiosulphate in the first titration is V$_1$ cm^3,
the number of mols of thiosulphate =V$_1$x0.1/1000
$\therefore$The number of mols of iodine liberated =½V$_1$x0.1/1000 (=m$_1$)
$\because\mathrm{IO_4^-+2I^-+2H^+\rightarrow IO_3^-+H_2O+I_2}$
$\therefore$The number of mols of IO$_4^-$=½V$_1$x0.1/1000 in 25 cm^3
$\therefore$[IO$_4^-$]=½V$_1$x0.1/25 mol dm^{-3}
$\because\mathrm{IO_3^-+5I^-+6H^+\rightarrow 3H_2O+3I_2}$
If the volume of thiosulphate in the second titration is V$_2$ cm^3,
the number of mols of iodine =½V$_2$x0.1/1000 (=m$_2$)
In this case, iodine is liberated from iodate already present and the iodate produced in the first titration.
$\therefore$Number of mols iodine liberated from iodate already present =m$_2$-m$_1$

∴The number of mols iodate =$(m_2-m_1)/3$
∴$[IO_3]^-=(m_2-m_1)x1000/(25x3)$ mol dm^{-3}

A8.4

The two preparations are only suitable for trained undergraduates and only carried out in a well-ventilated fume cupboard. The reaction of ICl_3 with CsCl can be used to prepare the interhalide $CsICl_4$, the large Cs ion stabilises the large ICl_4^-anion.

A8.4.3

The broad absorption band has a maximum wavelength of ~430,320 and 525 nm for ICl, Cl_2 and I_2 respectively. The bands are due to $\pi_g \rightarrow \sigma_u$ transitions.

A8.5.1

The distribution coefficient of iodine between tetrachloromethane and water is 85 at room temperature.

A8.5.2

The first experiments by this method were carried out in CS_2 which is not suitable because of its toxicity and flammability. The literature value for the equilibrium constant, determined by using other methods, is 825 at 20°C or 751 at 25°C (*Halogen Chemistry,*1(1967)p.247 Ed.V.Gutmann, Academic Press).

A8.6.1

$I_2+10HNO_3 \rightarrow 10NO_2+4H_2O+2HIO_3$
If the volume of 0.05 M thiosulphate is V cm^3,
the number of mols of iodine =½Vx0.05/1000
∴Number of mols of iodic acid =½Vx0.05/3000
∴Mass of iodic acid =½Vx0.05x175.9/3000 g(=m_1)
%Purity =m_1x100/mass weighed.

A8.6.2

$2HIO_3 \rightarrow I_2O_5(s)+H_2O(g)$ % Loss in mass =5.4
$2I_2O_5 \rightarrow 2I_2(g)+5O_2(g)$

A8.7.2

261.4 g of barium nitrate give 505.2 g barium iodate
% Yield =$(m_2$x261.4x100)/(m_1x505.2)
m_1 is the mass of barium nitrate and m_2 is the mass of product.
The condensed water of crystallisation turns the paper faintly pink. A crystal of blue self-indicating silica gel can be used instead of the paper.
$5Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2+4I_2$ (turns starch blue)+$9O_2$ (rekindles splint)

A8.7.3

505.2 g $Ba(IO_3)_2.H_2O$ gives 389.9 g $K[H(IO_3)_2]$
% Yield =(m_2x505.2x100/389.9xm_1)(m_1 mass of barium salt, m_2 =mass of product)
The compound reacts with NaOH which neutralises the acid
If the volume of NaOH is V cm^3, the number of mols =Vx0.05/1000
=mols of compound
∴Mass of preparation calculated =Vx0.05x389.9/1000=m_1 g
If mass taken for analysis =m_2 g % Purity =m_1x100/m_2

A8.7.4

214.00 g iodate give 230.0 g periodate

$\therefore$% Yield =$(m_2$x214.0x100)/(m_1x230.0)
(m_1=mass of iodate used, m_2=mass of periodate produced)
Calculation for % purity similar to A8.3.4.

A8.7.5

*J.Chem.Educ.*36(1959)191 describes a similar experiment for the determination of the dissociation constant of iodic acid but using copper(II) iodate.

The solubility product of calcium iodate is 64.4×10^{-8} at 18°C, pK_S=6.2 at 25°C. The dissociation constant of iodic acid at 25°C is 1.69×10^{-1}, pK_a=0.77. The plot of $2S^{3/2}$ against $[H^+]$ is expected to be linear within experimental error.

A8.8.1

126.91 g iodine give 347.11 g of complex
% Yield =(m_2x126.91)/(m_1x347.11)
(m_2=mass of product, m_1=mass of iodine)

A8.9.1

The reaction is second order with respect to iodide and first order with respect to Fe(III). Fe(II) retards the reaction.
Although the stoichiometry of the reaction is:
$2Fe(III)+2I^- \rightarrow 2Fe(II)+I_2$,
the rate law is represented by:
$-d[Fe(III)]/dt=k_1[Fe(III)][I^-]^2/(1+k_2[Fe(II)]/[Fe(III)]$

A8.9.3

The periodic change of colour from red to blue corresponds to the formation of Ce(III) and Ce(VI) during the oscillations. Oscillations also appear if a bromide sensitive electrode is used to monitor and/or record [bromide]. Small temperature oscillations may be also observed.

A8.10 Additional references and experiments

*Anal.Chem.*69(1997)3628 gives results of the determination of iodide in sea water by ion chromatography. Determination of bromate in drinking water is published in the same journal (*ibid.*69(1997)4275).

Electrochemical methods for the determination of iodide in HCl solution are described in *J.Chem.Educ.*75(1998)775.

The kinetics of oxidation of bromocresol green by NaOCl is studied in the same journal (*ibid.*64(1987)81. Fluoresence quenching by Cl^- and Br^- ions is used for their simultaneous determination (*ibid)*72(1995)A31.

N.Ikeda *et al* published a new radiochemical method for analysis of iodide and iodate in environmental water (*Radioisotopes,*20(1971)48).

Kinetics of the bromide/bromate reaction are discussed in *J.Chem.Educ.*47(1970)7775. The manganese dioxide-catalysed decomposition of potassium chlorate is demonstrated in the same journal (*ibid.*40(1963)78).

APPENDIX 9

A9.2.1

(a) Titanium dioxide is yellow when hot but becomes white when cold. The powder is inert to both acid and alkali.

(b)
- (i) Hydrous dioxide (white) precipitates, soluble in conc.HCl to give $TiCl_4$;
- (ii) the same precipitate is formed as above, due to hydrolysis;
- (iii) reduction to violet Ti^{3+}(aq.), Cd or Sn can also reduce Ti(IV);
- (iv) yellow or orange solution is formed and ascribed to peroxo-species $Ti(O_2)^{2+}$; in presence of F^-, the colour is discharged as $[TiF_6]^{2-}$ is formed;
- (v) brown $(TiO)_2[Fe(CN)_6]$ precipitates.

A9.2.2

(i) Hydrated dark Ti_2O_3 precipitates, slowly loses its colour in air by oxidation;
(ii) permanganate is reduced to Mn^{2+} and Ti(III) oxidised to colourless Ti(IV);
(iii) the colour fades as Ti(III) is oxidised by perchlorate to Ti(IV);
(iv) the colour becomes pale green, Fe(III) is reduced to Fe(II) and Ti(III) oxidised to Ti(IV).

A9.3.1

354.2 g $K_2[TiO(C_2O_4)_2].2H_2O$ give 176.04 g oxalate
If the volume of permanganate ≡m g of complex, is V cm^3
∴Number of mols of oxalate =2.5xVx0.02/1000
Number of mols of complex =2.5xVx0.02/2000
∴Mass of complex =2.5xVx0.02x354.2/2000=m_1 g
∴% Purity =m_1x100/m (Actual weight used is 10 m)
A commercial sample of the complex assayed 98%

A9.3.2

If the volume of Ti(III) used in the first titration is V cm^3,
the number of mols of Fe(III) =25x0.1/1000=number of mols of Ti(III).
∴$[Ti^{3+}]$=25x0.1/V mol dm^{-3}
Alternatively if the volume of Fe(III) solution used is V cm^3
$[Ti^{3+}]$=Vx0.1/25 mol dm^{-3}

A9.4.2

Results were published in *Polyhedron,* **13/14**(1989)1793. The paper includes results of the photoreduction of $[V(C_2O_4)_3]^{3-}$(aq.) (see its preparation in Sec.10.3.2)

A.A.Ginsberg; L.V.Shikheeva in *Russ.J.Inorgan Chem.***5**(1960)287 report the spectra and stability of Ti(IV)/oxalic acid complexes using Job's method (Sec.10.5.2). This method was used by V.V.Subbana *et al* (*J.Sci.Ind.Research (India)***18B**(1959)127) who reported the Ti(III)/oxalate complexes.

A9.4.4

Results were published by A.D.Buss *et al* (*J.Oil Col.Chem.Assoc.***59**(1976)369) and by M.A.Malati; N.J.Seager (*ibid.***64**(1981)231. A proton nmr spectrum of the distillate from butanol irradiated with anatase exhibited a peak at 4.3 ppm, suggesting hemiacetal formation.

A9.5

See *J.Colloid.Sci.,***27**(1968)305;**28**(1968)92

A9.5.1

Rank Brothers Mark II instrument was used fitted with a rectangular cell which was thermostatted at 27±0.5°C. The instruments microscope was used to determine the cell depth and its thickness. The stationary levels were determined (*J.Chem.Tech. Biotechnol.* **57**(1993)97). See also *J.Colloid Interface Sci.***65**(1978)548. Fig.A9.1 shows the results for some prepared titanias, the details of their preparation and their reflectance spectra are found in *Solar Energy*,**36**(1986)168.

Although the use of expensive platinum compounds has been avoided in the experiments described, it is worth mentioning that platinisation of anatase or rutile increased their photocatalytic activity. Details of photoplatinisation are found in *J.Am.Chem.Soc.***100**(1978)3456. Pt/TiO$_2$ was used to reduce carbonate to C (*J.Chem.Soc., Chem.Commun.*(1987)1418.

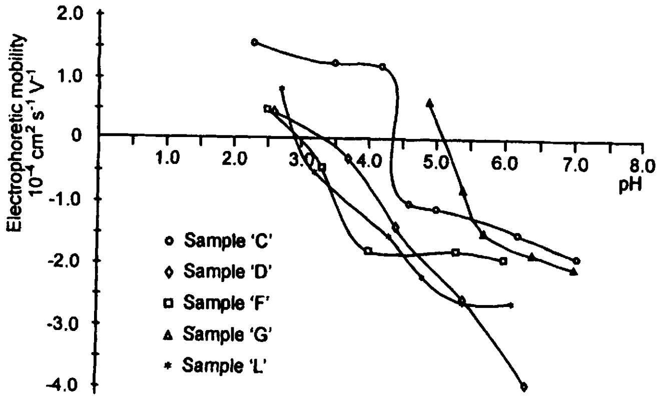


Fig. A9.1 The electrophoretic mobility of prepared titanias over a pH range.

A9.5.2

The results were published in *Powder Technology*,**22**(1979)279. For comparison with results on quartz see the reference in A3.5.3.

A9.5.3

See *J.Chem.Technol.Biotechnol.***58**(1993)387. Initial results on the adsorption of nitrite by the same anatase sample using a spectrophotometric method (Sec.6.3.4) was incomplete. Air should be excluded to prevent oxidation of nitrite.

A9.6 Additional experiments and references

If some of the solution of the product of photoreduction in Sec.9.4.2 is quickly dispensed into a vacuum 1 cm spectrophotometer cell and its spectrum is run over the visible range, a broad band appears at ~460 nm. A similar band is seen in the Ti(III) solution prepared in Sec.9.3.1. An examination of the generalised Orgel diagram (Fig.A9.2) shows that in both octahedral or tetrahedral complexes, only one d-d transition is expected. On the other hand, the single u.v. band of the complex analysed in Sec.9.3.1 is due to ligand to metal charge transfer since no d-d transitions are expected. (Fig.A9.3 sketches all the possible electronic transitions for a metal complex).

*Inorg.Synth.*9(1967)44 gives the preparation of hexa(urea)titanium(III) perchlorate. Another Ti complex is prepared in the same series:
$[Ti^{iv}(C_5H_7O_2)_3]_2[Ti^{iv}Cl_6]$ (*ibid.*2(1946)119).

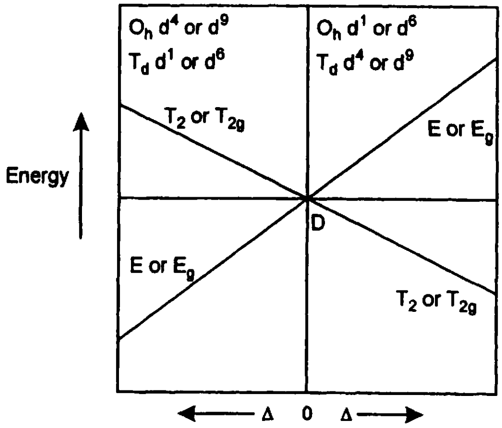


Fig. A9.2 Generalised Orgel diagram for $d^{1,6,4,9}$ in octahedral or tetrahedral ligand field.

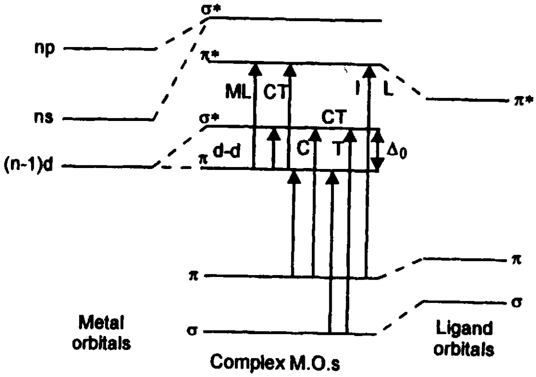


Fig. A9.3 A sketch of the electronic transition for an octahedral complex.

APPENDIX 10

A10.2.1.1 V(V)

(a) $2NH_4VO_3 \rightarrow H_2O(g)$ (turns cobalt paper pink)$+2NH_3(g)$ (turns litmus blue)$+V_2O_5(s)$
The solid (red or black) dissolves in dil.acid$\rightarrow VO_2^+$ and in alkali to give VO_4^{3-}(aq.).

(b) (i) The acidic solution contains VO_2^+(aq.) which is faintly yellow, but changes to blue VO^{2+}(aq.) when reduced by sulphite;
  (ii) colour changes to green V^{3+}(aq.) when reduced by Mg(with $H_2(g)$ evolved;
  (iii) colour changes to pale violet V^{2+}(aq.) when reduced by Zn;
  (iv) colour changes to blue VO^{2+}(aq.) when reduced by H_2S;
  (v) colour changes to red brown thiovanadate, which precipitates V_2S_5 with acid: (precipitate soluble in alkali);
  (vi) colour changes to deep red peroxoacid $HVO_2(O_2)$;
  (vii) yellow precipitate turns to white $Pb_3(VO_4)_2(s)$ on standing, and is soluble in acid;
  (viii) yellow $Ba(VO_3)_2(s)$ precipitates which is soluble in HCl;
  (ix) yellow or green basic copper vanadate is formed;
  (x) $VO_2^+ + 4H^+ + 2I^- \rightarrow 2H_2O + I_2(aq.)$ (brown)$+V^{3+}$(aq.) (green solution after volatilisation of iodine);
  (xi) yellow silver vanadate precipitates but becomes orange on boiling and is soluble in acid;
  (xii) oxidation of V(V) to yellow peroxovanadate.

A10.2.1.2 V(IV)

(a) permanganate oxidises VO^{2+} to VO_2^+ (pale yellow) with reduction to Mn^{2+}.
(b) magnesium reduces VO^{2+} to green V^{3+}aq.
(c) zinc reduces VO^{2+} to light violet V^{2+}.
(d) reduction of VO^{2+} to green V^{3+}
(e) oxidation of VO^{2+} to VO_2^+(aq.) with the formation of Fe(II) (gives red dipyridyl complex).
(f) dark precipitate VO_2aq. (s) is formed.
(g) intensely-coloured complex.

A10.2.1.3 V(III)

$Mg + 2VO^{2+} + 4H^+ \rightarrow 2V^{3+} + Mg^{2+} + 2H_2O$
(a) $V^{3+} + OH^- \rightarrow V(OH)_3(s)$ dark.
(b) $V^{3+} + Fe^{3+} + H_2O \rightarrow Fe^{2+} + 2H^+ + VO^{2+}$ (blue).
(c) Intensely coloured thiocyanate complexes are formed.
(d) Reduction to pale violet V^{2+}(aq.) takes place.
(e) Gradual change of colour to blue and eventually faint yellow VO_2^+.

A10.2.1 V(II)

$VO^{2+} + Zn + 2H^+ \rightarrow H_2O + Zn^{2+} + V^{2+}$ (pale violet).
(a) $V^{2+} + 2OH^- \rightarrow V(OH)_2(a)$ dark red, slightly soluble in excess.
(b) colour changes gradually to green then blue and eventually faint (yellow oxidation to $V^{3+}$and VO_2^+)
(c) $2VO_2^+ + V^{2+} + 2H^+ \rightarrow H_2O + 3VO^{2+}$ (blue).

A10.2.2

If the volume of permanganate used is V cm^3
the number of mols of permanganate =Vx0.02/1000
$\because 5VO^{2+} + MnO_4^- + H_2O \rightarrow 5VO_2^+ + Mn^{2+} + 2H^+$
$\because$Number of mols of V =5Vx0.02/1000
$\therefore$Mass of $VOSO_4$=5Vx0.02x163.0/1000 g in 25 cm^3=m_1
$\therefore$Mass in original solution =10m_1
$\therefore$Mass of water =mass weighed-10m_1=m_2
The ratio (10m_1/163.0):m_2/18.015) should be 1:5

A10.2.3

(i) If the volume of permanganate is V cm^3,
the number of mols of permanganate =Vx0.02/1000
The number of mols of V in the dilute solution =m/(10x116.98)
MnO_4^-:5V
The molar ratio will be 1 MnO_4^-:5V
∴Vanadium changes oxidation number by 1(m=mass of vanadate) ∴VO^{2+} is formed;

(ii) If the volume of permanganate required is V cm^3,
the number of mols permanganate =Vx0.02/1000
If the mass of $VOSO_4.5H_2O$ weighed is m_1 g
∴Number of mols V in the dilute solution =m_1/(10x253.1)
Mols permanganate : mols of V should be 3:5
∴Vanadium oxidation number is +2
$5V^{2+}+3MnO_4^- +4H^+ \rightarrow 5VO_2^+ +3Mn^{2+}+2H_2O$

(iii) If the volume of permanganate used in this is case~½the volume in part (ii), this indicates that the oxidation state of V is +3
$5V^{3+}+2MnO_4^-+2H_2O \rightarrow 5VO_2^+ +2Mn^{2+}+4H^+$

A10.3.1

If the mass of ammonium vanadate is m_1 g, the expected mass of the complex
=m_1x315.1/116.98=m_2
If the mass of the product is m_3, the percentage yield =m_3x100/m_2
If the volume of permanganate in the first titration is V_1 cm^3 and in the second titration is V_2 cm^3, the volume of permanganate equivalent to the oxalate =(V_1-V_2) cm^3
The number of mols permanganate ≡V(IV)=V_2x0.02/1000
The number of mols of V(IV) =5V_2x0.02/1000=m_1
The number of mols of oxalate =2.5x(V_1-V_2)x0.02/1000=m_2
The molar ratio m_1:m_2=1:2

A10.3.2

116.98 g vanadate gives 486.8 g complex
% Yield =(m_2x116.98x100)/(m_1x486.8)
m_1 is the mass of vanadate and m_2 is the mass of complex
If the volume of permanganate used in the first titration is V_1 cm^3 and in the second titration is V_2 cm^3, provided the mass of the complex was the same in the two titrations, V_2 corresponds to the oxalate alone and (V_1-V_2) corresponds to V(III)
Number of mols of oxalate =2.5xV_2x0.02/1000
The number of mols of V(III) =2.5x(V_1-V_2)x0.02/1000
The percentage purity can be also calculated from V_1 since
$5[V(C_2O_4)_3]^{3-}+8MnO_4^-+44H^+ \rightarrow 5VO_2^+ +8Mn^{2+}+30CO_2+22H_2O$
∴Mols of permanganate =V_1x0.02/1000
Mass of complex =5V_1x0.02x486.8/8000=m_1
% Purity =m_1x100/m_2 (m_2 is the mass weighed)
% Water lost on heating =m_3x54.05x100/486.8 (m_3=mass heated)

A10.3.3

Kinetics results are included in M.A.Malati, (*Chem.Labor.Biotech.***48**(1997)M19). They suggest two consecutive reactions presumably involving oxidation to V(IV) followed by oxidation to V(V). The oxidation by permanganate takes place more quickly and involves oxidation of V(III) to V(V) as well as oxidation of oxalate. The reference also includes results on the composition of V/ligand complexes (Sec.10.5.2) and the preparation of $[V(acac)_3]$ (Sec.10.4.2). The reference includes an ir spectrum and electronic spectra of the latter in some solvents.

A10.4.1

181.88 g vanadium pentoxide give 265.16 g of complex

% Yield =$(m_2$x181.88x100)/$(m_1$x265.16)

$(m_1$=mass of oxide, m_2=mass of product).

The reference gives 88% yield and analysis results: C45.09% (45.28), H5.33% (5.32), V19.32% (19.21), the values between brackets are the values calculated.

A10.4.2

The first reported preparative method was published in *Chem.Soc.Trans.*(1913)78. This was tried starting with anhydrous V(III) chloride (Aldrich) but the alternative method described in the reference in A10.3.3 uses the more stable and readily available $VO(SO_4).5H_2O$. The reference gives a yield of 61% as well as the m.p.187°-188°C and the ir spectrum and electronic spectra in various solvents (Sec.10.5.3).

253.08 g V(IV) salt give 348.28 g [V(acac)$_3$]

% Yield =m_2x253.08x100/$(m_1$x348.28)

$(m_1$=mass of V salt, m_2=mass of complex)

If the volume of 0.0167 M dichromate required =V cm^3

∴Mols of dichromate used =Vx0.0167/1000

$6V^{3+}+Cr_2O_7^{2-}+2H^+\rightarrow 6VO^{2+}+2Cr^{3+}+H_2O$

∴Mols of complex =6xVx0.0167/1000

% Purity =6Vx0.0167x348.28x100/(1000xm)

m is the mass of complex used. A slightly higher titre suggest some oxidation of the ligand.

A10.5.1

The literature (*Adv.Chem.Phys.*5(1963)33) gives the following absorption maxima for $[V(H_2O)_6]^{2+}$:813, 540 and 358 nm. The literature data for other species are found in the reference. The $V(II)/C_2O_4^{2-}$ mixtures had maxima at 840 nm and 570 nm

∴ $\Delta_O(H_2O)=119.7x10^{-3}/813x10^{-9}=147$ kJ mol^{-1}

$\Delta_O(C_2O_4)=119.7x10^{-3}/840x10^{-9}=143$ kJ mol^{-1}

The closeness of the data show that water and oxalate are close in the spectrochemical series.

The approximate literature absorption maxima of $[V(C_2O_4)_3]^{3-}$ are:640, 360 and 290 nm. The spectra of this complex and the corresponding $[VOOx_2]^{2-}$ complex are depicted and discussed in *Angew.Chem.*66(1954)768, together with those of aqueous (VIII) with maxima at 400 and 580 nm and V(II) sulphate double salts, other spectra of V complexes as well as Ti(III) species (Sec.9.3.2) and Cr(III) complexes (Sec.11.5.5). Spectra of Ni(II) complexes (Sec.15.6) are also depicted in the reference.

A10.5.2

Job's method for the composition of the V(II)/oxalate complex shows that $[V(C_2O_4)_2(H_2O)_2]^{2-}$ is formed in acid solution (see also Refs in Sec.A10.3.3; Sec.2.4.1). An attempt to prepare a solid potassium salt by reacting VSO_4(aq.) with oxalic acid and potassium oxalate produced an impure solid contaminated with Zn oxalato-complexes (the Zn^{2+} ions were formed during the reduction of VO^{2+} by Zn and sulphuric acid).

An electrolytic method for preparing V(II) salts and their solutions is described in *Z.Anorg.allgem.Chem.*65(1962)55, *ibid.*294(1958)155. This solution would be more suitable for preparing and studying V(II)/oxalate complexes. The composition of V(III)/SCN stable complex is given in the reference in Sec.A10.3.3. See also *J.Am.Chem.Soc.*73(1951)4528 for complexes of V(III) and V(IV) with SCN^-. R.Trujillo and F.Torres (*Anales de Fisica y Quimica* **52B**(1956)157 studied the stability of VO/oxalato-complexes and L.B.Levasheva and V.L.Zolotavin published corresponding studies of V(III) in *Russ.J.Inorg.Chem.10(1965)77.*

Preliminary results of the V^{3+}/urea system gave an absorbance at 620 nm of 0.397 for 1:4 molar ratio but the absorbance was 0.444 for 1:6 molar ratio, suggesting that the latter represents the most stable complex.

A10.5.3

The uv bands of the prepared [V(acac)$_3$] complex (see the reference in A10.3.3) in methanol or chloroform agreed with the literature values (*J.Inorg.Nucl.Chem.***21**(1961) 221). In this reference attention was drawn to the π interaction between the metal t_{2g} orbitals and the ligand π and π^* orbitals and its relation to the number of electrons in the metal orbitals.

The first reference in Sec.10.5.3 correlates the absorption bands of the first complex with the solvent E_T parameter. The second reference reports an empirical linear correlation between (ν_1-ν_2) and αDN+βAN(ν_1 and ν_2) are the wave numbers of the two long wavelength bands of the complex and α and β are empirical constants related to the donor number DA and acceptor number AN of the solvent. The reference also correlates these numbers with the hyperfine splitting constant of ^{51}V esr spectra. However, as Selbin (*Chem.Rev.***65**(1965)153) pointed out, meaningful theoretical interpretations are complicated by σ and π donor capacities of the ligands.

A10.5.4

The book reference in A4.6.3 reviews the ir spectra of the complexes containing oxalate or acetylacetonate ligands. A special feature of the V(IV) complexes is the bands ascribed to V=O bond. The $[VO(C_2O_4)_2]^{2-}$, unlike the corresponding Ti(IV) complex, is characterised by a band at ~960-1035 cm^{-1} (see Review cited above).

A10.5.5

The review mentioned in A10.5.3 lists magnetic data for VO^{2+} compounds and complexes. See also *J.Inorg.Nucl.Chem.***25**(1963)1359.

A10.6

The magnetic susceptibility of the $K_3[VC_2O_4)_3].3H_2O$ and of [V(acac)$_3$] measured by the Evans method in a commercial instrument was: $10^3\chi$=2.48 and 2.43 giving μ_e~2.4μ_B and 2.4μ_B respectively. For a prepared [VO(acac)$_2$], μ_e was found to be ~1.6μ_B (theoretical μ_e=1.73μ)$_B$.

A10.7 Additional experiments and references

A commercial sample sold as [V(acac)$_3$] was found to be largely oxidised as indicated by its colour and smell of the free ligand ketone. Its electronic spectra in acetone, methanol, ethanol, toluene and carbon tetrachloride were different from the prepared and analysed complex. Its C and H contents: 45.0 and 5.3% were close to the calculated values for the V(IV) complex. In addition a clear band at ~1000 cm^{-1} in its ir spectrum confirmed the conclusions, especially as the mass spectrum of the sample showed a molecular ion mass of 265. The spectrum was based on chemical ionisation (Sec.2.1.2)

*Inorg.Chem.*3(1964)1328 describes alternative preparation of [V(acac)$_3$] by reducing the VO complex with Zn under nitrogen. This is less satisfactory than the suggested preparations.

*J.Inorg.Nucl.Chem.*27(1965)297 contains studies of VO oxalate hydrates. Polaro- graphic characteristics of V in oxalate solutions are presented in *J.Am.Chem. Soc.* 69(1947)1021.

Diffuse reflectance spectra of VCl_2 are displayed in *J.Chem.Soc.*(1964)417, together with those of $CrCl_3$. Since both metal ions have a d^3 configuration, the longest wavelength band was used to calculate Δ_0. Evidence for an intermediate in the reaction of V(II) and V(IV) was reported in *Inorg.Chem.*3(1964)569.

APPENDIX 11

A11.2.1

(a) $Cr+2HCl\rightarrow CrCl_2(aq.)+H_2(g)$

(b) $CrCl_2(aq.)$ is sky blue, quickly oxidised in air to Cr(III) (green in acid).

(c) $2Cr^{3+}+Zn\rightarrow Zn^{2+}+2Cr^{2+}(aq.)$

(d) $2Cr^{2+}+4CH_3CO_2^-+2H_2O\rightarrow Cr_2(CH_3CO_2)_4.2H_2O$ (red).

A11.2.2

(a) $Cr_2O_7^{2-}+3SO_2+5H^+\rightarrow 2Cr^{3+}+3HSO_4^-+H_2O$. Crystals of $KCr(SO_4)_2.12H_2O$ separate.

(b) $[CrCl_2(H_2O)_4]^+$ (aq.) is green; $[Cr(H_2O)_6]^{3+}$(aq.) is violet. Cl^- and H_2O occupy different places in the spectrochemical series leading to shifts in the visible bands.

(c) $Cr^{3+}+3OH^-\rightarrow Cr(OH)_3$ aq. (grey-blue precipitate) soluble in excess to pink-violet ammine complexes.

(d) $Cr(OH)_3$ aq. Initially precipitates but it is soluble in excess to green $[Cr(OH)_4]^-$.

(e) Green $CrPO_4$ precipitates (soluble in dilute acids).

(f) In absence of nitrates, green Cr_2O_3 is formed; the nitrate oxidises Cr(III) to Cr(VI) (yellow).

A11.2.3

(a) $2CrCl_3+3H_2O_2+10NaOH\rightarrow 2Na_2CrO_4(aq.)$ (yellow)$+6NaCl+8H_2O$.

(b) $2Cr^{3+}+3S_2O_8^{2-}+7H_2O\rightarrow 6HSO_4^-+8H^++Cr_2O_7^{2-}(aq.)$ orange, Ag^+ catalyses the reaction (a black Ag(II) is formed and then reduced to Ag(I)).

(c) $Cr_2O_7^{2-}+OH^-\leftrightarrows 2CrO_4^{2-}$(yellow)$+H^+$, colour changes to orange on acidification.

(d) $2CrO_3+H_2O\rightarrow Cr_2O_7^{2-}+2H^+$; $CrO_3+2NaOH\rightarrow Na_2CrO_4+H_2O$.

(e) (i) Yellow $BaCrO_4$ precipitates, soluble in HCl;
    (ii) brick red Ag_2CrO_4 precipitates, soluble in acid and in ammonia
    $Ag_2CrO_4+4NH_3\rightarrow 2[Ag(NH_3)_2]^++CrO_4^{2-}$
    (iii) yellow $PbCrO_4$ precipitates soluble in acid;
    (iv) brown Hg_2CrO_4 precipitates, changes to a red form on heating.

(f) $Cr_2O_7^{2-}+6HCl+8H^+\rightarrow 2Cr^{3+}(aq.)+7H_2O+3Cl_2(g)$ (bleaches litmus).

(g) $4Cl^-+Cr_2O_7^{2-}+6H^+\rightarrow 3H_2O+2CrO_2Cl_2(g)$ red;
$CrO_2Cl_2+2H_2O\rightarrow 2Cl^-+4H^++CrO_4^{2-}$ (yellow).

(h) Violet complex of Cr(III) with the oxidised organic molecule. A spectrophotometric method is based on this colour change.

An additional test. Cool a solution of a chromate, acidify with dilute sulphuric acid, add 1 cm^3 of amyl alcohol (pentan-I-ol) and an equal volume of "10 volume" hydrogen peroxide dropwise while shaking. Note the blue colour in the organic layer. This is due to an unstable species:

$HCrO_4^-+2H_2O_2+H^+\rightarrow 3H_2O+CrO(O_2)_2$ (blue).

This decomposes to Cr(III) and oxygen quickly.

A11.3.1

If the volume of dichromate is V cm^3

the number of mols of Fe(II)=6xV/(60x1000)=number of mols of Cr(II) in 25 cm^3

Number of mols of Cr(III) in the salt weighed=10x6xV/(60x1000) in 250 cm^3

$\therefore$[Cr(III)]=Vx1000/(1000x250).

Calculated [Cr(III)]=mx1000/(250x499.4 mol dm^{-3}) (m=mass of double salt weighed)

A11.3.2

In the analysis, dissolving the prepared complex in an excess of Fe(III) solution, oxidises Cr(II) to Cr(III) while Fe(III) is reduced to Fe(II). The latter is equivalent to Cr(II) in the preparation. Permanganate cannot be used as a self indicating reagent because of the coloured solution.

$5Fe^{2+}+MnO_4^- + 8H^+ \rightarrow 5Fe^{3+}+Mn^{2+}+4H_2O$
If the volume of permanganate used is V cm^3
∴The number of mols Fe(II)=5xVx0.02/1000=number of mols of Cr(II)
The magnetic moment measured indicates that the solid is diamagnetic
In fact it is a dimer with quadruple Cr-Cr bonds:$Cr_2(CH_3CO_2)_4 2H_2O$
∴Its relative mass =376.20 of which 103.99 is Cr
Theoretical % Cr=27.6
Mass of Cr(II) found by titration =5xVx0.02x51.996/1000=m_1
% Cr=(m_1x100/m_2) (m_2 is the mass of solid weighed)
% Purity =%Cr found x100/27.7
The electronic spectrum of the blue $[Cr(H_2O)_6]^{2+}$ solution has an absorption band with a maximum at 714 nm. The broadness of the band is expected for a d-d band for a high spin species of d^4 configuration, subject to Jahn Teller distortion. (See Fig.A9.2). The titration can be performed electrochemically (Sec.2.5.1).

A11.4.1

294.19 g dichromate give 974.82 g complex (*Inorg.Synth.* **1**(1939)37).
Expected yield =m_1x974.82/294.19=m_2
% Yield =m_3x100/m_2 (m_1 mass taken of dichromate, m_3=mass of product).
% Loss of weight at 110°C is expected to be 54.0456x100/487.41=11.09
If the volume of permanganate used is V cm^3,
the number of mols of oxalate =2.5xVx0.02/1000
∴Mass of oxalate =2.5xVx0.02x88.02/1000 g
% Oxalate in preparation =2.5xVx0.02x88.02x100/(1000xm)
(m=mass of complex weighed)
% Oxalate for 100% pure solid =3x88.02x100/487.41=54.18%
% Purity =% oxalate found x100/54.18
Results of the spectra of this complex as well as those prepared in Sec.11.4.4 and Sec.11.4.5 are given in *Educ.Chem.* **17**(1980)115. The reference contains data of calculated Δ_O for these complexes from the wavelength λ of maximum absorption at the longest wavelength band. Fig.A9.3 shows the possible electronic transitions for a transition metal complex. Fig.14.1 is the simplified Orgel diagram for $d^{3,8,2,7}$ in O_h or T_d ligand field.

Observed λ_{max} for the complex prepared was 570 nm, which gives Δ_O of 210 kJ mol^{-1}. LFSE for d^3 species =-6/5(Δ_O) i.e.252 kJ mol^{-1}

The thermal decomposition of the complex was studied in *Sch.Sci.Rev.* **51**(1970)176; 634. Analysis of the decomposition products using titrimetric and instrumental methods is presented in this reference.

A11.4.2

Inorg.Chim.Acta. **12**(1975)L11 shows that the logarithm of the rate constant, k, of the aquation varied linearly with ionic strength, regulated by either sodium perchlorate or nitrate. Log k also varied linearly with the reciprocal of the dielectric constant, suggesting that the rate-determining step involves the reaction of the complex ion with a water molecule. The dielectric constant was varied by using dioxan/water mixtures.

A11.4.3

The results and discussion of these reaction are found in M.A.Malati; A.A.Abdul Azim *Egypt.J.Chem.* **2**(1959)47. It is suggested that dichromate ions are reduced by oxalic acid to Cr(III) which is then complexed with oxalate to form the complex-ion. The latter reaction is quantitative within a range of pH values. Mn^{2+} ions were required to catalyse the reduction step. (See J.*Am.Chem.Soc.* **95**(1972)3181).

A11.4.4

Results of analysis and spectra of this complex are found in the second Ref. in A11.4.1.

A11.4.4.1

294.19 g dichromate gives 678.38 g of the complex

$\therefore$% Yield=m_2x294.19x100/(678.38xm_1) (m_1=mass of dichromate used, m_2=mass of product)

Calculation of % purity from analysis of oxalate are similar to those in A11.4.1. Theoretical % oxalate =88.02x2x100/339.19=51.90

% Water =(36.03/339.19)x100=10.62 % Cr=51.996x100/339.19=15.39

A11.4.4.2

If the volume of thiosulphate used is V cm^3, the number of mols of iodine =½xVx0.05/1000

2Cr(III) in complex give 1 mol $Cr_2O_7^{2-}$

$\because Cr_2O_7^{2-}+6I^-+14H^+ \rightarrow 2Cr^{3+}+3I_2+7H_2O$

$\therefore$Number of mols of complex =$^1/_3$xVx0.05/1000

Mass of Cr=$^1/_3$xVx0.05x52.00/1000=m

%Cr=mx100/m_1=X(m_1=mass of complex)

% Purity =Xx100/15.3

Standardisation of thiosulphate is usually carried out using purest potassium iodate (Sec.7.3.3).

A11.4.4.3

(i) Water of crystallisation is lost (tested by blue cobalt paper); on further heating a green Cr_2O_3 appears. The residue effervesces with acid as CO_2 evolves from carbonate produced by decomposition.

(ii) Effervescence indicates CO_2 and darkened Pd(II) paper indicates CO (reduction to Pd).

(iii) Violet lilac flame colour (indicates K)

(iv) (a) Colour of supernatant changes to paler blue, indicative of reduction to Cr(II);
 (b) colour changes to orange dichromate (oxidation of Cr(III) to Cr(VI);

(v) Greenish blue hydrated Cr(III) oxide is formed (may dissolve in excess), colour changes to yellow with hydrogen peroxide (oxidation to Cr(VI).

(vi) Colour changes to deep green as a water ligand is replaced by OH, the colour reverts to purple complex on acidification. When the test is applied to the *trans*-isomer (Sec.11.4.5), a bright brown precipitate is formed, on adding dil.HCl, the roseo-violet complex is regenerated.

Calculation for the % oxalate is similar to Sec.A11.4.1.

A11.4.5

294.19 g dichromate give 714.7 g of the complex

Expected yield =m_1x714.7/294.19=m_2

% Yield =m_3x100/m_2 (m_3 is the mass of product, m_1 is the mass of dichromate used).

*Inorg.Chim.Acta.*19(1976)L5 gives the alternative preparative method as well as results for Sec.11.4.7 and 11.4.8.

A11.4.6

The isomerisation leads to an equilibrium mixture of *cis*-and *trans*-isomers. The kinetics and mechanism of this reaction are found in *J.Chem.Soc.A*(1971)1903. The acid catalysis is reported in *J.Inorg.Nucl.Chem.*16(1974)1355 together with results using heavy water and DCl solution. The kinetic isotope effects are discussed in this reference.

A11.4.7

Results are given in the reference in Sec.A11.4.5 in which data for Sec.11.4.8 are found.

A11.4.8

See the references in A11.4.3 and A11.4.1.

A11.5.1

A visible/near ir reflectance spectrum showed that the purification process slightly altered the spectrum.

A11.5.2

The procedure described was found satisfactory (*J.Chem.Educ.*49(1972)204). However, it is not always successful and is usually gives low yields. An alternative is described in *Inorg.Chem.*3(1964)1801. The first reference reports the results of conductivity measurements of solutions of the three isomers and depicts their visible spectra together with a titrimetric method for determination of ionisable chloride in the three isomers. Because of the different charges on the three isomers, their separation by ion-exchange resins is possible.

A11.5.3

499.39 g of the chromium alum give 266.45 g of the prepared isomer

Expected yield $=m_1x266.45/499.39=m_2$ (m_1=mass of alum)

% Yield $=m_3x100/m_2$ (m_3=mass of product).

A11.5.4.1

% Cl in AgCl=24.474

The success of the determination depends on keeping the solutions ~0°C throughout. An alternative is described in the first Ref. in A11.5.2 above.

A11.5.4.2

In the determination of Cr, boiling should continue until the colour is pure orange (dichromate colour).

$2Cr^{3+}+3S_2O_8^{2-}+7H_2O \rightarrow Cr_2O_7^{2-}+6HSO_4^-+8H^+$

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

If the volume of iron(II) solution is V cm^3, the number of mols dichromate =Vx0.05/6000

The number of mols of the isomer =2xVx0.05/6000

$\therefore$Mass of Cr =2xVx0.05x52.00/6000 g$=m_1$

% Cr$=m_1x100/m_2$ (m_2 is the mass taken).

Analytical data for compounds prepared in	11.5.1(G)	11.5.3(V)
% Cr (theor.19.52)	19.48, 19.43	19.12, 19.21
% Ionisable Cl	13.31, 13.35	39.89, 39.93
%Total chlorine (theor.39.92)	39.86, 39.83	39.89, 39.93

spectra of purified (G) in HCl showed little change in the longest wavelength band (over the range of [HCl]) at 634±2 nm. The next band showed a slight increase in λ from 446 nm in 1 M HCl to 451 nm in 10 or 11 M HCl. In ethanoic acid the corresponding wavelengths were 635 and 448 nm respectively (practically independent of [acid]). For complex (V) the corresponding bands were at 570 and 400 nm respectively in 11 M HCl. The absorption bands using the Nujol suspension (*Chem.Anal.*56(1967)36) gave less reliable results. The reflectance near ir (NIR)/visible spectra were less useful except for the complex $[Co(pn)_3][CrCl_6]$ (denoted as P). Its band at 753 nm is in fairly good agreement with literature value of 759 nm found for $[Rh(C_3H_{10}N_2)_3]$ $[CrCl_6]$ (*J.Am.Chem Soc.*85 (1963)265). The following Δ_O values in kJ mol^{-1} for the three complexes were as follows:

Complex	V	G	P
Δ_O	210	189	159

Using the law of average environment (eqn.11.8), the calculated Δ_O of the green isomer G is 1/6[(2x159)+(4x210)]=193 kJ mol^{-1} in fair agreement with the experimental value. The predicted

Δ_O for the $[CrCl(H_2O)_5]Cl_2.H_2O$ is 201.5 kJ mol^{-1} in fair agreement with the value in the second reference in A11.5.2.

A11.5.6

The red violet solid does not readily dissolve in water but in presence of Sn(II) or Cr(II), it dissolves readily. This could be due to electron transfer via a Cl bridge to Cr(III) in the solid which has a unique layer structure. Its reflectance spectra are displayed in the third reference in A10.6.

A11.6.1

499.39 g chrome alum give 589.82 g of the complex
Expected yield $=m_1x589.82/499.39=m_2$
% Yield $=m_3x100/m_2$ (m_3=mass of product)
% C:13.6, 13.2(13.9); % N:15.6,15.2(16.2). The first % is for the dried product prepared by the wet method, the second value was for the dried complex prepared by the dry method (the value between brackets is the calculated value).

A11.6.2.1

517.76 g dried complex from the above procedure gives 658.81 g of the pyridinium salt
Expected yield $=m_1x658.81/517.76=m_2$ (m_1=mass of dried reactant)
% Yield $=m_3x100/m_2$ (m_3=mass of product).

A11.6.2.2

% S in $BaSO_4$=13.74
If mass of the precipitate is m_1 g, the mass of S=(0.1374xm_1) g
% S in the complex $=0.1374xm_1x100/m_2$ (m_2=mass of complex weighed)
Theoretical % S=29.2
Calculation for determination of Cr as in A11.5.3.

The results for analyses of a sample prepared from the complex obtained by the wet method, referred to as W, and that prepared from the potassium salt prepared by the dry method, referred to as (D) were:

	%S	%Cr	%C	%N	%H
W	28.3	7.6	38.1	19.0	2.8
D	27.5	7.3	40.2	19.5	3.0
Theoretical	29.2	7.9	38.3	19.2	3.1

Molar ratio S:Cr~6: 1

A11.6.3

The %C, %N and %H in the product were 48.0(44.5); 15.3(15.7) and 3.3(2.9) respectively. The values between brackets are the theoretical percentages. The quinolinium complex lost its water of crystallisation under vacuum storage. See *Z.Anorg.Allgem.Chem.* **118**(1921)131.

The spectra of the dried product were recorded in MeOH, EtOH, DMF and DMSO. The longest wavelength band was at 553, 564, 558 and 557 nm respectively. The earlier results of the spectra of the two complexes in Sec.11.6.1 and 11.6.2 appeared in *Polyhedron,* **2**(1982)191. The conclusion was that the correct λ_{max} corresponding to Δ_O was 554 nm. Assuming that Δ_O for water was 210 kJ mol^{-1}, the expected Δ_O for the prepared complex $=1/6[(5x216)+210]=215$ kJ mol^{-1} corresponding to λ_{max} 557 nm close to the values in DMF and DMSO. The other bands in the spectra were at wavelengths near to those of the potassium complex. The uv spectra of thiocyanate were reported and discussed in *J.Chem.Soc.,Faraday Trans.*1,**77**(1981)1497. Reactions of $Cr(NCS)_5(DMSO)^{2-}$ were reported in *Aust.J.Chem.* **28**(1975)1907. Charge transfer spectra of the prepared complex in Sec.11.6.2 in various solvents are discussed in *Spectrochim.Acta.* **26A**(1970)1957 together with others.

A11.7

For spectrophotometric study of the equilibrium constants of equilibria 11.12-11.14 and related equilibria see *Inorg.Chem.*3(1964)1777,1804; *ibid.*5(1966)1902.

A11.8 Additional suggestions for experiments and references

The reaction between Cr(III) and malonate ion (propanedioate) is discussed in *J.Am.Chem.Soc.*77(1955)2083.

Preparation of other Cr(III)-oxalato-and other complexes is described in J.S.Wang, *Bull.Inst.Chem.Acad.Sinica.*(1964)64.

Cis-and *trans*-$[Cr(H_2O)_2(phen)_2]^{3+}$ were studied in *J.Inorg.Nucl.Chem.***20**(1961)290.

The *cis-trans*-isomerisation of $[Cr(OH)_2(en)_2]$ is reported in *Inorg.Chem.***2**(1963)415.

DTA was used to study the thermal *trans*-to *cis* isomerisation of $[CrCl_2(en)_2]Cl$ (*Bull.Chem.Soc.Japan.***45**(1972)646).

Separation of the isomers of $[CrCl_2(H_2O)_4]^+$ and their stability and spectra were reported in *J.Am.Chem.Soc.***80**(1958)5015. The equilibria of Cr(III) chloride acidic solutions are given in the same volume p.5011. Kinetics of the aquation of the chloro-complexes were studied in N.Nechaeva et al,*Ukr.Khim.Zh.***32**(1966)1273.

Kinetics of the reaction of Cr(II) with the isomers of $[CrCl_2(H_2O)_4]^+$ was published in *Inorg.Chem.*6(1967)906.

$[Cr(acac)_3]$

Preparation: *Inorg.Synth.*5(1957)130; dissociation (*Z.Anorg.Allgem.Chem.***359**(1968)305); electronic spectrum (*Inorg.Chem.***10**(1971)478); bromination (*J.Am.Chem.Soc.* **83**(1961) 531; *Inorg.Synth.*7(1963)134).

Cr(III)EDTA complex:

preparation and potentiometric study (*Educ.Chem.***12**(1975)12). Fe(III)-catalysed photoreduction of Cr(VI) by oxalate (*Environ.Sci.Technol.***31**(1977)160).

Kinetics of the oxidation of alcohols by H_2CrO_4 are discussed in *J.Chem.Educ.***45**(1968)269.

Photooxidation of Cr(II) chloride solution in water and in heavy water are compared in *J.Inorg.Nucl.Chem.*37(1975)1326. The apparatus developed for this study is described in *Lab.Practice*,**31**(1982)1172.

Spectral investigations of Cr(III) complexes including $[Cr(en)_3]Cl_3$ are discussed in *J.Chem.Educ.***44**(1967)101.

APPENDIX 12

A12.2.1

(a) $MnC_2O_4.2H_2O(s) \rightarrow MnCO_3+2H_2O(g)$ (turns paper pale pink)$+CO(g)$ (reduces $PdCl_2$ to dark Pd). Residue effervesces with HCl (evolution of CO_2).
(b) (i) White $Mn(OH)_2$ precipitates, insoluble in excess but soluble in HCl, and darkens in air due to oxidation to MnOOH, precipitates more quickly by adding H_2O_2;
(ii) $Mn(OH)_2$ precipitates, soluble in ammonium chloride (lowers $[OH^-]$);
(iii) flesh coloured MnS precipitates and is soluble in acetic acid;
(iv) flesh coloured $(NH_4)MnPO_4.7H_2O$ precipitates;
(v) PbO_2 oxidises Mn(II) to $[Mn(H_2P_2O_7)_3]^{3-}$(aq.) (violet); in absence of pyrophosphate, Mn(II) is oxidised to purple $HMnO_4$(aq.);
(vi) oxidation of Mn(II) to purple Mn(VII) with Ag^+ catalyst (black Ag(II) intermediate decomposes to Ag(I) on heating); best done on solid Mn(II) salt;
(vii) $2Mn^{2+}+5IO_4^-+3H_2O \rightarrow 5IO_3^-+6H^++2MnO_4^-$ (purple);
(viii)brown hydrated Mn(IV) oxide precipitates.

A12.2.2

(a) Mn(III) sulphate solution (faintly red in dilute solution) is formed besides Mn(II) sulphate.
(b) Only Mn(III) sulphate is formed.
(c) (i) Mn(III) disproportionates to Mn(II) and hydrated MnO_2 (dark precipitate soluble in acids);
(ii) $2Mn^{3+}+H_2O_2 \rightarrow 2Mn^{2+}+2H^++O_2(g)$ (rekindles splint);
(iii) faster disproportionation;
(iv) the aldehyde formed has a characteristic smell.

A12.2.3

(a) $Mn(NO_3)_2 \rightarrow MnO_2+2NO_2(g)$ (dark brown) (turns litmus red).
(b) (i) H_2O_2 decomposes quickly to water and oxygen;
(ii) reduction of Mn(IV) to virtually colourless Mn(II) solution;
(iii) reduction to Mn(II) with oxidation of oxalic acid to carbon dioxide;
(iv) reduction to MnOOH with evolution of nitrogen.

A12.2.4

(a) $MnO_2+NO_3^-+OH^- \rightarrow NO_2^-+H^++MnO_4^{2-}$ (green solid), the latter disproportionates to purple permanganate solution and a brown hydrated dioxide precipitate.
(b) Mn(II) is oxidised to Mn(VI) in alkali solution.

A12.2.5

(a) Green oily Mn(VII) oxide is formed (it is an explosive compound) which reacts with water to form purple $HMnO_4$.
(b) (i) Colour practically discharged due to reduction to Mn(II) with a yellow colloidal S precipitate;
(ii) colour discharged as in (i) but sulphate is formed;
(iii) reduction of Mn(VII) to Mn(II) with oxidation of Fe(II) to Fe(III) (pale yellow);
(iv) reduction of Mn(VII) with oxidation of iodide to brown iodine (turns starch blue);
(v) colour discharged, NO_2^- is oxidised to colourless NO_3^-;
(vi) $2MnO_4^-+5C_2O_4^{2-}+16H^+ \rightarrow 2Mn^{2+}+10CO_2+8H_2O$.
(c) Chlorine gas is formed (green, turns paper red then it is bleached).
(d) The dark crystals decompose to a dark powder (Mn_2O_3) and oxygen. The filtrate is colourless.

A12.3.1.1

If the volume of EDTA used is V cm^3,
the number of mols EDTA=number of mols of Mn(II)
=Vx0.05/1000 (in 25 cm^3)
∴[Mn(II)]=Vx0.05/25

A12.3.1.2

If the volume of EDTA used in the first titration is V_1 cm^3
the number of mols of Mn+Mg=V_1x0.05/1000=m_1
If the volume of 0.05 Mn(II) added is V_2 cm^3,
the number of mols of Mn(II) added =V_2 x0.05/1000=m_2
If the volume of ETDA equivalent to the excess Mn(II) is V_3
the number of mols of EDTA =V_3x0.05/1000=m_3
∴The number of mols of Mg=m_2-m_3 (EDTA liberated by the Mg complex is determined).
The number of mols of Mn=m_1-(m_2-m_3) (in 25 cm^3 of solution)
[Mg]=(m_2-m_3)x1000/25 mol dm^{-3}
[Mn]=(m_1-m_2+m_3)x1000/25 mol dm^{-3}

A12.3.1.3

If the volume of permanganate used is V cm^3
The number of mols of permanganate =Vx0.02/1000
∴The number of mols of Mn(II)=4Vx0.02/1000 in 25 cm^3
∴[Mn(II)]=4Vx0.02/25 mol dm^{-3}
The method is reported in *Ind.Engng.Chem.Anal.Edn.*15(1943)8, using polarography.

A12.3.1.4

The addition of Mn(II) to formaldoxime ($H_2C{=}NOH$) reagent gives an intense orange red colour in alkaline media. The wavelength of maximum absorption is 450 nm. Beer's law is applicable over the range 1-16 μmol dm^{-3}. The broad shape of the band suggests that it is a Mn(III) complex. (see Sec.12.7).

A12.3.2

Alternative preparation

Dilute 24 cm^3 of 66% HI to 50 cm^3, pass H_2S to remove any iodine and then add 600 cm^3 of 0.4 M barium hydroxide and heat to boiling. Add a solution of 53.5 g manganese(II) sulphate tetrahydrate in 50 cm^3 water, to the hot iodide solution. Filter off the precipitated barium sulphate and collect the filtrate in a clean dry dark bottle. A fresh solution is used for photolysis. Any brown colour is removed by drops of sodium thiosulphate solution.

A12.3.2.1

Calculation of iodide as in Sec.A8.3.1.
Alternative analysis by EDTA titration (as above Sec.12.3.2.1

A12.3.2.2

Adjust the pH of the analysed solution to 1.5, irradiate, in a reproducible position, under a low pressure mercury lamp.

40.0 cm^3 of the iodide solution (0.026 M) irradiated for 20 minutes under a Hanovia Chromatolite produced iodine equivalent to 9.0 cm^3 of 0.01 M thiosulphate solution. The quantum yield can be determined by replacing the iodide solution by a uranyl oxalate solution as in Sec.9.3.3.

A12.3.3

The procedure is based on an article: *J.Photochem.Photobiol.A Chem.*69(1992)237, which gives results of the photocatalysed oxidation.

A12.4.1

The preparation, analysis and reactions of Mn(III) are outlined in *Educ.Chem.*14(1977)146. Some electronic spectra are found in the reference.

When 6 M, rather than 3M, sulphuric acid is used in the preparation, a higher [Mn(III)] can be achieved.

For standardisation, freshly prepared Fe(II) solution should be made from purest iron(II) ammonium sulphate hexahydrate but it is less suitable than purest Fe(en) $(SO_4)_2.4H_2O$ which is more stable and has a higher RMM.

If the volume of 0.02 M Fe(II) is 25.0 cm^3 and it reduces V cm^3 of Mn(III) solution, the number of mols of Fe(II) =25x0.02/1000=the number of mols of Mn(III).

$\therefore$[Mn(III)]=25x0.02/V mol dm^{-3}.

Results of the spectrophotometric titration are found in the above reference as well as the solvent extraction.

Besides xylene, chloroform or DMF were used. The spectrum of the extracted complex by the latter liquid showed a narrower band when measured in a 2 cm cell. In all solvents, a little turbidity due to water in the organic solvent is overcome by drying with anhydrous sodium sulphate.

The analytical chemistry of Mn(III) solutions and its reactions with ascorbic acid and with hydrazine and hydrazinium salts are discussed in *Analyst,* 112(1987)511. The reference also gives analytical methods for the determination of Mn(III) and Mn(III)/(IV) complexes (Sec.12.4.3; 12.5.2; 12.5.3) and Ni(III) complexes (Sec.15.5.1).

A12.4.2

The results are found in *Polyhedron,* 13/14(1989)1874, including the energetics of the reaction and its mechanism. Similar kinetic data were published in M.W.Rophael, *Chimica Scripta,* 20(1982)171 using the difference in the absorption maxima of Cr(III), Mn(III) and dichromate i.e.580, 480 and 350 nm respectively. Purging the reaction mixture with nitrogen had no measurable effect on the rate of reaction. A lower [acid] led to a faster reaction as expected from the overall reaction.

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

A12.4.3.1

197.91 g Mn chloride give 352.27 g of the complex; $[Mn(C_5H_7O_2)_3]$ *Inorg.Synth.*6(1960) 164.

% Yield $=m_2$x197.91x100/(m_1x352.27) (*J.Am.Chem.Soc.*73(1951)4416;

(m_1=mass of Mn chloride used and m_2=mass of complex prepared).

A12.4.3.2

0.500 g of complex dissolved in 10.0 cm^3 0.1 M ascorbic acid required 52.45 cm^3 0.011 M Mn(III) solution to oxidise the excess ascorbic acid

Mols of excess ascorbic acid =52.45x0.011/(1000x2)=m_1

$2Mn^{3+}+C_6H_8O_6=C_6H_6O_6+2H^++2Mn^{2+}$

Mols of ascorbic acid reacting =(10x0.1/1000)-m_1=m_2

$\therefore$Mols of Mn(III)=2m_2

Mass of Mn(III)=2m_2x54.938

% Mn found in complex=2m_2x54.938x100/0.5=15.64%

Expected % Mn=54.938x100/352.27=15.60

% Purity =15.64x100/15.60=100%

A12.4.3.3

(a) $Sn^{2+} + 2Mn^{3+} \rightarrow 2Mn^{2+} + Sn(IV)$, the reagent solution reduces the dark complex to Mn^{2+}(aq.) which is hardly coloured.
(b) Solid complex disintegrates and a gas is evolved (N_2?)
(c) Iodide oxidised by the complex to iodine (brown solution formed), Mn(III) reduced to Mn(II), organic liquid extracts iodine giving a violet layer.
(d) A clear solution is formed due to reduction of Mn(III), and the oxalate is oxidised to CO_2.

A12.4.3.3

378.21 g oxalic acid gives 490.34 g complex
% Yield $=(m_2 x 378.21 x 100)/(m_1 x 490.34)$ (*J.Am.Chem.Soc.*58(1936)2061.
(m_1=mass of oxalic acid used, m_2=mass of complex formed).

The complex dissolves in dilute sulphuric acid decomposing to Mn(II). Its oxalate content and % purity can be obtained by titration with standardised permanganate solution.

The calculation for the determination of % Mn is similar to that shown above.

The complex should form dark violet crystals. Any white or colourless material indicates decomposition.

A12.4.3.4

(a) (i) With freshly prepared solution, the coloured crystals dissolve to a nearly colourless solution;
    (ii) as in (c) above;
    (iii) calcium oxalate precipitates, and dissolves in EDTA;
    (iv) Fe(II) oxidised to Fe(III), which gives red thiocyanate complex, Mn(III) is reduced to Mn(II).
(b) Water of crystallisation is lost at first; decomposition on stronger heating gives CO ($PdCl_2$ reduced to dark Pd)+ carbonate.

A12.4.3.5

The above reference in A12.4.3.3 describes the conversion to the bisoxalato-complex.

A12.4.3.6

References for preparation of EDTA complex: *Can.J.Chem.*40(1962)775; *Bull.Chem.Soc.Japan*,34(1961)1194. The references contain electronic spectra, XRD pattern and a thermogravimetric plot.
372.24 g sodium EDTA give 427.29 g of the complex
% Yield$=(m_2 x 372.24 x 100)/(m_1 x 427.29)$
(m_1=mass of EDTA, m_2=mass of complex).

A12.4.3.7

The wavelength of maximum absorption was taken at 545 nm, the [MnO_4^-] in the oxidised solution is interpolated from the calibration plot. Hence the % Mn is worked out from the mass of complex taken and the permanganate concentration found.

A12.4.3.8

$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$
If the volume of thiosulphate solution used is V cm^3,
the number of mols of thiosulphate =Vx0.01/1000
=mols of the Mn(III) compound assuming it is $Mn[(C_4H_9O)_2PO_2]_3$
$\therefore$Mass of Mn=Vx0.01x54.94/1000=m_1 g
%Mn=m_1x100/m_2 (m_2=mass of compound weighed)

% Purity =%Mn found x100/8.05.

This method is quicker and hence more suitable for the unstable solid. Because the available dibutylphosphate is not pure, its purity has to be taken into account in the calculation.

A12.4.4.1

The wavelength of maximum absorption of dichromate was found at 350 nm. Beer's law was applicable over the range 2.0-0.2x10^{-4} M. The results of the kinetic runs are found in *Surf.Technol.* 16(1982)243. The reference also contains results of the oxidation by Mn_3O_4 (see later).

A12.4.4.2

The violet solution obtained had an absorbance at 480 nm of 0.150 in a 1 cm cell. Using the literature ε 11.24 m^2 mol^{-1}, the concentration of the complex ion is 1.33x10^{-3} mol dm^{-3}.

Results of leaching of Mn_2O_3 and Mn_3O_4 (0.5 g of each with 10 cm^3 phosphate solution at 60°C).

Time/min	10	20	30	40	60	70
Absorbance	0.370	0.600[a]	0.881	1.021	1.769	0.207[c] (Mn_2O_3)
Absorbance	0.345	0.682[b]	1.094	1.661	0.299[c]	0.442[c] (Mn_3O_4)

[a] % Mn leached=0.83_9

[b] % Mn leached=1.38

[c] after 10 fold dilution

Example of calculation in (b)

[Mn(III)]=0.682/113=6.04x10^{-3} mol dm^{-3}. Amount formed =6.04x10^{-5} mol RMM Mn_3O_4=228.8;
Mols of Mn(III)=0.5x2/228.8=4.37x10^{-3}
% Leached =(6.04x10^{-5}x100)/(4.37x10^{-3})=1.38

The BET surface area, carried out commercially, gave the values of 8.83 m^2g^{-1} for Mn_3O_4 and 1.56 m^2g^{-1} for Mn_2O_3. The greater reactivity of Mn_3O_4 observed is likely to be related to its higher surface area indicative of a smaller particle size.

A12.4.3.3

Using 0.2 g of the prepared $Mn(acac)_3$ and shaking with the pyrophosphate solution for 5 minutes, the spectrum was similar to that of the Mn(III) pyrophosphate complex showing that ligand exchange has taken place in this heterogeneous reaction.

A12.5.1

The results are given in the above reference in A12.4.4.1, together with the XRD pattern before and after the oxidation of Cr^{3+}. The appearance of new lines after reduction of Mn(III) in the oxide indicates the appearance of a new phase.

A12.5.2.1

792.9 g phenanthroline hydrate give 1197.1 g of the complex

% Yield =(m_2x792.9x100)/(m_1x1197.1)(m_1=mass of phen, m_2=mass of product)

A12.5.2.2

Average	%C 47.6	%H 3.2	%N 9.4	%Mn 9.1
Theor.	48.1	3.0	9.3	9.0

% Purity =9.0x100/9.1=98.9 (see also *Trans.Met.Chem.* 1(1976)98).

A12.5.2.3

(a) (i) The solid is soluble in either acid, giving a red/brown solution;
    (ii) in both cases, a dark brown solution is obtained; whereas the aqueous solution is green.
(b) (i) The colour of the solid becomes lighter with the evolution of gas bubbles (O_2);
    (ii) the colour of the solid is discharged and faster gas evolution is observed;
    (iii) the colour of the solid is discharged and a gas is evolved (nitrogen);
    (iv) there was no colour change (no ligand exchange);

(v) brown iodine was liberated.

A12.5.3

632.6 Bipyridine give 1101.0 g of complex

% Yield =(m_2x632.6x100)/(m_1x1101)

(m_1=mass of bipyridine, m_2=mass of product)

% Purity =9.8x100/10=98% (%Mn as in A12.4.3.2)

Details of other analytical data as well as characterisation of the two mixed valence complexes were reported by M.A.Malati in *Chem.Labor.Biotechnol.*44(1993)36(M). Qualitative tests gave similar results to those given above except some exchange was observed with pyrophosphate.

A12.5.4

The kinetic results were included in the above reference.

Preliminary experiments of the interaction between hydrogen peroxide and the two manganese oxides mentioned above suggested that a second-order kinetics describes the reaction but it was not clear whether only a catalytic decomposition or a reduction /catalytic process was taking place.

A12.6.1

A room temperature magnetic moment of 5.9 μ_B is observed. The manual of the commercial Evans balance gives data for Mn(II) chloride.

The electronic spectra of Mn(II) salt solutions are reproduced in standard textbooks of Inorganic Chemistry. The sharp bands arise from transitions involving parallel levels in the Orgel or Tanabe-Sugano diagrams for high spin d^5 configuration. ε_{max} were an order of magnitude smaller than octahedral d^3 complexes.

A12.6.2

The electronic spectra Mn(III) species are found in the Ref. in A12.4.1. The wavelength of maximum visible absorption varies with the acid in solution being 472, 490 and 508 nm in perchloric, sulphuric and phosphoric acid media. The broadness of the band and other features confirm Jahn-Teller distortion. The shift in λ_{max} reflects the change in the corresponding Δ_o of the ligands. The single d-d band is expected from the Orgel diagram (Fig.A9.2), although the distortion leads to broadening or even splitting of the band.

The magnetic moment at room temperature for the mixed valence complexes was 2.9 μ_B per dimer as measured by the Evans method. In *J.Am.Chem.Soc.*99(1977)6623, the Authors measured the susceptibility in solution over a temperature range and used the NMR method. An earlier method gave a value of 2.5 μ_B per dimer which was taken as evidence of antiferromagnetic behaviour. The above reference also included results of cyclic voltametry (Sec.2.5.4.).

A12.7.1.1

Results of preparation and characterisation of βMnO_2 were reported in *J.Appl.Chem.Biotechnol.*21 (1971)200 including PZZ determination.

A12.7.1.2

The analytical method for the determination of χ in $MnO_{1+\chi}$ is described by G.Gattow in the reference in Sec.12.7.1.1, using the relation.

χ=titre of 0.01 M thiosulphate/2xtitre of 0.01 M EDTA.

A12.7.1.2

In the oxalic acid method, if the volume of oxalate added is 50 cm^3,

∴Total mols of oxalate=50x0.05/1000=m_1

If the volume of permanganate needed is V cm^3,

the number of mols of permanganate=Vx0.02/1000

∴The number of excess mols of oxalate=2.5xVx0.02/1000=m_2=mols of MnO_2

$MnO_2+H_2C_2O_4+2H^+ \rightarrow Mn^{2+}+2CO_2+2H_2O$

∴Mass of $MnO_2=(m_1-m_2)x86.94=m_3$ g

%$MnO_2=m_3x100/m_4$ (m_4=mass of βMnO_2 weighed)

A12.7.1.3

The results of PZZ of doped samples and their preparation are displayed in *Chem.Ind.* (1979)27,

A12.7.1.4

The values of PZC for two samples are given in *J.Electroanal.Chem.*89(1978)135 together with a discussion of the effect of crystal structure on PZC.

A12.7.1.5

The plot of the rate of adsorption of Ca ions on βMnO_2 appeared in *Chem.Ind.*(1972)768 together with the corresponding activation energies of a fast and a slower step.

A12.7.2.1

Some results of the kinetics of reduction by hydrazine, the catalysed decomposition of hydrogen peroxide are found in *Surf.Technol.*16(1982)235 and in *Power Sources,*10(1985) Ed.L.J.Pearce, The Paul Press, London, p237.

A12.7.2.2

For doped samples, the results are found in *J.Appl.Electrochem.* **10**(1980)315.

A12.7.2.3

Beer's law was found applicable up to a complex concentration of 0.02 M.

A12.7.2.4

A $MnO_{1.98}$ sample was found to be 92.4% pure. The reduced sample had a formula of $MnO_{1.87}$ and hence it is 90.5% pure (92.4x84.86/86.62)

∴Mass of pure oxide in the sample=0.5x0.905=0.453 g

The mass of Mn in the sample=0.453x54.94/84.86=0.293g

The number of mols of Mn=0.00533

If the molarity of the leached solution is 0.006 M

The number of mols of Mn leached in the 10 cm^3 aliquot=0.00006

∴%Mn(III) leached=0.00006x100/0.00533=1.12%

The results for quickly reduced or slowly reduced battery-active samples are found in *Electrochem.Acta,*26(1981)239, including calculation of diffusion coefficients. The samples were characterised by XRD, a useful characterisation technique for battery-active samples (see *Chem.Ind.*(1971)446).

A12.7.2.5

The green solution obtained by reacting MnO_2 and Cr^{3+} solution, run through a cation exchange resin, revealed a blue-violet coloured compound retained on the resin. The eluted orange/yellow liquid had an absorption maximum at 350 nm, identifying dichromate resulting from the oxidation of Cr(III). The liquid retained on the resin, eluted by HCl, displayed the spectrum of Cr(III) chloride.

The reference contains results of kinetic runs using 5 samples of Mn dioxides as well as Mn_3O_4. The effects of pH, temperature, rate of shaking and the anion of Cr(III) were also studied in the paper cited in the text.

A12.7.2.6

Although ascorbic acid can be determined titrimetrically using Fe(III), Ce(IV) or permanganate solutions, titration against Mn(III) sulphate was more suitable (Sec.12.4.1). Using a range of ascorbic acid solutions (0.01-0.05 M) and titrating each against 0.0121 M Mn(III) solution, the stoichiometry of the reaction was established. The molar ratio of MnO_2: ascorbic acid was found to be 2:1 using a range of [ascorbic acid]: 2.5-25x10^{-3} M.

A12.7.2.7

The rate constant, k_r, was calculated from the relation:

$k_r t=\chi/[a(a-\chi]$

where a is the concentration at time=0 and (a-χ) is the concentration at time=t. The duplicate results at 4 temperatures were used to calculate k_r using a computer program for straight line relationships. Applying the Eyring equation, the activation parameters were calculated from the linear plot of ln (k_rh/kT) against I/T where h and k are Planck's and Boltzmann's constants respectively and T is the thermodynamic temperature (Fig.A12.1). The values were ΔH_a=73 kJ mol^{-1} and ΔS_a=12 J mol^{-1} K^{-1}. In presence of 0.1 M HCl, the reaction at 293 K was practically complete in <2 minutes.

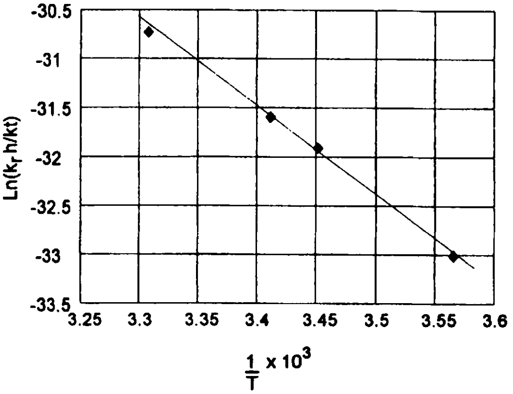


Fig. A12.1 The Eyring plot for the reaction of manganese dioxide with ascorbic acid.

A12.7.2.8

The solid isolated from the reaction gave the following elemental analysis: C13.9%, H2.3%, Mn29.4% (the latter was determined by atomic absorption), giving an empirical formula of $C_2H_4O_6$ Mn. The faint colour of the solid indicates a Mn(II) compound. The aniline blue test suggests an oxalate: $Mn(C_2O_4).2H_2O$. This was confirmed by ir spectra similar for the isolated solid and reagent grade oxalate. The mass spectrum showed the heaviest fraction with a mass of 149 near the mass of the residue $C_2H_4O_6$. Comparative neutron activation analysis confirmed that the solid had nearly the same Mn content as the reagent solid. TGA could be also used to add to the above evidence. The solid used, coded R2 had been fully characterised. Further results using this and other dioxide samples are found in the Power Sources reference mentioned above. This also compares the rates of the catalytic decomposition of hydrogen peroxide by R2 and four other battery-active samples.

A12.7.2.9

H_2O_2 should be used freshly from bottles stored in the fridge and standardised, usually after dilution, with standard Ce(IV) solution.

$2Ce(IV)+H_2O_2 \rightarrow 2Ce^{3+}+2H^{+}+O_2$

If the volume of Ce(IV) solution used is V cm^3

the number of mols of Ce=Vx0.1/1000

$\therefore$The number of mols of H_2O_2=½Vx0.1/1000 in 25 cm^3

$\therefore$Its concentration=½Vx0.1/25 mol dm^{-3}

A small scale set up to study the reaction is described in *J.Chem.Educ.*75(1998)213. For results of kinetic runs see the Power Sources reference in the above section.

A12.7.2.10

A standardisation plot relating the absorbance at 3.98μm and [D_2O] was used to find the heavy water content in the liquid collected from the evacuated solid and hence the percentage of lattice water exchanged with heavy water. A plot of this against (time)$^{1/2}$ suggest an initial fast step followed by a diffusion-controlled step. This was even clearer when tritiated water was used and the percent exchanged was calculated from measuring the tritium activity using liquid scintillation counting. The results were given by M.W.Rophael *et al*, *Manganese Dioxide Symposium*,**1**(1975)66 published by I.C.Sample Office c/o Union Carbide Corp.Cleveland.

A12.8.1

The kinetics and mechanism of the Mn^{2+}-catalysed reaction were published in *J.Am.Chem.Soc.* 77(1955)2036.

In presence of a drop of V(II) or V(III) solution, the titration can be carried out even at room temperature but it will be fast on warming to 40°C. The titre will be the same as in absence of V solution except for a small blank (using the same drop of V solution and oxidising with the same permanganate solution). The oxalate/permanganate reaction was also kinetically studied in *J.Chem.Educ.*65(1988)142.

A12.8.2

The results of the photocatalysed reaction are given by R.J.Cobb, M.A.Malati in *React.Kinet.Cat. Lett.*21(1982)397.

A12.9 Further references and experiments

Thermal analysis of $MMnO_4$ (M=alkali metal) are described in *Thermochimica Acta*,39(1980)281;293.

The kinetics and mechanism of the permanganate/ascorbic acid reaction are discussed in *Z.Phys.Chem.Leipzig.*263(1982)622.

Pulse-radiolysis of permanganate solution is described in *Pulse Radiolysis:Proceedings International Symposium,* Manchester 1965, p107.

Adsorption of Mn^{2+} and sulphite ions on β MnO_2 were reported in *J.Appl.Chem Biotechnol.* 21(1971)200 and of Ba ions in *International J.Mineral Processing,*1(1974)267. The rate of adsorption of Zn ions on doped manganese dioxide is studied in *J.Radioanal.Chem.*52(1979)677.

The photodecomposition of Mn(III) sulphate and the photosensitised oxidation of Mn(II) to Mn(III) are dealt with in M.W.Rophael; M.A.Malati, *Chem.Labor.Betribe.* 32(1981)158. In the same journal, an article by the same authors *ibid.*34(1985)51 describes neutron activation analysis of MnI_2(aq.), including its preparation, as well as activation analysis of other Mn, Cu and Ag compounds.

Voltammetry of Mn^{n+}(n=2-4) in 7.5 M sulphuric acid is given in *Electrochim.Acta.*13(1968)99.

The preparation of $[Me_4N]_2$ $[MnCl_4]$ is described in *Inorg.Synth.*9(1967)137.

APPENDIX 13

A13.2.1

(a) $FeSO_4.7H_2O \rightarrow FeSO_4+7H_2O$ (condenses on cold tube surface)
$2FeSO_4 \rightarrow Fe_2O_3(s)$ red brown+$SO_3(g)$ white acid fumes+$SO_2(g)$ (turns dichromate green).

(b) $FeCO_3(s) \rightarrow FeO(s)$ (oxidised in air to Fe_2O_3)+CO_2 (turns lime water turbid).

(c) $FeC_2O_4 \rightarrow FeO$ (as in b)+CO_2+$CO(g)$ (dark Pd formed by the reducing gas).

(d) (i) $Fe^{2+}+2OH^- \rightarrow Fe(OH)_2(s)$ grey/green (partial aerial oxidation) eventually oxidised to red brown Fe(III) oxide, the oxidation is immediate with H_2O_2;
(ii) $S_2O_8^{2-}+2Fe^{2+}+2H^+ \rightarrow 2HSO_4^-+2Fe^{3+}$ (forms red thiocyanate complex);
(iii) $KFe^{III}[Fe^{II}(CN)_6](s)$ pale Turnbull's blue precipitates;
(iv) $K_2Fe^{II}[Fe^{II}(CN)_6](s)$ blue (partial aerial oxidation) precipitates;
(v) no colour unless some aerial oxidation of Fe(II);
(vi) $6Fe^{2+}+Cr_2O_7^{2-}+14H^+ \rightarrow 6Fe^{3+}+7H_2O+2Cr^{3+}$ (the latter is green in acid solution).

A13.2.2

(a) $Fe_2(SO_4)_3H_2O \rightarrow H_2Og)+Fe_2O_3(s)+3SO_3(g)$ (see (a) above).

(b) $2Fe(NO_3)_3.9H_2O \rightarrow 18H_2O(g)+Fe_2O_3(s)+6NO_2(g)$ brown+$3/2O_2(g)$ (rekindles splint).

(c) (i) red brown Fe(III) hydrated oxide precipitates immediately;
(ii) dark Prussian blue: $KFe^{III}[Fe^{II}(CN)_6]$ precipitates;
(iii) brown (Berlin) green colour $Fe^{III}[Fe^{III}(CN)_6](aq.)$ is formed;
(iv) red complex e.g. $FeSCN^{2+}(aq.)$ is obtained;
(v) $2I^-+2Fe^{3+} \rightarrow 2Fe^{2+}+I_2$ (turns starch blue);
(vi) $Sn^{2+}+2Fe^{3+} \rightarrow Sn^{4+}+2Fe^{2+}$ (paler green solution);
(vii) brown basic iron(III) acetate precipitates.

A13.3.1.1

If the volume of Ce(IV) sulphate used is V cm^3,
the number of mols of Fe(II) complex=25x0.1/1000=the number of mols of Ce(IV)
∴[Ce(IV)]=25x0.1/V mol dm^{-3}=M

A13.3.1.2

If the volume of Ce(IV) solution used is V cm^3
the number of mols of Ce(IV)=VxM/1000=number of mols of Fe(II) in 25 cm^3
∴[Fe(II)]=VxM/25 mol dm^{-3} (M determined above)

Preparation of indicators

Dissolve 0.198 g phenanthroline hydrate in 50 cm^3 of 0.02 M iron(II) sulphate using purest solids.

A13.3.2

The purpose of adding phosphoric acid is to lower the Fe(III)/Fe(II) redox potential.

$SnCl_2$ solution is prepared by dissolving 30 g of purest dihydrate in 100 cm^3 conc.HCl, making up to 200 cm^3 with water. A little Sn prevents aerial oxidation.

If the volume of dichromate solution used is V cm^3
the number of mols of dichromate=Vx1/(60x1000)
∴The number of mols of Fe=6V/60,000 in 25 cm^3
∴[Fe(III)]=V/(10x25) mol dm^3

A13.3.2.1

The first titration gives [Fe(II)] only, which is calculated as above. The second titre gives the combined [Fe(II)+Fe(III)]. The difference between the two is equivalent to [Fe(III)].

A13.3.2.2

$2[Fe(CN)_6]^{3-}+2I^- \leftrightarrows 2[Fe(CN)_6]^{4-}+I_2(aq.)$
If the volume of thiosulphate used is V cm^3,
the number of mols of thiosulphate=Vx0.05/1000=the number of mols of Fe(III) complex in 25 cm^3.
$\therefore [Fe(CN)_6{}^{3-}]$ =Vx0.05/25 mol dm^{-3}

A13.3.3

Although $[Fe(phen)_3]^{2+}$ has a pronounced peak at 510 nm, in presence of the less strongly absorbing $[Fe(phen)_3]^{3+}$, measurements at 396 nm rather than 510 nm, are more appropriate. The peak at 510 nm is due to MLCT (see Fig.A9.3).

A13.3.4

Fe_2O_3 contains 69.94% Fe. If the mass of the precipitate is m_1 g,
$\therefore$the mass of iron in the original solution=m_1x0.6994=m_2 g
$\therefore$[Fe]=m_2x1000/(50x55.847) mol dm^{-3}.

A13.4.1

High spin Fe(II) compounds as in $[Fe(H_2O)_6]^{2+}$ have 4 unpaired electrons and their room temperature effective magnetic moment is ~5μ_B. However, the strong ligand cyanide gives the diamagnetic hexacyanoferrate(II). As a result, the ground state for this ion is ^1A_g. The spin-allowed d-d bands at 320 and 270 nm are ascribed to $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ respectively. This can be seen from the simplified Tanabe-Sugano diagram (Fig.14.2). These contrast the single broad band of the high spin species. The very strong band of the diamagnetic complex at ~220 nm is due to charge transfer (either from metal to ligand or metal to solvent). The spin-allowed band of the high spin complexes is expected from Orgel diagram (Fig.A9.2). The photodetachment of hydrated electrons from the low spin complex has been demonstrated, since in presence of N_2O gas, the electrons reduce it to N_2 which is measured by gas volumetric methods (*Proc.R.Soc., London.*A291(1966)340).

A13.4.2

The room temperature magnetic moment of iron(III) sulphate is 5.9 μ_B but the value for hexacyanoferrate(III) is 2.3 μ_B. The higher value than the spin only value of 1.73 μ_B is ascribed to orbital contribution to the magnetic moment.

The pale colour of solutions of Fe(III) nitrate or the ammonium iron(III) sulphate is reflected in the very weak absorption bands, similar to those of high spin Mn(II) salts. Spectra of Fe(III) chloride solution in HCl or in some oxygenated organic solvents are reported in both the visible and uv regions in *J.Am.Chem.Soc.*73(1952)5. It was concluded by the Authors that the tetrahedral $FeCl_4{}^-$ was the main absorbing species.

The spectrum of the low spin hexacyanoferrate(III) is dominated by the intense bands at 418, 304 and 260 nm which are ascribed to LMCT transitions whereas the ligand field bands appear as shoulders at 395, 322 and 282 nm. The LMCT bands involve transitions between ligand orbitals of t_{1u} or t_{2u} symmetry to the only vacant Fe(III) orbital of t_{2g} symmetry.

A13.5.1

The results of the preparation and characterisation of α iron(III) oxide are given in *J.Appl.Chem.Biotechnol.*25(1975)523. The solid was characterised by XRD, TGA and BET surface area. PZZ was determined in NaCl solutions and in presence of phosphate. The reference includes adsorption of phosphate at different pH values. The correlation between the ξ potential data and adsorption results is discussed in the reference.

A13.6.1.1

392.14 g of Fe(II) salt give 179.90 g of $FeC_2O_4.2H_2O$
Expected yield=m_1x179.90/(392.14)=m_2
(m_1=mass of iron(II) salt used)
% Yield=m_3x100/m_2 (m_3=mass of compound prepared)

A13.6.1.2

If the volume of permanganate used is V_1 cm^3,
the mols of iron(II) oxalate=7.5xV_1/1000
∴Mass of iron(II) oxalate=7.5xV_1x179.9/1000=m_1
∴% Purity=m_1x100/m_2 (m_2=mass of iron(II) oxalate weighed)
If the volume of permanganate in the second titration is V_2 cm^3
the number of mols of Fe(II)=5xV_2x0.02/1000
∴The mass of iron in the compound=5xV_2x0.02x55.85/1000=m_3
Theoretical mass of iron=m_2x55.847/179.9=m_4
∴% Purity=m_3x100/m_4
The two % purity values should be equal within experimental error.

A13.6.2.1

3 mols of oxalate ≡1 mol of complex RMM491.13
100% Yield=45x1.5x491.25/(3x1000)=11.05 g
%Yield=mx100/11.05 (m=mass of product)

A13.6.2.2

If the volume of permanganate used is V_1 cm^3
∴Mass of oxalate in the product=2.5xV_1x0.02x88.02/1000=m_1
%Oxalate=m_1x100/m_2=X
%Purity=Xx100/53.75 (m_2 is the mass of complex weighed)
If the volume of permanganate in the second titration is V_2
∴Mass of iron=5xV_2x0.02x55.547/1000
∴Mass of complex=5xV_2x0.02x491.25/1000=m_3
∴% Purity=m_3x100/m_2 (m_2=mass of complex weighed).

A13.6.2.3

(a) Water of crystallisation condenses on cool part of the tube (blue paper turns very faint pink).
(b) Solid becomes darker, $PdCl_2$ paper gives dark Pd (reducing CO formed). Carbonate residue effervesces with acid liberating CO_2 (tested with lime water).
(c) Decolourisation is due to reduction of permanganate by oxalate to Mn(II).
(d) The colour changes to pale green (reduction to Fe(II) chloride).
(e) Red Fe(III) thiocyanate complex is formed.
(f) White calcium oxalate precipitates.

When the solid is left exposed to light for a long time, the green crystals at the surface change to yellow indicating photoreduction to iron(II) oxalate.

A13.6.3

The advantage of this actinometric system is the high quantum yield and the sensitive detection of the product of photolysis as $[Fe(phen)_3]^{2+}$. For the details data of Φ and the mechanism see the book reference in Sec.2.10.2 and other references therein.

A13.7.1

The papers cited contain spectral data as well as a discussion of the solvent effect on the electronic spectra.

A13.7.2

Since both the reactant complex and its oxidised form are low spin and kinetically inert, even if the redox reaction involves a bridged species, there is no probability of transfer of the bridge after the reaction. When persulphate was used as an oxidant, the activation ΔG_a in a preliminary student's work was 95 kJ mol^{-1} compared to 220 kJ mol^{-1} when Ce(IV) sulphate was used as an oxidant.

A13.7.4

Preliminary students results showed that, although ΔG_{tr} (i.s.) decreased as [ethanol] increased, $\delta\Delta G_a$ showed a decrease at 25% v/v of alcohol, but there was an increase at 50% v/v of alcohol. The same trend was found for ΔG_{tr} (t.s.). Interestingly, the same trend was observed in another student's results using dimethylsulphoxide as the solvent. It was found that as the organic solvent concentration increased, the oxidant contribution to ΔG_{tr} increased i.e. it is increasingly destabilised in the less polar solvent, as expected for an ionic reactant. On the other hand, the reactant complex became more stable as the concentration of the organic solvent increased. This is not unexpected for a species with a large organic periphery of the molecule. However the sum ΔG_{tr} (i.s.) i.e. contributions of both reactants showed a small drop at 25% DMSO but a larger increase at 50% solvent composition. The same trend was observed in $\delta\Delta G_a$. See *J.Chem.Soc.Dalton Trans.*(1980)2442 and other references by the same Authors.

A13.8.1.1

Anhydrous iron(II) chloride is available commercially and is kept sealed before use. It can be used if available but its preparation given is based on the reaction:
$C_6H_5Cl+2FeCl_3 \rightarrow C_6H_4Cl_2+2FeCl_2+HCl$ (*Inorg.Synth.*6 (1960)1.

A13.8.1.2

126.75 g iron(II) chloride give 186.04 g ferrocene
% Yield =$(m_2 x 126.75 x 100)/(m_1 x 186.04)$
(m_1 is the mass of the chloride and m_2 is the mass of ferrocene).

The product can be compared with the commercially available ferrocene. Its m.p. is 175°C and it is diamagnetic.

A13.8.1.3

Absorption bands for ferrocene are observed at ~450 nm (intense in either solvent), at 255 and 207 nm (weak in methanol) or at 230 and 213 nm (in cyclohexane). The origin of the bands is thought to be associated with solvent effects. An intense band at ~307 nm is found in CCl_4.

The ir spectrum is better recorded using KBr discs but if Nujol is used, the bands due to the liquid have to be discarded. The main bands are at ~810 cm^{-1} and ~850 cm^{-1} (perpendicular H wagging), at 995 cm^{-1} (due to parallel H wagging), at ~1095 cm^{-1} (ring breathing), at ~1410 cm^{-1} (C-C stretch) and at ~3080 cm^{-1} (C-H stretch).

A13.8.2

186.04 g ferrocene give 228.07 g acetylferrocene
% Yield =$(m_2 x 186.04 x 100)/(m_1 x 228.07)$ (m_2=mass of product, m_1=mass of ferrocene)

A different preparation is given in *J.Chem.Educ.*43(1966)73. The paper also describes chromatographic separation of the product from the reactant. The m.p. of the product is 183-184°C.

The electronic bands of the acetylferrocene are at: 455 or 450 nm in MeOH or cyclohexane; at 285 and 260 nm in either solvent. The characteristic ir bands are at ~1265 cm^{-1} (as in alkyl ketones), 1460 cm^{-1} (weak, CH_3 bend) and at 1660 cm^{-1} (CO stretch).

A13.9

The large barium ion precipitates the large ferrate(VI) ion. The solid product quickly decomposes to iron(III) chloride solution and oxygen.

(i) a blood red Fe(III) complex is formed;
(ii) Prussian blue precipitates;
(iii) hydrated red brown iron(III) oxide precipitates.

A13.10 Further references and experiments

A brief review of ferrates(VI) (*Coord.Chem.Rev.*12(1974)151) gives the magnetic moment of the barium ferrate as 3.15 μ_B. This confirms the d^2 configuration of the tetrahedral ion. This is also indicated by the three spin-allowed d-d bands at 786, 510 and ~226 nm. If the solution obtained in the preparation is quickly transferred to a vacuum uv cell the spectrum can be recorded. DTA of the barium salt and other ferrates are also referred to in the above reference.

The reference also includes reviews of the chemistry of the higher oxidation states of Ni (Sec.15.5,15.6).

The preparation, analysis and properties of the potassium ferrate(VI) are given in *Inorg.Synth.*4(1953)164.

A table in *Acta Chem.Scand.*28(1974)p.630 compares the M-C bend and stretch ν as well as C≡N stretch ν in $K_3[Fe(CN)_6]$ with the corresponding cyano-complexes of Cr, Mn and Co.

A stopped-flow kinetics experiment of the formation of Fe(III)/thiocyanate complexes is described in *J.Chem.Educ.*74(1997)1214; see also *ibid.*40(1963)71; 41(1964)615.

The analytical chemistry of Fe(III)/Fe(II) is discussed in *J.Chem.Educ.*65(1988)183. Thermal analysis of $K_3[Fe(C_2O_4)_3]$ and other alkali metal and ammonium complexes as well as Fe(II) and Fe(III) oxalates are reported in *J.Chem.Soc.A*(1967)451. The paper includes XRD data.

The equilibria between Fe(II) and ascorbate ions and protons are studied in *Acta Chem.Scand.*A28(1974)631.

Reduction of Fe(III) oxide with various reductants are reviewed in *Adv.Inorg.Nucl. Chem.*3(1984)97.

Sunlight photochemistry of solutions of hexacyanoferrate(II) and (III) are described in *Environ.Sci.Technol.*27(1993)1875. In the same journal: *ibid.*31(1997)1426, a study of the kinetics of reduction of Cr(VI) by Fe(II) is published.

Since the complexes of Fe(III) with sulphosalicyclic acid are strongly absorbing, spectrophotometry can be used in conjunction with Job's method to determine the molar ratio of Fe(III): the acid. Iron(III) in chloride solution together with Co(II), can be separated in an ion exchange column. Iron(III) eluted can be monitored amperometrically using a rotating Pt electrode (*J.Chem.Educ.*51(1974)491).

APPENDIX 14

A14.3

(a) A blue basic salt precipitates, which gives with excess reagent, a pink $Co(OH)_2(s)$ which slowly darkens in air (oxidation to Co(III)).

(b) $4Co(OH)Cl+28NH_3+6H_2O+O_2 \rightarrow 4[Co(NH_3)_6](OH)_3(s)$ red $+4NH_4Cl$ the reaction is faster when hydrogen peroxide is added.

(c) $[Co(H_2O)_6]^{2+}$(aq.) pink $+4Cl^- \rightarrow [CoCl_4]^{2-}$(aq.) blue $+6H_2O$.

(d) $CoCl_2+2KNO_2 \rightarrow Co(NO_2)_2+2KCl$;
$Co(NO_2)_2+2KNO_2+2CH_3CO_2H \rightarrow Co(NO_2)_3+2CH_3CO_2K+NO+H_2O$;
$Co(NO_2)_3+3KNO_2 \rightarrow K_3[Co(NO_2)_6](s)$ yellow.

(e) $CoCl_2+4NH_4SCN \rightarrow (NH_4)_2[Co(SCN)_4]$(aq.) blue $+2NH_4Cl$; (blue complex extracted by the alcohol).

(f) $Co^{2+}+3CO_3^{2-}+H_2O_2 \rightarrow [Co(CO_3)_3]^{3-}$(aq.) dark green.

(g) Basic blue salt precipitates, which is soluble in excess giving brown Co(II) ammines (slowly oxidised in air to yellow Co(III) complexes).

(h) Grey green $Co_2[Fe(CN)_6](s)$ precipitates.

(i) Red $Co_3[Fe(CN)_6]_2$ precipitates.

(j) A blue solution is formed (probably tetrahedral $[Co(S_2O_3)_2]^{2-}$.

(k) Red brown basic chromate precipitates.

(l) Red $Co(C_2O_4)$ slowly precipitates.

(m) Black CoS precipitates from neutral or alkaline solution.

A14.3.1.2

If the volume of EDTA used is V cm^3
the number of mols of EDTA=Vx0.05/1000=number of mols of Co(II)
$\therefore$[Co(II)]=Vx0.05/25 mol dm^{-3}

A14.3.1.4

Mass of Co in precipitate =mx0.11982(m is the mass of precipitate)
Number of mols of cobalt =mx0.11982/58.933 in 25 cm^3 aliquot
[Co(II)]=(mx0.11982x1000)/(58.933x25) mol dm^{-3}

A14.3.2.1

257.93 g cobalt chloride give 316.10 g of complex $[CoCl_2(C_6H_5NH_2)_2]$
% Yield =(m_2x257.93x100)/(m_1x316.10)
(m_1=mass of cobalt chloride, m_2=mass of complex)

The blue colour of the tetrahedral complex changes on adding water to the paler pink colour of $[Co(H_2O)_6]^{2+}$.

A14.3.2.2

281.1 g cobalt sulphate give 491.8 g complex
$\therefore$% Yield =(m_2x281.1x100)/(m_1x491.8)
(m_1=mass of cobalt sulphate, m_2=mass of complex).

A14.3.2.3

257.93 g cobalt chloride give 843.6 g complex
% Yield =(m_2x257.93x100)/(m_1x843.6)
(m_1=mass of cobalt chloride, m_2=mass of complex)

See *J.Chem.Soc.*(1962)2552, which reports the preparation of other square planar en metal complexes, their colours, their magnetic moments, their reflectance electronic bands and ir frequencies.

A14.3.3 (see Fig.14.1)
The weak pink colour of aqueous Co(II) salt solutions is due to the Laporte-forbidden transition in the blue region of the spectrum and the band at ~540 nm is the major band in the visible region. The shoulder on the shorter λ is due to spin-orbit coupling. The ${}^4T_{1g}(F) \rightarrow {}^4t_{2g}$ is too weak to be observed. The more strongly coloured blue tetrahedral complexes e.g. tetrachlorocobaltate(II) have structured absorption in the region 610-700 nm (*Acta Chem.Scand.*9(1955)397). The fine structure is due to spin orbit coupling which splits the ${}^4T_1(P)$ state and allows transitions to the neighbouring doublet states. The spectra of other Co(II) octahedral complexes were reported in *J.Amer.Chem.Soc.*73(1950)4232. The value of ε_{max} ranges from 0.5-1.3 $m^2\ mol^{-1}$ whereas for tetrahedral complexes, the corresponding ε values are 30-60 $m^2\ mol^{-1}$.

For the high spin octahedral complexes, the number of unpaired electrons=3 and this is also the case for the tetrahedral complexes. For the octahedral complexes, orbital contribution to the magnetic moment leads to values appreciably >3.89 μ_B (the spin-only value). This is not expected for tetrahedral complexes, but mixing ${}^4T_2$ state with the ${}^4A_2$ ground state introduces orbital contribution. The difference between the observed moment and the spin-only moment increases as Δ_t decreases. The magnetic moment and reflectance spectrum of the complex prepared in Sec.14.3.2.3 are reported in *Bull.Chem.Soc.Japan*, **45**(1972)461 together with other low spin Co(II) complexes showing orbital splitting schemes.

Absorption spectra of anhydrous $CoCl_2$, (which is available commercially, or prepared by dehydrating the hexahydrate using $SOCl_2$), when dissolved in nonaqueous solvents show changes in the absorption spectra of the solutions suggesting coordination of the solvent to Co(II) (see *J.Chem.Soc.*(1961)5105, *Inorg.Chem.*1(1962)285).

A14.4.1
For the cyano-complex, the bands at 313 and at 260 nm are assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ spin-allowed transitions. The corresponding bands in the spectra of the ammonia complex are found at longer wavelengths: 530 and 360 nm respectively i.e. lower energies because ammonia is a weaker ligand than cyanide. However, a much more intense band at 220 nm is ascribed to LMCT transition. A similar band in the bromo-and iodo-complexes is shifted to a longer λ i.e. lower energy as the reducing power of the halide increases down the halogen group.

A14.5.1.1
118.94 g cobalt carbonate give 494.33 g of complex
% Yield =$(m_2$x118.94x100)/$(m_1$x494.33)
(m_1=mass of cobalt carbonate used, m_2=mass of complex obtained).

A14.5.1.2
If the volume of permanganate used is V_1 cm^3,
the number of mols of oxalate=2.5xV_1x0.02/1000
Mass of oxalate in 25 cm^3 aliquot=2.5xV_1x0.02x88.02/1000=m_2
% Oxalate in the solid=(100xm_2/25)x(1000/m_1)=χ_1
m_1=mass of complex used
% Purity =χ_1x100/53.42 (53.42 is the theoretical % oxalate)

A14.5.1.3
If the volume of thiosulphate used=V_2 cm^3
$\therefore$Mols of iodine liberated=$\frac{1}{2}V_2$x0.05/1000
$\because Co_2O_3+2I^-+6H^+ \rightarrow 2Co^{2+}+I_2+3H_2O$
$\therefore$1 mol complex$\rightarrow\frac{1}{2}$mol oxide$\rightarrow\frac{1}{2}$mol I_2
$\therefore$Mols of Co=V_2x0.05/1000
$\therefore$Mass of cobalt=V_2x0.05x58.93/1000 g
% Cobalt =V_2x0.05x58.93x100/(1000xm_1)=χ_2

% Purity $=\chi_2 x100/11.92$ (theoretical % Co=11.92)

This percentage is likely to be a little lower than the % purity based on oxalate since the determination of the latter was more direct.

A14.5.2

The results of the kinetics runs are found in M.A.Malati, *Chem.Labor.Biotech.*45(1994)61. The article also contains results of the reduction in Sec.14.8.3.

See also *J.Chem.Soc.*A(1968)1415; *ibid.*A(1967)298. The latter paper contains a comparison of the redox potentials of various Co(III)/Co(II) species. Analysis of kinetic data of reactions which are 1st order in both reactants are dealt with in *J.Chem.Educ.*66(1989)705.

A14.5.3

Reductant	ΔH_a kJ mol^{-1}	ΔS_a/JK^{-1} mol^{-1}
Sulphite *(14.5.3.1)*	50	-167
Hydrazine *(14.5.3.2)*	*96*	-31 (Fig.A14.1)

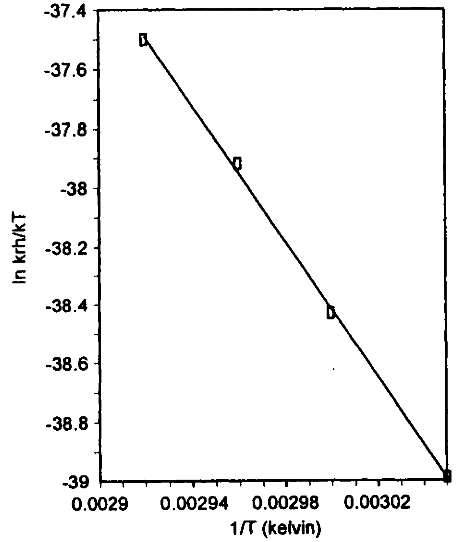


Fig. A14.1 The Eyring plot for the reduction of the cobalt (III) complex by hydrazine.

A14.5.3.3

Full details of the solid state photoreduction of this complex as well as the corresponding iron(III) complex (Sec.13.6.2) are found *J.Phys.Chem.*73(1969)2316. The effect of heating during irradiation, referred to as photothermographic, was demonstrated in *Photo-Sci.Engng.* 13(1969)147. The reflectance spectra of the irradiated solids are compared in the paper with spectra of blank samples which were heated but not irradiated.

The mass of complex (0.0117 g) spread on the slide, was irradiated for 1 hour with Hanovia Chromatolite low pressure mercury lamp. After reacting with iron(III) chloride and phenanthroline, the absorbance of the $[Fe(phen)_3]^{2+}$ complex formed, measured in a 1 cm cell, was 0.847 at 510 nm.

A14.5.4

118.94 g cobalt carbonate give 714.40 g of the complex
% Yield $=(m_2 x118.94x100)/(m_1 x714.40)$
(m_1=mass of carbonate, m_2=mass of complex obtained)

Infrared spectra of various binuclear Co(III) complexes are compared in the book reference in A4.6.3.

Evidence of the (OH) bridged complex, its preparation and analysis were reported in *J.Inorg.Nucl.Chem.*6(1958)310. The paper also deals with the Co(II) oxalate complex.

The thermal decomposition of the oxalate complexes of Al, V, Cr, Mn, Fe and Co are reported in *Bull.Chem.Soc.Japan*,45(1972)2166, together with $K_2[M(C_2O_4)_2].\chi H_2O$ (M=Cu,Zn,Rh,Pd and Pt). Infrared spectra of the complexes of Cr, Fe and Co after thermal treatment were reported in the same journal 40(1967)330.

A14.6.1.1

257.93 g cobalt chloride give 267.48 g of the complex
% Yield =$(m_2 x 257.93 x 100)/(m_1 x 267.48)$
(m_1=mass of cobalt salt; m_2=mass of complex obtained)

A14.6.1.2

If the volume of silver nitrate is V_1 cm^3,
the number of mols of silver chloride=V_1x0.1/1000
Mass of chlorine=V_1x0.1x35.45/1000=m_1
∴% Chlorine in complex=m_1x100/m_2=χ_1
(m_2 is the mass of complex weighed)
∴% Purity =χ_1x100/39.76 (theoretical % Cl=39.76)

A14.6.1.3

Number of mols HCl used=50x0.5/1000=m_1
If the volume of NaOH required to neutralise the excess acid is V_2 cm^3
the number of mols of excess acid=V_2x0.5/1000=m_2
∴Number of mols absorbing ammonia=m_1-m_2
∴Mass of ammonia in complex=(m_1-m_2)x17.03=m_3
% Ammonia=m_3x100/m_4 (m_4=mass of complex weighed)=χ_2
% Purity=χ_2x100/38.20 (theoretical % ammonia=38.20)

The % cobalt could be calculated by difference ($100-\chi_1-\chi_2$) or determined by titration as in Sec.14.5.1. However the molar ratio Co:NH_3:Cl will be near 1:6:3.

A14.6.2-A14.6.4

The preparation, analysis and ir spectrum of the complex are detailed in (M.A.Malati, *Chem.Labor.Betrieb*.39(1988)84). The analysis for ($V+C_2O_4$) suggested a formula: $[Co(NH_3)_6][V(C_2O_4)_3].3H_2O$. However, to ensure that the vanadium complex is not oxidised during the preparation, it is advisable to use boiled-out water for dissolving the V complex and to mix the solutions in a Buchmer flask under reduced pressure. The above reference contains similar results for the reactions in Sec.14.6.3 and 14.6.4. It is advisable to analyse for Co as in Sec.14.5.1.2. To ensure that the products are true compounds and not a mixture of the component complexes, XRD pattern of the reactants and products could be compared. A mass spectrum is equally useful.

An attempt was made to prepare the corresponding complex containing Fe(III) but the colour of the product was not distinctly different from the reacting Co complex. Using 2.67 g of the cobalt complex in a minimum of water and adding it to 100 cm^3 of a solution of 4.91 g the iron oxalato-complex (Sec.13.6.2), 4.77 g of a product was formed. On analysing for oxalate, its % was found to be 48.8%. This is in fair agreement with a calculated 49.4% assuming a trihydrate is formed. The % Co determined was higher than expected from an anhydrous product or a trihydrate. This may indicate the presence of cobalt complex contamination.

Infrared spectra of ammine complexes of Co(III), Co(II), Cr, Ni (as well as $[M(C_2O_4)_2]M_2^I$ (M=Cu,Pt and Pd) are collected in *Inorg.Chem.*3(1964)1805. Infrared spectra of some of these containing ^{15}N appeared in *J.Chem.Soc.Dalton Trans.*(1975)2199.

High frequency titration of the cobalt complex with trisoxalatechromate(III) was reported in the reference in A3.4.3.

A14.7.1

118.94 g cobalt carbonate give 250.45 g of the complex (*Inorg.Synth.*9(1967)160).

∴% Yield =(m_2x118.94x100)/(m_1x250.45)

(m_1=mass of carbonate used, m_2=mass of complex formed)

% Co=23.53 %NH_3=34.00. Conductivity measurements of a cooled solution will show that it is a 1:1 electrolyte when compared with the value for a KCl of the same molar concentration.

A14.7.2

291.05 g cobalt nitrate hexahydrate give 249.07 g of the complex (*Inorg.Synth.*4 (1963) 171).

% Yield =(m_2x291.05x100)/(m_1x249.07)

(m_1 is the mass of cobalt nitrate, m_2 is the mass of the complex formed)

A14.7.2.1

249.07 g of the complex give 250.45 g of the complex from Sec.14.7.1

∴5.00 g are expected to give 5.03 g of the chlorocomplex. The product is expected to be identical to the one obtained in Sec.14.7.1.

A14.7.4

250.45 g of the chloro-complex give 261.00 g of the nitrito-complex

% Yield =(m_2x250.45x100)/(m_1x261.00)

(m_1=mass of chloro-complex, m_2=mass of product).

A14.7.5

Calculation of % Yield is the same as above. Calculation of % purity of either isomer similar to the calculation in Sec.A14.5.1.

A14.7.6

118.94 g cobalt carbonate give 248.04 g of the complex

% Yield =(m_2x118.94x100)/(m_1x248.04)

(m_1=mass of carbonate, m_2=mass of complex)

The complex can be analysed for cobalt and for NH_3 as before (Sec.14.6.1.3; 14.5.1).

A14.7.7

The neutral complex has a similar ir spectrum as the nitro-isomer but the latter will have a conductivity of its solution comparable to solutions of 1:2 electrolyte e.g. $CaCl_2$ of the same molar concentration. The neutral complex will have a low solubility in water and even in solutions in organic solvents, it has a very low conductivity. The two isomers are characterised by their ir spectra depicted in *Educ.Chem.*3(1966)285. See also *Trans.Faraday Soc.*52(1956)1590. Their electronic absorption maxima are listed in *Bull.Chem.Soc.Japan*,29(1950)311 together with numerous Co(III) complexes. Their electronic spectra are depicted in *Inorg.Chem.*7(1968)1398 where the photochemistry of the nitro-complex is studied.

The solid state isomerisation is clearly demonstrated by the absorption spectra of the solutions after various heating times or by their ir spectra.

A14.8.1

129.84 g cobalt chloride give 285.49 g of the complex

% Yield =(m_2x129.84x100)/(m_1x285.49)

(m_1=mass of cobalt salt used, m_2=mass of complex obtained)

*Inorg.Synth.*2(1946)222 gives the preparation of both the *cis*-and *trans*-isomers and the resolution of the *cis*-form. The equilibrium between the two isomers in DMF and dimethylacetamide was studied in *J.Chem.Soc.*(1962)4614. Initially the crystals of the *trans*-complex contain 1HCl molecule per molecule of complex but HCl(g) is lost on heating. The reference also contains the preparation of the *cis*-form and its resolution. See also

*J.Am.Chem.Soc.*75(1953)227; 75(1953)3089). The latter reference contains a different titrimetric method for Cl^- determination, which was found to be less satisfactory than the suggested method. The reference also contains rates of aquation of the *trans*-complex and other analogous complexes.

Preparation of diphenylcarbazone mixed indicator: dissolve 0.5 g of the purest solid and 0.05 g of purest bromophenol blue in 100 cm^3 of ethanol (95%).
The reaction in the titration is:
$Hg^{2+}+2Cl^-\rightarrow HgCl_2(aq.)$ (slightly dissociated)
0.01 M $Hg(NO_3)_2$ is prepared by weighing the purest solid, dissolving in 200 cm^3 water to which 5 cm^3 2 M nitric acid has been added and making up to 250 cm^3.
If the volume of mercury(II) solution used is V cm^3,
the number of mols of chloride=2x0.01V/1000
$\therefore$Mass of chloride=2xVx0.01x35.45/1000=m_2
$\therefore$% Chloride =m_2x100/m_1=χ (m_1 is the mass of complex used)
% Purity =χx100/12.42 (12.42 is the theoretical %Cl^-)
If the solution was heated before titration, the %Cl will be 24.82.

A14.8.2

Results of the kinetics of the aquation of the complex as well as the aquation of the *cis*-isomer and the *cis*-and *trans*-isomers of $[Co(en)_2Cl(OH)]^+$ ions are reported in *J.Chem.Soc.*(1961)4637. The reference proposes a mechanism of the reactions.

A14.8.3

The results of the kinetics of reduction in aqueous or in water/MeOH solution are given in the reference in A14.5.2. It is essential to use boiled-out water for the preparation of the solutions and to use freshly prepared cooled ascorbic acid solutions. The reference contains spectra of the complex before and reduction compared to the spectrum of $[Co(en)_2(H_2O)Cl]^{2+}$. The activation energy for the reduction was 40 and 26 kJ mol^{-1} for ascorbic acid or hydrazine as reductants respectively.

A14.9.1

First order kinetics with respect to the complex was established, by the linear variation of log(A_t-A_f) against time t (A denotes absorbance at 620 nm and t and f refer to time=t or infinity, i.e. long time, respectively). Using Eyring's equation (2.77), the approximate activation (a) parameters were ΔH_a=87 kJ mol^{-1} and ΔS_a=-45 J K^{-1} mol^{-1}. The literature E_a was 92 kJ mol^{-1} in water, indicating that replacing chloride by DMF is slightly easier than replacing it by water. Possibly the mainly hydrophobic periphery of the complex ion makes it easier for the organic solvent to attack the complex. (See also *J.Chem.Soc.Dalton Trans.*(1973)2514; 2518).

A14.9.2

First order kinetics with respect to the complex was established as above.

A14.9.2.1

The freshly mixed reactants had absorption maxima at ~680 and ~610 nm and low absorbances below 580 nm. As the reaction proceeds, the colour changes from green to a much darker blue/violet. The maximum at ~680 nm decreased and a new maximum appeared at ~525 nm. A much stronger absorption started at ~400 nm, peaking at 390 nm. The absorbance at this peak was about 2.5 times the absorbance at ~525. The intense colour of the reduction product contrasts with the faint pink colour of the reduction product in water or water/alcohol solutions; suggesting that a tetrahedral Co(II) complex in DMF is formed. The small energy difference between octahedral and tetrahedral Co(II) complexes leads to a large number of tetrahedral Co(II) complexes. The isomerisation of the *trans*-isomer has been studied in *J.Chem.Soc.(*1962)4614.

The linear variation of log (A_t-A_f) against time indicated first order kinetics with respect to the complex (A is absorbance at 390 nm at time=t or after >3 hours, denoted by f, respectively). An activation energy of 34 kJ mol^{-1} was calculated from results at two temperatures.

A14.9.2.2

Fig.A14.2 depicts the free energy changes ΔG with the % alcohol (v/v) in the reduction of the complex by ascorbic acid. In this figure ΔG_{tr} for the complex (C) and for ascorbic acid (A) and the sum of these ΔG_{tr} (i.s.) are shown for different MeOH/water ratios. The variation with the solvent composition of the change in the free energy of activation $\delta\Delta G_{-}$ and of ΔG_{tr} (t.s.) are also depicted where t.s. refers to the transition state.

As water is gradually replaced by MeOH in the solvent, both the complex ion and, to a lesser extent, ascorbic acid are destabilised in the less hydrophilic solvent. The activated complex is destabilised to a greater extent than the reactants as the % MeOH increases. This is not unexpected if an inner sphere mechanism is operative. The ΔG_{tr} for the complex ion were taken from *Trans.Met.Chem.*9(1984)193.

Example of calculating ΔG_{tr} of ascorbic acid from water to 25% MeOH/75% water solution. [ascorbic acid] were:
In saturated solution in aqueous MeOH=1.198 M
Saturated aqueous solution is 1.506 M
ΔG_{tr}=0.56 kJ mol^{-1}. (eqn.13.9)
The points at 43% alcohol refer to EtOH/water solution.

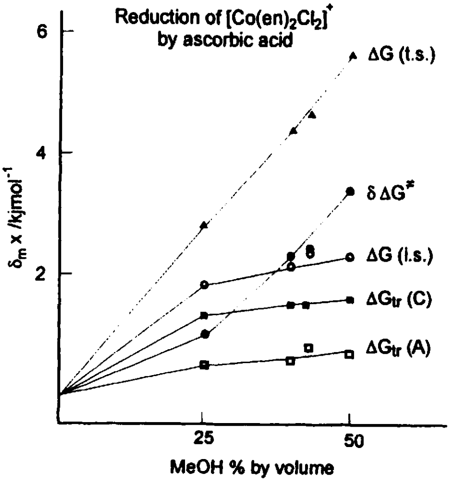


Fig. A14.2 The change in free energy as a function of methanol % (see text for details).

A14.10.1

118.94 g cobalt salt give 521.02 g of complex
% Yield =(m_2x118.94x100) / (m_1x521.02)
(m_1=mass of cobalt salt, m_2=mass of complex produced)

The reference contains results of %C, %H, %N and %Br for this complex and the complex prepared in the following section, together with λ_{max} and ε_{max} of 0.01 M solutions. Five other complexes were prepared and characterised in the same references.

A14.10.2

118.94 g cobalt carbonate give 521.02 g of the complex
% Yield =(m_2x118.94x100)/(m_1x521.02)
(m_2=mass of complex, m_1=mass of carbonate)

A14.10.3

257.93 g cobalt chloride give 313.54 g of complex
% Yield =$(m_2x257.93x100)/(m_1x313.54)$
(m_1=mass of cobalt salt, m_2=mass of complex formed). For electronic spectra of this and analagous Co(III) complexes see *J.Phys.Chem.*63(1959)780, which also includes the effect of alcohols on the spectra.

A14.11 Miscellaneous references

Oxalato-complexes of Co and other metals: ir spectra (*.Spectrochim.Acta* 9(1957)51); crystallographic and other data (*J.Chem.Soc.*A.(1969)3006.

Kinetics of isomerisation in methanol solution of *cis*- to *trans*- $[Co(en)_2Cl_2]^+$ is described in *J.Amer.Chem.Soc.*80(1958)788. For the study of nucleophilic substitution of Cl^- in the *trans*-isomer by other anions in methanol see *J.Chem.Soc.Dalton Trans.*(1973)2514.

The kinetics of aquation of $[Co(NH_3)_5X]^{2+}$(X=Cl or Br) is reported in *Trans.Met. Chem.*12 (1987)25.

Simultaneous determination of Co(II) and Cr(III) is described in *J.Chem.Educ.* 74(1997)848; 75(1998)878. The Authors use a spectrophotometric analysis with a standard additions method.

APPENDIX 15

A15.2

(a) Green NiO turns black (partial oxidation) on heating in air.

(b) (i) $2NaOH+NiCl_2=2NaCl+Ni(OH)_2(s)$;

(ii) $(NH_4)_2S+NiCl_2\rightarrow 2NH_4Cl+NiS(s)$ (black) insoluble in dil.HCl, but it dissolves in conc. hot HNO_3;
$3NiS+8HNO_3=3Ni(NO_3)_2+2NO+3S+4H_2O$
(NO combines with O_2 near the top of the test tube producing brown NO_2/N_2O_4);

(iii) initially $Ni(OH)_2$ or a basic salt precipitates but in excess ammonia a soluble complex is formed: $[Ni(NH_3)_6](OH)_2$, transition 3d metals tend to form complexes with N- containing ligands more readily than with O- coordinating ligands;

(iv) green white $Ni_2[Fe(CN)_6](s)$ precipitates but it is soluble in ammonia forming complexes;

(v) grey/yellow $Ni_3[Fe(CN_6]_2(s)$ is formed but it is soluble in ammonia forming complexes;

(vi) green $Ni_3(PO_4)_2(s)$ precipitates but is soluble in acetic acid;

(vii) Ni(s) is formed due to reduction (a metallic mirror may be seen on the sides of the tube).

A15.3.1

0.1 M Ni^{2+}:26.286 g purest $NiSO_4.6H_2O$ dissolved in distilled water, slightly acidified with dil.H_2SO_4 and made up to 1000 cm^3 or 23.769 g purest $NiCl_2.6H_2O$ similarly made up.
0.1 M Disodium salt of EDTA (37.224 g made up to 1000 cm^3) Eriochrome black T indicator and buffer pH10 as in Sec.A3.4.1.
0.1 M Zinc solution:28.755 g purest $ZnSO_4.7H_2O$ dm^{-3}
Mols of 0.1 M Zn^{2+} used=$V\text{x}0.1/1000\equiv V\text{x}10^{-4}$ (V cm^3 used)
Mols EDTA$\equiv Ni^{2+}=(5.0\text{x}10^{-3})-(V\text{x}10^{-4})=\chi$mols in 25 cm^3
Ni^{2+} and EDTA react in 1:1 molar ratio (though a penta-coordinate complex is formed)
$\therefore[Ni^{2+}]=\chi\text{x}1000/25$ mols $dm^{-3}=\chi\text{x}1000\text{x}58.69/25$ g dm^{-3}

To help the students to identify the end-point, 25.0 cm^3 of the Zn^{2+} solution are titrated with 0.1 M EDTA solution to obtain the red end-point, then 25.0 cm^3 of Ni^{2+} solution diluted to about 50 cm^3 are added.

A15.3.2

The determination does not always give good results. The red precipitate does not settle. To check for complete precipitation, a drop of the reagent is run down the side of the beaker and carefully watched. Only a slight excess is recommended.
$CH_3.C(NOH)C(NOH)CH_3$ or H_2DMG for short. RMM 116.12
$Ni^{2+}+2H_2DMG=Ni(HDMG)_2$ (Fig.15.1) $+2H^+$
Mass of Ni in the precipitate $=m_1\text{x}0.2031$ (m_1=mass of precipitate)
%Ni in the salt used=$m_1\text{x}0.2031\text{x}100/m_2$
(m_2=mass of Ni salt used)
%Ni assuming 100% purity and 100% recovery=14.86

The red precipitate is a sensitive qualitative test for Ni^{2+} (a drop of the solution+a drop of H_2DMG solution, the addition of a drop of dil.NH_3 produces a red precipitate or colour).

A15.4.1

$NiCl_2.6H_2O\rightarrow[Ni(NH_3)_6][BF_4]_2$
237.69 g Nickel salt give 334.47 complex
% Yield $=(m_2\text{x}237.69\text{x}100)/(m_1\text{x}334.47)$
(m_1=mass of nickel salt, m_2=mass of complex obtained)

The blue/green colour of the crystals confirms the octahedral arrangement of ammonia ligand.

A15.4.2.1

$2CuI \rightarrow [Ni(H_2N.CH(CH_3).CH_2.NH_2)_2][CuI_2]_2$ or $[Nipn_2][CuI_2]_2$

380.89 g CuI give 841.64 g Ni complex

% Yield=$(m_2$x380.89x100)/(m_1x841.64)

(m_1=mass of CuI used, m_2=mass of complex obtained)

A15.4.3

Hot dil. nitric acid oxidises both Cu^+ and I^- to Cu^{2+} and I_2 respectively:

$CuI_2^- + NO_3^- + 4H^+ \rightarrow Cu^{2+} + I_2 + NO + 2H_2O$

$[Nipn_2][CuI_2]_2 \rightarrow 2Cu^{2+}$

In presence of excess I^-: $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

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

$\therefore Cu^{2+} \equiv S_2O_3^{2-}$

If the volume of thiosulphate used is V cm^3,
the number of mols of thiosulphate=Vx0.05/1000

The number of mols of Cux½=number of mols of the complex

∴The mass of the complex=½xVx0.053841.64/1000=m_2 g

% Purity =m_2x100/m_1 (m_1=mass weighed)

If the analysis shows an impure product, it can be purified by washing with concentrated KI solution, followed by alcohol and acetone as in the preparative procedure.

A15.4.2.2

$2AgNO_3 \rightarrow [Ni(H_2N.CH(CH_3).CH_2NH_2][AgI_2]_2$

339.75 g silver nitrate give 930.30 g of the complex

∴% Yield =(m_2x339.75x100)/(m_1x930.30)

(m_1=mass of silver salt, m_2=mass of complex obtained).

The colour of the two $[Ni(pn)_2]$ complexes are orange indicating square planar Ni(II). On the other hand, $[Ni(NH)_6][BF_4]_2$ has an octahedral arrangement of NH_3 round Ni.∴Ni configuration $(t_{2g})^6(e_g)^2$ similar to $[Ni(H_2O)_6]^{2+}$

Analysis of [Ni(pn)2][AgI2]2

Heat 0.3 g of the preparation with 25 cm^3 dil.HNO_3 gently in a round bottom flask in the fume cupboard until all the iodine has been expelled. Wash the solid with CCl_4 thoroughly and filter through a G4 sintered crucible, heat at 110°C to constant weight and weigh as AgI.

$[Ni(en)_2][CuI_2)]^2$ can be prepared and analysed similar to $[Ni(pn)_2][CuI_2]_2$.

$[Ni(en)_2][AgI_2]_2$ can be also prepared and analysed as $[Ni(pn)_2][AgI_2]_2$

A15.5.1

$NiSO_4.6H_2O \rightarrow K[Ni(NHCONHCONH)_2]$

262.87 g salt give 299.91 g of the complex

% Yield =(m_2x262.87x100)/(m_1x299.91)

(m_1=mass of nickel sulphate used, m_2=mass of complex).

A15.5.2

Preparation and standardisation of Mn(III) sulphate solution were given in Sec.12.4.1, together with the stoichiometry of the reaction of ascorbic acid with Mn(III) solution.

The number of ascorbic acid mols added=50x0.028/1000=m_1

[Mn(III)] when prepared in 6 M sulphuric acid is usually ~0.019 M

If the volume of this Mn(III) used in the titration is V cm^3

the number of mols of Mn(III)=Vx0.019/1000

∴The excess mols of ascorbic acid=½Vx0.019/1000=m_2

∴Mass of Ni in the complex=2(m_1-m_2)x58.69

%Ni in the complex=2(m_1-m_2)58.69x100/m_3=χ

(m_3=mass of complex weighed)
% Purity=χx100/19.57 (theoretical % of Ni=19.57)
(Ni(III) is assumed to react with ascorbic acid with the same stoichiometry as Mn(III)).

A15.6.1

237.70 g Ni salt give 482.2 g anhydrous complex
% Yield =(m_2x237.70x100)/(m_1x482.2)
(m_1=mass of Ni salt used, m_2=mass of complex formed).

The reference gives calculated % elemental analysis based on a wrong formula. The expected Ni content=12.2%. The reference gives also alternative oxidation conditions as well as the kinetics of the formation of the anion, electronic and ir spectral data, ^{1}H nmr spectral results and a spectrophotometric titration.

Other Ni(IV) octahedral complexes are reported in *Inorg.Chem.*14(1975)2178, including the preparation of the ligands and characterisation of the complexes by magnetic measurements, electronic and ir spectra and Ni(IV)/Ni(II) redox potentials.

A15.7.1

A simplified Orgel diagram for octahedral Ni^{2+} is qualitatively similar to that of octahedral V^{2+} or Cr^{3+} (Fig.14.1). Three bands are expected corresponding to the transitions:
$^3A_{2g} \rightarrow ^3T_{2g}$ (gives Δ_O); $^3A_{2g} \rightarrow ^3T_{1g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$
Δ_O and B' can be calculated. Δ_O is lower than Δ_O for the corresponding Cr^{3+} complexes due to the lower charge on Ni^{2+}. Since NH_3 is lower than en in the spectrochemical series, the position of the first band of $[Ni(NH_3)_6]^{2+}$ is at longer wavelength (it is in the ir region and not recorded in the spectrum except when the range of the spectrophotometer extends to 1000 nm). The energy of the longest wavelength transition gives Δ_O which increases in the series: water<ammonia<en.

The spectra (electronic and ir) of the complexes prepared in Sec.15.4.2.1 and 15.4.2.2 are reported in *Synth.React.Inorg.Met.-org.Chem.*11(1981)463 together with the corresponding Cu(II) complexes (Sec.16.4.3.2).

The reference also gives elemental analysis. The reference in A14.3.2.3 gives results on the corresponding $[Ni(en)_2]^{2+}$ complexes.

The diamagnetism of the above complexes as well as $Ni(HDMG)_2$ demonstrates their square planar geometry. On the other hand, the octahedral complex prepared in Sec.15.4.1 has a $(t_{2g})^6(e_g)^2$ configuration and 2 unpaired electrons with a magnetic moment a little >2.83 μ_B, the increase is due to the mixing of the ground level with the $^3T_{2g}$ level, thus introducing some orbital contribution to the magnetic moment. Simple Ni salts will exhibit similar magnetic behaviour.

The ir spectra are reported in the above references. The ir spectrum of $[Ni(NH_3)_6]^{2+}$ will be similar to other ammine complexes.

A15.7.2

*Inorg.Chem.*10(1971)1202 gives the preparation of the complex and its characterisation by spectral data (electronic and ir), magnetic measurements and polarographic data as well as elemental analysis. The reference also includes some substituted biuret complexes, and oxamidato-complexes. The electronic spectrum has bands at 461 nm, a shoulder at 410 nm and a strong band at 215 nm (ε_{max} 800 m^2 mol^{-1}). The effective magnetic moment is 2.5 μ_B, indicating considerable orbital moment. (See also *Educ.Chem.*12(1975)145, where biuret was prepared from urea).

A15.7.3

The reference in Sec.15.6.1 concludes that the lack of any significant esr signal confirms the oxidation state of Ni. This is also confirmed by its diamagnetism. Although no ir spectra have been reported in the reference the organic ligand is responsible for the ir bands which can be compared with those of $[Ni(HDMG)_2]$. The displayed uv spectrum is not extended to the visible region where absorption bands are expected from the colour of the complex. The electronic spectrum in the reference in A15.6.1 covers the visible and uv regions. The assignment of the bands can be based on the analagous diamagnetic Co(III) complexes.

A15.8 Further references

*Inorg.Chem.*4(1964)427 describes the preparation of Ni(II) alcohol complexes and their characterisation by spectral (electronic and ir) studies and elemental analysis. The kinetics of the dissociation of $[Ni(phen)_3]^{2+}$(aq.) was followed spectrophotometrically in *J.Chem.Educ.* 40(1963)264, including calculation of the activation energy. Tetrahedral $[M\ X_4]^{2-}$ complexes (M=Mn→Cu, X=Cl→I) were prepared as described in *J.Chem.Soc* (1959)3997 and their charge transfer spectra were recorded and discussed on the basis of a molecular orbital model in *J.Chem.Soc.*(1964)6226. Although $K_2[Ni(CN)_4]$ is easy to prepare and is also available commercially, it is unlikely to be used by students except by senior undergraduates under strict supervision. Another interesting related cyano-complex: $[Ni(NH_3)_2][Ni(CN)_4]$ forms clathrates where aromatic compounds can be incorporated as guests in the host Ni compound (*J.Chem.Educ.*40(1963)646).

Macrocyclic complexes of Ni(II) are reported in *J.Chem.Educ.*54(1977)580. This reference includes the preparation of the ligands as well as ir and nmr spectra. Such complexes are particularly stable due to the **macrocyclic effect.** Other Ni(II) complexes can be easily prepared e.g. $[Ni(NH_3)_6]Br_2$ (Inorg.Synth.3(1950)194; $[Ni(en)_3]Cl_2$ (.*ibid* 6(1960)198) and $[NEt_4]_2[NiCl_4]$ (*ibid.*9(1967)139.

The voltammetric determination of Ni and Co is described in *J.Chem.Educ.*74(1997) 1444 employing the standard addition method.

APPENDIX 16

A16.2.1

(a) (i) Cu dissolves slowly in the hot acid exposed to air, giving green $CuCl_2$(aq.);
    (ii) $Cu+2H_2SO_4 \rightarrow CuSO_4(aq.)+2H_2O+SO_2(g)$ (turns dichromate green);
    (iii) $3Cu+8H^++2NO_3^- \rightarrow 3Cu^{2+}(aq.)+4H_2O+2NO(g)$
    (in air gives brown NO_2 which is an acid anhydride);
    (iv) $Cu+4H^++2NO_3^- \rightarrow Cu^{2+}(aq.)+2H_2O+2NO_2(g)$ (tested as above);
(b) (i) $Cu^{2+}+H_2S \rightarrow 2H^++CuS(s)$ black, soluble in hot acid:
    $3CuS+8H^++2NO_3^- \rightarrow 4H_2O+2NO(g)+3S(s)+3Cu^{2+}(aq.)$;
    (ii) $Cu^{2+}+2OH^- \rightarrow Cu(OH)_2(s)$ blue precipitate, giving soluble hydroxo-complexes in excess hydroxide; converted to black CuO(s) on boiling;
    (iii) pale blue basic salt precipitates which is soluble in excess forming deep blue $[Cu(NH_3)_4]^{2+}$(aq.), which forms the paler EDTA complex;
    (iv) red brown $Cu_2[Fe(CN)_6]$ precipitates;
    (v) $2Cu^{2+}+4I^- \rightarrow I_2(aq.)+2CuI(s)$, flesh coloured precipitate which is soluble in boiling KI, producing $K[CuI_2]$; iodine in the filtrate turns starch blue;
    (vi) black $Cu(SCN)_2$ precipitates, changing to the white CuSCN(s) with H_2SO_3 or ascorbic acid;
    (vii) $Cu^{2+}+Fe \rightarrow Cu(s)+Fe^{2+}$ (turns red with phenanthroline due to the formation of $[Fe(phen)_3]^{2+}$);
    (viii)green colour or precipitate is formed (the reagent is a 5% (w/v) of the solid).
(c) Cu^{2+} in HCl imparts a green colour to the flame.
(d) $CuSO_4.5H_2O \rightarrow 4H_2O+CuSO_4.H_2O$ white, turns blue with water.

A16.2.2

(a) (i) Pale yellow hydrated Cu_2O precipitates which changes to red on heating;
    (ii) colourless $[Cu(NH_3)_2]^+$(aq.) (absorbs oxygen giving ultimately green basic precipitate of Cu(II) chloride);
    (iii) flesh-coloured CuI precipitates.
(b) The solid darkens before melting to a darker liquid.
(c) $2CuCl+2en \rightarrow [Cu(en)_2]Cl_2(aq.)+Cu(s)$ (dark red precipitate).

A16.3.1

499.36 g copper sulphate give 143.08 g copper(I) oxide
% Yield =(m$_2$x499.36x100/(m$_1$x143.08)
(m$_1$=mass of salt used, m$_2$=mass of oxide obtained)
$Cu_2O+2H^+ \rightarrow Cu^{2+}+H_2O+Cu(s)$
Molar ratio $1Cu^{2+}$:1Cu(s)

A16.3.2.1

190.45 g CuI gives 391.50 g of the complex
% Yield =(m$_2$x190.45x100)/(m$_1$x391.50)
(m$_1$=mass of CuI used, m$_2$=mass of product)
% CuI precipitated=48.7.% CuI=m$_3$x100/m$_4$=χ
(m$_4$=mass of complex used, m$_3$=mass of CuI produced)
% Purity=(χx100)/48.7

Nitric acid decomposes the complex to CuI and I_2. The latter reacts with iodate in conc.HCl according to:
$IO_3^-+2I_2+6H^++5Cl^- \rightarrow 5ICl+3H_2O$
If the volume of iodate used is V cm^3,
the number of mols of iodine=2xVx0.01/1000

Since 1 mol of complex gives ½ mol of iodine, the number of mols of complex=4xVx0.01/1000
The mass of complex=4xVx0.01x391.5/1000=m_2
∴ Purity=mx100/m_1 (m_1 is the mass of complex weighed)

A16.3.2.2

380.90 g CuI give 530.80 g of the complex
% Yield =(m_2x380.90x100)/(m_1x530.8)
(m_1=mass of CuI, m_2=mass of complex formed)
% CuI (for 100% purity)=71.76

The reference in A15.4.2.2 gives the quantum yield of iodine production as 0.02. The reference also contains analyses, spectra (electronic and ir) and any changes on uv irradiation of the complexes prepared in Sec.16.3.2.1, 16.3.2.2, 16.4.3.1, 16.10.1, 16.10.2, 16.10.3.

A16.4.1.1

CuSCN contains 52.24% Cu
∴Mass of Cu in 25 cm^3=0.5224xm (m mass of precipitate)
Mass of Cu dm^{-3}=0.5224xmx1000/25 g dm^{-3}

A16.4.1.2

If the volume of thiosulphate used is V cm^3
∴The number of mols of iodine=½xVx0.05/1000
The number of mols of Cu(II)=Vx0.05/1000
∴[Cu(II)]=Vx0.05/25 mol dm^{-3}

A16.4.2

The results of the kinetic study and the mechanism of the reaction are found in *J.Chem.Tech. Biotechnol.*33A(1983)116.

A16.4.3.1

249.68 g copper sulphate give 245.74 g of complex
% Yield =(m_2x249.68x100)/(m_1x245.74) (m_1=mass of copper salt, m_2=mass of complex)
% loss in mass at 150°C=35.05%
% Cu if pure=25.86

A16.4.3.2

170.47 g copper chloride give 846.52 g of the complex
% Yield =(m_2x170.47x100)/(m_1x846.52)
(m_1=mass of copper salt, m_2=mass of complex obtained)
If the volume of thiosulphate used is V cm^3
the number of mols of Cu(II)=Vx0.05/1000
∴Mass of Cu in the sample=Vx0.05x63.546/1000=m_2
∴% Cu in the sample=m_2x100/m_1=χ(m_1=mass of complex used)
% Purity=χx100/22.5 (theoretical %Cu is 22.5)

The corresponding $[Cu(en)_2][CuI_2]_2$ can be prepared and analysed in a similar way. Complexes of the cation with $[PbX_4]^{2-}$(X=Br or I) are reported by C.M.Harris; H.N.S.Schafer in *J.Proc.Roy. Soc.N.S.W.*, **Part 85**(1952)148.

A16.4.4

The Cu(II) complexes have one unpaired electron with a magnetic moment near 1.7μ_B. The spectra of the Cu(II) ammonia complexes are reported and discussed in F.A.Cotton, G.Wilkinson, *Advanced Inorganic Chemistry*, 5th edition, Wiley, 1988, p.770. The maxima of absorption at 790 nm for $[Cu(H_2O)_4(H_2O)_2]^{2+}$, at 590 nm for $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and at 640 nm for [[illegible]$)_4(NH_3)(H_2O)]^{2+}$ correspond to Δ_O values of 151, 203 and 187 kJ mol^{-1} respectively. The unique low value for the latter is due to a weaker LF where the two *trans*-ligands are further away from the rest.

The absorption band in DMF solution at 269 nm is close to the bands in the (en) complexes of Cu(II) and Ni(II) and are ascribed to the anion. The reference for the ir spectra was given in A15.4.2.2.

A16.5

249.68 g of copper sulphate give 304.77 g of complex $K[Cu(NHCO.NHCO.NH)_2]$

% Yield $=(m_2 x 249.68 x 100)/(m_1 x 304.77)$

(m_1=mass of copper salt, m_2=mass of complex formed)

Although the copper content can be determined by dissolving in 2 M sulphuric acid and titrating Cu(II) as in Sec.16.4.1.2, the method suggested was developed for the determination of the Cu(III) content of the superconductor YBCO (Sec.18.11.2). The Cu content of a pure sample=20.85%.

The values of ε_{max} for the chlorides of Fe(III), Cu(II) and Fe(II) were 165 , 61.5 and 1.6 $m^2\ mol^{-1}$ respectively. The corresponding λ_{max} were 335, 245 and 260 nm respectively. In the case of the prepared complex, the [Cu(III)] is obtained from the absorbance at either 335 or 245 nm (the latter corresponds to the Cu(II) formed by reduction).

A16.6

Silver nitrite and silver sulphate are slightly soluble. In (v) and (ix), a white precipitate is only formed from concentrated solutions; whereas metaphosphates give no precipitate with silver nitrate in (xii). White AgCl(i), Ag_2SO_3(v), $AgBrO_3$(vii), $AgIO_3$(viii), $Ag_4P_2O_7$(xii), Ag(OH)(xviii) precipitate with silver nitrate. $AgBO_2$(s) also precipitates:

$Na_2B_4O_7+3H_2O+2AgNO_3 \rightarrow 2H_3BO_3+2NaNO_3+2AgBO_2(s)$(xvi).

$Ag_2S_2O_3$(s) in (vi) is also white but dissolves quickly in excess solution, so it is necessary to add silver nitrate dropwise with shaking. The precipitate darkens on warming. All these precipitates are soluble in dilute ammonia. $AgBrO_3$ is soluble in hot water. Of the coloured precipitates: AgBr(in(ii)) is only soluble in conc.ammonia but yellow AgI(iii) is insoluble in ammonia. Yellow Ag_2SiO_3(a) in(xvi) and pale yellow Ag_3PO_4(s) in(x) and light brown Ag_2CO_3 in(xiii) are also soluble in dil.ammonia. Black Ag_2S is precipitated in (xvi) and dark brown Ag_2O(s) is precipitated in (xvii). Brown Ag_5IO_6 precipitates from periodate solutions.

A16.6.1

(a) A stain of AgCl is coloured black by Ag: $2Ag^++4OH^- +Mn^{2+} \rightarrow MnO_2+Ag+2H_2O$

(b) Red Ag_2CrO_4 appears as colour or precipitate.

A16.6.2

(a) These metals are above Ag in the electrochemical series, hence they replace it in its salt solutions, when dark silver particles precipitate.

(b) Ascorbic acid also reduces Ag^+(aq.) to Ag(s).

A16.6.3

(a) Ag^+ ions catalyse the oxidation of Mn(II) to purple permanganate.

(b) Ag^+ ions also catalyse the oxidation of Cr(III) to dichromate. In both cases a dark Ag(II) intermediate is formed but decomposes on heating.

(c) Decolourisation of Ce(IV) by Cl^- is rapid in presence of Ag^+ ions as catalysts.

A16.8

Even daylight will produce dark specs of Ag on thin layers of $AgNO_3$ solution. Using a low pressure mercury lamp and irradiating 200 cm^3 water, in which 0.2 g silver nitrate was dissolved together with 2.0 g anatase, for 30 minutes, the darkened P25 anatase was found to have gained 0.098 g. The silver deposit is easily dissolved by hot dilute nitric acid. Thus silver can be recovered from dilute aqueous solutions. The silverised P25 was found to have efficient photocatalytic properties (see Sec.5.4 and 5.14).

A16.9

^{110m}Ag was used to determine the adsorption of Ag^+ ions on rutile or anatase TiO_2. Atomic absorption and, in some cases, polarography were used to study the adsorption of Ag^+ ions by precipitated silica or pyrogenic silica. The results are found in *Surface Technology,*17(1982)165, including ΔG (for specific adsorption) and adsorption isotherms (Langmuir type).

A16.10.1

169.87 g silver nitrate give 234.77 g AgI
% Yield =$(m_2 x169.87x100)/(m_1 x234.77)$
(m_1=mass of silver nitrate, m_2=mass of AgI).
234.77 g AgI produce 670.60 g of the complex
% Yield =$(m_2 x234.77x100)/(m_1 x670.60)$
(m_1=mass of AgI, m_2=mass of complex)
Calculation of %I is similar to A16.3.2.1
% Ag in AgI=45.95

A16.10.2

The spectra are found in the reference in A15.4.2.2. The change in colour was reflected by the appearance of new peaks in the region 400-600 nm.

A16.10.3

245.74 g copper complex yield 855.03 g of the Cu/Ag complex
% Yield =$(m_2 x245.74x100)/(m_1 x855.03)$
(m_1=mass of copper complex, m_2=mass of complex prepared)
% Ag in AgI as above
% Ag in the 100% pure complex=25.23%

A16.10.3.1

The colour of the irradiated layer changes from green to brown, which suggests loss of iodine. The % loss in mass was 22.0%. The peaks in the electronic spectrum of a solution in acetonitrile did not appear after heating. Under prolonged irradiation, a yellow substance appeared at the edges. This substance: the original complex and AgI produced, showed fluorescence under uv irradiation.

A16.11.1.1

169.87 g silver nitrate give 482.27 g Ag(I) complex $[Ag(bipy)_2](NO_3)$
% Yield =$(m_2 x169.87x100)/(m_1 x482.27)$
(m_1=mass of silver nitrate, m_2=mass of complex obtained)
See *J.Chem.Soc.*(1930)2594.

A16.11.1.2

$[Ag(bipy)_2](S_2O_8)+4KI \rightarrow AgI+2K_2SO_4+2bipy+{}^3/_2I_2$
If the volume of thiosulphate used is V cm^3,
the number of mols of iodine=½xVx0.05/1000
% Purity=$({}^1/_3 xVx0.05x612.36x100)/(mx1000)$
(m=mass of complex weighed, 612.36 is its RMM).

A16.12 Miscellaneous references

A study of various $[Cu(N\text{-}N)_2]X_2$(N-N =diamine, X univalent anion) found a correlation between the far ir Cu-N stretching ν and the main electronic band (*Inorg.Chem.***10**(1971) 817).

The equilibrium and redox kinetics of the Cu(II)thiourea complexes are studied in *ibid*,**35**(1996)3210.

Copper(II)/D-galacturonic acid complex stability constant was determined by potentiometry (*J.Chem.Educ.*74(1997)1329). Various complexes, especially cationic and anionic Ag complexes are studied in *ibid*, **61**(1984)729.

The crystal growth of Ag during the electrodeposition on Cu substrates, studied by electron diffraction, was studied in *Z.Physik.Chem.Neue Folge.*1(1957)196.

Although the chemistry of gold is rich and interesting, the price of its compounds makes any experiments with them prohibitively expensive. See however, a study of Au sols in a reference in A18.14.1

The preparation of $K_2[Cu(C_2O_4)_2].2H_2O$ is given in *Inorg.Synth.*6(1960)1.

A study of its thermal decomposition is found in *J.Chem.Educ.*49(1972)365.

APPENDIX 17

A17.2.4

(a) NaOH precipitate the hydroxide $M(OH)_2$(M=Zn or Cd), the former is soluble in excess giving $[Zn(OH)_4]^{2-}$. Yellow HgO is obtained from Hg(II) solution.
(b) Ammonia also precipitates $M(OH)_2$, (M=Zn or Cd) soluble in excess to give ammine complexes. Hg(II) solutions give white $HgNH_2Cl(s)$ and $Hg_2NCl.H_2O(s)$.
(c) White ZnS is precipitated from alkaline or acetic acid solutions and is soluble in dil.mineral acids, yellow CdS precipitates from solutions acidified with 0.3 M HCl, soluble in hot dilute acids. Black HgS precipitates soluble in dil.nitric acid.
(d) White MNH_4PO_4 precipitates (M=Zn or Cd). Hg(II) solutions give double and basic phosphate solids.
(e) White $M_2[Fe(CN)_6]$ precipitates, the colour of the mercury compound slowly darkens in air, and eventually gives Prussian blue.

A17.2.1

(a) ZnO becomes yellow when hot, returning to white on cooling (surface partial loss of oxygen).
(b) (i) White zinc sulphite precipitates from acetic acid solution;
 (ii) orange zinc hexacyanoferrate(III)(s) precipitates;
 (iii) Mg replaces Zn which is formed as a dark powdery solid.

A17.2.2

(a) Yellow cadmium chromate precipitates.
(b) Colourless complex solutions $Cd(SCN)_x^{(x-2)-}$ are produced.
(c) Granules covered by precipitated Cd powder.

A17.2.3

(a) White Hg(II) thiocyanate precipitates, soluble in excess giving colourless complexes.
(b) Yellow HgI_2 precipitates and then changes to the red form which changes back to yellow on heating.
(c) White Hg_2Cl_2 is first precipitated, changing to dark grey Hg in excess of the reagent.
(d) Grey film of Hg is formed on cleaned Cu foil.

A17.2.4

(a) White Hg_2Cl_2 precipitates (blackened in ammonia giving $(Hg(NH_2)Cl)$.
(b) Black $Hg_2O(s)$.
(c) Black Hg+Hg/N compounds are formed.
(d) Yellow/green $Hg_2I_2(s)$ precipitates soluble in excess giving $[HgI_4]^{2-}$+black Hg(s).
(e) Golden $Hg_2CrO_4(s)$ precipitates.
(f) Grey/black Hg(s) is formed.
(g) Same as in (f) above.

A17.3.1

The preparation of the buffer solution is given in A3.4.1.
If the volume of EDTA used is V cm^3,
the number of mols of Zn ions=Vx0.01/1000
$[Zn^{2+}]$ in solution=Vx0.01/25 mol dm^{-3}

A17.3.2

Indicator solution: 1% solution of solid indicator in conc.sulphuric acid.
Dissolve 0.3 g of purest $K_3[Fe(CN)_6]dm^{-3}$ in the solution of the hexacyanoferrate(II). The reaction is represented by:

$3Zn^{2+}+2K_4[Fe(CN_6]\rightarrow K_2Zn_3[Fe(CN)_6]_2(s)+6K^+$

When Zn(II) is quantitatively precipitated, the excess $[Fe(CN)_6]^{4-}$ causes a sudden change in the redox potential, which is indicated by the change in colour of the redox indicator. The titration should be carried out with vigorous shaking, avoiding rapid addition of the hexacyanoferrate(II) solution.

If the volume of this solution used is V cm^3,
the number of mols of $Zn^{2+}={}^3/_2xVx0.05/1000$ in 25 cm^3
$\therefore[Zn(II)]={}^3/_2xVx0.05/25$ mol dm^{-3}

A17.3.4

% Zn in the precipitate $[Zn(C_9H_6ON)_2]$=18.49
If the mass of the precipitate is m g, the mass of Zn is 0.1849 m
[Zn(II)]=0.1849xmx1000/(25x65.38) mol dm^{-3}

A17.3.5

The reference in Sec.4.5.2.1 gives fluorescence spectra of zinc oxinate.

A17.4.1

287.54 g zinc sulphate give 307.11 g of the complex
% Yield $=(m_2x287.54x100)/(m_1x307.11)$
(m_1=mass of zinc sulphate, m_2=mass of complex)
The HCl neutralises the ammonia in the complex, the excess acid is titrated with NaOH.
Mols of HCl used=50x0.1/1000=m_1
Mols of NaOH used=Vx0.1/1000=m_2 (V is the volume of NaOH used)
Mols of NH_3 in the sample=m_1-m_2
Mass of NH_3 in the weight used=$(m_1-m_2)x17.03$
% Ammonia $=(m_1-m_2)x17.03x100/m_3=\chi$ (m_3 mass of complex weighed)
% Purity $=\chi x100/22.18$ (22.18 is the theoretical % of ammonia)

A17.4.2

287.54 g zinc sulphate give 281.61 g of the complex
% Yield $=(m_2x287.54x100)/(m_1x281.61)$
(m_1=mass of zinc salt, m_2=mass of complex obtained)
For ir data see reference in A4.6.3.

A17.5.1

For preparation of indicator see A4.6.3
If the volume of EDTA used is V cm^3,
the number of mols of Cd(II)=Vx0.05/1000
[Cd(II)]=Vx0.05/25 mol dm^{-3}

A17.5.3

% Cd in Cd oxinate=27.91 If the mass of the precipitate is m g
Mass of Cd in original solution=mx0.2791x1000/25 g dm^{-3}
[Cd(II)]=(mx0.2791x10000/(25x112.41) mol dm^{-3}

A17.7.1

$Hg_5(IO_6)_2+34KI+24HCl=5K_2[HgI_4]+24KCl+12H_2O+8I_2$
If the volume of thiosulphate is V cm^3,
the number of mols of iodine=½xVx0.05/1000
$\therefore$The number of mols of Hg=5xVx0.05/(1000x16) in 25 cm^3
$\therefore$[Hg(II)]=5xVx0.05/(16x25) mol dm^{-3}

A17.7.2

λ_{max} was at 480 nm. A calibration curve of absorbance against [Hg(II)] in the range of 0.2-2.0 g dm^{-3} was drawn. A recent modification of the extraction is described in *J.Chem.Educ.* 67(1990)608. The article also describes a similar process for the determination of low lead concentrations.

A17.7.3

% Hg in $Hg_5(IO_6)_2$=69.23

The mass of Hg in the precipitate (m g)=0.6923xm g in 25 cm^3

[Hg(II)] in original solution=(0.6923xmx1000)/(25x200.59) mol dm^{-3}

A17.8.1

The reference gives the transition temperature in (a) at 50°C and in (b) at 67°C.

A17.8.1.1

$Cu_2[HgI_4]+2KI \rightarrow 2CuI(A)+K_2[HgI_4](B)$

$CuI+KSCN \rightarrow CuSCN(C)+KI(D)$

$3CuSCN+8HNO_3+2H_2O \rightarrow 8NO+3CO_2+3NH_4^{+}+3CuSO_4(aq.)$

$6I^{-}+16H^{+}+2CrO_4^{2-} \rightarrow 2Cr^{3+}+8H_2O+3I_2(aq.)$, this is extracted by carbon tetrachloride to give a violet organic layer.

(i) $[HgI_4]^{2-}$+Cu, deposit of Hg on the surface of Cu ;

(ii) black HgS precipitates eventually. Initially $2HgS.HgCl_2$ may be formed. In (i) and (ii), the presence of Hg^{2+} ions, formed in equilibrium with $[HgI_4]^{2-}$ is responsible for the reactions observed.

A17.9

Hg-Hg distances in Hg_2Cl_2 were found to be 253 nm, appreciably smaller than the sum of the atomic radii: 310 nm. The three prepared solutions are 0.05 M assuming Hg(I) nitrate is $Hg_2(NO_3)_2$. Its molar conductivity is close to that of $Ba(NO_3)_2$, both are ionised to three ions unlike KNO_3. The diamagnetism confirms that no Hg^{+} is found in the solid which would have an unpaired electron.

A17.10.1

Low pressure mercury lamps emit mainly the resonance line at 254 nm. The corresponding energy would promote valence electrons from either of the three photocatalysts to their conduction band. On reaching the surface, these electrons reduce Ag^{+} ions to metallic silver which is deposited as a dark layer on the catalyst particles. The increase in mass after irradiation indicates the mass of silver deposited. H_2O_2 restores the colour of ZnO to white by converting Ag to Ag^{+}(aq.).

A17.10.2

Table A10.1 gives the results of removal of Hg(II) using Hanovia chromatolite for 30 minutes.

Table A10.1

$[Hg(NO_3)_2]$/M	% Hg left	Photocatalyst
0.05	1.5	P25
0.05	3.3	WO_3
0.005	10	P25
0.005	20	ZnO
0.005	15	WO_3
$[HgCl_2]$/M		
0.05	5.4	P25
0.05	7.5	ZnO

A17.10.3

The % Cd(II) in the irradiated suspension dropped quickly in the first two hours but was little changed beyond 2 hours. The mass of Cd deposited on the catalyst (P25 anatase) increased linearly as the mass of catalyst increased up to 2.0 g/500 cm^3. The increase in the % reduction with [MeOH] is depicted in Fig.A17.1. The little change in the % of reduction after 2 hours could be due to the deposited Cd on the P25 surface which does not allow the uv light to reach the catalyst particles. The increase in the extent of reduction with [MeOH] is expected since the alcohol is an efficient hole scavenger, thus preventing the hole/electron recombination. Measurements of [Cd(II)] were carried out using an inductively coupled plasma-optical emission system.

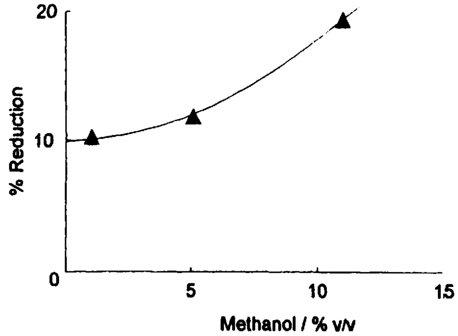


Fig. A17.1 The % reduction in cadmium concentration as a function of % methanol.

A17.10.4

See *Solar Energy Materials and Solar Cells*,**40**(1996)1 for some results.

A17.11 Miscellaneous references

Determination of low concentrations of Hg in the gas phase or in solution are best carried out by atomic absorption (N.S.Poluektov *et al*, *Zh.Anal.Khim.***19**(1964)873; *Analyst*,**96** (1971)847).

Fluorescein mercury(II) acetate is available commercially and was used for the determination of its emission lifetime (*J.Chem.Educ.***74**(1997)853).

The effect of ionic strength on the solubility product of $Cd(NO_3)_2$ is discussed in *J.Chem.Educ.* **36**(1959)125. Ionic strength $=\Sigma(m_iZ_i^2)/2$ where m_i and Z_i are the molar concentration and charge respectively of the ions i.

The separation of metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) as chloro-complex anions can be affected on an anion exchange resin (*J.Amer.Chem.Soc.***72**(1950)4293).

APPENDIX 18

A18.2

The results show that $t_{1/2}$~70s. Quick work gives higher count rates and hence better results. Longer shaking time for solvent extraction gives lower count rates in spite of a greater extent of extraction. The procedure was used for A level classes. If the aqueous layer is counted, the growth of the Pa activity will be demonstrated. In this case, it is essential to decontaminate the liquid counter immediately by soaking in Decon solution. It was noticed that the counting efficiency of the liquid counters was somewhat different in different counters. A standard ^{90}Sr cylinder, supplied by Amersham International, can be used to compare the efficiency of the different counters.

A18.3

A strip of ^{90}Sr was cut into smaller strips for use by more than one student. The lead castle used was IDL710A (newer models of this and the other counting equipment have been introduced) together with NE scaler 7000 and quench unit 2130 connected to the G-M counter (Mullard MX123). Fig.18.1 shows the arrangement of the source ^{90}Sr, the thin and thick aluminium plates: Al and the other metal absorber M, which may be Al, Fe, Cu or Pb. In absence of the absorber, only the β^- particles scattered by the thin lining of the castle will be counted if it reaches the end window of the G-M counter through the holes in the plates. In a typical experiment this was 0.39 cps. Using Al plates of different thicknesses for back scattering the following corrected count rates were observed.

Thickness/mg cm^{-2}	21.6	55	82	240	430	712	1335	1693
count rate/c.p.s.	5.24	8.66	12.01	13.34	13.31	14.16	14.50	14.47

The results show clearly that the back scattering increases rapidly with the metal thickness until it reaches a plateau value (the difference between the two latter values is a result of the expected scatter in the count rate when the counting period is not long enough).

Using thick metal plates, plotting the corrected count rates against log (atomic number Z) nearly a line can be drawn for Al, Fe, Cu and Pb. Keeping the source in the same position but moving the thick Al absorber further away from the source, the back scatter count rate decreased as expected. Keeping the absorber in the same position but changing the position of the Sr source led to a clear change in the back scatter count rate. It is also known that the back scatter percentage depends on the maximum β^- energy. The saturation thickness is about a fifth of the extrapolated range of the β particles in the metal. See also *Anal.Chem.***29**(1957)969.

A18.4

Full results are found in *J.Phot.Sci,***29**(1981)249. The reference also includes results of the exchange between Ag-labelled nitrate solution and inactive AgI (prepared as in the procedure described) and the effect of heating the solid prior to the exchange. See also *Z.anorg.allgem. Chem.***304**(1960)296.

A18.5

A stock labelled sulphate solution (5 m Ci or 185 M Bq in 10 cm^3):0.05 cm^3, measured with a micropipette made up to 150 cm^3.

I The time to collect 40,000 counts from each planchet was measured. For the planchet backed by Al, 38.60 min. and 38.19 min. were measured using the same set-up as in Sec.18.3. The other planchet with steel backing gave 25.56 min.

II The count rate for the thin precipitate was 1814.3 cpm whereas the thick sample gave a count rate of 1625.7 cpm. Using various amount of ^{35}S solution, it can be seen that the count rate increases to a plateau as the thickness of the precipitate increased.

A18.6.1
For typical results using MnO_2, In or Cu foil as targets see M.W.Rophael; M.A.Malati, *Praxis Naturwissenschaften*,**23**(1974)262; *Phys.Educ.*13(1978)353. The neutron source and the principle of neutron activation are discussed in these references

A18.7.1
The NE system used has been improved in the new models. The plot of corrected count rate *vs* time, using semilog paper, was extrapolated to the time of withdrawal from the source to give the initial count rate in cps. The initial activity of the standard was 15.24 cps and its V content was 0.126 g. The V content of V(III) complex, whose initial activity was 13.55 cps was 15.6% compared to the expected % of 14.6. For the V(IV) complex, the % V found=18.9% compared to the expected 19.2%.

A18.8
From the end-point of titration, the lanthanum solution was 0.099 M i.e. 3.2 g of the nitrate and 1.1 g of water of crystallisation.∴The formula is $La(NO_3)_3.6H_2O$. For another example of $Na^{187}WO_4/BaCl_2$ titration see *Educ.Chem.*21(1984)158. Even when the labelled element has a shorter half-life, it is possible to carry out the titration, allowing for the decay of the activity during the experiment. Thus it was possible to titrate $^{116m}InCl_3$ against $K_3[Fe(CN)_6]$ solution.

A18.9
See Malati, *Isotopen praxis*,**27**(1991)305 for results of Szilard-Chalmers and exchange processes.

A18.10.1.1
See Chem.Ind.(1970)649 and references therein for results of the determination of [sodium oleate].

A18.10.1.2
The cmc of sodium oleate was $\sim 10^{-3}$M at 25ºC using surface tension/concentration plots where there is an intersection between a rapidly decreasing nearly linear part and the slightly decreasing linear part. The ring method was used for the measurements. Modern Tensiometers are automated to measure surface or interfacial tension as well as the cmc. See also NSRDS, NBS.**36**, National Bureau of Standards, U.S. Government Office, Washington, 1971.

A18.10.2
See *J.Appl.Chem.*17(1967)1 for the results.

A18.10.3
See A.A.Yousef; T.R.Boulos, *Tenside*,6(1969)322 for results, including aromatic hydroxy compounds and their frothing behaviour.

A18.11
See also A.Henglein; H.Weller in *Photochemical Energy Conversion*, Eds. J.R.Norris; D.Meisel, Elsevier Science, 1989, which includes other "size-quantised" semiconductors.

A18.12.1
For a brief background information and results of preparation and characterisation see M.A.Malati, *Chem.Labor Betrieb*,**42**(1991)M42.

A18.12.2
A summary of the analysis is given in *Anal.Proceedings*,**29**(8)(1992)371.
Using m g of superconductor, if the mass of barium sulphate precipitate is m_1,

% Ba=0.5885xm_1x100/m
If the mass of CuSCN is m_2 g,
% Cu=0.5224xm_2x100/m

The average of duplicate determinations for two prepared samples was 41.3 and 40.8% Ba and 28.9 and 27.9% Cu.

The % Cu(III) using the titrimetric method (*J.Solid State Chem.*69(1987)182) was 1.85 and 2.41 for the two samples. A potentiometric modification is described in *J.Chem.Educ.*71(1994)A115.

A18.12.3

The spectrum of standard Y arsenazo solutions in HCl, measured against the indicator solution showed a maximum at 648 nm. A linear calibration plot of absorbance at this wavelength against [Y] was established over the range 0.1- 4x10^{-5} M. Using this method the % Y was 12.8 and 15.4 for the two samples. An EDTA titration (*Anal.Chem.*30(1958)1111) gave the % Y of 13.5 and 13.8 for the two samples. In applying this titration, the pH was adjusted to 5.5-6.5. Diethyldithiocarbamate was used as a masking agent. The metal dithiocarbamates were removed by chloroform extraction, adding sulphosalicylate to prevent rare earth hydroxide precipitation during extraction.

A18.12.5

The results are found in *J.Chem.Tech.Biotechnol.*51(1991)71; the catalytic effect on $N_2H_5^+$ decomposition is also discussed in *ibid.*61(1994)117.

A18.13.1

The reference gives results at two temperatures and reports the effect of pH and solvent on the rate of decay and the catalytic role of Ag and Cu ions.

A18.13.2

If the total volume of iodine solution is V_1 cm^3,
the number of mols of iodine added=V_1x0.05/1000=m_1
If the volume of thiosulphate reacting with the excess iodine is V_2 cm^3
the number of mols of excess iodine=½V_2x0.05/1000=m_2
∴The number of mols of iodine reacting with ascorbic acid
=m_1-m_2
$\because I_2+C_6H_8O_6\rightarrow C_6H_6O_6+2H^++2I^-$
∴The number of mols of ascorbic acid=(m_1-m_2 (in 25 cm^3)
[$C_6H_8O_6$]=(m_1-m_2)x1000/25

See *J.Chem.Educ.*51(1974)488. Several other oxidants have been used for the titration, see G.G.Rao, V.N.Rao *Z.Anal.Chem.*147(1955)338. J.Barek; A.Berka, *Anal Lett.* 8(1975)57. A thermometric titration method using Ce(IV) is described in *Analyst*, 112(1987)507. The kinetics and mechanism of the reaction were studied in K.C.Rajanna *et al*, *Indian.J.Chem.*17A(1979)66. The kinetics and mechanism of the oxidation by permanganate are reported in *Z.Phys.Chem. Leipzig.*263(1981)622.

A18.13.3

Several papers deal with this reaction e.g. the effect of ionic strength (*J.Chem.Educ.*57(1980)158), using flow injection technique (*ibid*,74(1977)560), the equilibrium constant of the reaction (*ibid*, 71(1994)438); the alkali metal catalytic effect on the reaction (*J.Chem.Soc., Faraday Trans.* 89(1993)3571) and the reaction at elevated pressure (*Inorg.Chem.*33(1994)1881). The latter reference includes study of the corresponding Ru(III) and Os(III) complexes and values of ΔV_a. An example of the wide range of the reducing power of ascorbic acid is its reduction of Ag(I) (*J.Chem.Soc., Dalton Trans.*(1974)1460.

A18.14.1 Miscellaneous colloid chemistry experiments

Further colloid/surface chemistry experiments references: coagulation kinetics using AgI hydrosol (*J.Chem.Educ.*68(1991)523; verification of the Schulze/Hardy rule using Au hydrosol (*ibid.* 71(1994)624); determination of critical micelle concentration of surfactants using a colorimetric method (*ibid.*70(1993)254); density gradient columns displaying acid/base and metal ion (V, Cr, Fe, Co, Ni) equilibria (*ibid.*63(1986)148).

A18.14.2 *Miscellaneous experiments*

Other general physical chemistry experiments include: using cyclic voltammetry and the quinone/hydroquinone equilibrium to illustrate the Nernst equation (*ibid*,74(1997)1195), the effect of ionic strength on the dissociation of bromocresol green (*ibid*,40(1963)252); kinetics of consecutive reactions (*ibid*,75(1998)917); deuterium kinetic isotope effect in the hydrolysis of acetic anhydride (*ibid*,74(1997)562). Double wavelength spectrocopy is discussed in (*ibid*, 44(1972)73A including application to Ce/Er.

A18.4.3 *Miscellaneous nuclear and radiochemical references*

Other neutron activation experiments are given in M.W.Rophael; M.A.Malati, *Chem. Labor. Betrieb*,34(1983)51; *Educ.Chem.*12(1975)35; *ibid.*21(1984)158; *J.Radioanal. Chem.* 42(1978)35; 54(1979)399; *Radiochem.Radioanal.Letters* 32(1978)141; *J.Chem. Technol. Biotechnol.* 31(1981)11.

Other radiochemical experiments using other radioisotopes include: *J.Radioanal.Chem.*52(1979)477;*Radiochem.Radioanal.Letters*.35(1978)305;*J.Appl.Chem. Biotechnol.*24(1974)113; *Internat.J.Mineral Processing*,1(1974)267.

The above references in this section were published jointly with my collaborators.

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