X.1 AN INTRODUCTION TO SOLUTION CHEMISTRY TECHNIQUES

1 PURPOSE

How do chemists analyze a sample quantitatively? The purpose of this experiment is to give you an early opportunity to investigate this question. There are many possible methods, from instrumental methods, such as atomic absorption spectroscopy, to measurements of the conductivity of a solution, or titration methods that rely on the colour change of an indicator. Here you will determine the concentration of calcium, fluoride and copper ions using different methods, and be asked to assess the relative value of each one.

In this two-day experiment you will:

Prepare solutions of precisely known concentration; (sections 4, 5 & 6)

Perform titrations to determine calcium concentrations using both an indicator and a pH probe; (section 4) $\,$

Use a calcium ion specific electrode to determine the concentration of calcium ion in a sample; (section 5)

Record electronic spectra using an ultraviolet / visible spectrometer to determine the concentration of a copper solution, and follow the kinetics of a reaction; (sections 6 and 7)

Perform a critical analysis of results;

Compare your results with those of others who have completed the experiment, to develop experience in the statistical analysis of data (post-experiment).

Before starting, read the instructions and appendices in full.

Record your measurements in the boxes below. The write-up for this experiment consists of these boxes fully completed, together with your calculations, plots, spectra and comments.

2 IMPORTANT NOTE

This experiment is in two parts, each of which require about a day to complete. The first comprises sections 4 and 5, and requires the use of pH and ion specific electrodes, while sections 6 and 7 form the second part and require the use of a uv/visible spectrometer. In order to accommodate the maximum number of students, some pairs will start at section 4 and others section 6.

If you are in an odd-numbered pair (i.e., X 1.1, X 1.3 or X 1.5) please start at section 4 and work consecutively through all experiments. If you are in an even-numbered pair (X 1.2 or X 1.4) please complete sections 6 and 7 first, then move on to sections 4 and 5.

3 SAFETY

You must wear safety glasses whenever you handle corrosive or toxic chemicals. Wear them throughout this experiment.

None of the chemicals required for this experiment is particularly hazardous, but you will be using acids (corrosive), Cu(II) solutions (poisonous) and dilute base (harmful if splashed in the eyes). Work carefully, and ask the demonstrator or technician for advice if you are in any doubt about an operation.

COSHH assessments are available in the laboratory; you can find further information at http://ptcl.chem.ox.ac.uk/~ hmc/tlab/experiments/X1.html In addition, a summary of safety information for each chemical is given at the end of these instructions.

4 CALCIUM-EDTA TITRATION

You will be familiar with simple titrations, which can often be used to measure the concentration of a chemical in solution. To begin, you will titrate Ca^{2+} with EDTA (ethylene diamine tetraacetic acid); the two form a complex according to the equation

$$Ca^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Ca(EDTA)]^{2-}(aq)$$



Fig. 1. EDTA.

4.1 Preparation of Solutions

You will need to prepare solutions of EDTA, calcium carbonate and the unknown, according to the instructions given below. If you have not already done so, read Appendices A-E, which discuss the preparation of solutions.

- 1. Prepare 250 cm³ of standard EDTA solution by weighing accurately about 1g disodium EDTA and dissolving it in demineralized water.
- 2. Weigh accurately into a 250 cm³ Erlenmeyer (conical) flask about 1g calcium carbonate. Using a Pasteur pipette, add 1M HCl until the solid dissolves. Add 10 - 20 cm³ demineralized water, then raise the solution to boiling point on the hot plate to drive out CO₂. Cool the solution under cold water to a temperature at which you can hold the flask, then dilute with demineralized water to 1000 cm³ in a labeled volumetric flask.
- 3. Weigh accurately about 1g of the unknown, and prepare 1000 cm³ solution from it using the procedure used in part 2 above. Label the flask. The unknown is a mixture of CaCO₃ and ZnCO₃.2Zn(OH)₂.H₂O (FW 342.16 Daltons).
- 4. Complete the box below. You will need to include error limits for some values during this experiment; if you are unsure how to determine an error limit, read the background note on experimental error provided with this manual.



4.2 Titration of the standard calcium solution

1. Wash a 250 cm^3 flask with a little EDTA solution to remove adsorbed calcium ions. Discard the washings and rinse the flask with demineralized water.

Comment: Small amounts of calcium are present in most aqueous samples. Calcium ions readily adsorb on (that is, attach to) silica (glass) surfaces. For accurate results these surfaces must be calcium-free before the experiment starts.

- Pipette 25 cm³ of the standard calcium solution into the flask and add demineralized water to give a total volume of around 50 cm³. Using a small graduated cylinder add about 5cm³ 1M NaOH to the flask.
- 3. Check the pH of the solution using a pH electrode; if it is less than 11, add small amounts of 1M NaOH until the pH reaches 11. Remove the pH electrode, washing it clean into the flask with a little demineralized water.
- 4. Add GBHA indicator to give a cherry red colour (which may take a few seconds to develop), then titrate with EDTA solution; at the end-point the indicator is golden yellow. Complete the box below.

EDTA titration against standard Ca²⁺ solution

Starting volume of EDTA

Final volume of EDTA

Titre {give error limits}

4.3 Titration of the unknown

1. Pipette 25 cm³ of the unknown solution into a clean flask, add some demineralized water to bring the total volume to around 50 cm³, adjust the pH to approximately 11 as before, and titrate against the EDTA solution. The volume of EDTA solution you need should be no more than about 35 cm³. Complete the box below.

EDTA titration with unknown

Number of unknown

Starting volume of EDTA

Final volume of EDTA

Titre {give error limits}

Moles of calcium in unknown solution {give error limits}

Percentage by weight of calcium in unknown sample

Comment: The colour change in this second reaction is again from light pink to yellow. However, the end-point will be less clear this time because the addition of alkali causes precipitation of zinc hydroxide which tends to mask the colour change.

4.4 Determination of zinc in the presence of calcium by potentiometric titration

As you will have found in part 4.3, it is not always easy to find the end-point in a titration using an indicator. Results will be reproducible only when, near the end-point, small additions of titrant cause large changes in appearance. More accurate data can be found by continuous measurement of some property of the solution. This can conveniently be done potentiometrically - in other words, by making the solution part of an electrochemical cell and monitoring the cell potential as the titration proceeds.

You might not think of a pH probe as being an electrochemical tool, but it is, as you will learn in the electrochemistry course later this year. In this step you will carry out a potentiometric titration, recording the pH as the titration is performed.

4.4.1 Apparatus

pH meter with combined glass electrode, magnetic stirrer and burette. The bottom of the electrode is a thin and very fragile glass membrane so <u>the electrode must be handled with great</u> <u>care</u>. The membrane must not be allowed to touch any surface, even that of a cleaning tissue.

4.4.2 Titration

- 1. Before starting, calculate the approximate pH at which zinc hydroxide will precipitate, using the value for K_{sp} in Appendix H and a rough estimate for $[Zn^{2+}]$. Show your answer here \rightarrow
- 2. Weight out accurately about 1g of the unknown, dissolve this in dilute hydrochloric acid and heat the solution briefly to boiling, as in the previous section.
- 3. Cool the solution to below 40°C, then pour it into a conical flask. Wash out with demineralized water, and add the washings to the flask.
- 4. Arrange the pH probe so that its end dips into the solution. Add demineralized water, if necessary, to ensure that the electrode tip is covered, then titrate the solution with 1M NaOH, recording the pH after each addition of alkali. Add alkali in small portions near the points of inflection.

Comment: Before starting, think about what the titration curve should look like. Make sure that you include <u>all</u> the chemicals that are in your solution!

5. Plot pH as a function of added alkali, and attach your graph. Indicate on it the points at which you believe zinc precipitation starts and ends. Complete the box overleaf.

Potentiometric Titration

Volume of 1M NaOH needed to fully precipitate zinc hydroxide {give error limits}

Moles of NaOH used

Moles of Zn salt in solid sample {give error limits}

Weight of zinc salt in sample

Weight of calcium salt in sample

Percentage by weight of calcium in sample

5 USE OF AN ION SPECIFIC ELECTRODE (ISE)

5.1 Solutions

1. By diluting the stock calcium solution, prepare four solutions of Ca²⁺ with concentrations in the range 0.01M to 0.0001M.

5.2 Measurement

- 1. Clamp the calcium ISE vertically with the membrane in a measured volume of your most dilute standard. Clamp the reference electrode in the same solution, but do not allow the electrodes to touch.
- 2. Connect both electrodes to the ion analyzer (do not press the reference electrode connector hard into the meter or it may be difficult to remove).
- 3. Record the potential when it becomes steady.
- 4. Repeat with the remaining standards in order of increasing concentration. Measure the calcium ion concentration of the unknown calcium solution (obtain from the technician), using the ISE.
- 5. Wash the electrode well in demineralized water and return it dry to its tube.
- Complete the table on the next page. Prepare a suitable plot of ISE reading as a function of concentration and hence determine the concentration of calcium in your sample {give error limits}

Comment: You may wonder why we do not provide a "real" sample containing calcium for you to use, such as milk. ISE probes are very convenient, but their readings are frequently affected by the presence of other species in solution. Calcium electrodes are sensitive to the presence of zinc, magnesium, proteins and other materials in milk, which would need to be

removed before you could get a reliable reading. Therefore we have supplied you with a pre-treated sample.

Comment: In the electrochemistry course to come later in your 1st year, you will meet the Nernst equation. This shows that the emf generated by an electrochemical cell or half-cell (of which an ISE is an example) is related to the logarithm of the concentration of the active species. You might want to take this information into account when plotting data from this part of the experiment.

Concentration	ISE reading
Unknown solution and number	

6 SPECTROPHOTOMETRIC DETERMINATION OF COPPER

6.1 Solutions

1. From the stock solution of 0.5M copper (II) sulfate, prepare solutions of concentration 0.08M, 0.09M, 0.1M and 0.2M.

6.2 Recording spectra

- 1. Consult the instructions beside the spectrometer.
- 2. Record the spectrum of your most concentrated solution between 300nm and 900nm and find the wavelength of maximum absorption.

6.3 Absorbance versus concentration plot

- 1. Follow the instructions by the spectrometer to make a quantitative measurement of the concentration of copper, using your standard solutions and the unknown.
- 2. Choose a suitable wavelength at which to measure the absorption by copper ions. For each standard solution in turn and for your unknown solution determine the absorption at the chosen wavelength.

Comment: According to Beer's law, absorbance is proportional to concentration, provided that the total absorbance is not large.

3. Tabulate your readings in the box on the next page.

Spectrophotometric Determination of Copper		
Wavelength of maximum ab	sorption:	
Concentration	Absorption	
unknown 0.08 M 0.09 M 0.1 M 0.2 M		
Sample number		
Concentration of unknown {	give error limits}	
Use your spectrum to explain below why the solution appears blue		
If the absorption of the unknown was 0.6 (or lower than the absorption of your most diluted solution) would using your calibration line still give you a reliable result? State your reasons.		
When the absorption gets very but approaches a constant val	large, it is not linearly dependent on the concentration any more ue. Discuss possible explanations with the demonstrator.	

7 KINETICS OF HYDROLYSIS OF AN ESTER

This section is designed to give you further practice using the spectrometer, and to remind you of the derivation of rate equations from kinetic data.

You will investigate the hydrolysis of 4-nitrophenyl ethanoate, which is rapidly converted into 4-nitrophenoxide ion in the presence of base. A colour change occurs during the reaction, so its

progress can conveniently be followed by monitoring how much visible light is absorbed as a function of time.

7.1 Procedure

- 1. Find a suitable wavelength to monitor the absorption change during the reaction, as follows. Add a tiny amount of 4-nitrophenyl ethanoate to about 10 cm³ 0.1M NaOH solution and mix. Record the spectrum of the yellow product to find the wavelength of maximum absorption which lies between 350 and 900 nm. Record the wavelength here.
- 2. While one partner is doing this, the other should prepare 100 cm³ of 0.01M 4-nitrophenyl ethanoate in methanol.
- 3. Check that you understand how the spectrometer can be used for kinetics studies, since the reaction is rapid, and you will not have time to read the instructions once it has begun!
- 4. Measure accurately 2.5 cm³ of the 10.9 buffer solution (solutions bench) into the spectrometer cell. Inject 100 μ l of ester solution. Stir the contents of the cell using the steel loop provided, then place the cell in the spectrometer without delay and record the change in absorbance.
- 5. Determine the initial rate of reaction and record it in the box below.
- 6. Make three further measurements of the initial rate for fresh solutions of the same strength.

Determine the initial reaction rate for the first run; include units and an error estimate.

Determine the mean and standard deviation of your four values for the initial rate of reaction.

Comment: Recall that the initial rate of reaction is the initial rate of change of concentration divided by the rate of change of time; in other words, the gradient of the absorption versus time plot at t = 0. It is easiest to quote this directly as $\Delta A/\Delta t$, but you should also consider what information you would need in order to convert this into more conventional units of Δ (concentration)/ Δt .

8. Choose several other concentrations of ester and measure the initial rates of reaction for each. Determine the dependence of the rate of reaction on the ester concentration and show your working in the space below (continuing overleaf if necessary).

8. COMPARISON WITH RESULTS FROM OTHER STUDENTS

- 1. Enter the value you have found for the percentage by weight of calcium in your sample on the appropriate section of the student data sheets (available by the demonstrators' table) or on the spreadsheet available for this purpose.
- 2. Compare your result to the last eight entries for the sample you used. Record those entries, then work out the average of those values and record it here.
- 3. Use the procedure discussed in the background notes on experimental error to determine whether your result differs significantly from the results of other students. Comment in the space below and overleaf if necessary.

APPENDIX A. WEIGHING

Choose a suitable balance; it is a waste of time to use an analytical balance if you need only to weigh to 0.1 g. Unless the instructions indicate otherwise, do not try to weigh the exact amount of material specified in instructions; if you are asked to weight 5g accurately, an amount such as 5.017g is sufficiently close. When weighing solids,

either

Place a weighing boat on the balance and tare the balance (set the balance reading to zero). Add the appropriate amount of solid to the weighing boat. Transfer the solid to your container and, if preparing a solution, wash all traces of the solid into it with a stream of solvent,

or

Place a sample vial or a weighing boat on the balance. Add the appropriate amount of solid. Tip the solid into a container and re-weigh the sample vial to determine the weight of solid transferred.

APPENDIX B. TO PREPARE SOLUTIONS OF ACCURATELY-KNOWN CONCENTRATION FROM A SOLID

- 1. Calculate the quantity of solid needed to give a solution of the required strength. Weigh the solid into a clean glass vial or weighing boat, using a metal spatula. Weigh to 1mg.
- 2. Transfer the solid to a clean volumetric flask. Fill the flask two thirds full, and swirl to dissolve the solid.

Safety Note: Never hold large volumetric flasks by the neck alone; provide support at the bottom.

Safety Note: You can speed the dissolution of most solids by warming the flask in warm water, but do NOT use a Bunsen burner or hot plate to heat a volumetric flask, since such flasks are fragile and easily broken through thermal shock.

Question: What does the observation that solubility usually increases with temperature tell us? Hint: think Le Chatelier!

3. Once the solid is dissolved, fill to the mark on the neck of the flask, using a dropping pipette to add the last few cm³ of liquid. Label the flask with the pen provided; do not use an adhesive label.

APPENDIX C. TO PREPARE SOLUTIONS OF ACCURATELY-KNOWN CONCENTRATION FROM A LIQUID

Safety Note: In one of the most common injuries in undergraduate chemistry laboratories students cut themselves trying to fix a pipette filler onto a pipette. <u>Use the minimum force only</u> when attaching a pipette filler. If in doubt, ask for help from a technician or demonstrator. Hold the pipette about 1 cm from the point at which it enters the aid. Use a gentle twisting motion to insert the pipette. Never pipette any solution - even aqueous solutions - by mouth.

- 1. Calculate the amount of liquid needed. Choose a clean and dry pipette and volumetric flask of suitable size.
- 2. Using a pipette filler, suck up enough liquid to nearly fill the pipette, then allow the meniscus to fall to the mark. Transfer the liquid to the volumetric flask, touching the end of the pipette against the inside of the flask to allow the last of the liquid to drain out. Do not blow out the liquid unless the pipette specifically states it is of the blow-out variety.
- 3. Make up to the mark with solvent and mix well. Label with the pen provided; do not use an adhesive label.

APPENDIX D. TO PREPARE SOLUTIONS OF LOW CONCENTRATION BY SUCCESSIVE DILUTION

Very dilute solutions may contain only a few milligrams of solute per litre. It is very poor practice to try to make up such solutions by weighing directly this small amount of material and dissolving in solvent. Instead prepare a small amount of a more concentrated solution, then dilute a precisely-measured portion of this in a volumetric flask. If necessary repeat the procedure.

Comment: You will have heard of homeopathy, in which patients are treated with solutions of "active" ingredients that have been diluted so many times that no molecules at all of the "active" ingredient are likely to be present. There is further information on this type of alternative medicine at http://www.bbc.co.uk/science/horizon/2002/homeopathy.shtml

APPENDIX E. USING THE DIGITAL PIPETTE

- 1. Push the tip gently but firmly onto the end of the pipette.
- 2. Set the required volume as follows: Adjust the top of the white screw thread (visible inside the plunger) to the required volume (volumes are in cm³) as closely as possible on the scale by twisting the outside of the plunger. Align the dot with the large pointer by twisting the outside of the plunger. The pipette will now deliver the volume set.
- 3. Depress the plunger until you feel it 'bottom'.
- 4. Immerse the tip 3-4 mm into the liquid to be dispensed, keeping the pipette vertical. Gently release the plunger.
- 5. To dispense, place the tip against the inside wall of the receiving container and dispense by pushing the plunger down slowly. A small amount of liquid will remain in the tip; this is allowed for in calibration.
- 6. After use, remove and wash the tip with demineralized water; it is reusable. Be careful not to allow any liquid to get into the pipette never leave it lying in a position in which liquid might drain into it.

APPENDIX F. TITRATION

- 1. Ensure that all equipment is clean, and all measuring equipment (pipettes and burettes) is dry, or has been rinsed with the solution you will use.
- 2. Titration volumes should be in the region of 15 50 cm³ (if you use very small volumes the percentage error in your measurements becomes large; if you use large quantities of solutions, you waste chemicals), so start by estimating the volume of material you need in the flask for the titration. Fill up the burette, but do not attempt to get the meniscus exactly on the 0.00 mark. This is difficult and pointless.
- 3. Remove the funnel from the top of the burette, so that liquid does not drop from the funnel into the burette during the titration, thus affecting your readings.
- 4. Add an indicator to the material in the flask, or clamp a suitable probe (pH, ISE or conductivity) in the flask.
- 5. Ensure the end of the probe, which may be very fragile, is well away from the stirring bean if you are using one; check that the end of the probe is covered with solution. If it is not, add a little solvent until it is. If you are using an indicator, place the flask on a white tile which will make the change of colour more easily visible.

6. Standard practice is for a titration to be done three times (though you need not do replicates in this experiment). A fast rough titration to locate the end point approximately is followed by a pair of accurate titrations in which the end point is approached slowly and with care.

APPENDIX G. THEORY OF pH TITRATIONS

pH is defined in terms of proton concentration:

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

pH can be measured by an electrode whose e.m.f. depends upon $[H^+]$. The Pt $|H_2$ electrode, which you will learn about in the 1st year electrochemistry course, would be one possible choice of electrode. However, oxidizing and reducing solutions, sulfur and proteins all interfere with platinum, and the hydrogen electrode is a clumsy and expensive tool for routine use, so in this experiment we instead use a glass electrode, which is really a half-cell. The cell is completed by the test solution and reference electrode. The two electrodes are often incorporated into a single unit. The emf between the electrodes is measured by a millivoltmeter (usually labeled as a pH meter) calibrated to display pH directly.

A normal commercial combination pH electrode contains a silver, silver chloride electrode dipping into a solution of hydrochloric acid of known concentration. To make a measurement, the following cell might be set up:

Hg | Hg₂Cl₂ | KCl (sat) | glass membrane | test solution | HCl(0.1M) | AgCl | Ag

In the standard notation used above, a vertical line represents the boundary between two phases. The test solution affects the e.m.f. of this cell at two points. A small and constant potential, (usually ignored), arises at the liquid junction between the saturated KCl and the test solution. A larger, variable contribution arises from the effect of the test solution on the potential across the glass membrane. The electrode is standardized using a buffer of known [H⁺]. The constant term may then be evaluated, and the pH of other solutions deduced from the e.m.f. generated when the combination electrode is immersed in them. Solutions are standardized by placing the electrode in buffer solution and adjusting the pH meter to give the correct pH.

The idea that glass membranes are semi-permeable to H^+ ions is a simplification. The membrane potentials appear because the hydrated silicate network of the glass has an affinity for certain cations, notably H^+ and Na⁺. These are adsorbed into the silica, and are in equilibrium with free ions in the solution next to the glass membrane. The migration of these ions inside and outside the electrode into the silica generates a potential difference, whose size is determined by the concentration of sodium and hydrogen ions in the solution. Sodium ions are of little consequence at low sodium concentration, but at high pH, the quantity of sodium ions in solution may be considerable if NaOH is used to perform the titration, and the electrode then adsorbs significant amounts of sodium, which affects the measured potential. At high pH, therefore, the electrode is measuring some composite concentration of both hydrogen and sodium ions, and the potential becomes increasingly dependent on sodium ion concentration, and may, for example, register a pH of 12.8 in a solution 0.01M in Na⁺ at pH 12.

APPENDIX H. CHEMISTRY UNDERLYING THE HYDROXIDE TITRATION

If hydroxyl ion is added to a solution containing calcium and zinc ions, zinc and calcium hydroxides will be precipitated if the product $[Ca^{2+}][OH^{-}]^2$ or $[Zn^{2+}][OH^{-}]^2$ exceeds the appropriate solubility product. (The solubility product is the equilibrium constant for the dissolution process. You might expect this equilibrium constant to be given by

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm OH}^{-}]^2 / [{\rm Ca}({\rm OH})_2]$$

but when writing an equilibrium constant we leave out any species whose concentration is constant. The 'concentration' of solid calcium hydroxide is the same as its density, which, of course, does not change. Thus the concentration of the calcium hydroxide solid does not appear in the expression for the solubility product. Furthermore, the expression for K_{sp} should strictly be written in terms of activities, not concentrations, but for sparingly-soluble salts the concentration is a good approximation to the activity. You'll learn about "chemical activity" later this year.)

 $Ca(OH)_2 (s) \Rightarrow Ca^{2+} (aq) + 2OH^- (aq)$ $K_{sp} = [Ca^{2+}] [OH^-]^2 = 1.1 \times 10^{-8}$ $Zn(OH)_2 (s) \Rightarrow Zn^{2+} (aq) + 2OH^- (aq)$ $K_{sp} = [Zn^{2+}] [OH^-]^2 = 1.8 \times 10^{-14}$

As zinc hydroxide has the lower solubility it precipitates at a lower pH (smaller [OH⁻]) than calcium hydroxide. As long as zinc ion is present in the solution in significant quantity, the concentration of OH⁻ as NaOH is added cannot exceed the point at which precipitation occurs. However, when almost all Zn^{2+} has been removed from solution by precipitation, the concentration of OH⁻ will rise rapidly, increasing eventually to a value sufficient to precipitate the calcium. This increase, once the zinc has precipitated out, defines the end-point (and appears as a second point of inflection in the titration curve, the first being due to neutralization of the excess acid used to dissolve the sample. A point of inflection is a point on a line at which the gradient is neither increasing nor decreasing, so the second derivative is zero).

A third end point should, in principle, also be observable. This end point defines the pH at which precipitation of calcium hydroxide is complete, but it is difficult to observe both because of the relatively high solubility of the hydroxide, which means the rate of precipitation is noticeably affected by the growth in the volume of solution as the titration proceeds, and the 'alkali error' of the electrode, whereby the readings of the glass electrode become progressively more in error as the pH of the solution increases - see Appendix G.

APPENDIX I. ION-SPECIFIC ELECTRODES

Ion-specific electrodes function very much like pH electrodes, and may resemble them in construction. They measure selectively the concentration of a single type of cation or anion, though for most electrodes certain other cations or anions interfere with the operation of the electrode, and must be removed from solution before the electrode can be used. In this experiment, no such interfering ions are present.

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APPENDIX J. A BRIEF INTRODUCTION TO SPECTROSCOPY

You may not have come across much spectroscopy yet, but you will encounter several different techniques in lectures and practicals. This appendix covers some to basic principles.

Two electronic energy levels (or 'states') of an atom, molecule or ion are separated by an energy ΔE :

A transition from the ground state to the excited state can be brought about if the electron absorbs an energy equal to the separation between the two states. The energy of a photon of wavelength λ is given by:

$$E = \frac{hc}{\lambda}$$



Alternatively, this expression can be rewritten in terms of frequency:

$$v = \frac{c}{\lambda}$$

therefore,

$$E = hv$$

If the energy of the photon does not match the gap between two energy levels, no transition can occur and the photons are not absorbed. You can think of the energy levels as being a ladder: if the electrons don't take steps of the right size they have nothing to hold on to:



The general rule for a transition is:

$$\Delta E = hv$$

A spectroscopic absorption measurement consists of passing light through a sample and measuring the intensity of the transmitted light as a function of wavelength. Wavelengths

corresponding to the energy separation between two energy levels are absorbed by the sample and the rest of the photons are transmitted (and scattered). In the absorption spectrum, you see peaks of the wavelengths that have been absorbed by the sample, which are not present in the light beam that has passed it.



So why do the spectra in this experiment show wide peaks instead of sharp lines at discrete wavelengths, as shown to the right?

In solution, the energies of molecules are affected by their interactions with others very close by. The molecules are also rotating and vibrating and, as you will see in the lecture course, all three effects mean that transitions occur at a range of different energies so we observe a broad band of absorption rather than a single strong line.



The Beer-Lambert Law relates the ratio of the initial intensity of the light beam and its intensity once it has passed through the sample to the concentration of the sample:

$$\frac{I}{I_o} = e^{-\alpha cl}$$

In this expression I_0 is the initial light intensity, I the measured intensity after absorption by the sample, α is the "absorption coefficient", c the concentration of the absorbing species and l is the path length, in other words, the distance the light travels through the absorbing material.

For small x, exp(-x) can be approximated as 1-x and the expression becomes

$$\frac{I}{I_o} = -\alpha cl$$

Therefore, the fraction of light which is absorbed is proportional to the concentration of the absorbing species as long as this fraction of is small. This is the basis for much of the use of spectroscopy for quantitative analysis.

APPENDIX K. CHEMICAL PROPERTIES, HAZARDS AND EMERGENCY TREATMENT

Gloves are not necessary for this experiment, but may be worn if you wish. Neoprene or nitrile are both suitable materials.

Buffer solution, pH 10.9

White powder, white tablets or colourless solution. Harmful if swallowed in quantity. Skin or eye contact: wash off with water. If swallowed: wash out mouth with water.

Calcium carbonate

White powder. Dust may irritate the eyes or lungs. Skin or eye contact: wash off with water.

Copper (II) sulfate

Blue crystals dissolving to give deep blue aqueous solution. Harmful if swallowed or breathed in. Skin contact: wash off with water. Eye contact: wash out with water and seek medical attention. If swallowed; wash out mouth with water, drink plenty of water and seek medical attention.

Disodium EDTA

White crystalline powder. Harmful if swallowed. Skin or eye contact: wash off with water. If swallowed: wash out the mouth with water, drink plenty of water and seek medical help.

GBHA

Off-white powder or colourless solution containing ethyl alcohol. Irritant. Skin or eye contact: wash with water. If swallowed: wash out mouth with water, drink plenty of water and seek medical help.

Hydrochloric acid (dilute)

Colourless solution. Harmful if swallowed, and in contact with the eyes. Brief skin contact is relatively harmless, but extended contact may lead to burns. Skin contact: wash off with water. Eye contact: wash off with water and seek medical help. If swallowed: wash out mouth with water, drink plenty of water and seek medical help.

4-Nitrophenyl ethanoate

Off-white powder. Skin, respiratory and eye irritant. Skin or eye contact: wash with water. If swallowed: wash mouth with water. If swallowed in quantity seek medical help.

Sodium hydroxide (dilute)

Colourless solution with a slippery feel. Harmful in contact with the skin or if swallowed. **Potentially very harmful in contact with the eyes**. Skin contact: wash well with water. Eye contact: rapid action is essential: wash the eyes for several minutes with water and call for immediate medical help. If swallowed: wash out the mouth with water, drink plenty of water and call for medical help.

Zinc carbonate hydroxide

White powder. Irritant. May be harmful if swallowed in quantity. Eye or skin contact: wash off with water. If swallowed: wash out mouth with water.

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