1
Introduction

Inorganic Experiments, Third Edition. Edited by J. Derek Woollins

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1.1
Introduction

J. Derek Woollins

Chemistry remains a practical subject and for many of us the topics we recollect most sharply (and understand most thoroughly) are often derived from our own experiences in the laboratory. Meaningful experiments which develop laboratory skills, introduce interesting chemistry and are reliable are not always easy to find. This text seeks to address the problem for inorganic chemists. The following compilation of experiments in no way attempts to cover all of inorganic chemistry. However, I hope that there is sufficient range to demonstrate the majority of the important techniques in the context of some interesting and stimulating chemical examples. The experiments have generally come from laboratory courses where they have been tried and tested or they have been checked so we can optimistically assume that they 'work'. For convenience, the experiments have been classified (by me — not the authors) into 'introductory', 'intermediate' and 'advanced'. Clearly, laboratory course organisers must make their own assessment as to the level of difficulty of individual experiments in the context of their laboratory facilities, experience of the students, etc. In general, we have not described measurement methodology in great detail, again on the assumption that facilities differ from one laboratory to the next. Furthermore, some experimental arrangements differ depending on the origin of the submission. This is the case in research and in industry and I have made no effort to impose any house style, there is much to be learnt from the differences!

The experiments are usually prefaced by a section detailing any special safety precautions. Although this is an aid for the user, it should not be assumed that all aspects of safety have been dealt with — the laboratory course supervisor and the student performing the experiment **must** make their own assessment as to the hazards which the chemicals and procedures represent. Although we have made every reasonable effort to test experiments and to provide appropriate safety data and instructions, the authors and the editor do not assume any responsibilty or liability for any mishaps or accidents that may occur in the use of any part of this text as a laboratory manual.

In this revised edition, I have added 18 additional experiments, bringing the total available to just under 100. I am grateful to Petr Kilian, who has provided a brief chapter dealing with reporting of data. I have taken the opportunity to reorganise the order of the experiments into coherent groupings. Alert readers will

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also notice that there are possibilities to link together experiments, e.g. the synthesised Ph_3PO from Experiment 2.20 can be utilised in a coordination chemistry Experiment 2.14.

I wish to express my gratitude to all the authors who have so readily contributed experiments to this third edition.

1.2
General Spectroscopic Techniques and Report Writing

Petr Kilian

The following sections are derived from 'good practice' at St Andrews. They do not represent the only way to collect and report spectroscopic data, but it is hoped that they will serve as indications of good practice.

1.2.1
General Spectroscopic Techniques

1.2.1.1
Preparation of Samples for Infrared Spectroscopy

A) Use of NaCl (or KBr) Sample Plates

Note: Alkali metal halide plates used in IR spectroscopy must be handled only by their edges, never by their polished faces. They dissolve on contact with water!

The sample plates are mounted in a plate holder and placed in the sample beam of the spectrometer. After use, the plates are wiped clean with a tissue dampened with dichloromethane and stored in a tube containing silica gel.

a) Liquid Samples

For liquids, it is normally appropriate to measure IR spectra as thin films. A small drop of the substance is placed on a polished face of a sodium chloride plate. A second plate is placed on top and the two plates are squeezed firmly together. Any excess sample squeezed out is wiped off with a clean tissue.

b) Solid Samples

Solids may be run as a KBr disc or a paste in Nujor (Nujol mull).

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B) Nujol Mull Preparation

Nujol is a mixture of alkanes and therefore contains only C–C and C–H bonds; hence it has a comparatively simple spectrum (see Fig. 1.2-1), the principal absorptions of which are associated with C–H vibrations. These absorptions should be subtracted from the final spectrum to obtain the spectrum of the solid.

1. A small amount of the solid is placed in the agate mortar and ground thoroughly to a very fine powder.
2. A small drop of Nujol is added and the mixture ground again to give a thick paste.
3. The paste is placed on the polished face of a sodium chloride plate.
4. A second plate is placed on the first and the mull is squeezed between the plates until it appears to be a thin translucent smear between the plates.

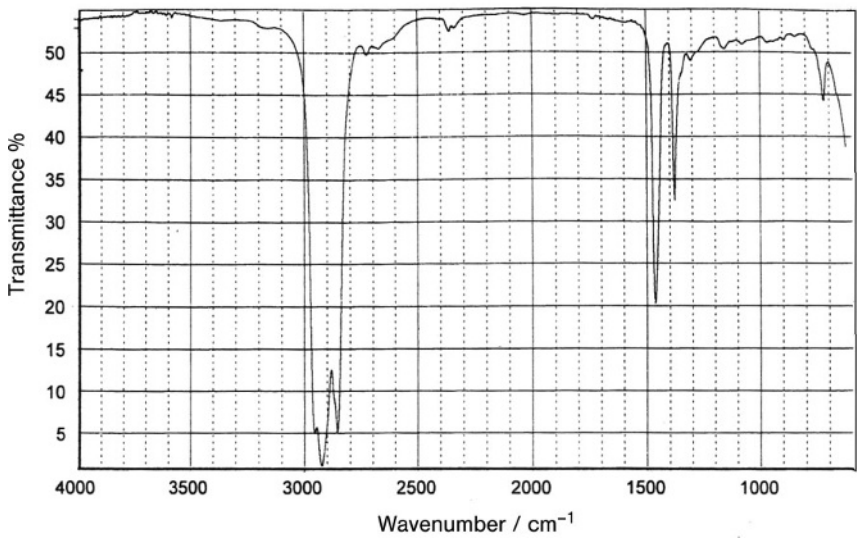

Fig. 1.2-1 IR spectrum of Nujol.

C) Use of a Mini-Press for KBr Pellet Preparation

a) Sample Grinding

Dried spectroquality potassium bromide (KBr) is used as the matrix. Thoroughly grind approximately 2–3 mg of solid sample (with experience you will see that this is enough to cover the tip of a microspatula) with 100 mg of KBr in a dry agate mortar and pestle. Grind thoroughly for 3–5 minutes, until the resulting powder is like talc.

b) Forming the Pellet

Place one dry bolt into the dry barrel and advance five full turns. Deposit ground matrix and sample on the surface of the bolt inside the barrel. Tap the unit gently to spread the sample uniformly over the lower bolt. Insert second bolt and advance until finger tight. Using two ring spanners, gradually exert pressure on each bolt. To operate more easily, the lower bolt may be placed in a bench vice and the top tightened with a wrench. Apply pressure for about 1 minute, then remove bolts. If one bolt holds tight in the barrel, use a vice on the flats of the barrel with wrench on the bolt.

c) Clean-Up

The pellet is best removed, and the barrel and bolts cleaned, using hot water followed by rinsing with acetone, blotting with a tissue, then oven drying for a few minutes. **Note:** Do not attempt to punch out the pellet or to drive it out with one of the bolts – this may damage the barrel or the polished die surface. Take care in the oven not to scratch the polished bolts. Ensure that the KBr is removed completely, then return the barrel and bolts to the desiccator. Ensure the clean-up is performed for the benefit of the next user!

The quality of spectrum is affected by the grinding and by the amount of sample in the matrix; see the example spectra in Figures 1.2-2 and 1.2-3.

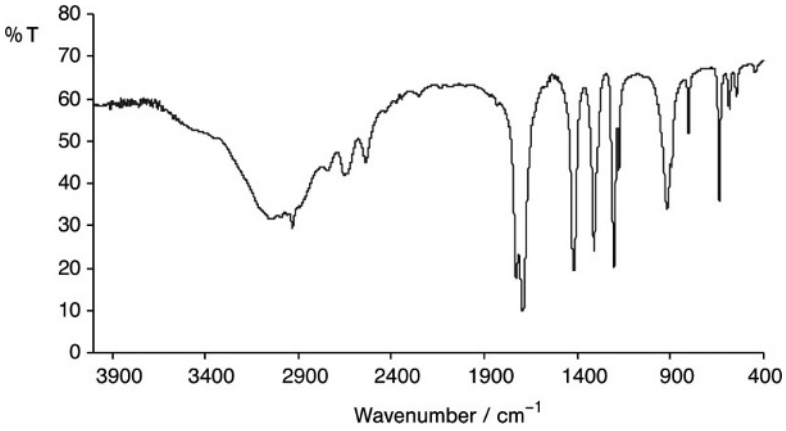

Fig. 1.2-2 Good-quality IR spectrum.

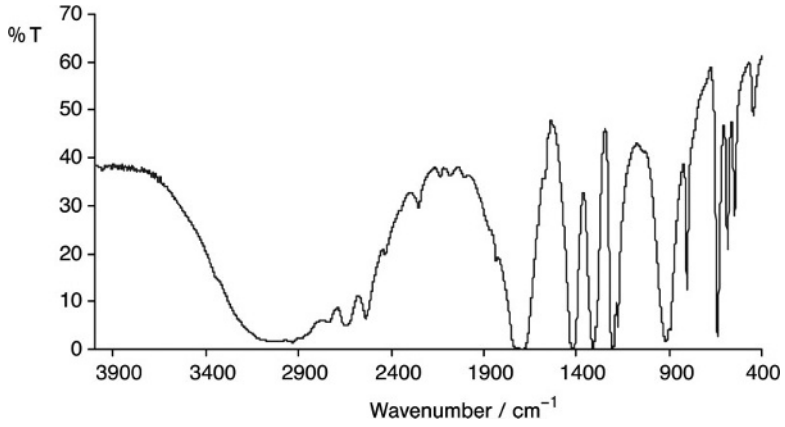

Fig. 1.2-3 Spectrum with too much sample in the pellet.

Further Reading (including help with assignments)

K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc., New York, **1978**.

1.2.1.2

Preparation of Samples for Raman Spectroscopy

Use of glass sampling accessories (e. g. melting point capillary) is possible in Raman spectroscopy, as the spectrum is usually obtained using a near-infrared laser beam which is not absorbed by ordinary glass. Seal one end of a melting point capillary using a Bunsen burner. Fill the capillary to *ca*. 10 mm height with your sample by scooping it from a sample vial and compact by gentle tapping. The open end of the capillary can be sealed using Blu-Tack.

1.2.1.3

Preparation of Samples for UV-Vis Spectroscopy

The sample concentration should be chosen such that the maximum absorbance of the band of interest does not exceed 2 and is preferably close to 1. Remember that the absorbance is usually proportional to concentration (Beer's law: $A = \varepsilon cl$, where ε (epsilon) is the extinction coefficient in units of $dm^3\ mol^{-1}\ cm^{-1}$, c is concentration in mol dm^{-3} and l is the pathlength in cm.

1.2.1.4 Preparation of Samples for ^{1}H NMR Spectroscopy

To run an NMR experiment, the sample compound must be dissolved in a deuterated solvent (normally $CDCl_3$) and transferred to an NMR tube. It is important to filter the sample prior to running the experiment since small solid particles can lead to a distorted NMR spectrum. The NMR tube must first be cleaned and thoroughly dried. You will soon find out that acetone is not as volatile as you think; it is the most common contaminant in NMR spectra. Wash tubes with water, then rinse with acetone and finally with dichloromethane.

For each ^{1}H spectrum, *ca.* 10 mg of sample is required. Note that it is not advantageous to put in more than this as this will reduce the resolution of the spectrum. The sample is dissolved in ca. 0.7 cm^3 of the appropriate deuterated solvent, usually deuterated chloroform ($CDCl_3$) unless otherwise instructed in the experimental procedure. If there is any undissolved material in the sample, then the solution **MUST** be filtered (through e.g. a cotton-wool plug in a disposable pipette) before it is placed in the NMR tube. The depth of sample is also very important; it has to be between 50 and 60 mm. It is also very important that the outside of the tube is clean, so give it a wipe with some tissue.

Make up your sample as instructed above and write a legible sample code on the side of the NMR tube (e.g. for J. A. Smith the code might be JAS001) and place the tube in the appropriate sample rack for your NMR queue. Add your name and details of the sample to the list. These details will be necessary for subsequent identification of your spectrum.

Remember when analysing the spectrum obtained from your sample to watch for the signal due to the solvent. The signal for residual $CHCl_3$ present in $CDCl_3$ is at 7.27 ppm. Further common contaminants include the solvent used in the reaction and work-up (e.g. hexane), water and vacuum grease. To help you identify these, a table of chemical shifts of residual protons in common deuterated solvents is given in Table 1.2-1.[1)]

Table 1.2-1 Chemical shifts of residual protons in common deuterated solvents.

	Proton	Multiplicity	$CDCl_3$	$(CD_3)_2CO$	C_6D_6	D_2O
Solvent residual peak			7.26	2.05	7.16	4.79
H_2O	OH	s	1.56	2.84	0.4	
Acetone	CH_3	s	2.17	2.09	1.55	2.22
Benzene	CH	s	7.36	7.36	7.15	
Chloroform	CH	s	7.26	8.02	6.15	
Dichloromethane	CH_2	s	5.30	5.63	4.27	
Diethyl ether	CH_3	t	1.21	1.11	1.11	1.17
	CH_2	q	3.48	3.41	3.26	3.56
Ethanol	CH_3	t	1.25	1.12	0.96	1.17
	CH_2	q	3.72	3.57	3.34	3.65
	OH[a)]	s	1.32	3.39		

1) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

Table 1.2-1 (continued)

	Proton	Multiplicity	$CDCl_3$	$(CD_3)_2CO$	C_6D_6	D_2O
Ethyl acetate	CH_3CO	s	2.05	1.97	1.65	2.07
	CH_2CH_3	q	4.12	4.05	3.89	4.14
	CH_2CH_3	t	1.26	1.20	0.92	1.24
Grease	CH_3	m	0.86	0.87	0.92	
	CH_2	br s	1.26	1.29	1.36	
n-Hexane	CH_3	t	0.88	0.88	0.89	
	CH_2	m	1.26	1.28	1.24	
Methanol	CH_3	m	3.49	3.31	3.07	3.34
	OH	br s	1.09	3.12		
Silicone grease		s	0.07	0.13	0.29	
Toluene	CH_3	s	2.36	2.32	2.11	
	CH(*o*, *p*)	m	7.17	7.1–7.2	7.02	
	CH(m)	m	7.25	7.1–7.2	7.13	

a) The signals from exchangeable protons are not always identified.

1.2.1.5 Preparation of Samples for ^{13}C NMR Spectroscopy

The same rules apply for preparation of samples for ^{13}C NMR as for ^{1}H NMR analysis, the only difference being the concentration of the sample needed. As the sensitivity of ^{13}C NMR is two orders of magnitude lower than that of ^{1}H NMR, **very concentrated sample** is needed (the recommended amount to obtain a good spectrum is 100 mg). ^{13}C chemical shifts of common solvents as trace impurities are shown in Table 1.2-2.[2)]

Table 1.2-2 ^{13}C chemical shifts of common solvents as trace impurities.

	Carbon	$CDCl_3$		Carbon	$CDCl_3$
Solvent residual peak		77.16	Grease	CH_2	29.8
Acetone	CO	207.1	*n*-Hexane	CH_3	14.1
	CH_3	30.9		CH_2(2	22.7
Benzene		128.4		CH_2(3)	31.6
Dichloromethane		53.5	Methanol	CH_3	50.4
Diethyl ether	CH_3	15.2	Silicone grease		1.0
	CH_2	65.9	Toluene	CH_3	21.5
Ethanol	CH_3	18.4		C(*i*)	137.9
	CH_2	58.3		CH(*o*)	129.1
Ethyl acetate	CH_3CO	21.0		CH(*m*)	128.3
	CO	171.4		CH(*p*)	125.3
	CH_2	60.5			
	CH_3	14.2			

2) The signals from exchangeable protons are not always identified.

1.2.1.6
Conductivity

In brief, with the exception of H^+ or OH^-, which have hydrogen-bonding chain conduction mechanisms, most singly-charged ions have a molar conductivity of roughly 60 Ω^{-1} cm^2 mol^{-1} and thus a 1:1 electrolyte MX has a conductivity of around 120 Ω^{-1} cm^2 mol^{-1}. Comparisons with molar conductances of known ionic substances allow one to determine the number of ions present in a given salt. Slow-moving large or highly charged ions will give lower values; for complex ions this can reach the point where the determination becomes uncertain. Typically, 10^{-3} mol dm^{-3} solutions are used for measurements.

Typical molar conductances (Ω^{-1} cm^2 mol^{-1}) in water for various ion conductors are as follows:[3)]

	1:1	1:2	1:3	1:4
Λ_m	96–150	225–273	380–435	~540

1.2.1.7
Magnetic Susceptibility

Background

Magnetic susceptibility is a measure of the tendency of molecular magnets to align themselves with an applied field, and from the degree of paramagnetism observed we can assess the number of unpaired electrons in a sample. The effect is temperature dependent, since thermal vibration causes some magnetic randomisation and a number of other magnetic influences cannot be compensated for. Hence the result is approximate although generally unambiguous.

In the traditional Gouy method (after French physicist Louis Gouy), a cylindrical sample is suspended from a traditional balance, weighed, then partially immersed in a strong magnetic field by introducing a powerful magnet around it. The consequent displacement of the sample is registered on the balance: diamagnetic materials are forced away from the field and appear to become lighter; paramagnetic materials are pulled in and appear to become heavier.

In the *Johnson Matthey apparatus* or Evans' balance as it is sometimes called (Fig. 1.2-4), the same principles apply but, instead of the sample, the magnet is attached to one arm of a balance much more sensitive than the analytical balance. Introducing a sample causes a displacement of the magnet, which is restored to its original position by altering the current flowing through electromagnet acting on the opposite arm of the balance. The reading displayed digitally on the front of the instrument is proportional to the apparent change in weight that would have been observed using the Gouy method; that is, net diamagnetic materials repel the magnet, giving a negative reading, and net paramagnetic materials attract it, giving a positive reading.

3) *Source*: S. Girolami, T. B. Rauchfuss, R. J. Angelici, *Synthesis and Techniques in Inorganic Chemistry*, 2nd edn, Saunders, Philadelphia, **1997**.

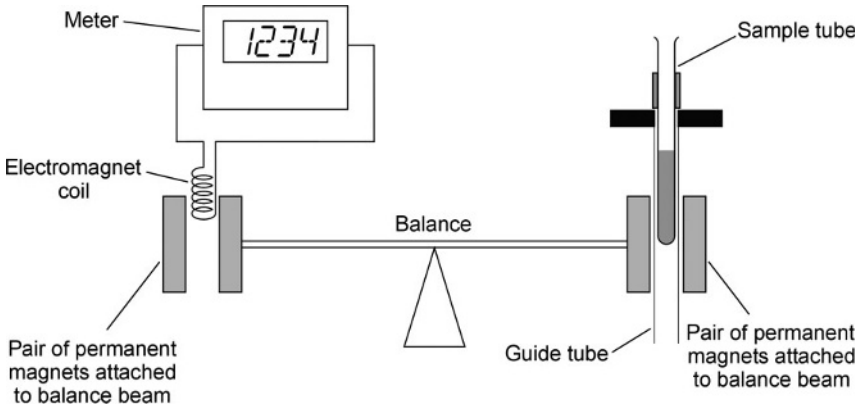

Fig. 1.2-4 Johnson Matthey/Evans' apparatus.

It is important that part of the sample remains outside the magnetic field – there is no net effect when it is fully immersed in the field. Since you cannot alter the position of the magnet in the Johnson Matthey apparatus, you must instead insert a sample of adequate height.

Further details of the Johnson Matthey balance, the method and the underlying theory are provided in manual available with the balance. Please note in particular:

- The balance is very sensitive! Moving the balance even slightly will alter the zero position and sudden movements may cause damage.
- The magnet is very strong! Ferromagnetic materials (including spatulas) should be kept away from the balance and must never be inserted.

Measurements

The method provided below applies for the magnetic susceptibility balance manufactured by Johnson Matthey, Catalytic Systems Division, UK. Although the following notes apply to all similar instruments, particular details may differ and should be checked against the manual supplied with your instrument.

The balances should be level and have been switched on for 10 minutes before any measurements are made.

1. With the sensitivity knob on the Johnson Matthey magnetic balance set at "×1", adjust the "ZERO" knob until the digital display reads "000".
2. Carefully insert a clean sample tube, then note the reading, R_0, which should be negative since the glass is diamagnetic. Keep the tube vertical to avoid damaging the very thin internal guide and draught shield. The rubber ring on the sample tube ensures the same height of sample is immersed every time in the magnetic field — check that the ring is 48.0 mm from the bottom of your sample.
3. Zero the analytical balance, then weigh the empty sample tube to 0.1 mg.

4. The greatest experimental error in this method arises from uneven packing. Grind your sample briefly (mortar and pestle) to obtain a small and regular grain size, but avoid creating a very fine powder, which tends to form clumps.
5. Fill the sample tube a few mm at a time to a depth of at least 1.5 cm and ideally 2.5–3.5 cm, compacting the powder by gently tapping the tube on the bench between additions. Note the room temperature.
6. Zero the magnetic balance, then insert the filled sample tube. Note the reading, R, carefully remove the tube, gently tap it on the bench a few times, then re-insert it. Repeat until consistent results are obtained.
7. Carefully remove the tube without disturbing the sample then measure the length, l, of the sample column to the nearest 0.5 mm.
8. Zero the analytical balance, then weigh the filled sample tube to 0.1 mg. Find, by difference, the mass of the sample, m.
9. Tap out the powder then repeat from step 4 or 5 to calculate an average R.
10. Clean the sample tube by tapping out the powder followed by careful use of water and a length of pipe cleaner. Rinse the tube with distilled water, followed by acetone, then blot dry internally with a clean length of pipe cleaner. Continue from step 4 with your next sample or return the clean tube and collar to the box.

Calculations

First, the *calibration constant*, K, for your instrument has to be determined by measurement of a sample with known magnetic properties. The K for your instrument is given by

$$K = \frac{\chi_g \times m \times 10^9}{l \times (R - R_0)}$$

where
l = length of the sample (cm)
R = the reading when a sample is introduced
R_0 = the reading for the empty sample tube
m = mass of the sample (g)

A standard, such as $HgCo(SCN)_4$ (a deep blue powder)m needs to be provided in order to determine K of your instrument. Compact the standard, then measure its R_0, m, l and R. The literature value of χ_g for $HgCo(SCN)_4$ is

$$\chi_g = \frac{4981 \times 10^{-6}}{283 + T} = 16.44 \times 10^{-6}\text{cgs}$$

at 20 C, where T is temperature in °C.

In the second step, proceed with measurements of your sample with unknown magnetic properties. Record its R_0, R, l and m in order to determine the **gram magnetic susceptibility**, χ_g:

$$\chi_g = \frac{K \times l \times (R - R_0)}{m \times 10^9}$$

The **molar susceptibility** of an unknown sample is obtained by multiplying χ_g by the molecular weight:

$$\chi_M = \chi_g \times M$$

Now correct for the diamagnetism of the sample by using the appropriate values of diamagnetic molar susceptibilities from the literature (a few examples are given in Table 1.2-3).[4)]

Table 1.2-3 Diamagnetic molar susceptibilities ($\chi_D \times 10^{-6}$ cgs units) for selected ions, molecules and atoms.

Co^{3+}	12.56	NH_3	22.62	H_2O	16.34
O (ether)	5.79	O (ketone)	2.17	SO_4^{2-}	50.39
H	3.68	NO_3^-	23.75		

Remember that diamagnetic corrections are **added**. This gives the **corrected molar susceptibility**, χ'_M:

$$\chi'_M = \chi_M + \chi_D$$

For a sample of known χ'_M the **magnetic moment**, μ, is given by the Curie law:

$$\mu = \frac{(3RT\chi'_M)^{1/2}}{N_A}$$

where N_A is Avogadro's number (6.023×10^{23} mol^{-1}). This equation (after substituting for the value of R converted to cgs units) gives μ in cgs units. A more convenient unit for μ is the Bohr magneton, the magnetic moment of a single electron, which has a value of $\mu = eh/4\pi m_e = 9.273 \times 10^{-24}$ A m^2, so that μ/μ_B represents the **magnetic moment in Bohr magnetons** (also known as μ_{eff}). Thus the previous equation eventually gives

$$\mu/\mu_B = 2.828\sqrt{\chi'_M T}$$

where T is in kelvin. This is then related, by the "spin only" approximation, to the **number of unpaired electrons**, n, per formula unit:

$$\mu/\mu_B = \sqrt{n(n+2)}$$

4) For extensive tables of molar susceptibilities of molecules, ions and atoms, see R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 53rd ed, CRC Press, Cleveland, OH, **1972**, p. E-108.

This can be solved as a quadratic equation, where the positive (real) solution is

$$n = \sqrt{(\mu_{\text{eff}}^2 + 1)} - 1$$

The value of n is often non-integral. Nonetheless, the experimentally obtained μ_{eff} value serves as a practical means of determining the number of unpaired electrons in a complex.

1.2.1.8 Cyclic Voltammetry (CV)

The CV technique is useful for surveying the position (volts) of the redox potentials of molecules in solution and also gives a measure of the relative stability of the different oxidation states. The potential of an electrode is swept over as wide a range as possible while the current at the electrode is simultaneously monitored. A positive current flow indicates that the molecule is being oxidised, while a negative current flow indicates reduction.

The theoretical cyclic voltammogram for a single one-electron oxidation process is shown in Figure 1.2-5. The first process seen is an upward peak (e.g. oxidation of Fc to Fc^+) and a reverse peak (e.g. due to reduction of the Fc^+). The upward peak arises because diffusion is slow on the electrochemical time-scale and during the scan the product Fc^+ builds up near the electrode, blocking the diffusion of unoxidised Fc to the electrode, leading to a fall in current. The standard sweep rate is 100 mV s^{-1}, although faster/slower scans can be used when we wish to investigate the kinetic stability of the Fc^+.

Many laboratory classes record the cyclic voltammograms of ferrocene and its derivatives. Detailed instructions on actual measurement are specific to the potentiostat. Usually nowadays the measurement is fully automated and driven by a PC. The software will determine the quantities E_p^a, i_p^a, E_p^c and i_p^c and calculate the redox potential

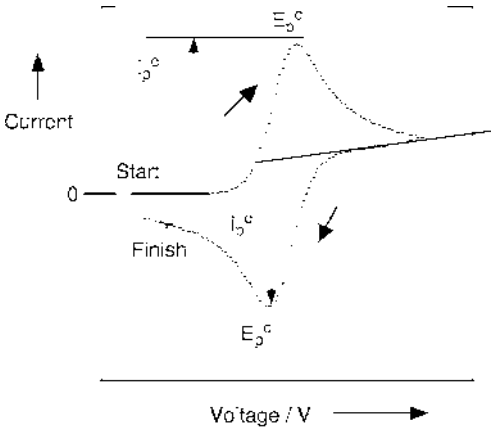

Fig. 1.2-5 Theoretical cyclic voltammogram for a single one-electron oxidation process.

(E) by taking the average of the peak voltages. Calculate the difference in peak positions $E_p^a - E_p^c$, which should be $59/n$ mV, where n is the number of electrons transferred in the redox process. Your measured $E_p^a - E_p^c$ will be somewhat larger than expected for a one-electron process (this is due to resistance effects).

1.2.1.9 Polarimetry

Optical rotation, α, is usually measured using the sodium emission wavelength (589 nm). Solutions of two concentrations (e.g. 0.01 and 0.025 mol dm^{-3} solutions) are measured and the average value of optical purity from the two measurements is taken. Read the instructions provided with your instrument and obtain α values for both solutions.

Calculate the specific rotation of your complex at 589 nm [ϕ] from

$$[\phi]_{589} = \frac{\alpha}{lc}$$

where l = pathlength of sample in decimetres and c = concentration in g cm^{-3}.

Knowing the specific rotation of pure enantiomer $[\phi]_{pure}$ (e.g. +60°), it is possible to estimate the *optical purity* (= enantiomeric excess, *ee*) for your product as an average of the two values obtained from the two solutions of differing concentrations:

$$\text{optical purity (\%)} = 100[\phi]_{obs}/[\phi]_{pure}$$

Knowing optical purity, calculate how much of each isomer (Λ and Δ) is in your product (in %).

1.2.2 Laboratory Reports

All reports should be **concise**, organised and tidy. They may be typed (strongly preferred) or hand-written, with (preferred) or without the use of chemical structure drawing software, such as ChemBioDraw or IsisDraw.

The following information should be included in a typical report:

1. Name of the experiment (as heading) and date.
2. Short abstract of the experiment. The abstract should include a brief description of syntheses performed and summarise characterisation methods and the most important findings (possibly including brief answers to questions posed in the manual).
3. A fully balanced equation for each reaction should be included for every experiment.
4. Detailed experimental procedure: write what you actually did and do not simply copy the procedure out of the manual. Details of the equipment used and of stan-

dard procedures, such as sublimation, are not required (see below); the degree of detail provided should be such that an experienced experimentalist will be able to reproduce the experiment based on your description. Note that for quantities of reagents and starting materials employed in a procedure *both* the mass (or volume) *and* the number of moles must be quoted, e. g. (0.25 g, 10 mmol).

5. Yield of product, i. e. actual weight and percentage yield. Calculation of the yield should be based on limiting component, which should be indicated.
6. Physical properties of product:
   - colour, state;
   - melting point (m.p.); or
   - boiling point (b.p.)/pressure.
7. Spectral and chromatographic data (e. g. IR, NMR and GC) with assignments and interpretation. The NMR and IR data should be given in the format which is discussed in more detail later. Spectra should be clearly labelled and attached to the report.
8. A short discussion of the spectral data (if there are some interesting trends, any unusual patterns in spectra, how the signals were assigned, etc.) and answers to any questions posed in the manual.

Generally, a good report will not be longer than three pages (12 point font size, 2.5 cm margins each side). The number of additional pages with spectra and other attachments is not limited.

Samples of each product must also be submitted with every report. They should be packed in sample tubes and clearly labelled with the following information:

- name of the student,
- experiment number,
- name or structure of the compound.

A more detailed example of a report is given below (covering points 1, 2 and 4–7) (remember to also include points 3 and 8). The idea of using this format is to give you practice in the way in which chemists write up their work for publication in the chemical literature.

Note that reports should be *CONCISE* and *NOT* of excessive length.

1.2.2.1 Example Report

Preparation of Ferrocene

Abstract

Ferrocene was prepared by the reaction of iron(II) chloride with cyclopentadiene in the presence of base (KOH). Crude ferrocene was purified by sublimation and was characterised by m.p., IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy. Ferrocene was reacted with acetic anhydride in the presence of phosphoric acid to afford acetylferro-

cene. Acetylferrocene was purified by column chromatography on alumina and by recrystallisation from cyclohexane; it was characterised by m.p., IR, UV-Vis, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and by cyclic voltammetry. The presence of the electron-withdrawing/donating acetyl group on one of the cyclopentadienyl rings of ferrocene resulted in the shift of *E* by *xx* V. In contrast to ferrocene, acetylferrocene was not oxidised to the corresponding ferricenium (Fe^{III} ion) on addition of concentrated sulfuric acid as determined by UV-Vis spectroscopy.

Experimental Procedure

Ferrocene

A three-necked flask equipped with magnetic stirrer, reflux condenser, dropping funnel and nitrogen inlet was charged with 1,2-dimethoxyethane (30 cm^3) and flake potassium hydroxide (15 g, 0.27 mol). Cyclopentadiene (2.75 cm^3, 34 mmol), prepared by cracking of its dimer, was added with vigorous stirring. Stirring was maintained as a solution of finely powdered iron(II) chloride tetrahydrate (3.25 g, 16.3 mmol) in degassed dimethyl sulfoxide (25 cm^3) was added dropwise over 30 min. The exothermic reaction resulted in gentle boiling. The reaction mixture was stirred for an additional 30 minutes, after which time it was neutralised with HCl (6 M, 45 cm^3) and ice (50 g). Ferrocene, as an orange precipitate, was collected by filtration, washed with water and dried in air (5.3 g, 25%). Purification by sublimation yielded orange crystalline material, which was used for spectroscopic characterisation, m.p. 174–176 °C.

Spectral Data

Ferrocene

IR:	ν_{max} (Nujol mull)/cm^{-1} 3050m (υCH), 1118s, 1002s, 835vs.
^{1}H NMR:	δ_H (300.0 MHz, $CDCl_3$, Me_4Si) 4.18 (10H, s, CH).
^{13}C NMR:	δ_C (67.8 MHz, $CDCl_3$, Me_4Si) 123.3 (s, CH).
MS (exact mass):	*m*/*z* (EI) 186.0134 (M^+); $C_{10}H_{10}Fe$ requires 186.0132.

1.2.2.2
Writing Up Spectral Data

A more detailed explanation of the format to be used for reporting the spectroscopic data is given in this section. The spectroscopic data can be listed in several ways, but here the standard format is that required for publication in *Dalton Transactions*. An important part of this laboratory class is to learn how to do this in the correct way. If unsure, consult Guidelines for Layout of Articles for Submission at RSC webpage (www.rsc.org).

Below is an example of data in the correct format.

Infrared Data

ν_{max} (Nujol mull)/cm^{-1} 3350 m (O–H stretch), 1670 s (C=O stretch), 1000 s, 850 m (aromatic C–H deformation).

Notes: List the peaks in decreasing order. List only major or significant peaks (typically this will be 3–10 peaks). You must record how the spectrum was run, most commonly as a Nujol mull or KBr disc (for solids) or a thin film (for oils and liquids). One of the main points is not to go overboard with assignments. The most important functional groups observed by IR are OH and NH, carbonyl groups (where we can often tell the type of carbonyl compound from the position), C–O bond and whether the compound is aromatic from strong peaks at the lower end of the spectrum (850–700 cm^{-1}) due to aromatic C–H deformations. C–H stretches for aromatics are at >3000 cm^{-1}, whereas for aliphatics they appear at <3000 cm^{-1}. The type of signal (s, m, w, vs, br) should be indicated by appended letters (e.g. 1670 s). Do NOT give IR data with excessive accuracy. Peaks should only be reported to the nearest whole number.

Raman Data

The same format as for IR can be used to list Raman data.

^{1}H NMR Data

δ_H (300.1 MHz, $CDCl_3$, Me_4Si) 7.50–7.30 (2 H, m, Ar-H), 7.23–7.12 (2 H, m, Ar-H), 7.16 (2 H, d, *J* 5.0 Hz, H-5), 6.58 (1 H, s, =C<u>H</u>), 4.30–4.10 (2 H, m, C<u>H</u>S), 4.05–3.97 (2 H, m, C<u>H</u>S), 3.84 (2 H, s), 3.82 (12 H, s), 3.43 (1 H, q, ^{3}J 2.5 Hz, H-3), 3.38 (1 H, br s, N–H), 2.68 (1 H, d of t, ^{3}J 10.2, ^{4}J 2.6 Hz, H-7) and 1.86–1.72 (1 H, m, H-6).

Notes: We start by giving the frequency at which the spectrum was run, the solvent employed and reference compound. Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{1}H NMR, an accuracy of two decimal places is normal for δ and one decimal place for *J*. In parentheses after each, first put the number of protons (from the integral trace) then the form of the peak (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), then if possible the coupling constant *J* in Hz and finally the assignment. A ppm range must be given for a complex multiplet arising from more than one proton, whereas only the centre value is given for a simple signal.

^{13}C{^{1}H} NMR Data

δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 164.4 (s, C=O), 144.9 (s, 4ry, C-1), 127.3 (s, CH, C-3,5), 127.2 (s, CH, C-4), 124.2 (d, $^{3}J_{CP}$ 2.5 Hz, CH, C-2,6), 79.1 (d, $^{1}J_{CP}$ 60.5 Hz, 4ry, C-7), 65.2 (s, CH, C-9), 54.8 (s, CH_2, C-10) and 52.4 (s, CH_3, 9-OMe).

Notes: As for ^{1}H NMR spectra, we start by giving the frequency at which the spectrum was run, the solvent employed and reference compound. Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{13}C NMR, an accuracy of one decimal place is normal for both δ and *J*. In parentheses after each put the assignment. The form of the peaks (s, d, t, etc.) can be omitted if all peaks appear as singlets (e.g. no heteronuclear coupling such as from P or B is present). The number of carbon atoms cannot be determined from integral trace in $^{13}C\{^{1}H\}$ NMR spectra and therefore is usually not listed.

$^{31}P\{^{1}H\}$ and ^{31}P NMR Data

δ_P (121.5 MHz, $CDCl_3$, 85% H_3PO_4) 25.3 (s). In the non-decoupled ^{31}P NMR spectrum the signal was split into a doublet, $^{1}J_{PH}$ 121.0 Hz.

Notes: As for ^{1}H NMR spectra, we start by giving the frequency at which the spectrum was run, the solvent employed and reference compound.[5)] Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{31}P NMR, an accuracy of one decimal place is normal for both δ and *J*. The non-decoupled experiment provides information on PH coupling constants; the number of bonds between the two coupled atoms should be indicated if known (e.g. $^{1}J_{PH}$, $^{2}J_{PH}$).

2D NMR Spectra

The 2D correlations are supplied to help you with the assignment of the peaks observed in 1D spectra; there is no need to list peaks found in these in your report.

Mass Spectrum (Normal Resolution)

m/z (EI) 670 (M^+, 47%), 655 (M^+ – Me, 4), 488 (23), 368 (21), 306 (10), 279 (12), 248 (80), 222 (100), 220 (88) and 149 (62).

Notes: Remember to give the ionisation technique used (EI, ES) and mode in case of ES (positive or negative). List the peaks in decreasing order. For the molecular ion peak, put in parentheses M^+ and the relative intensity (100% is defined as the largest or base peak – in our example *m/z* 222). List the other main peaks up to a maximum of 8–10 with their intensities and, where known, assignments. Remember in ES, not only ($M + H^+$) but also other clusters such as ($M + Na^+$) and/or ($M + K^+$) are often observed.

5) In contrast to Me_4Si, often used as an internal standard in ^{1}H and ^{13}C NMR, 85% H_3PO_4 is rarely used as an internal standard. Instead, a sample with reference compound is measured in a separate experiment (hence external standard).

Mass Spectrum (Exact Mass Measurement)

Exact mass measurement can be reported as follows:

m/*z* (EI) 186.0134 (M^+), $C_{10}H_{10}Fe$ requires 186.0132

For your own PC, a very useful piece of freeware, Molecular Weight Calculator, is available from http://ncrr.pnl.gov/software/. It is very convenient for calculations of molecular weights, including isotopic weights (for exact mass measurement). Molecular weight, exact mass and isotopic patterns can also be calculated conveniently using the 'Analysis' tools in ChemBioDraw software.