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Laboratory Safety

SAFETY RULES

Many experiments in chemistry use potentially dangerous chemicals and procedures. Providing you follow appropriate laboratory and safety rules, the risks associated with laboratory work can be minimised. The following is taken from the Australian Standards for Laboratory Practice (AS 2243.1-1990). Always follow these rules.

Behaviour

1. Never adopt a casual or reckless attitude in the laboratory and always be conscious of the potential hazards.
2. Never run in the laboratory or along corridors.

Clothing

3. Ensure that personal clothing is suitable for laboratory conditions, e.g. non-slip, closed-in footwear. Do not wear open-toed shoes in the laboratory.
4. Always wear eye protection when in the laboratory.
5. Use protective clothing and devices appropriate to the operation being carried out, giving due thought to the work being carried out near you.

Due care

6. Always exercise care when opening and closing doors and entering or leaving the laboratory.
7. Take additional care when carrying any potentially hazardous substance.
8. Clean up spills immediately and report accidents or breakages to the teacher.

Emergency

9. Keep all fire escape routes completely clear at all times.

Food and poisons

10. Do not handle or consume food in the laboratory.
11. Regard all substances as hazardous unless there is definite information to the contrary.
12. Always use a fume hood when working with highly toxic, volatile or odorous substances.
13. Wash skin areas that come in contact with chemicals, irrespective of the concentration.
14. Dispose of specialised wastes (e.g. broken glassware and organic substances) in containers reserved for the particular type of waste.

SAFE LABORATORY PRACTICES

Following safe laboratory practices and being aware of potential hazards can avoid most accidents in the laboratory.

Acids and alkalis

- If spilt on the skin, acids and alkalis should be thoroughly washed off under running water. Affected clothing should be removed immediately.
- If acids need to be diluted, always add the acid to the water. Never add water to acid.

Burns

- Take care not to handle hot glassware.
- Extinguish Bunsen burners when not in use.
- If the Bunsen burner is to be left for a short time, adjust the flame to an easily visible yellow colour.

Chemical spills

- If chemicals are spilt on the skin, remove affected clothing and wash the affected area thoroughly with running water.
- Do not carry bottles by the neck.

Cuts

- Take care when setting up glassware to avoid putting the glass under stress. Never force glass tubing through a cork or rubber stopper. Lubricate the tubing with water or inert grease and gently work the tubing into the stopper.
- When boring a cork or stopper, lubricate the borer with 1:1 ethanol/glycerol and place the stopper on a piece of wood, not on your hand.

Eye injuries

- Safety glasses must be worn. If you wear prescription glasses, you should wear over-glasses, safety goggles or a visor.
- Acids and alkalis are particularly dangerous. If any material gets into the eye, it should be washed immediately and very thoroughly with running water. Note the location of the laboratory eyewash.
- Eye injuries occurring in the laboratory (including splashes) must be referred to medical staff.

Fire

- Never panic.
- Safety of people comes first. Know the escape routes and keep them clear.
- Remember the location of the fire extinguisher and fire blanket. Do not use a naked flame in the presence of flammable organic solvents such as alcohols, ketones and carboxylic acids.
- If a person's clothing catches fire, put the victim on the floor and extinguish the fire with a laboratory coat or fire blanket.
- If a fire gets out of control, if possible turn off gas and electrical appliances, evacuate, shut the doors of the laboratory, and raise the alarm.

Heating test tubes

- This can be dangerous if the top of the test tube is pointed towards others and if the test tube is heated too rapidly. Point the top of the test tube away from others and heat gently by holding the test tube above the flame.

Ingestion

- Never taste chemicals.
- Do not pipette by mouth. Use manual pipette pumps.

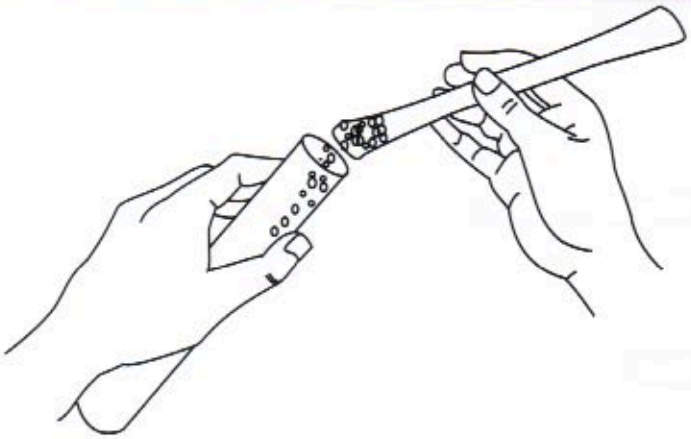
Poisonous gases or vapours

- Generally avoid inhaling any gases or vapours.
- If testing the odour of gases, gently waft the gas towards your nose and cautiously sniff.
- Use the fume hood when generating or using poisonous gases or vapours.
- Report mercury spills immediately to the teacher.

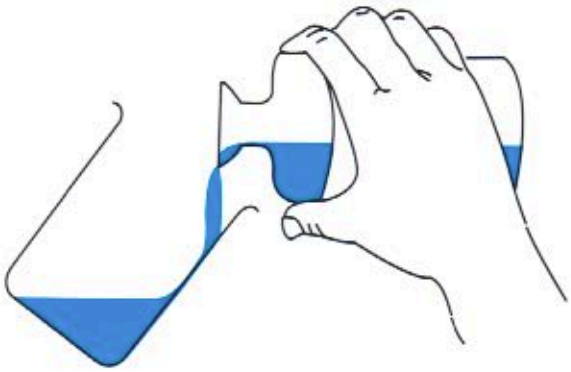
Laboratory techniques

Transferring solids

A spatula is used to transfer small quantities of solid material from a stock bottle to a test tube, beaker or watch glass. The spatula must be thoroughly cleaned between uses by washing with water and thoroughly drying. Solid material must never be returned to a stock bottle as this may cause contamination. Discard any excess into the rubbish bin.



Transferring liquids by pouring

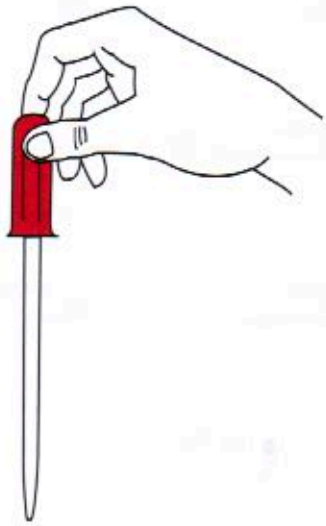


When pouring from a reagent bottle, the receiving vessel (beaker, flask, test tube, etc.) should be tilted so that the liquid can run down the side of the vessel without splashing.

When pouring from a beaker, the liquid stream can be directed using a stirring rod. The stirring rod is held against the beaker lip and directs the liquid stream into the receiving vessel.

Transferring liquids with a dropper

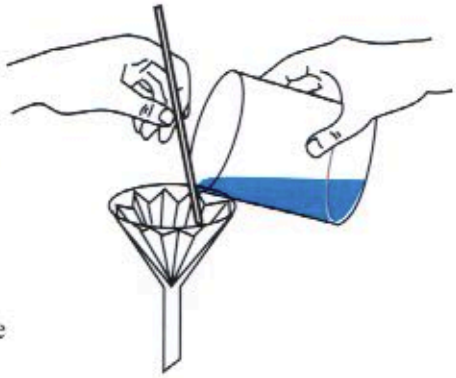
A dropper or Pasteur pipette can be used if a small volume of liquid is required. Sometimes reagent bottles are provided with their own dropper. Be careful not to exchange these droppers between bottles nor allow the droppers to touch the bench or the insides of test tubes or beakers.



If the reagent solution is not provided with a dropper, do not use your own dropper to make the transfer, as this will contaminate the liquid. Wash a test tube or beaker, rinse with distilled water, rinse with a small amount of reagent and then transfer some of the reagent into the test tube or beaker. Use a clean dropper to obtain the required quantity of liquid from the test tube or beaker.

Do not invert the dropper when transferring liquids. Hold the dropper upright as atmospheric pressure is sufficient to support the liquid in the dropper. If the dropper is inverted, liquid may run into the rubber bulb at the end of the dropper, which tends to rot the rubber and contaminate liquids transferred on future occasions.

Filtration



Filtration is a technique used to separate a solid from a liquid. Depending on the situation, the solid may be an impurity that is discarded, or it may be the required product. In gravity filtration, separation of the mixture is achieved by adding it to a filter paper supported in a filter funnel. The filter funnel is itself supported by either a funnel holder (metal ring) or a filter funnel stand (wooden stand). The filter paper is folded in one of two ways.

Method 1: The filter paper is folded into halves and then quarters. One of the segments is opened and the filter paper is placed into the funnel.

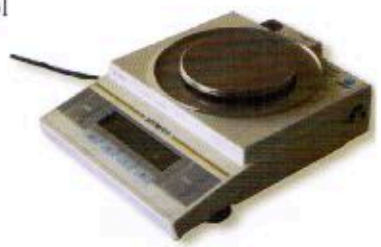
Method 2: A fluted filter paper is obtained by folding the filter paper so that there are sixteen segments. The filter paper is then opened. A maximum filtering area is obtained with minimum contact between the filter paper and the funnel. (This type of folded filter paper is shown in the image)

Filtering to separate a solid:
Place the filter paper in the filter funnel and moisten it with a small amount of water. The liquid to be filtered is transferred from the beaker using a glass rod to direct the liquid into the filter paper. Care must be taken to ensure that the liquid does not come above the edge of the filter paper, and that the glass rod does not come in contact with the filter paper.

If the solid is required, extra liquid may need to be added to the beaker to wash out any residual material. Depending on the solubility of the solid, the filtrate or distilled water from a wash bottle may be used.

Measuring mass

The accuracy with which you want to measure the mass of a particular substance will depend on the purpose of the activity. In some experiments you will only want to carry out a rough measurement within 0.1 g, but in other experiments you will want to measure an accurate mass, within 0.001 g or even 0.0001 g.
The accuracy of your measurement depends on the equipment available within your school laboratory and the best you might be able to do is 0.01 g.



Using a top-loading electronic balance.

1. Place the container on the balance pan and either tare the balance so the readout is 0.0 g or 0.00 g or 0.000 g depending on the accuracy of the balance being used, or record the initial balance reading.
2. Carefully add the required amount of substance and note the new reading.

Measuring liquid volumes

A range of glassware is used for measuring liquid volumes. This includes graduated cylinders, pipettes, burettes and volumetric flasks.

A graduated cylinder is used to deliver variable approximate volumes of liquid with moderate accuracy. Graduated cylinders, or measuring cylinders as they are often called, come in various sizes:

10 mL (with 0.1 mL graduations),
25 mL (0.5 mL),
50 mL (1 mL),
100 mL (1 mL),
250 mL (2 mL),
500 mL (5 mL) and
1 L (10 mL).

Laboratory techniques

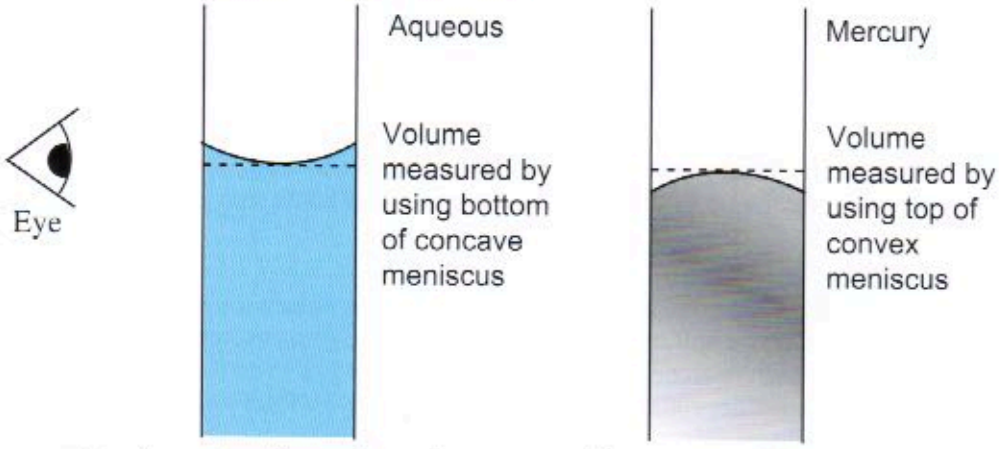
Cleanliness of glassware

In all situations it is essential that glassware is clean and free from grease. To test for clean glassware, pour in some distilled water and swirl it gently. The glassware is clean if, when the water is poured out, an unbroken film remains on the glass surface, which drains uniformly under gravity. If the glass is dirty or greasy, the water will form droplets that stick to the sides of the glass and cause errors in volume measurements.

If glassware is dirty, it should be cleaned with dilute detergent solution. This is then drained, rinsed several times with tap water, and finally rinsed with distilled water.

The liquid meniscus

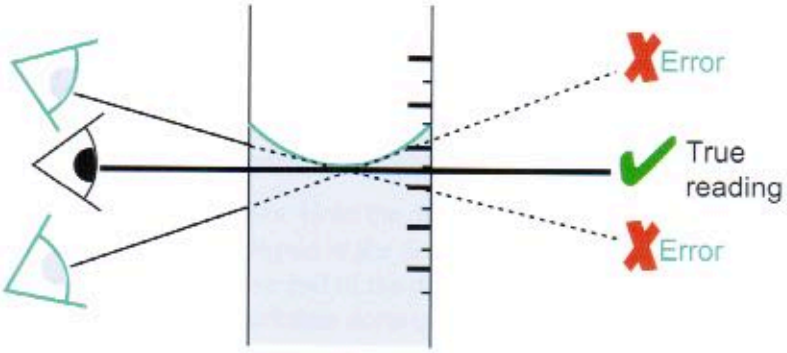
The measurement of a liquid volume involves comparing the liquid level in a glass container with an accurately etched or printed line on the container. The surface of a liquid is curved and with water, occurs as a concave meniscus. The bottom, curved line of the meniscus is used when measuring the volume. In some intensely coloured aqueous solutions, such as potassium permanganate solution, it may be necessary to use the top of the meniscus, although this procedure is less accurate as the top of the meniscus is more difficult to identify.



If the liquid is mercury, as in a barometer, the meniscus is convex and the top curved line of the meniscus is used. When using a graduated cylinder or burette, the bottom of the meniscus may not coincide with a particular graduated line. In these cases, where the bottom of the meniscus lies between two graduations, the volume reading is estimated from the position of the meniscus relative to the two adjacent graduations.

Parallax error

Reading analogue scales such as those on metre rules or measuring cylinders, is more challenging than reading digital scales. A major difficulty in reading analogue scales is 'parallax error'.



Laboratory techniques: Volumetric analysis

Volumetric analysis is one method of determining the amount of a particular substance present in a given sample. It is used as a form of quality assurance in many industries, such as wine making. In order to maintain the quality of wine a number of components are assessed on a regular basis. The acid content of wine, for example, is closely linked to appearance and taste. The acid concentration can be determined by volumetric analysis.

In industry there are now automated forms of volumetric analysis, but the manual form that you will be learning is still used, particularly by small companies and laboratories.

Titration

The process of adding one solution to another until reaction between them is complete is known as titration. One solution, the standard, contains a known quantity of one reactant and information about the other solution can be deduced from knowledge of the reaction involved.

It is essential that all glassware used in volumetric analysis is extremely clean and free from grease. Glassware should be thoroughly cleaned with dilute detergent solution, followed by several rinses with tap water and finally a rinse with distilled water.

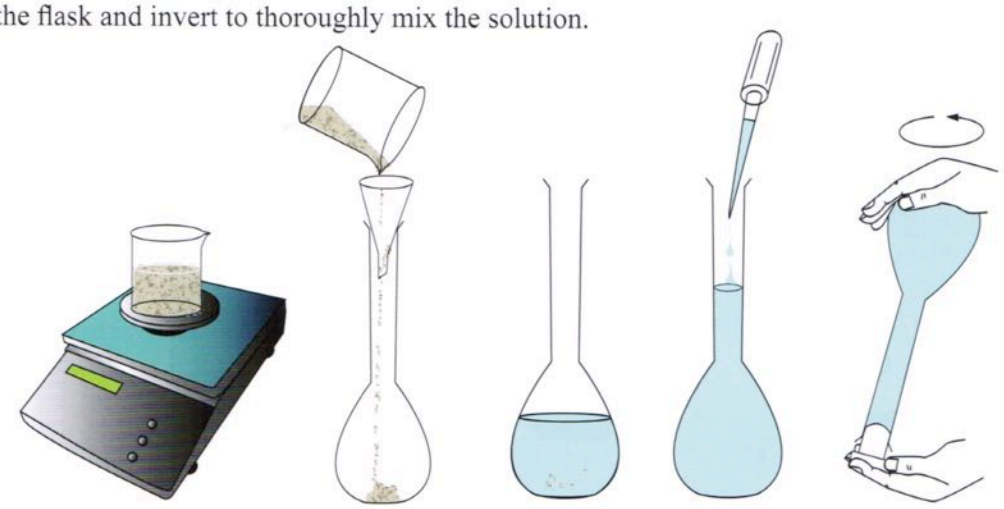
If a solution is to be placed in a vessel from which precise volumes are to be dispensed or withdrawn, this vessel should be rinsed with a small portion of the solution to be placed in it. Such vessels include the burette, pipette, storage bottles, and beakers used for filling burettes and pipettes. As a general rule, if you want to maintain an accurate concentration, wash the vessel with some of the solution to be used in it. If you want to maintain the number of moles, wash the vessel with distilled water.

Some of the techniques used in volumetric analysis are described below.

Using a volumetric flask to prepare a standard solution

Volumetric flasks are used in the preparation of standard solutions. These are often prepared by dissolving an accurately known mass of a pure solid to prepeare an accurately known volume of solution. The preparation of a standard solution involves the following steps:

1. Transfer approximately the required quantity of solid to a suitable beaker and measure its mass accurately.
2. Dissolve the solid in distilled water ensuring that only about one half the final solution volume of water is used.
3. Transfer the solution to the volumetric flask ensuring complete transfer by washing the beaker several times with distilled water, then pouring the washings into the flask.
4. Add distilled water from a dropper to make the solution up to the calibrated mark.
5. Stopper the flask and invert to thoroughly mix the solution.



1. 2. 3. 4. 5.

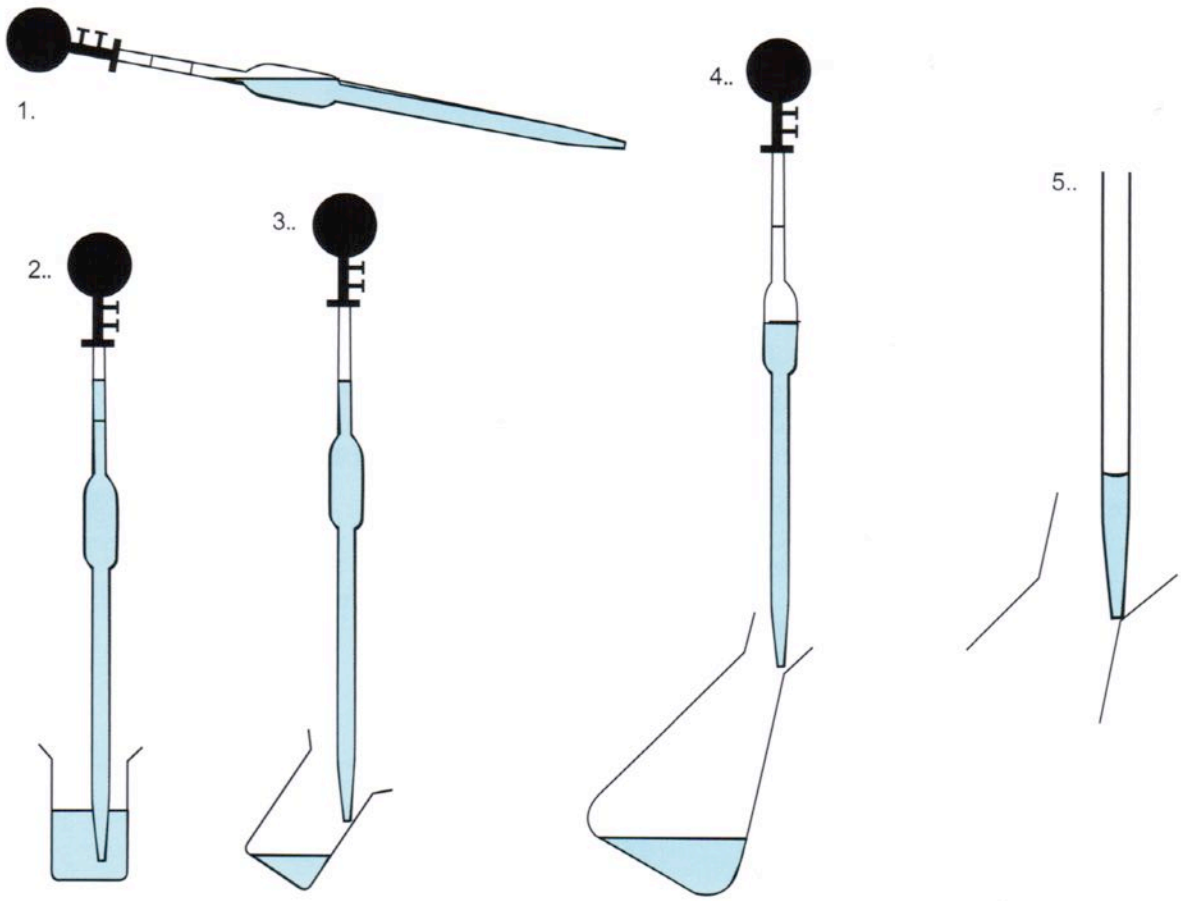
Laboratory techniques: Volumetric analysis

Using a pipette to transfer a fixed volume of solution

Pipettes are used to accurately deliver a fixed volume of solution. This fixed volume is sometimes called an **aliquot**.

The procedure for using a pipette is as follows:

1. After thorough cleaning, the pipette should be rinsed out with a few millilitres of the solution to be used.
2. Making sure that the tip of the pipette is held well below the surface of the solution being sampled, the solution is drawn up by suction to a point just above the etched mark.
3. Raise the tip of the pipette above the solution being sampled, wipe adhering liquid from the outside of the pipette, then allow the solution to run out of the pipette until the bottom of the meniscus coincides with the etched mark. Touch the tip of the pipette against the side of the beaker to remove any drops of solution adhering to it.
4. Allow the solution to run into the receiving vessel with the tip of the pipette touching the inner wall of the vessel.
5. When the solution has finished running out, the tip of the pipette should remain touching the side of the vessel for a further 15 seconds. After this time, the correct volume should have been delivered in spite of the small amount of solution remaining in the tip. Do not blow this liquid out.



Using a burette in a titration

Burettes are used to deliver, at a controllable rate, any volume of liquid up to 50 mL. The procedure for using a burette in a titration is as follows:

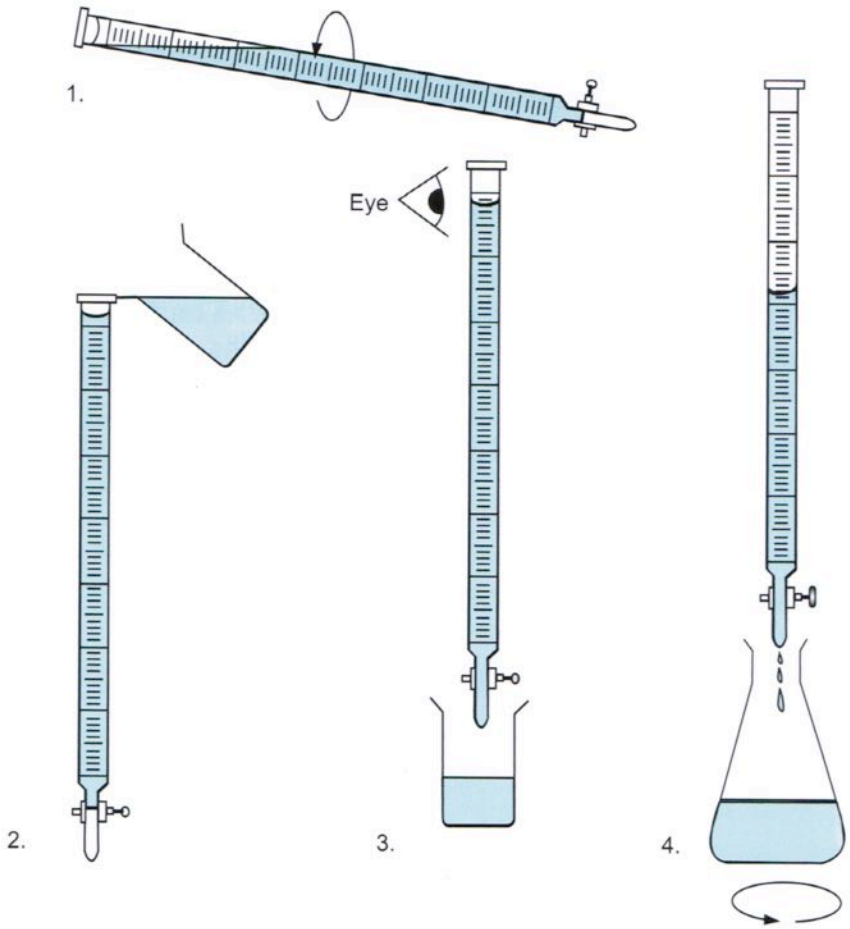
1. After thorough cleaning (Fig 1), rinse the burette with a few millilitres of the solution to be used.

2. Place the burette in its stand, ensuring it is vertical. Lower the burette so that the top is at eye level (Fig 3) when it is being filled. Add liquid from a 100 mL beaker until the burette is filled to a point a little above the 0.00 mL mark (Fig 2).

3. Run the liquid out through the tap to ensure that the tip below the tap is filled with liquid and contains no air bubbles. The level should now be at or below the 0.00 mL mark. It is a waste of time trying to obtain an 'initial reading' of exactly 0.00 mL. Take an initial reading of the level of the solution in the burette. This reading should be estimated to the nearest 0.01 mL. Take this reading with your eye level with the meniscus in the burette.

4. Open the burette tap and allow the solution to run into the flask containing the solution being titrated. While the solution is being added from the burette the receiving flask should be swirled (Fig 4) to ensure mixing of the solutions. Occasionally the inside surface of the flask should be washed with distilled water from a wash bottle.

5. Near the end of the titration the solution should be added drop-wise from the burette so that the end point can be determined accurately. A final reading of the burette is then taken, and the volume of solution used, **the titre**, can be calculated from the difference between the initial and final readings.



A guide to writing practical reports

Introduction

In general your practical report should reflect as accurately as possible all measurements and observations you made. It should also clearly illustrate your knowledge and understanding of the subject covered by the practical work.

Practical reports should include the following headings:

Aim, purpose or hypothesis

This should be a short sentence or two, describing briefly what you are trying to find out from the experimental procedure you are conducting.

Equipment list and procedure

These should only be included for investigations where you need to design the experiment yourself. There is no point copying equipment lists and instructions when writing a report for a skill building experiment.

Results and/or observations

Results are numerical quantities which you measure during the experiment.

- You should record all measured quantities in your report.
- Record these quantities in a suitable table, particularly if there are a large number of measurements.
- You must include units for each quantity that you measure and record.
- Each measurement must be written to the appropriate number of significant figures. You may also be required to estimate the uncertainty involved in each measurement.

A useful rule of thumb is that the uncertainty in a measurement is half the smallest scale division. For more detail read the 'Uncertainty and error' section on page 16.

Observations are qualitative descriptions of what you actually see, hear, smell and detect by touch during an experiment.
What you infer or conclude from the observations or from your knowledge about the experiment must not be included as observations.

Example 1

If you place a piece of zinc metal into hydrochloric acid solution one observation you might make is that colourless bubbles are produced on the surface of the zinc.
This is an **observation.**
From your knowledge of this type of reaction you may infer that the bubbles contain hydrogen gas.
This is an **inference** not an observation.

Example 2

If you drop an object one observation you might make is that you hear it hit the ground.
This is an **observation.**
You may infer that some of the kinetic energy of the object is converted to sound energy.
This is an **inference** not an observation.

Processing of results and questions

Written answers or calculations

- Include answers to all questions in your report.
- You will often use calculations to generate new quantities from numerical results. Full details of these calculations must be included in your report. If large numbers of similar calculations are required, then details of only one example of each type should be included.
- Always quote numerical results to an appropriate number of significant figures.
- One-word written answers are not acceptable. You must always include some justification or explanation in your answer.

Significant figures represent an approximate system of indicating the degree of accuracy of results. The precision with which an instrument is manufactured, the measurement scale provided and the skill of the experimenter contribute to the level of uncertainty of a measurement. For more detail read the 'Uncertainty and error' section on page 16.

Graphs

- These should be drawn on graph paper and to an appropriate scale.
- These should not be smaller than half an A4 page.
- Label the axes with a suitable scale, the quantity being graphed and the units used. Give your graph a title.
- You should draw the line or curve of best fit (by eye) since the quantities plotted are measured values and so must contain uncertainties. The graphing process will remove outliers.

Conclusion

The conclusion for an experiment or investigation should relate to the aim, purpose or hypothesis of the experiment or investigation. It should answer the question asked or implied in the aim. The conclusion may be stated as the answer to one of the questions. If this is so, then there is no need to write a separate conclusion, otherwise a conclusion must be included.

If the aim of the experiment is to experimentally verify a quantity, which has a known, generally accepted value, some comparison between the measured and established value should be made.

Risk Assessment: Laboratory reports and investigations

In planning your investigations and preparing practical work you should be aware of the possible hazards of some chemicals.
You can download an iphone/android app: **"Material Safety Data Sheets"** at no charge.
You should ensure you are fully informed of any necessary precautions you should take in handling chemicals.

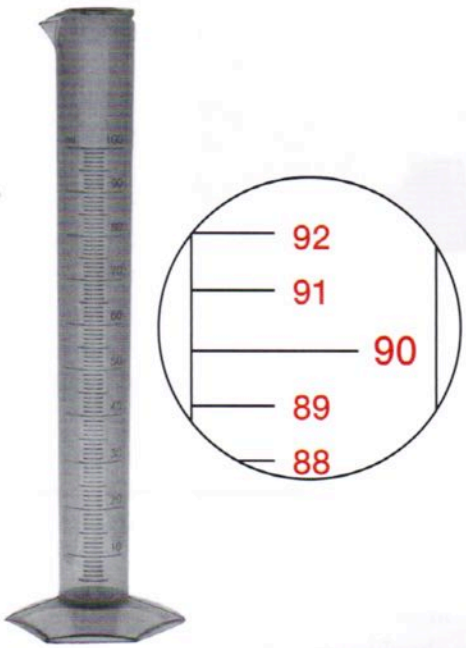
Uncertainty and error

Uncertainty in measurement

Measurement is an important part of laboratory work in chemistry. When any measurement is made, such as determining mass, volume or temperature, it is subject to a degree of uncertainty. What this means is that any quantitative data you record actually occurs within a range of values that could represent the true value.

Different pieces of apparatus have different levels of uncertainty associated with them and so it is important to carefully consider the piece of equipment you select for a task. Think of the variety of glassware available for measuring volume. There are beakers, measuring cylinders, volumetric pipettes, burettes and volumetric flasks of various grades, shapes and sizes. Selection of the most appropriate piece of glassware depends on the accuracy that is required for the task you are carrying out and your budget. The volume of water in a beaker being used as a water bath to cool a test-tube does not need to be measured to the nearest 0.1 mL whereas the volume of water added to reactions when investigating rate of reaction is critical.

Uncertainty in analogue equipment/instruments



If you were measuring 90 mL using a 100 mL measuring cylinder the uncertainty of that measurement would be +/- 0.5 mL as the smallest scale division is 1.0 mL. This means that the true value of the volume measured is in the range 89.5- 90.5 mL. The measured volume could be above or below the 90 mL you are trying to achieve.

A beaker would be unsuitable for measuring a volume of 100.0 mL accurately. The most accurate measuring device for a volume of 100.0 mL in a school laboratory would usually be a 100.0 mL volumetric flask. There is only one line on the flask so you cannot calculate the uncertainty using the half the smallest scale division rule; however, in this case there is generally a manufacturer's uncertainty written on the apparatus. Different grades of glassware can be purchased. The best quality grades have the lowest uncertainty. A Grade A 100.0 mL volumetric flask has an uncertainty of +/-0.10 mL.

Uncertainty in digital equipment

When reading a digital scale the uncertainty is plus or minus the smallest scale division. For example if you use an electronic balance that reads to one decimal place its uncertainty would be +/- 0.1 g. A balance that reads to two decimal places has an uncertainty of +/- 0.01 g.

Experimental error

All measurements have a degree of uncertainty resulting in experimental error. The experimental error in a result is the difference between the experimental value and the published or theoretical value. There are two types of experimental error: random error and systematic error. Both should be considered when evaluating any quantitative investigation.

Random error

Random errors come from measurements that have an equal chance of being above or below the actual value. Values taken from any analogue or digital scale have random error that can be stated in the uncertainty of the reading. Random errors can never be completely eliminated from measurements. Random errors affect the reliability or precision of the results. Precision refers to how close the values are to each other. A reliable method is one that produces consistent results with similar data readings.

If a number of experimental trials are carried out it is possible to reduce the effect of random errors on the final result. If an anomalous result is obtained, repeating trials and calculating the average minimizes the impact of the outlier if there is no justification for discarding it from the data set.

Another source of random error that must be considered is that humans may not be as accurate as the device being used for the measurement. For example human reaction time must be considered if using a stopwatch. The stopwatch may read to hundredths of a second; however human reaction time is far greater than this at around 0.1 s. In this case the uncertainty of the measuring device has minimal effect on the results compared to the human impact. Reaction time may impact on experimental data in a random manner.

An experiment with low random error will be more reliable or precise; however, it may not necessarily produce accurate results. The precision of a measurement refers to the consistency among a number of measurements made in the same way.

Systematic error

Systematic errors are a result of flaws in the experimental method or apparatus that lead to a result that is always either above or below the true value. Examples of things that result in systematic errors include the type of equipment used, calibration of the equipment and human judgement.

Systematic errors cannot be reduced by increasing the number of experimental trials carried out. They must be overcome by altering the method in some way, generally by using different equipment. Enthalpy changes such as the heat of neutralisation can be estimated experimentally by measuring temperature change when acid and alkali are mixed together in a beaker. The increase in temperature and other data can be used to estimate the enthalpy of reaction. The enthalpy change obtained is lower than the true value due to heat loss from the reaction vessel. The heat loss is the most significant source of systematic error in this experiment. Altering the method to minimize heat loss by adding insulation to the beaker will achieve a more accurate result. Human colour perception could impose systematic or random errors in an experiment. You need to use your common sense when evaluating a particular experiment to judge whether the error is random or systematic. Removing the need for human judgment in the experimental design by choosing a piece of equipment that can measure colour intensity (a colorimeter) or using a digital pH meter that gives continuous monitoring of pH rather than a chemical indicator that changes colour can reduce systematic error.

Section 1: Investigating in Chemistry

Exploring Chemistry Year 12: Experiments, Investigations and Problems **provides opportunities for students to continue developing their science inquiry skills.**

Section 1: Investigating in Chemistry involves identifying and posing questions; planning, conducting and reflecting on experiments and investigations; processing, analysing and interpreting data; and communicating findings.

The chemistry experiments and investigations in this book are activities in which chemical concepts are explored and ideas, predictions or hypotheses are tested and conclusions are drawn in response to a question or problem. The collection and analysis of data is an important component of the experiments and investigations. This can involve collecting or extracting information and reorganising data in the form of tables, graphs, flow charts, diagrams, text, keys, spreadsheets and databases.

Chemical Equilibrium

Understanding the behaviour of materials helps in interpreting chemical processes. For example, collision theory and Le Châtelier's Principle help to explain and predict energy changes in reactions, reversible reactions and equilibrium. As well as knowing the theory, you must be able to read, write and interpret chemical equations and to perform quantitative investigations and calculations in order to communicate your understanding of change processes in chemistry. Investigating the relationships between concepts, models and principles, and sustainable chemical practices in industrial processes helps you to see how a maximum yield at the lowest possible cost can be achieved.

Fritz Haber, airbags and blood

Accessible nitrogen is a vital component in soils for the healthy growth of plants. Historically the nitrogen in soils was replenished by the use of natural fertilisers such as manure and growing nitrogen-fixing plants such as beans (legumes). However, with heavy cropping, it was found that this was not sufficient to maintain the nitrogen levels and food shortages were predicted.

Fritz Haber, a German scientist, was interested in finding a way to convert atmospheric nitrogen into ammonia, a compound containing nitrogen that could be used to make nitrogen based fertilisers for plants. As the reaction between hydrogen and nitrogen tends to equilibrium at a low yield, conditions to improve the yield needed to be identified. He and his colleagues found that high temperatures and pressures produced an acceptable yield of ammonia.

$$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g)$$

They also developed a method for achieving these conditions in the laboratory. This was something that had never been done before. They also recognised the need for a catalyst for, although the conditions produced a reasonable yield, the reaction proceeded too slowly to be economic. Haber's choice of catalyst was a combination of osmium and uranium. When the process went into commercial production an iron oxide catalyst was found to be effective and economical.

Fritz Haber © Science Museum/Science & Society Picture Library

The production of ammonia from atmospheric nitrogen allowed Germany to be less reliant on imported chemicals during World War I. The ammonia was converted into fertilisers and explosives. It is believed that Haber's process was responsible for the prolonging of the war.

Haber was also known for his contribution to the development of chemical weapons. He led a team of chemists who were responsible for the use of chlorine gas as a chemical weapon in the trenches during World War I.

Haber was awarded the Nobel Prize in 1918 for his work on ammonia and became a very rich man. The personal cost, however, was high. His wife committed suicide because of his involvement in the development of chemical weapons. In 1933 he was forced to leave Germany because of his Jewish background. Haber died in 1934.

Airbags

Airbags were developed to reduce impact injuries in car accidents. Many modern cars have multiple airbags to reduce injuries from both head-on and side impact collisions. An airbag contains sodium azide (NaN_3) that reacts very rapidly upon the application of an electrical current (which is designed to occur during a collision) to produce sodium metal and nitrogen gas.

An equation for the reaction is: $2\,NaN_3(s) \rightarrow 2\,Na(s) + 3\,N_2(g)$

It is the formation of the nitrogen which inflates the airbag. An understanding of the relationship between mass of sodium azide and volume and pressure of nitrogen produced is important in order to calculate the appropriate amount of sodium azide to inflate the airbag to the correct pressure given the volume of the airbag.

Career profile 1: Toxicologist

Blood: Oxygen transport and carbon monoxide poisoning

Haemoglobin is an iron based protein in the blood that is responsible for the transport of oxygen around the body. Over 90% of the carbon dioxide produced by cellular respiration returns to the lungs by dissolving in the blood plasma, but some is involved in the following equilibrium (Hb represents haemoglobin):

$HbO_2 + CO_2 \leftrightarrows HbCO_2 + O_2$

In regions of high oxygen concentration, such as in the lungs, carbon dioxide is displaced from the haemoglobin and the reverse is true in regions of high carbon dioxide concentration, such as in the cells.

If carbon monoxide is present the following equilibrium occurs: $HbO_2 + CO \leftrightarrows HbCO + O_2 \quad K_c = 2 \times 10^7$

This second equilibrium favours the products significantly, reducing the haemoglobin's ability to transport oxygen around the body.

Profile of a Toxicologist

The use of drugs and alcohol has been associated with an increased incidence of injury and death in the workplace. (Refer to the Australian Government Occupational Health and Safety Act)

This is where testing for drugs and alcohol comes into play, especially in industries such as mining and construction, where there is a potentially high risk of injury. We all know that use of substances such as drugs and alcohol are potentially mind altering and if consumed in high enough amounts seriously affect one's judgment.

So, who does the testing? Biochemistry or Toxicology Departments of Pathology Laboratories do the testing. The sensitive nature of this work requires anonymity of the scientists and pathology centre that have provided information for this article. The sample, usually urine is either collected at the worksite or the worker provides a sample at a collection centre. Either way, it needs to be collected under supervision to prevent tampering and sample substitution. The sample is then put through a machine for screening. This initial testing (called an immunoassay) uses specific antibodies to which compounds of interest attach.

If the screening test is positive, then it is followed up by a confirmatory test using a more specific and sensitive analytical technique called Gas Chromatography with Mass Spectrometry (GCMS) that looks for specific drugs, which could be illicit or prescibed. The Scientist in Charge of Biochemistry of a local Pathology company says "its really interesting to be working with sophisticated technology such as GCMS."

Some examples of drugs tested for include; opiates (such as codeine used in pain-killers or the illicit form, heroin), amphetamine type substances (such as pseudoephedrine found in some cold & flu medications or illicit forms like ecstasy and methamphetamine) and cocaine to name a few.

There are various staff levels in a pathology laboratory biochemistry department. They include Laboratory Assistants, Laboratory Technicians and Medical Scientists. Laboratory Assistants do not require special qualifications and can be trained on the job. As a Laboratory Technician, you would require a certificate of laboratory practices or equivalent at a minimum. The Medical Scientists are the highest qualified personnel authorized to sign off on laboratory results and possess a science degree with specialization in the areas of biochemistry, chemistry or toxicology.

Toxicology scientist in biochemistry provided courtesy of a local pathology provider

Experiment 1: Rate of reaction

Notes

The rate of a chemical reaction is how quickly the reactants are changed to products. Reaction rates can therefore be determined by measuring the rate of disappearance of reactants or the rate of appearance of products.

Factors that affect the rate of a reaction are
- the nature of reactants
- state of subdivision of the reactants
- concentration or gas pressure of the reactants
- temperature of the reaction system
- the presence of a catalyst

These factors can be explained, and their effects on the rate of a reaction predicted, using the collision theory. The collision theory of reactions uses the idea that particles must first collide before a reaction can occur. A successful collision is one where products are formed.

In this experiment you will investigate the reaction between marble chips, $CaCO_3$, and dilute hydrochloric acid solution, $HC\ell$ (aq).

Equipment

cotton wool
an electronic or triple beam balance
250 mL conical flask
50 mL measuring cylinder
100 mL beaker
spatula or spoon
timer: stop-watch or stop-clock
approximately 2 g (equivalent masses) of $CaCO_3$:
  large marble chips,
  small marble chips
40 mL of:
  2.0 mol L^{-1} hydrochloric acid solution [$HC\ell$]
  1.0 mol L^{-1} hydrochloric acid solution [$HC\ell$]

Procedure

Experiment 1

1. Accurately weigh approximately 2 g of large marble chips in a 100 mL beaker. Record the mass in a table similar to Table 1.1.
2. Using the 50 mL measuring cylinder, measure 25 mL of 2.0 mol L^{-1} hydrochloric acid and pour into the 250 mL conical flask.
3. Place the conical flask of acid and the beaker of marble chips onto the balance and record the total mass against time zero in a results table.
4. Pour the marble chips into the beaker of acid and start the timer.
5. Replace the beaker onto the balance with the reaction flask.
6. Record the mass of the full setup (see Figure 1.1) every 30 seconds.

Notes

7. Continue to record the time until the reaction is complete, when all the marble chips have reacted. The reaction may take up to 15 minutes.

8. Describe your observations of the reaction.

Experiment 2

9. Repeat steps 1 to 8 using small marble chips.

Experiment 3

10. Repeat steps 1 to 8 using small marble chips and 1.0 mol L^{-1} $HC\ell$ in step 2

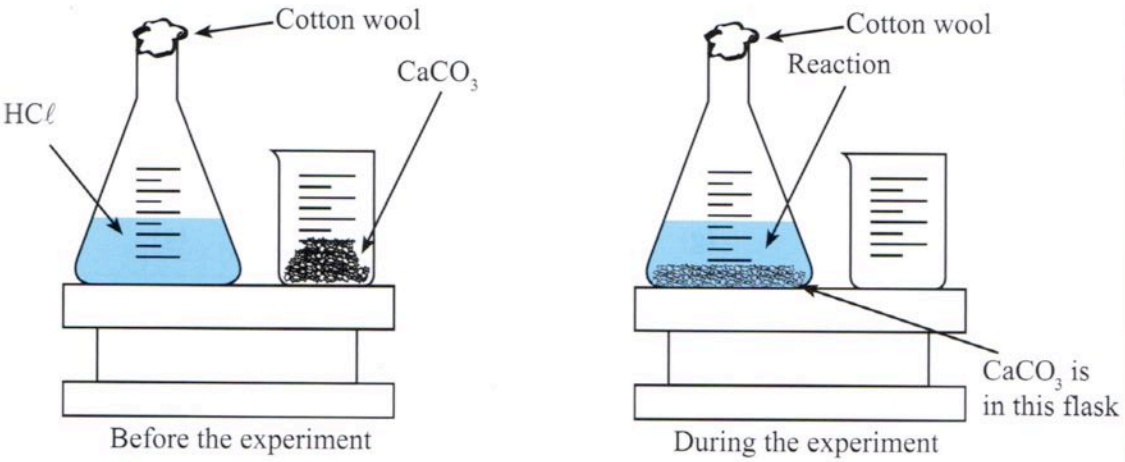


Figure 1.1 Experiment setup

Starting mass of $CaCO_3$	g	g	g

		Experiment 1	**Experiment 2**	**Experiment 3**
Time (s)	Total mass of set up	Large marble chips 2 mol L^{-1} $HC\ell$ (g)	Small marble chips 2 mol L^{-1} $HC\ell$ (g)	Small marble chips 1 mol L^{-1} $HC\ell$ (g)
0		0	0	
30				
60				
90				

Table 1.1: Results $CaCO_3$ + $HC\ell$ reaction

Experiment 1: Rate of reaction

Notes

Processing of results and questions

1. Write an equation for the reaction between calcium carbonate and hydrochloric acid solution.

2. The loss in weight of the reaction system is equal to the mass of carbon dioxide that is formed during the reaction and escapes into the air. Construct and complete a table similar to Table 1.2 below to record the rate of formation of carbon dioxide for each of the three experiments: Experiment 1, 2 and 3.

Mass of carbon dioxide formed (g) = loss in weight			
Time (s)	**Experiment 1** Large marble chips 2 mol L^{-1} $HC\ell$ (g)	**Experiment 2** Small marble chips 2 mol L^{-1} $HC\ell$ (g)	**Experiment 3** Small marble chips 1 mol L^{-1} $HC\ell$ (g)
0	0	0	0
30			
60			

Table 1.2: The rate of formation of carbon dioxide

3. On one set of axes, draw graphs of mass of carbon dioxide formed (vertical axis) against time for experiments 1 and 2.

4. After what time did the reaction stop
   (a) in experiment 1?
   (b) in experiment 2?

5. Explain the effect of particle size on the rate of reaction.

6. For a given mass of marble, how is particle size related to surface area?

7. Draw a graph (on the same axes) of mass of carbon dioxide formed (vertical axis) against time for experiments 2 and 3.

8. Approximately how many times faster or slower is reaction 2 than reaction 3?

9. What is the effect of decreasing the acid concentration on the initial rate of reaction?

10. How many moles of hydrochloric acid are used:
    (a) in experiment 2?
    (b) in experiment 3?

11. Why is the mass of carbon dioxide formed in experiment 3 half that formed in experiment 2?

Experiment 2: Temperature and gas solubility

Notes

Alka-Seltzer and other 'fizzing' drinks are mainly a combination of a solid weak acid and a carbonate (or hydrogencarbonate). When they are added to water, the acid dissolves and reacts with the carbonate to produce carbon dioxide gas. That is the fizzing you observe. Carbon dioxide is slightly soluble in water and produces a slightly acidic solution. This can be represented by the following equations:

$$CO_2(g) \leftrightarrows CO_2(aq)$$

$$CO_2(aq) + H_2O(\ell) \leftrightarrows H_2CO_3(aq) \leftrightarrows HCO_3^-(aq) + H^+(aq)$$

Bromothymol blue is an acid-base indicator. It is yellow in acidic solutions and blue in basic solutions.

Equipment

Alka-Seltzer tablets or soluble paracetamol
0.2 mol L^{-1} sodium hydroxide solution [NaOH] (approximately 20 mL)
bromothymol blue indicator (approximately 10 mL)
250 mL beakers × 3
test tubes
dropper pipettes (Pasteur pipettes)
ice bath
hot plate/hot water or Bunsen burner
thermometer (-10 to 110 °C)

Procedure

1. Place 150 ml of water into three 250 mL beakers.

2. Leave one beaker on the bench as a control; put one beaker in an ice bath, and a third on a hot plate and heat to about 80 °C.

3. Cut the tablet into two equal halves.
   Weigh out two 1.0 g samples of Alka-Seltzer or paracetamol.

4. When the beaker on the hot plate reaches a temperature of about 80 °C, remove it from the heat. Also remove the other beaker from the ice bath. Place 3 mL of bromothymol blue indicator into each of the three beakers. The colour should be a bright blue – add a drop or two of NaOH to the beaker if the water is not blue.

5. Simultaneously drop each tablet into the hot and cold beakers of water. Record your observations.

6. When the Alka-Seltzer stops bubbling, note the appearance of the liquids in each beaker.

7. Remove 10 mL samples from each beaker and place each sample in its own test tube.

8. Add drops of NaOH to the samples from the hot and the cold beakers of water, until their colours correspond to the colour of the water from the control. Record the number of drops of NaOH used for each test tube in an appropriate table.

Experiment 2: Temperature and gas solubility

Notes

Processing of results and questions

1. In which beaker did the tablet dissolve faster? Explain your answer in terms of your understanding of rates of reactions.

2. In which beaker does the colour change to a more distinct yellow?

3. What do the colour changes signify?

4. To which test tube was more NaOH added? What does this mean in terms of the solubility of carbon dioxide?

5. Which liquid, the hot or the cold, dissolves more gas? How do you know?

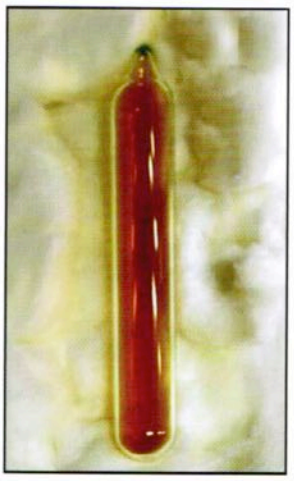
6. From your observations, is the dissolving of gas in water an endothermic or exothermic reaction? Justify your answer with respect to your understanding of equilibrium.

Experiment 3: Le Châtelier's Principle and gases

Many reactions proceed almost to completion. In reactions that do not proceed to completion the products of the reaction begin to react to reform the reactants until the rates of the forward and reverse reactions are equal. When such a situation exists, a state of chemical equilibrium has been achieved. Actually, all chemical reactions are reversible to some extent, but in many cases the reactions effectively go to completion.

With a reversible reaction it is possible to alter the relative proportions of products and reactants by altering one of the factors which affect the state of equilibrium. The effect of such changes can be predicted using Le Châtelier's Principle.

An understanding of Le Châtelier's Principle has been useful for identifying the conditions that are most likely to lead to higher yields in industrial processes. The conditions that lead to higher yields in the Haber process can be predicted using Le Châtelier's Principle.



NO_2/N_2O_4 equilibrium

In this experiment the equilibrium that occurs between the brown gas, nitrogen dioxide and the colourless gas, dinitrogen tetroxide, will be investigated.

$$2\,NO_2(g) \leftrightarrows N_2O_4(g) + 57\text{ kJ}$$

brown *colourless*

Because NO_2 is brown and N_2O_4 is colourless it is possible to observe qualitatively the effect of various changes on the relative proportions of reactants and products. You will observe the container of gas become more brown or less brown.

Equipment

large transparent glass syringe with sealed end, containing NO_2/N_2O_4
two sealed tubes or flasks containing NO_2/N_2O_4 at the same pressure
ice bath at about 0 °C
hot water bath at about 90 °C
thermometer (-10 to 110 °C)
test tube rack
test tube holder/tongs
Bunsen burner
bench protector
matches

Procedure

(Your teacher will conduct this experiment as a demonstration.)

Part A: Effect of pressure or volume on the equilibrium

1. Carefully observe the colour intensity of the gas mixture in the syringe.

2. Push in the gas syringe quickly so that the volume occupied by the gas mixture is instantaneously reduced. Note the immediate change in colour of the gas mixture.

3. Carefully observe the change in colour intensity which occurs over several seconds after the immediate colour change.

Notes

Experiment 3: Le Châtelier's Principle and gases

Notes

Part B: Effect of temperature on the equilibrium

1. Compare the colours of the two flasks containing the NO_2/N_2O_4 gas mixtures.

2. Place one of the flasks in an ice bath for five minutes and compare the colour in this flask with that in the flask at room temperature.

3. Remove the flask from the ice bath and place it in a hot water bath. Compare the colour in this flask with that in the flask at room temperature.

Processing of results and questions

1. (a) In part A, what happened to the concentration of the two gases immediately after the volume was reduced, but before the system adjusted to re-establish equilibrium?

   (b) Explain the immediate change of colour that occurred when the volume of the system was reduced.

   (c) From the colour change that occurred after the volume was reduced, identify the direction in which the net reaction took place as the system re-established equilibrium.

   (d) Describe your observations using Le Châtelier's Principle.

2. If the volume of the NO_2/N_2O_4 system were increased, predict the effect this would have on the equilibrium and hence the colour intensity in the syringe.

3. Given that the reaction is exothermic, explain your observations made in part B.

$$2\ NO_2(g) \leftrightarrows N_2O_4(g) + 57\ kJ$$

4. Sketch concentration vs time graphs for
   (a) the effect of changing volume on the system.
   (b) the effect of changing the temperature

5. Sketch the rate vs time graphs for
   (a) the effect of changing volume
   (b) the effect of changing the temperature

6. Explain, with reference to collision theory, the effect of changes in concentration or partial pressure on the system.

7. Predict the effect of injecting argon into the NO_2/N_2O_4 gas mixture at fixed volume. Justify your prediction with reference to Le Châtelier's Principle, and explain your prediction with reference to collision theory.

Experiment 4: Le Châtelier's Principle and aqueous solutions

Many industrial processes involve equilibrium in solution. An understanding of how changes to those systems will impact on the yield is useful for maximising return for a given cost.

This experiment contains two activities concerning chemical equilibrium in aqueous solution. The purpose of the activities is to observe the effect of various changes on these equilibria and to determine whether the observed effects are those expected from an application of Le Châtelier's Principle.

Chromate dichromate equilibrium

The two reactions to be investigated are:

1. **The chromate-dichromate equilibrium**
   In any aqueous solution of a chromate or dichromate salt an equilibrium exists between the chromate and dichromate ions. This equilibrium can be represented by the equation

$$2\,CrO_4^{2-}(aq) + 2\,H^+(aq) \leftrightharpoons Cr_2O_7^{2-}(aq) + H_2O(\ell)$$

yellow orange

In a solution of potassium chromate (K_2CrO_4) the concentration of CrO_4^{2-} ions (yellow) is relatively large and the concentration of $Cr_2O_7^{2-}$ ions (orange) is relatively small. In a solution of potassium dichromate ($K_2Cr_2O_7$) the concentration of $Cr_2O_7^{2-}$ ions (orange) is relatively large and the concentration of CrO_4^{2-} ions (yellow) is relatively small.

2. **The equilibrium between $[Co(H_2O)_6]^{2+}$ and $[CoC\ell_4]^{2-}$**
   When $CoC\ell_2{\cdot}6H_2O$ is dissolved in water it forms a pink solution due to the hydrated cobalt ion, $[Co(H_2O)_6]^{2+}$. In this ion, six water molecules are bonded to a central cobalt ion. If the $CoC\ell_2{\cdot}6H_2O$ is dissolved in concentrated $HC\ell$ it forms a deep blue solution due to the formation of the $[CoC\ell_4]^{2-}$ ion. In this anion four chloride ions are attached to the central cobalt ion.
   The equilibrium between the $[Co(H_2O)_6]^{2+}$ and $[CoC\ell_4]^{2-}$ ions can be represented by the following equation:

$$[Co(H_2O)_6]^{2+}(aq) + 4\,C\ell^-(aq) \leftrightharpoons [CoC\ell_4]^{2-}(aq) + 6\,H_2O(\ell)$$

pink blue

Equipment

four strips of cobalt(II) chloride paper
potassium chromate solution [K_2CrO_4] 0.1 mol L^{-1} (5 mL)
potassium dichromate solution [$K_2Cr_2O_7$] 0.1 mol L^{-1} (5 mL)
sodium hydroxide solution [NaOH] 0.2 mol L^{-1} (5 mL)
hydrochloric acid solution [$HC\ell$] 0.2 mol L^{-1} (5 mL)
hydrochloric acid solution [$HC\ell$] 1.0 mol L^{-1} (5 mL)
distilled water
test tubes (four large)
graduated cylinder (100 mL)
beaker (100 mL) or Petri dish
dropper
forceps or gloves

Notes

Preparation of cobalt chloride paper:

- Dissolve 5 g of hydrated cobalt(II) chloride in 100 mL of water (solution is TOXIC see 'Risk assessment', page 15).
- Soak filter paper in this solution, drain and dry in an oven (set at no more that 100°C), so that it is a definite blue colour.
- The filter paper can be cut into small strips and stored in a desiccator with dry silica gel.

Experiment 4: Le Châtelier's Principle and aqueous solutions

Notes

Procedure **Part A: The chromate-dichromate equilibrium**

1. Place about 1 mL of 0.1 mol L^{-1} K_2CrO_4 solution into each of two test tubes and note the colour of the solution. Use one of the test tubes for comparison of colours.

2. Place about 1 mL of 0.1 mol L^{-1} $K_2Cr_2O_7$ solution into each of two test tubes and note the colour of the solution. Use one of the test tubes for comparison of colours.

3. To one of the test tubes of K_2CrO_4 solution add 0.2 mol L^{-1} $HC\ell$ solution dropwise until a colour change is noted.

4. To the same solution now add 0.2 mol L^{-1} NaOH solution dropwise until another colour change is observed. Record your observations.

5. To one of the test tubes of $K_2Cr_2O_7$ solution add 0.2 mol L^{-1} NaOH solution dropwise until a colour change is observed.

6. To the same solution now add 0.2 mol L^{-1} $HC\ell$ solution dropwise until another colour change occurs. Record your observations.

Procedure **Part B: The equilibrium between $[Co(H_2O)_6]^{2+}$ and $[CoC\ell_4]^{2-}$**

SAFETY NOTE:
- **Cobalt chloride is toxic and a possible carcinogen. The indicator papers should be handled with forceps or gloves and hands washed after use.**

1. Using the forceps place a piece of the blue cobalt(II) chloride paper into a 100 mL beaker or Petri dish.

2. Add water drop-wise until a definite colour change is noted. Record your observations.

3. To the same piece of paper add 1.0 mol L^{-1} $HC\ell$, drop-wise until a definite colour change is noted. Record your observations.

Processing of results and questions

1. By referring to the collision theory, account for the observed colour change that occured when $HC\ell$ solution was added to the K_2CrO_4 solution.

2. When NaOH solution was added to a solution containing $HC\ell$, the concentration of H^+ ions was reduced because of the neutralisation reaction:

   $$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$$

   By referring to the collision theory, account for the observed colour change that occured when NaOH solution was added to the acidified K_2CrO_4 solution.

Notes

3. By referring to the collision theory, account for the observed colour change that occured when NaOH solution and then $HC\ell$ solution were added to the $K_2Cr_2O_7$ solution.

4. Explain, with reference to collision theory, the colour changes that occurred when water and then $HC\ell$ solution were added to the cobalt (II) chloride paper.

5. The equilibrium between the $[Co(H_2O)_6]^{2+}$ and $[CoC\ell_4]^{2-}$ ions can be represented by the following equation:

$$\underset{\text{pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4\,C\ell^-(aq) \leftrightarrows \underset{\text{blue}}{[CoC\ell_4]^{2-}(aq)} + 6\,H_2O(\ell)$$

(a) When the solution is heated it changes from pink to blue, predict whether the reaction, as written, is exothermic or endothermic.

(b) Explain your choice.

Acids and Bases

Acids and bases have particular characteristics and are vital chemicals in many processes including those involved in wine making, refining metal ores, and improving agriculture and human health. Acid-base theory and indicator theory are used to explain solution equilibria and the existence of acidic and basic salts. Buffers play an important role in both biological and industrial processes. Investigating the chemistry of buffers, such as the carbonic acid/hydrogencarbonate buffering of blood plasma, and in swimming pools, helps to build further understanding of equilibrium and acid-base chemistry. Developing and practising volumetric analysis skills and applying them to the analysis of industrial and household goods such as vinegar, household cleaning solutions and wine, facilitates a deeper understanding of quantitative investigations and calculations.

Swimming pools and oceans

Authorities warn of the heath risks of a poorly maintained swimming pool.

If not properly maintained, the water in a backyard swimming pool becomes home to a range of microbes. The bacteria and algae that grow can cause health problems such as ear, nose and throat infections.

Water used in most swimming pools is essentially fresh water containing small amounts of salts. To prevent the growth of microorganisms a solution of sodium hypochlorite is added. This solution and its decomposition product, chlorine, are toxic to microorganisms as well as to algae and fungi. The rate of decomposition of the hypochlorite ion is dependent on the pH of the water.

Increasing and decreasing pH

The optimum pH value for pool water is from 7.2 to 7.6, slightly alkaline. This range provides for optimum use of free chlorine and is comfortable to the human eye (pH of 7.2).

The slightly alkaline pH also maintains water that is not corrosive or scale forming. Hydrochloric acid is most often used to neutralise the excess hydroxide ions and lower the pH. To raise pH, soda ash (sodium carbonate) is usually added.

Australian Standards for pH of pool water is 7.0 to 7.8 with 7.2 to 7.6 recommended and 7.0 to 7.2 for fibreglass pools.

Buffers

To help reduce major fluctuations in the pH, buffers are often added to pool water. The H_2CO_3/HCO_3^- buffer system (carbonic acid/hydrogencarbonate) is most commonly used. Its addition increases the water's buffering capacity, "total alkalinity". Addition of a buffer tends to resist changes in the pH due to the production of hydroxide ions as the hypochlorite ion hydrolyses.

$$C\ell O^- + H_2O \rightleftharpoons HC\ell O + OH^-$$

$$H_3O^+ + HCO_3^- \rightleftharpoons H_2CO_3 + H_2O$$

Ocean acidification: a complex buffer system

*Due to **Greenhouse Gas emission**, the level of CO_2 in our oceans is steadily rising.*

The extra carbon dioxide in the oceans is resulting in:

- Increased acidity
- Increased bicarbonate ion concentrations
- Decreased carbonate ion concentrations

Atmospheric carbon dioxide is in equilibrium with dissolved carbon dioxide in the ocean (equation 1). The dissolved carbon dioxide undergoes hydrolysis forming carbonic acid, H_2CO_3 (equation 2).

Equation 1 $CO_2(g) \rightleftharpoons CO_2(aq)$

Equation 2 $CO_2(aq) + H_2O(\ell) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $\quad K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}$

The ocean is a saturated solution of calcium carbonate (equation 3). The excess H^+ formed as the ocean becomes more acidic reacts with soluble carbonate in the ocean resulting in an increase in the concentration of bicarbonate (hydrogen carbonate), HCO_3^- (equation 4).

Equation 3 $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $\quad K_2 = [Ca^{2+}][CO_3^{2-}]$

Equation 4 $CO_3^{2-}(aq) + H^+(\ell) \rightleftharpoons HCO_3^-(aq)$ $\quad K_3 = \frac{[HCO_3^-]}{[H^+][CO_3^{2-}]}$

Corals and shellfish use the ocean's source of carbonate ions to create their exoskeleton. Coral body is built from calcium carbonate when the carbonate ions combine with calcium ions from the water (equation 5).

Equation 5 $Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$

In accordance with Le Châtelier's Principle as the hydrogen ion removes carbonate ion in Equation 4 it will force Equation 3 to the right to maintain K_2. Thus th Ca^{2+} rises and this results in a decreased carbonate ion concentration causing a reduction in the ability of the coral polyp skeleton to form. This ultimately results in stunted growth of corals.

Career profile 2: Viticulturalist and Laboratory Assistant

Profile of a Viticulturist

As Viticulturist of Leeuwin Estate Wines in Margaret River, David Winstanley, says "Viticulture is all about the weather, soil, landscape, plant physiology, planning, people and chemistry." As you can see from David's qualifications, BSc (Geology), Grad Dip (Natural Resources) and Grad Dip (Viticulture), he is more than well qualified to address the demands of a viticulturist.

The Margaret River Region of WA is world renown for the quality of its exported wines. The moderate climate of our South West Region is ideal for grape growing.

As an Agricultural Science, Viticulture requires much outdoor work including: pruning, spraying, pest and disease management and sample collecting. Grape maturity sampling is performed in a laboratory, where parameters such as pH, sugar and sulfur content are measured. Volumetric analysis is a vital technique.

Volumetric analysis

Acid concentration can be easily determined by volumetric analysis. Volumetric analysis is one method of determining the amount of a particular substance present in a given sample. It is used as a form of quality assurance in many industries, such as the wine industry. In order to maintain the quality of wine a number of components are tested for on a regular basis. The acid content of wine, for example, is closely linked to appearance and taste.

Profile of a Laboratory Analyst

Shift Relief Analyst, Daryl Stout, BSc of the ALCOA Pinjarra Refinery Labs, says with pride, "The best part of my work is taking people through the lab as well as involving myself with project work, especially when there is a high degree of difficulty associated with the problem or problems the chemist is trying to solve!"

Being a Laboratory Analyst at the Pinjarra Refinery, involves looking at raw materials (bauxite, caustic soda), intermediates (process solutions, red muds, hydrates and impurities) and the final product of the refinery (alumina) with respect to normal values. This provides an indication that the refinery is operating properly.

Daryl explains, "To analyse for the element or elements we are determining, we prepare some standards in dilute acid. These usually comprise a blank which is just the acid and water the standards are made from, followed by increasing concentrations of analytes (the stuff we're trying to measure, e.g. alumina, soda etc) in the water and acid, using an Inductively Coupled Plasma (ICP) to heat a fine mist of the solution we're analysing." It measures elemental concentration by "exciting" the atom and measuring the light emitted. "When heated enough, every element has at least one signature light colour. If we can measure this light colour, then we can usually measure its intensity or brightness. A brighter colour usually indicates a higher concentration of analyte (material being analysed). We use an inbuilt detector to measure the different colours and intensities. This gives us a calibration curve."

The processing of samples and use of instrumentation in a busy laboratory environment requires excellent time management, communication and organisational skills, as well as a minimum educational qualification of a Certificate III in Laboratory Practices & Techniques. Where instrumentation is to be used for more complex analyses, a BSc in Applied Chemistry may be required.

Investigation 5: Properties of acids and bases

Notes

Acids and bases are two classes of compounds that have wide application in industrial and household chemistry.

The Brønstead-Lowry theory, defines acids as substances that donate protons. Commonly encountered acids include spirits of salts (hydrochloric acid), battery acid (sulfuric acid) and vinegar (ethanoic or acetic acid). While bases are substances that accept protons, and in aqueous solutions produce hydroxide ions (OH^-). Sodium carbonate (soda ash), sodium hydroxide (caustic soda), sodium carbonate-10-water (washing soda) and ammonia are commonly used bases.

The task

Design and carry out a qualitative test that represents each of the following acid base properties and reactions:

1. Effect of acids and bases on litmus
2. Reaction of an acid with a reactive metal
3. Reaction of an acid with a metal oxide
4. Reaction of a strong acid with a carbonate
5. Reaction of a strong acid with a hydrogencarbonate
6. Reaction of a strong acid with an ethanoate (acetate)
7. Reaction of a strong acid with a strong base

Planning the investigation

Select your chemicals, reactants and equipment for each test and reaction from the materials provided.

For each of the properties and reactions:

1. Write a procedure including the reactants to be used, equipment needed, setup and safety requirements.
2. Describe any test or tests that may need to be conducted to identify products.
3. Check the proposed procedure with your teacher.

Equipment

Bunsen burner
dropper
test tubes (six)
taper and matches
hydrochloric acid [$HC\ell$] 2 mol L^{-1} (30 mL)
sodium hydroxide solution [NaOH] 2 mol L^{-1} (30 mL)
limewater [$Ca(OH)_2$] (20 mL)
vinegar [3-4% CH_3COOH] (2 mL)
two pea-sized pieces of:
- aluminium [$A\ell$], copper [Cu], iron [Fe], magnesium [Mg] and zinc [Zn]

about 1 g each of:
- copper(II) oxide [CuO]
- sodium hydrogencarbonate [$NaHCO_3$]
- calcium carbonate (marble chips) [$CaCO_3$]
- sodium ethanoate (sodium acetate) [$NaCH_3COO$]

blue litmus paper
red litmus paper
stopper fitted with gas delivery tube

SAFETY NOTE:

- **Hydrochloric acid and sodium hydroxide solutions are corrosive and should be handled with care.**
- **If any solution gets in contact with your skin or eyes immediately wash off with *copious* quantities of water. Sodium hydroxide spills should be washed continuously for 20 minutes.**

Notes

Conducting the investigation

Conduct each test and reaction using your teacher-approved procedure. Record your observations of the reactions and the results of tests for products.

Processing of results

Write balanced equations for the reactions and for any chemical test that you used to identify the products. Explain how your observations and results from product tests support the balanced equations that you have written for each reaction.

Summary

Summarise the properties of acids and bases by completing the following general equations:

Acid + Reactive Metal →
Acid + Metal Oxide →
Acid + Carbonate →
Acid + Hydrogencarbonate →
Acid + Ethanoate (Acetate) →
Acid + Strong Base →

Investigation 6: Acid and base strength and concentration

Notes

Acids and bases are electrolytes, that is, they conduct an electric current when in aqueous solution. For acids and bases, electrolyte strength is also referred to as acid or base strength. Strong acids and bases exist essentially as ions in aqueous solution. Weak acids and bases are those in which only a small proportion of the molecules or ions react with water to form hydronium ions, H_3O^+ (hydrogen ion attached to a water molecule) or hydroxide ions, OH^- in aqueous solution.

In this experiment you will investigate the electrical conductivity of acid and base solutions of different strengths and concentrations.

The task

Compare the electrolyte strength of:

- Strong verses weak acids and bases
- Concentrated versus dilute solutions of a strong acid

Equipment

power supply (0 to 12 V)
plate electrode system as shown in Figure 6.1
switch
ammeter
electrical leads (four)
beakers (two 100 mL)
50 mL samples of the following solutions:

hydrochloric acid [$HC\ell$] 1 mol L^{-1}	hydrochloric acid [$HC\ell$] 0.1 mol L^{-1}
hydrochloric acid [$HC\ell$] 0.01 mol L^{-1}	hydrochloric acid [$HC\ell$] 0.001 mol L^{-1}
nitric acid [HNO_3] 1 mol L^{-1}	acetic acid [CH_3COOH] 1 mol L^{-1}
sodium hydroxide [NaOH] 1 mol L^{-1}	ammonia [NH_3] 1 mol L^{-1}

Planning the investigation

Select chemicals and equipment from the materials provided.
Set up the circuit and the electrodes as shown in Figures 6.1 and 6.2. Set the power supply to 6 V DC. SEE CAUTION.

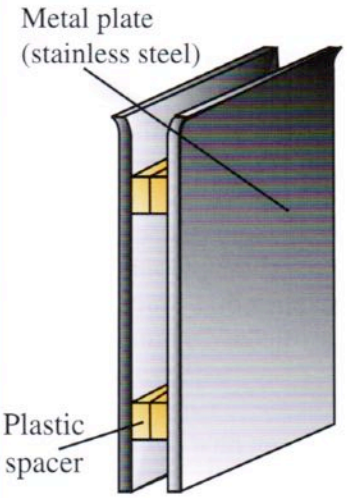


Figure 6.1. Plate Electrode System

Figure 6.2

CAUTION!
Connect the red terminal of the power supply to the red terminal of the ammeter that uses the least sensitive scale.

Notes

For each of the properties and reactions:

1. Write a procedure to test and compare the electrolyte strength of the strong and weak acids and bases.
2. Write a procedure to test and compare the electrolyte strength of the different concentrations of the strong acid, $HC\ell$.
3. Check the proposed procedure with your teacher.

Conducting the investigation

Conduct each test and record your observations / results in a table.

Processing of results and questions

1. Explain why these solutions conduct an electric current.

2. Look at your results for the $HC\ell$ solutions. Draw a graph of concentration *vs* amps for $HC\ell$. What conclusion can you draw concerning the conductivity of a solution and the concentration of ions in it?

3. Were the conductivities of 1.0 mol L^{-1} $HC\ell$ and 1.0 mol L^{-1} CH_3COOH different? If so, explain why they were different.

4. Were the conductivities of 1.0 mol L^{-1} NaOH and 1.0 mol L^{-1} NH_3 different? If so, explain why they were different.

5. Acids and bases are referred to as being 'strong' or 'weak' as distinct from being 'concentrated' or 'dilute'. Explain how these two variables, electrolyte strength and solution concentration, affect the conductivity of aqueous solutions.

Summary

Draw diagrams to help describe the difference between a:

- Strong acid and a weak acid
- Concentrated acid solution and a dilute acid solution

Experiment 7: Using indicators

Notes

To maintain the correct acid balance in a swimming pool you need to check the pH and if necessary adjust it to the correct level (7.2 to 7.6). This is conducted using a test kit that contains an acid – base indicator. The indicator has a different colour in solutions having a different pH.

Acid-base indicators are dyes whose colours depend upon the hydrogen ion concentration in solution. Each indicator changes colour at a unique $[H^+]$.

In this experiment you will use two indicators that have colour changes in the acid range, methyl orange and methyl red, and two indicators that have colour changes in the basic range, indigo carmine and alizarin yellow R.

Indigo Carmine

Alizarin Yellow R

Methyl Orange

Methyl Red

In parts A and B of the experiment you will prepare solutions of known $[H^+]$ from standard hydrochloric acid and sodium hydroxide solutions. These solutions, with indicator added, will serve as standards. You will use these standards in part C to estimate the $[H^+]$ values in solutions of acetic acid (ethanoic acid) and calcium hydroxide.

Equipment

test tubes (20)
beaker (250 mL)
graduated cylinder (100 mL)
hydrochloric acid solution [$HC\ell$] 0.1 mol L^{-1} (20 mL)
sodium hydroxide solution [NaOH] 0.1 mol L^{-1} (20 mL)
acetic acid solution [CH_3COOH] 0.1 mol L^{-1} (5 mL)
limewater solution [$Ca(OH)_2$] (5 mL)
lemon juice or orange juice (5 mL)
A few mL of each of the indicators
- indigo carmine
- alizarin yellow R
- methyl orange
- methyl red

Procedure **Part A: Preparation of acid standards (10^{-1} to 10^{-4} mol L^{-1} $HC\ell$)**

Notes

1. Take four test tubes and place about 10 mL of 0.1 mol L^{-1} $HC\ell$ in the first tube and label it $[H^+] = 10^{-1}$ mol L^{-1}.

2. Place another 10 mL of 0.1 mol L^{-1} $HC\ell$ in a 100 mL graduated cylinder and add water to the 100 mL mark. Thoroughly mix the 100 mL of solution by pouring it into a clean 100 mL beaker, then back into the cylinder and finally into the beaker again. Pour 10 mL of this solution into a clean test tube and 10 mL, back into the graduated cylinder. Discard the remaining solution. Label the test tube $[H^+] = 10^{-2}$ mol L^{-1}.

3. Again add water to the 10 mL of acid in the graduated cylinder and make it up to the 100 mL mark. Mix thoroughly as above. Pour 10 mL into the third test tube and 10 mL back into the graduated cylinder. Discard the remaining solution. Label this test tube $[H^+] = 10^{-3}$ mol L^{-1}.

4. Repeat the procedure to prepare a 10^{-4} mol L^{-1} solution of $HC\ell$. Pour 10 mL into the fourth test tube. Discard the remaining solution. Label this test tube $[H^+] = 10^{-4}$ mol L^{-1}.

5. Pour half the contents of each test tube into four clean test tubes, so that you have two sets of standards. Label the second set of test tubes.

6. Add two drops of methyl red solution to each of the four test tubes in the first set of standards. Add two drops of methyl orange to each of the test tubes in the second set.

7. Draw up a table and record the colours observed in each of the solutions for the various values of $[H^+]$. Save the standards for part C of the experiment.

Procedure **Part B: Preparation of base standards (10^{-1} to 10^{-4} mol L^{-1} NaOH)**

1. Follow the directions in the first four steps in part A to prepare solutions for the basic range using 0.1 mol L^{-1} NaOH instead of 0.1 mol L^{-1} $HC\ell$. Label the solutions prepared as $[OH^-] = 10^{-1}$ mol L^{-1}, $[OH^-] = 10^{-2}$ mol L^{-1}, $[OH^-] = 10^{-3}$ mol L^{-1} and $[OH^-] = 10^{-4}$ mol L^{-1} respectively. Calculate the corresponding $[H^+]$ and add these to the labels.

2. Divide the solutions to obtain two sets of four standards. Add two drops of indigo carmine solution to each of the four test tubes in the first set of standards and two drops of alizarin yellow R solution to each of the test tubes in the second set.

3. Draw up a table and record the colours observed in each of the solutions for the various values of $[OH^-]$. Save the standards for use in part C of the experiment.

Experiment 7: Using indicators

Notes

Procedure

Part C: Determination of the $[H^+]$ of some aqueous solutions

1. Place about 2 mL of 0.1 mol L^{-1} acetic acid into each of four test tubes.

2. Add two drops of methyl red solution to one test tube, two drops of methyl orange to the second test tube, two drops of alizarin yellow R to the third test tube and two drops of indigo carmine to the fourth test tube.

3. Compare the colours with those of the standards containing the same indicator. Estimate and record the $[H^+]$ of the acetic acid solution.

4. Repeat steps 1, 2 and 3 using calcium hydroxide solution.

5. Repeat steps 1, 2 and 3 using lemon juice and/or orange juice.

Processing of results and questions

1. Compare the $[H^+]$ of the 0.1 mol L^{-1} acetic acid solution with the 0.1 mol L^{-1} $HC\ell$ solution. Explain any difference you observe.

2. Compare the $[H^+]$ of the 0.1 mol L^{-1} calcium hydroxide solution with the 0.1 mol L^{-1} NaOH solution. Explain any difference you observe.

3. When making up the standard solutions in this experiment describe the precautions you took to make sure that the concentrations of the solutions remained accurate.

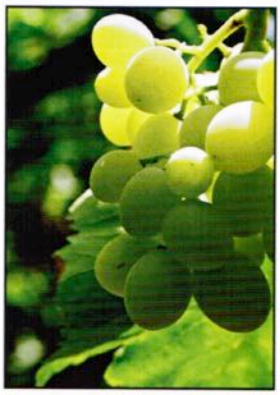
4. Calculate the $[H^+]$ of the acetic acid and calcium hydroxide solutions, using the pH identified in the experiment.

5. Calculate the $[H^+]$ of the lemon juice and/or orange juice, using the pH identified in the experiment.

6. Which indicator or combination of indicators used in this experiment could you use to test swimming pool water?
   Describe the colour of the indicator or indicators chosen you would expect for pool water at the correct pH level. Check your ideas by testing a sample of swimming pool water.

Investigation 8: Determining pH using indicators

The water used to irrigate grape vines is often sourced from underground and brought to the surface via bore holes from below the water table. Water reservoirs, lakes and rivers are also important sources of water for irrigation. The water pH should be close to neutral to be useful for irrigating vines.



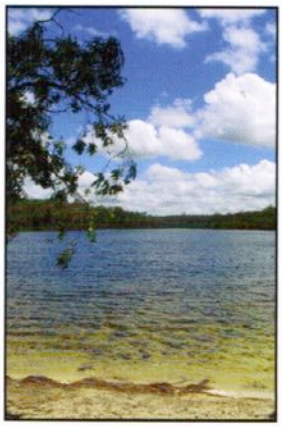
Grapes

The pH of underground water supplies, water supply reservoirs, rivers, lakes, soils and the grapes that are produced by the vines have a significant effect on the quality of the wine produced from the grapes. Measurement of the pH of these factors is therefore necessary if high quality wine is to be produced. Often an approximate value is sufficient. This can be obtained by using a number of indicators to test suitably prepared samples.

The task

Determine the pH of two water samples from different sources (chosen by you or your teacher).

Note: To successfully conduct this investigation you need to have completed Experiment 7: Using indicators



Irrigation water

Equipment

test samples - two water samples from different sources
hydrochloric acid solution [$HC\ell$] 0.1 mol L^{-1} (30 mL)
sodium hydroxide solution [NaOH] 0.1 mol L^{-1} (30 mL)
5 mL of indicator solutions of:

- indigo carmine
- alizarin yellow R
- methyl orange
- methyl red

Write a list of additional equipment and materials you will require to complete the investigation.

Planning the investigation

1. Write a clear set of steps you will use to conduct this investigation. Include a risk assessment – a description of the precautions and safety procedures you will follow to ensure that you carry out the investigation safely.
2. Draw up a suitable table to record your results.

Conducting the investigation

Conduct the investigation collecting and recording observations and results as you proceed.

Processing the data

Write a report summarising your results. Your report must include your conclusion, and an explanation of the reasons you reached your conclusion as a result of your observations. A comparison of the two samples with a possible explanation of any difference in pH is also essential.

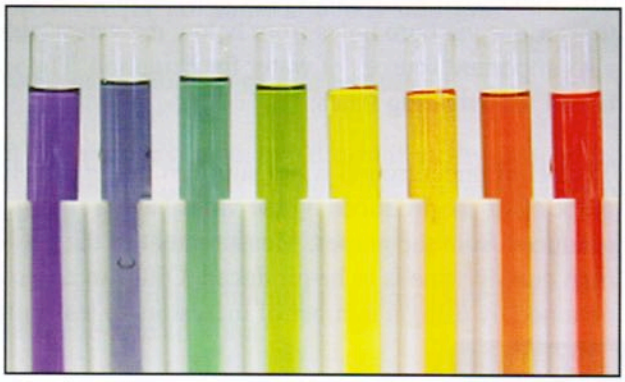
Evaluating the investigation

Identify and describe any changes that you could make to the experimental design that could improve the accuracy of the results obtained.

Notes

Experiment 9: The pH of some salt solutions

Notes



Basic —— Universal Indicator™ ——► Acidic

For optimum growth and production plants need the correct balance of water-soluble elements in the soil. This is particularly true for winemaking varieties of grape vines. Not only is the amount of fruit produced important but also the flavour characteristics of the grapes are critical to the production of high quality wine. There are many environmental factors that contribute to the quality of the grapes, one of which is the adequate availability of elements in the soil and the soil pH. The required elements in a soluble form are found in the soil as salts and if the quantity present is inadequate then fertilisers, either natural or synthetic, containing the appropriate salts must be added.

Salts are ionic compounds containing a cation other than H^+ and an anion other than O^{2-} or OH^-. Sodium chloride ($NaC\ell$), potassium carbonate (K_2CO_3), copper(II) sulfate ($CuSO_4$) and ammonium nitrate (NH_4NO_3) are all examples of salts.

Soils may contain a variety of salts. Some important factors that determine the type and quantity of salts in soils are:

- the parent rock from which the soil formed,
- materials added to the soil such as fertilisers,
- vegetation grown and
- water movement in the soil.

Typically soils can contain ions such as sodium, potassium, aluminium, chloride, carbonate, hydrogencarbonate and sulfate. With the addition of fertilisers it is possible that soils can also contain nitrate, ammonium and phosphate ions.

When ions associated with weak acids or bases are dissolved in water they undergo hydrolysis: that is they react with water. This can make the solution and therefore the soil either acidic or basic.

In this experiment you will test the pH of a number of salts dissolved in water.

Equipment

test tubes (eight)
Universal Indicator™ solution (5 mL)
Universal Indicator™ colour chart
approximately 2 mL of 0.1 mol L^{-1} solutions of the following:

ammonium chloride [$NH_4C\ell$]
sodium chloride [$NaC\ell$]
potassium nitrate [KNO_3]
sodium carbonate [Na_2CO_3]
sodium acetate [$NaCH_3COO$]
sodium hydrogencarbonate [$NaHCO_3$]
sodium sulfate [Na_2SO_4]
sodium phosphate [Na_3PO_4]

Procedure

1. Place 2 mL of each solution into separate test tubes.
2. Add four drops of Universal Indicator™ and, using the colour chart provided with the indicator, note the pH of the solutions and record your results in suitable table.

Processing of results and questions

1. Classify the salt solutions as acidic, neutral or basic.

2. Explain why some salt solutions are
   (a) neutral
   (b) acidic
   (c) basic

3. Write balanced ionic equations to show how the salts you tested when in solution could make a soil
   (a) acidic
   (b) basic

4. Sodium hydrogenphosphate produced a basic solution when dissolved in water.
   (a) Write two equations showing that hydrogenphosphate can act as an acid and as a base with water.
   (b) Explain, with the aid of these equations, why a sodium hydrogenphosphate solution is basic.

Notes

Experiment 10: Making and testing buffer solutions

Blood

A pH buffer is used to maintain a relatively constant pH in an aqueous solution. The H_2CO_3/HCO_3^- buffer system that is found in the blood is also used in swimming pools.

Biological systems involve complex solutions, many of which contain buffers. Human blood should be maintained at a constant pH of 7.4 as higher or lower pH values will damage cells and alter proteins. Two of the buffering systems found in blood involve carbon dioxide and phosphoric acid. The one that has the greater effect is the one involving carbon dioxide and the hydrogencarbonate ion. The phosphoric acid buffer has a much smaller effect, as the concentrations are very low.

Buffers are also important in agriculture, for example, in maintaining the pH balance of aquaculture solutions and in nutrient solutions for plant growth.

In this experiment you are going to make two simple buffer solutions and compare their behaviour with solutions of the same pH that do not contain buffers.

Notes

Equipment

4 beakers (100 mL)
graduated cylinder (50 mL)
glass stirring rod
2 Pasteur pipettes (droppers)
1 mol L^{-1} solutions of:
- acetic acid solution [CH_3COOH] (10 mL)
- ammonia solution [NH_3] (10 mL)
- sodium acetate solution [$NaCH_3COO$] (40 mL)
- ammonium chloride solution [$NH_4C\ell$] (40 mL)

0.1 mol L^{-1} solutions of:
- hydrochloric acid solution [$HC\ell$] (30 mL)
- sodium hydroxide solution [NaOH] (30 mL)

Universal Indicator™
Universal Indicator™ colour chart

Procedure

This experiment can also be performed with a pH meter.

1. Place 10 mL of 1 mol L^{-1} CH_3COOH into a clean dry 100 mL beaker. To this add 40 mL of 1 mol L^{-1} $NaCH_3COO$ and mix thouroughly.
2. Transfer 25 mL of this solution to another clean dry 100 mL beaker. Label both these beakers as acetic acid-acetate buffer.
3. Add 5 drops of Universal Indicator™ to each of the beakers. Using the Universal Indicator™ chart, estimate and record the pH of the solution. Retain these beakers for further testing.
4. Place 50 mL of distilled water into a 100 mL beaker then add 10 drops of Universal Indicator™. Add 0.1 mol L^{-1} $HC\ell$ solution dropwise until the colour of the indicator is the same as in the buffer solution.
5. Transfer 25 mL of this solution into another clean dry beaker. Label both beakers "Unbuffered acid solution".
6. (a) To one of the beakers containing acetic acid-acetate buffer add one drop of 0.1 mol L^{-1} $HC\ell$, stir the solution then record the colour. Repeat this until you have added 40 drops. Estimate the pH after the 40 drops have been added.

(b) Repeat this with one of the beakers containing unbuffered solution. Again record any colour changes after the addition of each drop and estimate the pH after the 40 drops have been added.

7. Repeat procedure 6 (a) and (b) with the remaining beaker of buffered and unbuffered solution but this time use the 0.1 mol L^{-1} NaOH solution.

8. Repeat procedures 1 to 7 using ammonia solution (10 mL) and ammonium chloride solution (40 mL) and 0.1 mol L^{-1} NaOH solution to make an unbuffered solution of the same colour (pH) as the ammonia-ammonium chloride buffer solution.

Notes

Processing of results and questions

1. Compare the behaviour of the buffered solutions with the unbuffered solutions when either acid or base was added.

2. (a) Using the collision theory and rate of reaction explain the behaviour of the acetic acid-acetate buffer as
   (i) H^+ ion is added (ii) OH^- ion is added
   (b) Support your explanation by writing equations to represent the processes occurring.

3. (a) Using the collision theory and rate of reaction explain the behaviour of the unbuffered acidic solution as
   (i) H^+ ion is added (ii) OH^- ion is added
   (b) Support your explanation by calculating the $[H^+]$ before the addition of the 40 drops of acid or base, the $[H^+]$ after 40 drops of 0.1 mol L^{-1} $HC\ell$ was added to one beaker and the $[H^+]$ after 40 drops of 0.1 mol L^{-1} NaOH was added to the other beaker. Calculate the pH for each $[H^+]$.
   (c) Compare the estimated pH in each solution with the calculated value.

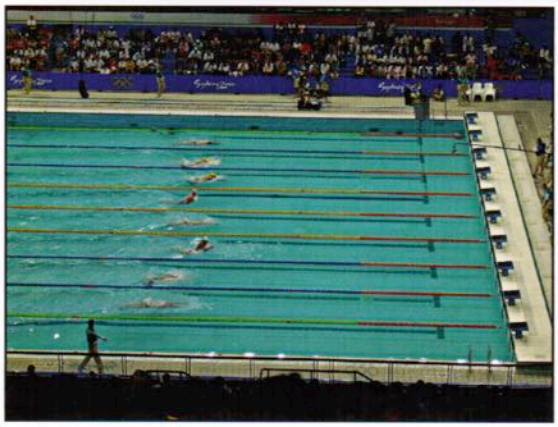
4. (a) Using the collision theory and rate of reaction explain the behaviour of the ammonia-ammonium chloride buffer as
   (i) H^+ ion is added (ii) OH^- ion is added
   (b) Support your explanation by writing equations to represent the processes occurring.

5. (a) Using the collision theory and rate of reaction explain the behaviour of the unbuffered basic solution as
   (i) H^+ ion is added (ii) OH^- ion is added
   (b) Support your explanation by calculating the $[H^+]$ before the addition of the 40 drops of acid or base, the $[H^+]$ after 40 drops of 0.1 mol L^{-1} $HC\ell$ were added to one beaker and the $[H^+]$ after 40 drops of 0.1 mol L^{-1} NaOH were added to the other beaker. Calculate the pH for each $[H^+]$.
   (c) Compare the estimated pH in each solution with the calculated value.

6. For the acetic acid-acetate buffer, research how buffers of pH values other than that obtained in your experiment could be produced.

7. Describe two different examples where buffers play an important role in maintaining a relatively constant pH. In each case describe the buffer system and indicate the likely source of H^+ and /or OH^- ions that can potentially change the pH.

Investigation 11: Buffering capacity of swimming pool water



Buffering capacity is a measure of the resistance of a solution to a pH change. The term "total alkalinity" is used in the swimming pool maintenance industry to refer to the buffering capacity of the pool water.

Before you attempt this investigation you should complete Experiment 10: Making and Testing buffer solutions.

The measurment of 'total alkalinity' in pools is a measure of OH^- and HCO_3^-. The OH^- is formed by the hypochlorite reaction:

$$C\ell O^-(aq) + H_2O(\ell) \rightleftharpoons HC\ell O(aq) + OH^-(aq)$$

and the $HCO_3^-(aq)$ is formed by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + H_2O(\ell)$$

If the total alkalinity is too low, then bicarbonate in the form of $NaHCO_3$ is added.

Notes

The task

Test the buffering capacity of a number of samples of swimming pool water taken from:

- the same swimming pool at a number of different times, or
- a number of different swimming pools at the same time.

Apply your knowledge and skills for testing buffer solutions for changes in pH, identify the samples of pool water that are well buffered and those that show little resistance to changes in pH.

Equipment

At least 3 samples of pool water.

Write a list of additional equipment and materials you will require to complete the investigation.

Planning the investigation

1. Write a clear set of steps you will use to conduct this investigation. Include a risk assessment – a description of the precautions and safety procedures you will follow to ensure that you carry out the investigation safely.
2. Draw up a suitable table to record your results.

Conducting the investigation

Conduct the investigation collecting and recording observations and results as you proceed.

Processing the data

Write a report summarising your results. Your report must include your conclusion, and an explanation of the reasons you reached your conclusion as a result of your observations. A comparison of the three samples with a possible explanation of any difference in pH is also essential.

Evaluating the investigation

Identify and describe any changes that you could make to the experimental design that could improve the accuracy of the results obtained.

Experiment 12: Preparation of standard sodium carbonate solution

Notes

Analyses of acids and bases often requires the determination of an accurate concentration of a solution. The wine industry, for example, relies on pH testing using titrations during the fermentation process. The grape juice 'must' is titrated with a standard solution of a base such as sodium hydroxide. Standard solutions are solutions whose concentrations are accurately known. Volumetric techniques rely on accurate measurement of quantities. Mass and volume are the usual quantities measured. This experiment is the first in a series that prepares some standard solutions. Once prepared the standard solutions can be used to determine the concentrations and pH of unknown samples such as a wine.

Anhydrous sodium carbonate of analytical reagent (A.R.) quality can be used as a primary standard as it is very pure and it is not hygroscopic (does not readily pick up moisture from the air). By dissolving a precisely known mass of Na_2CO_3 and making it up to a definite volume of solution it is possible to prepare a standard solution of Na_2CO_3, that is, one with an accurately known concentration.

In this experiment you will prepare 500 mL of approximately 0.05 mol L^{-1} Na_2CO_3 solution whose concentration is accurately known.

Equipment

balance
volumetric flask (500 mL)
oven
desiccator
beaker (250 mL)
washbottle
storage bottle (approximately 500 mL)
distilled water
anhydrous sodium carbonate [Na_2CO_3] (4 g)
Pasteur pipette

Procedure

1. Calculate the mass of anhydrous Na_2CO_3 required to make up 500 mL of 0.05 mol L^{-1} solution.
2. Place a little more than the required amount in an oven at 270 °C for 30 minutes to remove any water. After drying, place the anhydrous Na_2CO_3 in a desiccator to cool.
3. Accurately weigh out into a 250 mL beaker a mass of Na_2CO_3 approximately equal to that calculated. You should not waste time trying to weigh out exactly the mass calculated but the mass must be known precisely so that the exact concentration can be calculated.
4. Dissolve the solid in about 100 mL of distilled water.
5. Transfer this solution to a 500 mL volumetric flask. Rinse the beaker several times with about 20 mL portions of distilled water, adding each washing to the volumetric flask.
6. Make up the solution to precisely 500.0 mL with distilled water, adding the last few millilitres dropwise from a Pasteur pipette.

Experiment 12: Preparation of standard sodium carbonate solution

Notes

7. Place the stopper in the volumetric flask and mix the solution thoroughly by repeatedly inverting the flask.

8. Transfer the solution to a clean storage bottle which should first be rinsed with a little of the Na_2CO_3 solution. Label the storage bottle with the type of solution, its date of preparation and your name.

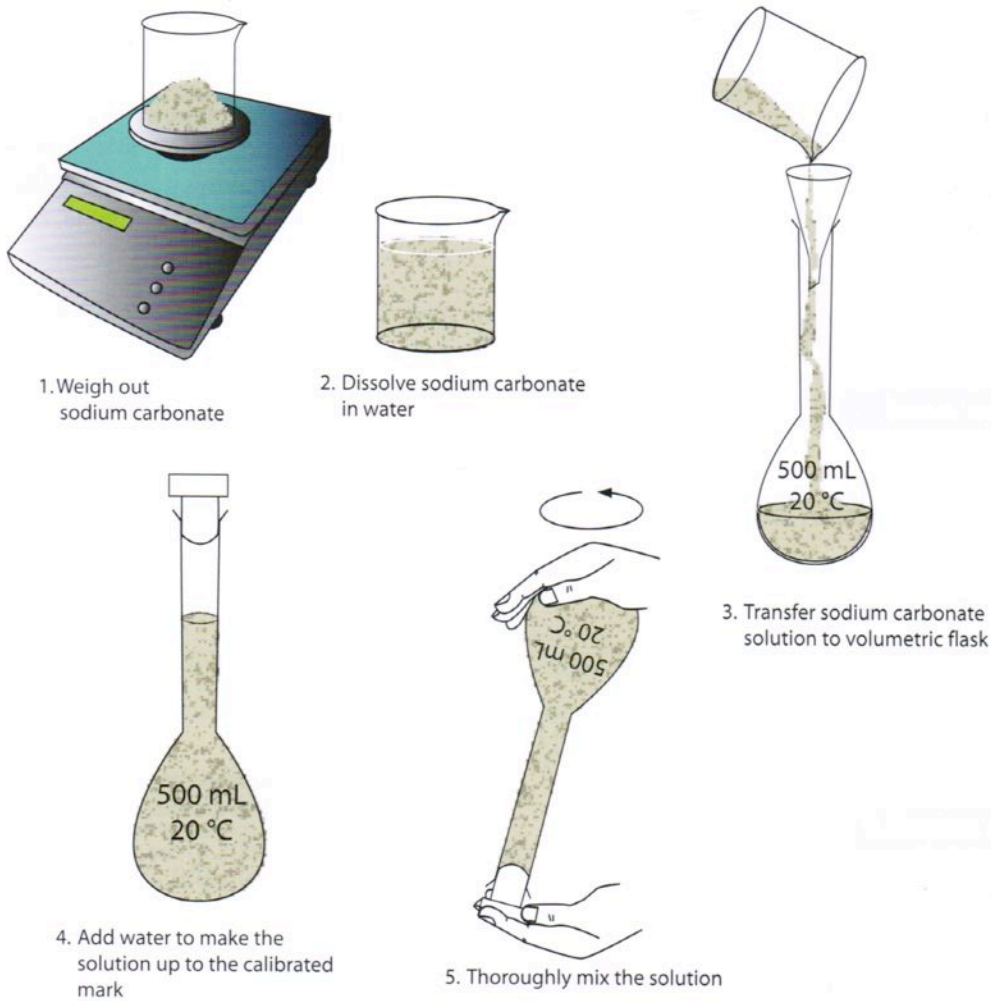


Figure 12.1: Preparing standard sodium carbonate solution

Processing of results and questions

1. Calculate the precise solution concentration in mol L^{-1}. Add this information to the label.

2. The concentration of the solution you have made should be accurately known. List some possible ways that minor inaccuracies could occur in determining the concentration.

3. Calculate the percentage error for the concentration of sodium carbonate.

Experiment 13: Preparation and standardisation of hydrochloric acid

Notes

If you remove the lid from a bottle of $HC\ell$ solution and gently waft the odour to you, you will detect the acrid smell of $HC\ell$. The acid solution is losing concentration and cannot be used as a primary standard solution. In this experiment you will prepare an approximately 0.1 mol L^{-1} solution and determine its exact concentration by titration against the standard Na_2CO_3 solution prepared in Experiment 12. The equation for the reaction is:

$$2\ H^+(aq) + CO_3^{2-}(aq) \leftrightarrows H_2O(\ell) + CO_2(g)$$

Note that one mole of Na_2CO_3 reacts with two moles of $HC\ell$.

Since the solution at the equivalence point is somewhat acidic (pH ~ 3.5), an indicator that changes colour in this region must be used. Methyl orange (yellow to red when pH changes from 4.4 to 3.1) or bromophenol blue (blue to yellow for pH change from 4.6 to 3.0) are most suitable.

Equipment

concentrated hydrochloric acid [$HC\ell$] (6 mL)
graduated cylinder (10 mL)
volumetric flask (500 mL)
storage bottle (approximately 500 mL)
beakers (two 100 mL)
burette and stand
funnel
pipette (20 mL)
pipette filler
conical flask (250 mL)
standard sodium carbonate solution [Na_2CO_3] approximately 0.05 mol L^{-1} from Experiment 12 (150 mL)
methyl orange or bromophenol blue (a few drops)
distilled water
Pasteur pipette

Procedure

Part A: Making the approximately 0.1 mol L^{-1} hydrochloric acid

SAFETY NOTE:

- **Concentrated hydrochloric acid is very corrosive and must be handled with extreme care. You must wear eye protection.**
- **If any concentrated $HC\ell$ gets in contact with your skin, immediately wash it off with *copious* quantities of water.**

1. Calculate the volume of concentrated (approximately 12 mol L^{-1}) $HC\ell$ that would be required to prepare 500 mL of 0.1 mol L^{-1} solution.

2. Measure out this volume of concentrated $HC\ell$ in a graduated cylinder and transfer to a 500 mL volumetric flask that is about half filled with distilled water. Make the solution up to the mark using distilled water added dropwise from a Pasteur pipette.

3. Place the stopper in the volumetric flask and mix the solution thoroughly by repeatedly inverting the flask.

Experiment 13: Preparation and standardisation of hydrochloric acid

Notes

4. Transfer the approximately 0.1 mol L^{-1} $HC\ell$ to a clean storage bottle that has been rinsed with a little of the $HC\ell$ solution.

5. Label the storage bottle with "0.1 m $HC\ell$", the date of preparation and your name.

Procedure **Part B: Standardisation of the hydrochloric acid solution**

1. Place about 100 mL of the standard Na_2CO_3 solution into a clean beaker. If the beaker is wet, rinse with a little of the Na_2CO_3 solution first.

2. Rinse a clean 20 mL pipette with some of the Na_2CO_3 solution (Fig 13.1: 1). Pipette 20 mL of the Na_2CO_3 solution into a 250 mL conical flask. Add 2-3 drops of your chosen indicator to the flask (Fig 13.1: 2).

3. Place about 100 mL of the newly made $HC\ell$ solution into a clean beaker. Again, if necessary, rinse the beaker with a little of the $HC\ell$ solution first

4. Rinse a clean burette with some of the $HC\ell$ solution and then fill the burette with the solution.

5. Note and record the level of acid in the burette. Obtain a rough estimate of the titration volume by running acid quickly from the burette while constantly swirling the liquid in the conical flask. Stop delivery of the acid as soon as a permanent colour change is obtained (Fig 13.1: 3). Note and record the acid level in the burette and determine the approximate volume of acid required.

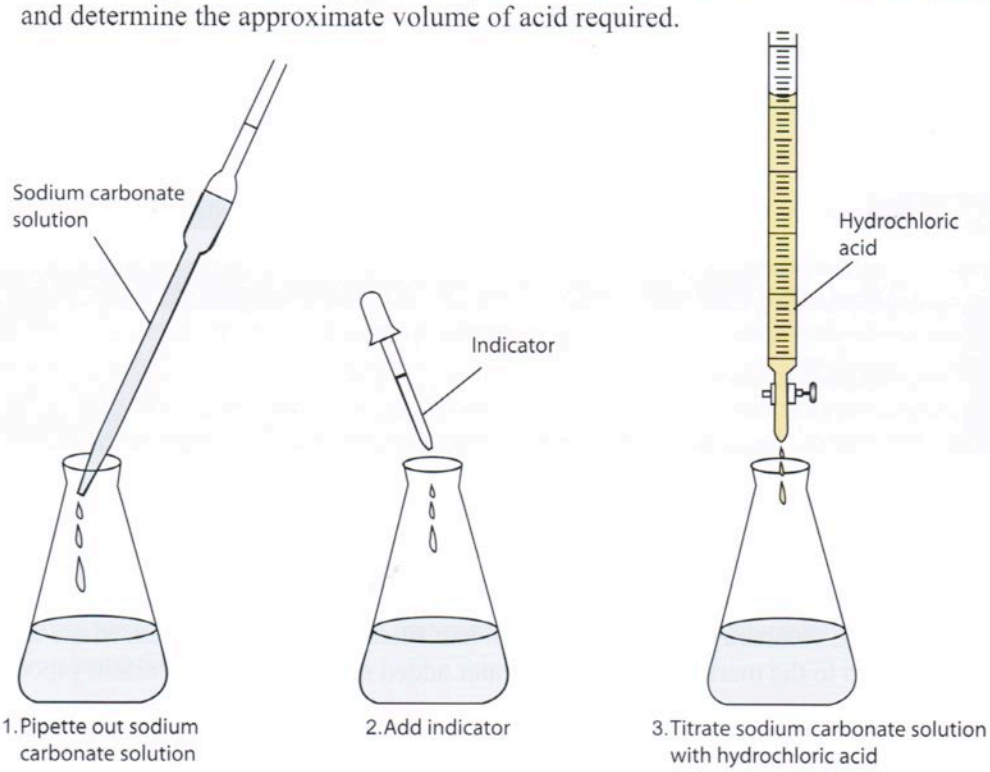


Figure 13.1

Notes

6. Record your results in a table similar to the one shown below.

	Rough estimate	Accurate titrations		
		1	2	3
Final reading (mL)				
Initial reading (mL)				
Titre (mL)				

7. Prepare another conical flask containing a 20 mL aliquot of the Na_2CO_3 solution and 2-3 drops of indicator. This time add the acid quickly from the burette with constant swirling of the flask, until the volume added is within 2-3 mL of the approximate volume required. Rinse the inside of the conical flask with a jet of distilled water from a wash bottle to return any splashed solution to the bulk solution. Continue adding acid drop by drop, and with constant swirling, until the addition of one drop is sufficient to produce a permanent colour change. Note and record the level of the acid in the burette at the end point.

8. Repeat the accurate titration with further 20 mL aliquots of Na_2CO_3 solution until consistent titration volumes are obtained. These should be within 0.2 mL of each other.

Processing of results and questions

1. Using the equation for the reaction, calculate the number of moles of Na_2CO_3 used in each titration.

2. From the equation determine the number of moles of $HC\ell$ that react with each mole of Na_2CO_3. Use this to determine the number of moles of $HC\ell$ used in the titration.

3. Calculate the average volume of $HC\ell$ solution used in the titrations. Use only those results that are concordant, that is within 0.2 mL of each other. From this determine the concentration of the $HC\ell$ solution. Mark this information on the label of the storage bottle.

4. Distinguish between `equivalence point' of a reaction and 'end point' of a titration.

5. In the introduction it was stated that the solution at the equivalence point is 'somewhat acidic'. Explain why this is so.

6. Explain why hydrochloric acid solution cannot be used as a primary standard.

7. Suppose that phenolphthalein, whose colour change is in the vicinity of pH 9, had been used instead of one of the indicators recommended would:
   a) the volume of acid required for the titration be more or less than that obtained in this experiment?
   b) the calculated concentration of the $HC\ell$ solution be higher or lower than the result obtained in this experiment?

8. What are possible sources of error in this experiment?

9. Calculate the uncertainty for the average titration volume of your hydrochloric acid solution.

Experiment 14: Preparation and standardisation of sodium hydroxide

Notes

A standard sodium hydroxide solution is often used to determine the acid content of wine.

Sodium hydroxide cannot be used as a primary standard as it readily absorbs water and carbon dioxide from the air, it is deliquescent. In this experiment you will make up a solution of NaOH that is approximately 0.1 mol L^{-1} and standardise this with standard approximately 0.1 mol L^{-1} $HC\ell$ prepared in Experiment 13.

The equation for the titration is:

$$\underset{\text{(from NaOH)}}{OH^-(aq)} + \underset{\text{(from HC}\ell\text{)}}{H^+(aq)} \rightarrow H_2O(\ell)$$

At the equivalence point of the reaction, the pH changes from about 10 to 4 over the addition of only 0.1 mL of acid. Consequently any indicator that changes colour within this pH range is suitable.

Equipment

sodium hydroxide [NaOH] (3 g)
balance
beaker (250 mL)
volumetric flask (500 mL)
storage bottle (approximately 500 mL)
beakers (two 100 mL)
washbottle
burette and stand
conical flask (250 mL)
funnel
pipette (20 mL)
pipette filler
standard hydrochloric acid [$HC\ell$] approximately 0.1 mol^{-1} from Experiment 13 (150 mL)
methyl orange or phenolphthalein (a few drops)

Procedure

Part A: Making approximately 0.1 mol L^{-1} sodium hydroxide solution

1. Calculate the mass of NaOH needed to make up 500 ml, of 0.1 mol L^{-1} solution.

SAFETY NOTE:
- **Sodium hydroxide pellets are very corrosive and must not be allowed to come in contact with your skin. If sodium hydroxide comes in contact with your skin, wash under running water for 20 minutes.**
- **Use a spatula or plastic spoon to handle the NaOH pellets.**

2. Quickly weigh out this amount, to the nearest pellet, in a clean dry 250 mL beaker. Ensure you do not leave the lid off the jar.

3. Dissolve the NaOH in about 100 mL of distilled water and transfer the solution to a 500 mL volumetric flask.

4. Stopper the flask and swirl the contents to mix them. If the solution is warm, wait until it cools, and then make it up to the graduation mark with distilled water. Place the stopper in the top and invert and swirl the flask several times to ensure that the water in the neck is mixed thoroughly with the solution in the bottom.

5. Transfer the approximately 0.1 mol L^{-1} NaOH to a clean storage bottle that has been rinsed with a little of the NaOH solution. Label the storage bottle.

Notes

Procedure **Part B: Standardisation of the sodium hydroxide solution**

1. Using the appropriate technique, pipette 20.00 mL of NaOH solution into a 250 mL conical flask. Add 2-3 drops of methyl orange or phenolphthalein.

2. With your standard $HC\ell$ solution from Experiment 13 in the burette do a rapid titration to obtain a rough estimate of the volume of $HC\ell$ solution needed to neutralise the 20.00 mL of NaOH solution.

3. Carry out repeat titrations, adding the acid more slowly near the end point, until concordant titration volumes are obtained, as in Experiment 13. Record your results in a similar table.

Processing of results and questions

1. From the equation for the reaction, the volume of NaOH used, and the volume and concentration of the standard $HC\ell$, calculate the concentration of the NaOH solution. Record this on the label of the NaOH storage bottle.

2. What is meant by deliquescence? Why is a substance that is deliquescent unsuitable for use as a primary standard?

3. Calculate the uncertainty for the average titration volume of your hydrochloric acid solution.

4. Why did procedure 2 ask you to keep the lid on the NaOH pellets? What effect would leaving the lid off have on the concentration of the solution?

5. For procedure 4, why did the solution become warm?

6. Why did the procedure allow either methyl orange <u>OR</u> phenolphthalein, while in other experiments there is no choice?

Experiment 15: Acetic acid content in vinegar

Notes

Commercial vinegar usually contains about 3-5% acetic acid (CH_3COOH) by mass. The purpose of this experiment is to determine the exact acetic acid content of a commercial brand of vinegar. This is achieved by titration with standard approximately 0.1 mol L^{-1} NaOH from Experiment 14.

Acetic acid reacts with hydroxide ion according to the equation:

$$CH_3COOH(aq) + OH^-(aq) \leftrightarrows CH_3COO^-(aq) + H_2O(\ell)$$

The pH at the equivalence point of this reaction is approximately 8.7, making phenolphthalein (colourless to pink when the pH changes from 8.3 to 10) a suitable indicator.

Equipment

balance
vinegar (40 mL)
volumetric flask (250mL)
washbottle
conical flask (250 mL)
pipettes (20 mL and 25 mL)
pipette filler
burette and stand
funnel
beakers (two 100 mL)
standard sodium hydroxide solution [NaOH] approximately 0.1 mol L^{-1} from Experiment 14 (150 mL)
phenolphthalein (a few drops)

Procedure

1. Determine the density of the vinegar by weighing out a known volume delivered from a pipette or by using a hydrometer.

2. Using a pipette place 25.0 mL of vinegar into a 250 mL volumetric flask. Make the volume up to precisely 250.0 mL with distilled water. Mix well by repeatedly inverting the volumetric flask.

3. Titrate the diluted vinegar solution from a burette against 20.0 mL portions of the standard NaOH solution each with 1-2 drops of phenolphthalein indicator. Record your results in a table as before.

Processing of results and questions

1. Write the equation for the reaction of acetic acid solution with sodium hydroxide solution and calculate the number of moles of
   (a) NaOH in the 20.0 mL samples of standard NaOH solution
   (b) acetic acid from the average volume titrated.

2. Calculate the concentration of acetic acid in the diluted vinegar.

Notes

3. Determine the concentration of acetic acid in the undiluted vinegar.

4. Calculate the mass of acetic acid in 1000 mL of undiluted vinegar.

5. Use the density of the vinegar to calculate the mass of 1000 mL of vinegar.

6. Determine the mass of acetic acid per 100 g of vinegar, that is, the percentage by mass of acetic acid in the vinegar.

7. What volume of the 0.1 mol L^{-1} NaOH solution would be required in a titration with 20.0 mL of the undiluted vinegar, using phenolphthalein as indicator?

8. Suppose that methyl orange, which changes colour at about pH 3.7, had been used instead of phenolphthalein in your experiment. Would you expect the calculated percentage of acetic acid to be too high or too low? Explain.

9. What are the possible sources of error in this experiment?

10. Calculate the uncertainty for the average titration volume of your sodium hydroxide solution.

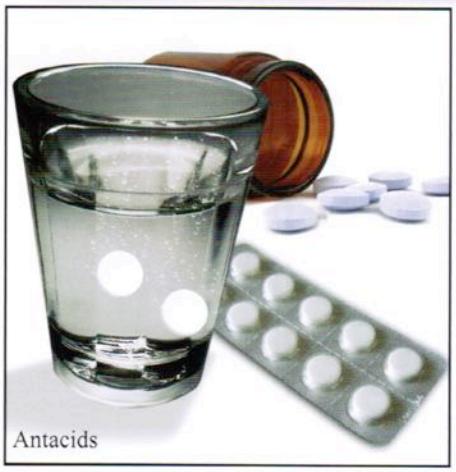
11. For the last four experiments you titrated

    Na_2CO_3 with $HC\ell$
    $HC\ell$ with NaOH
    NaOH with vinegar.

    Why did we not just titrate Na_2CO_3 against vinegar in one experiment rather than three?

12. In Experiments 13, 14 and 15 you have conducted a series of titrations and calculations of various solutions. Predict and justify the impact on the total uncertainty/experimental error on the acetic acid concentration.

Investigation 16: Effectiveness of antacids


Antacids

Gastric juice can be considered to be an $HC\ell$ solution.
Antacid preparations are prescribed to neutralise excess stomach acidity suffered by some people. These antacid preparations contain chemical substances capable of neutralising excess acidity.

The task

Determine the effectiveness of a soluble antacid preparation in neutralising excess stomach acidity.

Equipment

use the volumetric equipment that you have used in Experiments 12 -15
soluble antacid powder, e.g. Andrews, Eno, Dexsal or equivalent (about 2 g)
standard hydrochloric acid solution [$HC\ell$] approximately 0.1 mol L^{-1} from Experiment 13 (150 mL)
standard sodium hydroxide solution [NaOH] approximately 0.1 mol L^{-1} from Experiment 14 (150 mL)

Notes

Planning the investigation

1. Plan an investigation to determine the volume of gastric juice (assumed to be 0.15 mol L^{-1} $HC\ell$) that would be neutralised by a recommended dose of an antacid preparation.

   Conduct a preliminary trial to determine a suitable mass of antacid to use in your titrations. A suitable mass of antacid should react with about 20 mL of 0.1 mol L^{-1} $HC\ell$. It is suggested that in your trial you use about 0.2-0.3 g of antacid. You may find it difficult to obtain a distinct end point in the titration.

2. Write out your proposed plan, list the chemicals and equipment you need and identify the safety requirements.

3. Check the proposed plan with your teacher.

SAFETY NOTE:
- **Check your plan with your teacher before you commence**

Conducting the investigation

Conduct the investigation, collecting and recording the data in a table as you proceed.

Processing the data

Determine the volume of gastric juice neutralised by a recommended dose of antacid powder.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure and describe any modifications you would make to improve the accuracy of the results and your organisation of the investigation.

2. Compare your results with those of other class members and discuss possible sources of error.

3. What other household substances could you investigate, applying the principles you have learned in acid-base titrations?

Investigation 17: Ammonia content in household cleaning solutions

The task

In this investigation you will determine the percentage of ammonia in a solution of household ammonia.

Equipment

use the volumetric equipment that you used in Experiments 12 - 15
household ammonia or window cleaner (50 mL)
standard hydrochloric acid [$HC\ell$] - approximately 0.1 mol L^{-1} from Experiment 13 (150 mL)

Household ammonia and window cleaner

Planning the investigation

1. Plan an investigation to determine the percentage by mass of ammonia in household ammonia. When planning your procedure consider the fact that the household ammonia contains about 3% by mass of ammonia (about 2 mol L^{-1}) and your standard $HC\ell$ solution is approximately 0.1 mol L^{-1}.

2. Write out your proposed plan, list the chemicals and equipment you need and identify the safety requirements. Be sure to explain why you chose a particular indicator.

3. Check the proposed plan with your teacher.

SAFETY NOTE:
- **Check your plan with your teacher before you commence**

Conducting the investigation

Conduct the investigation, collecting and recording the data in a table as you proceed.

Processing the data

Determine the percentage by mass of ammonia in the household ammonia.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure and describe any modifications you would make to improve the accuracy of the results and your organisation of the investigation.

2. Compare your results with those of other class members and discuss possible sources of error.

3. What other household substances could you investigate, applying the principles you have learned in acid-base titrations?

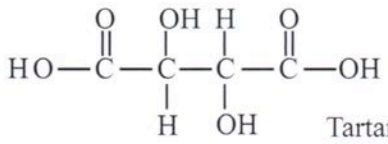
Notes

Investigation 18: Acid content in wine

Notes

The acid content of a wine is determined by titration. The titratable acidity, referred to as total acidity is measured in grams per litre. It can also be expressed as a percentage. Total acidity of wines can range from 6.0 – 8.5 g L^{-1}. A dry wine has a lower total acidity than a sweet wine.

There are many acids in wine. Tartaric acid is the main acid and gives the wine a tart, crisp taste, while citric acid gives the wine a fruity flavour. Tartaric acid, the most concentrated acid in wine, is diprotic. When titrating to determining the total acidity of a wine all the acid is assumed to be tartaric acid.



Tartaric acid

The task

Determine the total acidity of a sample of white wine. Express your determination of total acidity of the wine in grams per litre and as a percentage.

Equipment

Use the volumetric equipment that you have used in Experiments 12 - 15
white wine (40 mL) - non-alcoholic wine and grape juice can be used in place of an alcohol wine
standard sodium hydroxide solution [NaOH] approximately 0.1 mol L^{-1} from Experiment 14 (150 mL)

Planning the investigation

1. Plan an investigation to determine the concentration of acid in your white wine sample.
2. Write out your proposed plan, list the chemicals and equipment you need and identify the safety requirements.
3. Check the proposed plan with your teacher.

SAFETY NOTE:
- **Check your plan with your teacher before you commence**

Conducting the investigation

Conduct the investigation, collecting and recording the data in a table as you proceed. Use an appropriate degree of accuracy in your measurements.

Processing the data

Determine the concentration of acid in the white wine sample.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure and describe any modifications you would make to improve the accuracy of the results and your organisation of the investigation.
2. Compare your results with those of other class members. Do your results fall within the range of concentrations described in the introduction? Discuss any discrepancies and possible sources of errors.

Oxidation and Reduction

Oxidation and reduction are best understood as different aspects of an electron transfer process. Investigating the interrelationships between chemical change and electrical energy in galvanic and electrolytic cells demonstrates and consolidates understanding of applications of oxidation and reduction. This understanding can be further reinforced through the construction and testing of electrochemical cells and with the examination of the oxidising potential of various chemicals. Exploring the relationships between chemistry, industry and modern lifestyles, for example the development of batteries, fuel cells used in spacecraft and the impacts of corrosion, exemplifies the importance of the oxidation-reduction process to our 21st century lifestyle.

Free radicals, antioxidants and rusting

Free radicals are the 'bad guys' that pose a serious threat to our good health and longevity.
Fortunately chemistry can isolate and target free radicals, which damage the human body and contribute to cancer, Type 2 diabetes, heart disease and ageing. The ideal weapons to combat the destructive nature of free radicals have been identified as antioxidants. They are found in foods such as fruit and vegetables and some drinks including tea and red wine. Antioxidants mop up the free radicals before destructive oxidising reactions within the body can occur.
There are a number of sources of free radicals. Some free radicals appear normally during metabolism, and sometimes the body's immune system creates them to neutralise bacteria and viruses. **Environmental factors** such as cigarette smoke and herbicides, pollution and radiation can also produce free radicals.
The body can normally handle free radicals, but if antioxidants are in short supply, or if free radicals are produced in excess, then damage can occur. Unfortunately, free radical damage accumulates with age.

Vitamin E – The most abundant fat-soluble antioxidant in the body is found in almonds, in many oils, wheat germ, safflower, corn and soybean, and also in mangoes, nuts, broccoli and other foods.

Vitamin C – The most abundant water-soluble antioxidant in the body can be found in large amounts in many fruits and vegetables but is also found in cereals, fish, beef, and poultry.

Investments in improving health reduce costs to the health system. In a media release on 8 April 2002, Department of Health (Government of Western Australia) Director General Mike Daube said people who regularly had diets high in vegetables and fruit had substantially lower risk of many diseases. "This includes a reduced risk of cardiovascular disease, stroke, several major cancers, and possibly hypertension, Type 2 diabetes and cataracts," he said. Health authorities around Australia joined forces in 2002 to highlight this issue with the launch of the **Go for 2&5 campaign**. The campaign recommends that we eat at least five serves of vegetables and two serves of fruit every day. Unfortunately health experts are still saying that most Australians continue to place their health at unnecessary risk by not eating enough fruit and vegetables.

The **chemistry** behind the seven servings per day of anti-oxidant rich fruits and vegetables lies in the way free radicals and **antioxidants** interact in oxidation and reduction processes. During a reaction bonds are broken and new bonds resulting from the transfer or sharing of electrons are formed. Normally the new bonds satisfy the conditions of maximum stability for the compound or molecule with full outer valence shells. Sometimes bonds split and leave a free radical, an atom or molecule with an unpaired electron or an otherwise incomplete valence shell. From a medical viewpoint the two main free radicals are the hydroxyl radical (OH) and the superoxide radical, which consists of two linked oxygen atoms (O_2^-) with a single, unpaired electron.
These free radicals are very unstable and react quickly with other compounds. They try to capture the needed electron to gain stability. The gaining of one or more electrons is called reduction. Free radicals attack the nearest stable molecule, stripping off an electron and become reduced. The "attacked" molecule loses its electron and is oxidised. As a result it becomes a free radical itself, and so begins a chain reaction. Free radical attacks on tissue are known as oxidative stress and feature the chemical reaction known as oxidation.

Career profile 3: Corrosion Scientist

Profile of a Corrosion Scientist

Sustainability is one of the buzzwords of today, but traditionally it has not been used much by corrosion scientists and engineers - even though they have been practising some of the core sustainability principles for decades. Corrosion, like death and taxes, is the third certainty of our lives and every day it has the potential to adversely affect our health, safety, lifestyle, and environment. Andrew Peek, Principal Materials Scientist at GHD, says "food processing & packaging, energy production & distribution, water & wastewater services, all forms of transport, buildings, bridges, manufacturing and mineral processing, are just some of the areas in our every day lives affected by corrosion". Corrosion science is truly multidisciplinary, combining many facets of chemistry, physics, engineering, and sometimes biology - the mix and role vary from one industry to another. Corrosion Scientists use all techniques from classical wet chemistry (titrations, etc.) and microbiological methods to the latest in separation sciences, x-ray microscopy and infra-red spectrometry to diagnose causes of failures and investigate the corrosion mechanisms. They also draw on the various technologies in paints and plastics, corrosion inhibiting chemicals, environment modification, and metals and alloys to develop and provide solutions to corrosion issues. If you have a desire to contribute to a sustainable, safe, and healthy lifestyle for all - this could be a career for you.

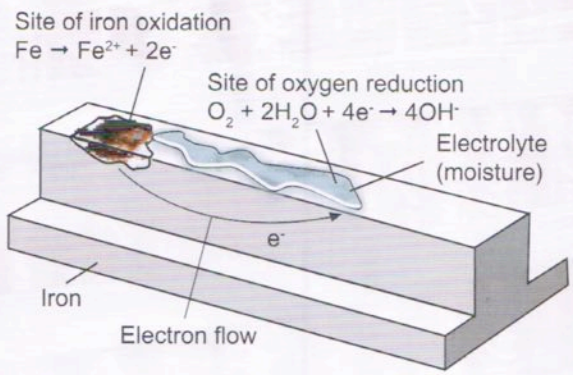
Source: Andrew Peek, Principal Materials Scientist, Materials Testing Group GHD Pty Ltd. Perth. www.ghd.com.au

Rusting nanoparticles of iron cleanup toxic chemical spills

Corrosion of metals costs Australia about three billion dollars annually. However, it is not only a monetary cost due to constant maintenance or replacement of metal; there is also a cost in human lives. For example, corroded structures, such as bridges, buildings, cars, and machinery are weakened and become dangerous. In the corrosion process a metal reacts with oxidants in the environment, and, as a result, an electric current is established just as in an electrochemical cell (see the diagram "Corrosion of iron").

However, researchers from the University of New South Wales have shown that rusting iron can actually be very useful in cleaning up toxic spills. They have found that molecular-sized 'nanoparticles' of iron, rust extremely rapidly and in the process produce powerful oxidants called hydroxyl radicals. These hydroxyl radicals are capable of breaking down many toxic organic compounds, such as pesticides, and industrial waste chemicals.

We usually think of corrosion as a destructive process in which a metal is attacked in an electrochemical reaction. Has nanotechnology turned corrosion into a friend?



Corrosion of iron

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Experiment 19: Oxidation and reduction reactions involving metals

Notes

Oxidation occurs when a species loses electrons. These electrons are transferred to another species that gains electrons and is reduced. Oxidation and reduction processes must therefore proceed simultaneously.

Oil Rig
Oxidation is the loss of electrons. Reduction is the gain of electrons.

In this experiment two common types of redox reactions are investigated. These are the reaction of dilute hydrochloric acid with metals to produce hydrogen gas, and metal displacement reactions.

Equipment

test tubes (three)
pea sized samples of copper [Cu], lead [Pb], magnesium [Mg] and zinc [Zn] (four samples of each)
hydrochloric acid [$HC\ell$] 2 mol L^{-1} (10 mL)
taper and matches
10 mL 0.1 mol L^{-1} solutions of:
- copper(II) nitrate [$Cu(NO_3)_2$]
- lead(II) nitrate [$Pb(NO_3)_2$]
- magnesium nitrate [$Mg(NO_3)_2$]
- zinc nitrate [$Zn(NO_3)_2$]

Procedure

Part A: action of dilute hydrochloric acid on various metals

1. Place a piece of zinc metal in a test tube and add about 2 mL of dilute $HC\ell$. Observe what happens.
2. Collect any gas that is evolved in another test tube by inverting it over the first test tube, as shown in figure 19.1. Apply a lighted taper to the mouth of the inverted test tube and identify the gas present from the result of this test.
3. Repeat this procedure for magnesium, lead and copper, noting any difference in behaviour from the zinc.

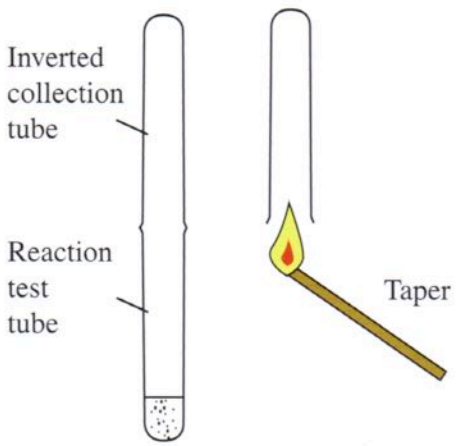


Figure 19.1: Collecting and testing for hydrogen

Procedure

Part B: metal-metal ion displacement reactions

1. Place a piece of zinc in each of three test tubes and add sufficient $Mg(NO_3)_2$ solution to the first tube, $Pb(NO_3)_2$ solution to the second tube and $Cu(NO_3)_2$ solution to the third tube to cover the zinc. Observe and note any reactions that occur.
2. Repeat this procedure for the magnesium, covering the metal with $Zn(NO_3)_2$, $Pb(NO_3)_2$ and $Cu(NO_3)_2$ solutions respectively.
3. Repeat this procedure for the lead, covering the metal with $Mg(NO_3)_2$, $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solutions respectively.
4. Repeat this procedure for the copper, covering the metal with $Mg(NO_3)_2$, $Zn(NO_3)_2$ and $Pb(NO_3)_2$ solutions respectively.

Processing of results and questions

1. Write the oxidation and reduction half equations and the overall redox equation for any reactions that took place. (See set 19 and 20 for examples)
2. For each reaction you observed identify the oxidising and reducing agents.
3. List the four metals observed in this experiment in order of decreasing strength as reducing agents.

Notes

Experiment 20: Halogen displacement reactions

Notes

The halogens, the group 17 elements, are all oxidising agents. The halogens tend to gain electrons to form halide ions. For example, chlorine tends to gain electrons to form chloride ions.

$$C\ell_2(aq) + 2\,e^- \rightarrow 2\,C\ell^-(aq)$$

In this experiment the strength of chlorine, bromine and iodine as oxidising agents in aqueous solution (chlorine water, bromine water and iodine water) will be compared. Although solutions of chlorine, bromine and iodine in water exhibit different colours, the identification of a particular halogen is made more simple if a solvent such as dichloromethane is used. The halogens dissolve preferentially in the dichloromethane and exhibit characteristic colours. In part A of this experiment the colours of the halogens in dichloromethane are identified. This information is used in part B where several halogen displacement reactions are investigated.

Equipment

test tubes (six) and stoppers
5 mL 0.5 mol L^{-1} solutions of:
- potassium bromide [KBr]
- potassium chloride [$KC\ell$]
- potassium iodide [KI]

5 mL chlorine water [$C\ell_2$(aq)]
5 mL bromine water [Br_2(aq)]
5 mL iodine water [I_2(aq)]
10 mL dichloromethane [$CH_2C\ell_2$]

Procedure **Part A: colour of halogens in dichloromethane**

SAFETY NOTE:
- **The halogen solutions are poisonous and must be handled with care.**
- **Do not breathe the vapours given off from these solutions.**
- **If the solutions come in contact with your skin immediately wash the affected with plenty of water.**
- **Dichloromethane is poisonous and should be handled with care.**
- **Do not breathe in $CH_2C\ell_2$ vapour or allow it to come in contact with your skin.**
- **Carry out the experiment in the fumehood.**

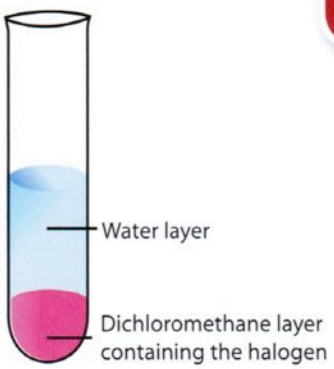


Figure 20.1

1. Prepare a table to record the colours of the halogens and halide ions in water and the halogens in dichloromethane.
2. Record the colour of the bromine water, which contains the halogen molecule, bromine. Record the colour of the potassium bromide solution, KBr, which contains the bromide ion, Br^-.
3. Place about 2 mL of bromine water in a test tube, add 1 mL of dichloromethane, stopper and shake vigorously for a few seconds. Allow the liquid layers to separate, as shown in figure 20.1. Record the colour of the dichloromethane layer (the bottom layer), which contains the halogen molecule, bromine. Keep the test tube sample for comparison in part B.

4. Repeat procedures 2 and 3 for chlorine water and iodine water.

5. Be sure that you keep the test tubes of the three samples as a colour reference for making comparisons in part B. The colours will help to identify the halogen molecule present.

Notes

Procedure

Part B: halogen displacement reactions

1. Add about 2 mL of chlorine water to 2 mL of KBr solution in a test tube and shake. Observe any changes that occur.

2. Add about 1 mL of dichloromethane to the same test tube. Shake and allow the dichloromethane layer to settle, and note its colour. From the colour of the dichloromethane can you identify the halogen it has dissolved?

3. Repeat this procedure for solutions of the other halogens and halide ions, using the following combinations:

chlorine water	+	KI solution;
bromine water	+	KCℓ solution;
bromine water	+	KI solution;
iodine water	+	KCℓ solution;
iodine water	+	KBr solution.

In each case add some dichloromethane and shake and identify any newly formed halogen that might be present.

4. Draw up a table to summarise the results of the six reactions above.

Processing of results and questions

1. Write the oxidation and reduction half equations and the overall redox equation for any reactions that took place. (See set 19 and 20 for examples)

2. a) Which of the halogens have been reduced?
   b) Which of the halide ions have been oxidised?
   c) Which of the halogens is the strongest oxidising agent?

3. List the halide ions in order of increasing strength as reducing agents.

Experiment 21: Redox reactions 1

Notes

Sometimes bonds split and leave a free radical, an atom or molecule with an unpaired electron or an otherwise incomplete valence shell. Free radicals, like the hydroxyl radical (OH, note it has no charge - it is not OH^-) in our bodies, are very unstable and react quickly with other compounds. They try to capture an electron to gain stability. The gaining of one or more electrons is called reduction. Free radicals attack the nearest stable molecule, stripping off an electron and become reduced. The "attacked" molecule loses its electron and is oxidised. Free radical attacks on tissue are known as oxidative stress and feature the chemical reaction known as oxidation.

A free radical is an oxidising agent.

The following reactions will help you better understand how an oxidising agent like a free radical works and how an antioxidant can neutralise a free radical. Your teacher may choose to demonstrate these reactions.

The permanganate ion is commonly used as an oxidising agent in an acidified aqueous solution. The permanganate ion (MnO_4^-), which is deep purple in colour, may be reduced to manganese(II) ion (Mn^{2+}) which is almost colourless at this concentration. The equation for the half reaction is

$$\underset{\text{purple}}{MnO_4^-(aq)} + 8\,H^+(aq) + 5\,e^- \rightarrow \underset{\substack{\text{colourless}\\ \text{(very pale pink)}}}{Mn^{2+}(aq)} + 4\,H_2O(\ell)$$

Equipment

test tubes and stoppers (seven)
watch glass
dropper
potassium permanganate solution [$KMnO_4$] 0.02 mol L^{-1} (3 mL)
potassium dichromate solution [$K_2Cr_2O_7$] 0.05 mol L^{-1} (3 mL)
potassium chloride solution [$KC\ell$] 0.5 mol L^{-1} (5 mL)
potassium bromide solution [KBr] 0.5 mol L^{-1} (5 mL)
potassium iodide solution [KI] 0.5 mol L^{-1} (5 mL)
hydrogen peroxide solution [H_2O_2] 6% (5 mL)
sulfuric acid [H_2SO_4] 2 mol L^{-1} (6 mL)
dichloromethane [$CH_2C\ell_2$] (6 mL)
iron(II) sulfate-7-water [$FeSO_4 \cdot 7H_2O$] (about 1 g)
graduated cylinder (10 mL)
copper turnings
concentrated nitric acid (10 mL)
blue litmus paper

SAFETY NOTE:

- **Dichloromethane is poisonous and must be handled with care.**
- **Do not breathe in $CH_2C\ell_2$ vapour or allow it come in contact with your skin.**
- **Use dichloromethane in a fumehood.**

Notes

Procedure **Part A: permanganate ion oxidising agent**

1. Make up a stock solution of acidified potassium permanganate solution by mixing 3 mL of 0.02 mol L^{-1} $KMnO_4$ with 3 mL of 2 mol L^{-1} H_2SO_4.
2. Place 2 mL of 0.5 mol L^{-1} KI into a test tube. Using a dropper add dropwise about 1 mL of the stock permanganate solution and shake well. If a redox reaction occurs the purple permanganate colour will disappear, or at least be greatly reduced in intensity.
3. Add 1 mL of dichloromethane to the test tube and shake well to see if any halogen has been formed. (Refer to experiment 20.)
4. Place a small quantity of $FeSO_4 \cdot 7H_2O$ in a test tube and dissolve in about 2 mL of water. Repeat step 2 using the $FeSO_4$ solution in place of the KI solution.
5. Repeat step 2 using hydrogen peroxide, H_2O_2, solution in place of the KI solution.

Procedure **Part B: reaction of Cu metal with concentrated nitric acid**

Concentrated nitric acid does not act like a normal acid. It is a powerful oxidizing agent. It reacts thus:

$$NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2\,(g) + H_2O(\ell)$$

SAFETY NOTE:

- **Conduct the Cu metal concentrated HNO_3 experiment in the fumehood.**
- **Nitric acid is corrosive: handle with care and avoid contact with the skin. If spilt wash thoroughly with water or cover spilt acid with hydrogen carbonate or the acid spill material available in the laboratory.**
- **The brown gas, nitrogen dioxide, is poisonous and must be handled with care. Do not breathe in NO_2 gas or allow it come in contact with your skin.**

1. Place about 1 g of copper turnings into a 100 mL beaker. (Figure 21.1)
2. Cover the copper metal with about 10 mL of concentrated nitric acid. Carefully swirl the mixture a few times then cover with the watch glass.
3. Occasionally feel the side of the beaker.
4. Moisten the blue litmus paper while holding with metal tongs. Carefully lift one edge of the watch glass and hold the litmus paper in contact with the brown gas.
5. Record all observations as the reaction proceeds.

Processing of results and questions

1. Using the permanganate half equation (given in the introduction), write the oxidation and overall redox equation for each the reactions observed in part A.
2. Write the oxidation and reduction half equations and the overall redox equation for the copper, nitric acid reaction in Part B.
3. Explain any temperature changes observed during the copper, nitric acid reaction in Part B.
4. Identify sources and list environmental hazards that could result from the release of large quantities of nitrogen dioxide gas into the atmosphere.

Figure 21.1: Copper/nitric acid reaction

Experiment 22: Redox reactions 2

Notes

Energy is a useable product of redox reactions as demonstrated in respiration occurring in living cells. A more obvious example is the welding and metal cutting capacity of the oxidation of acetylene in an oxy-acetylene torch. Oxygen is the most common oxidiser. As well as the examples already described its oxidising power includes the combustion of fuels, the formation of metal oxides (such as found in hematite and bauxite) and in the rusting of iron.

This experiment explores a number of different redox reactions. Conduct the experiments and identify the oxidising and reducing reagents and write half and full oxidation and reduction equations for the reactions.

Equipment

3 large test tubes with stoppers
retort stand and clamp
test tube rack
hydrochloric acid [$HC\ell$] 2 mol L^{-1} (10 mL)
2 cm magnesium ribbon
matches and wax tapper
6% hydrogen peroxide (5 mL)
potassium iodide [KI] solid (2 g)
test tube holder
250 mL beaker
calcium hypochlorite [$Ca(OC\ell)_2$] (pool shock/chlorine) (2 g) or sodium hypochlorite [$NaOC\ell$] (household bleach) (5 mL)
0.5 mol L^{-1} potassium iodide solution [KI] (5 mL)

Procedure

Part A: Making and testing hydrogen gas

1. Set up the gas generating equipment to collect the hydrogen by the downward displacement of air as shown in Figure 22.1. Support the reaction tube using a retort stand and clamp.
2. Into the reaction tube place 2 cm length of magnesium ribbon and add 2 mol L^{-1} $HC\ell$ solution to a depth of about 3 cm. Replace the stopper assembly.
3. Collect a test tube of hydrogen gas by placing an inverted test tube over the delivery tube for 1-2 minutes. Finally stopper the test tube of hydrogen and place it in a test tube rack.
4. Have a laboratory partner light the taper and bring it to the mouth of the stoppered test tube. In one action remove the stopper and hold the burning taper above the mouth of the test tube.
5. Record your observations.

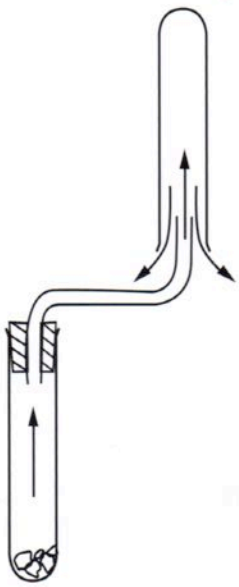


Figure 22.1

SAFETY NOTE

- **Safety glasses must be worn.**
- **Hydrochloric acid is corrosive and must be handled with care.**
- **Hydrogen peroxide is corrosive and must be handled with care, avoid contact with the skin and wash after handling the container.**
- **Hypochlorites are corrosive and must be handled with care.**

Notes

Procedure **Part B: Decomposing hydrogen peroxide**

5. Pour 5 mL of 6% hydrogen peroxide solution into a test tube.
6. Using the test tube holder, hold the test tube upright in the centre of the 250 mL beaker and add a half a teaspoon (approx. 1 g) of potassium iodide solid.
7. Gently mix then hold the test tube upright in the centre of the 250 mL beaker.
8. Record your observations.

Procedure **Part C: The oxidising power of hypochlorite**

9. Pour 5 mL of 0.5 mol L^{-1} potassium iodide solution into a test tube.
10. To the same test tube add 5 mL of household bleach, sodium hypochlorite or a teaspoon (approx. 2 g) of calcium hypochlorite.
11. Record your observations.

Processing of results and questions

1. Write an equation for the reaction of magnesium and hydrochloric acid in part A. Is it a redox reaction? If so, explain your reasons for making that decision. (If appropriate use half equations to help your explanation)

2. Write an equation for the reaction used to test for the presence of hydrogen gas in part A. Is this redox reaction? If so, then write the two half equations, identifying the oxidising agent and the reducing agent.

3. Using equations explain your observations in part B.

4. Write half equations and an overall redox equation for the reaction in part C that demonstrates the oxidising capacity of hypochlorite. Identify the oxidising and reducing agents for the reaction and explain the changes observed.

Experiment 23: Sulfur dioxide; reducer and oxidiser

Common uses of SO_2

- *A fruit-preserving agent*
- *A food preservative*
- *A disinfectant in food factories and breweries*
- *A fumigant for grapes, citrus fruits and grains*
- *A bleach for textile fibres*
- *In the manufacture of paper*
- *To store grape juice and in the fermentation stage of wine making*

Notes

Sulfur dioxide is an important compound to the wine industry. In winemaking, SO_2 serves as an antibiotic and antioxidant, protecting wine from spoilage by bacteria, fungus and oxidation. It is present in wine at concentrations of up to 10 parts per million (10 ppm). The upper limit of SO_2(present as SO_{21}, HSO_3^- and H_2SO_3) allowed in wine is 350 ppm. An SO_2, water and citric acid mixture is commonly used to clean and sanitize winery equipment as chlorine based disinfectants like bleach cannot be used. Today, compounds like ozone (O_3) are becoming more extensively used as cleaning products in wineries. They are efficient and compounds made by reacting ozone do not affect the wine or the equipment.

Sulfur dioxide's antioxidant properties are due to its ability to reduce other substances. Nevertheless it is capable of acting as an oxidiser in the presence of a strong reducer. In this experiment you will prepare SO_2 and test its oxidising and reducing capabilities. Sulfur dioxide is a poisonous gas with a pungent suffocating odour. Because of the poisonous nature of the gas the experiment should be carried out in a fumehood.

Equipment

large test tube fitted with gas delivery tubing (a length of plastic tubing connected to a 10 cm piece of glass tubing which fits the stopper)
retort stand and clamp
Bunsen burner
matches
6 test tubes
test tube rack
blue litmus paper (four small pieces)
red litmus paper (one small piece)
sodium sulfite [Na_2SO_3] (2 g)
sulfuric acid [H_2SO_4] 2 mol L^{-1} (10 mL)
5 mL, 0.1 mol L^{-1} solutions of:
- potassium dichromate solution [$K_2Cr_2O_7$]
- potassium permanganate solution [$KMnO_4$]
- sodium sulfide solution [Na_2S]

Procedure

(Your teacher may prefer to carry out this experiment as a demonstration).

SAFETY NOTE:

- **Sulfur dioxide is a poisonous gas which must be handled with care.**
- **Do not breathe the SO_2 it could also trigger an asthma attack.**
- **This experiment should be carried out in the fumehood.**

1. Place about 2 g of Na_2SO_3 into a test tube, label as the "reaction tube". Clamp the reaction tube to the retort stand.
2. Into a second test tube carefully add 2-3 mL of 0.1 mol L^{-1} $K_2Cr_2O_7$. Label the test tube "$K_2Cr_2O_7$" and place into the test tube rack.
3. Into a third test tube carefully add 2-3 mL of 0.1 mol L^{-1} $KMnO_4$. Label the test tube "$KMnO_4$" and place into the test tube rack.

4. Into a fourth test tube carefully add 2-3 mL of 0.1 mol L^{-1} Na_2S. Label the test tube "Na_2S" and place it into the test tube rack.

5. Set up the gas generating equipment as shown in Figure 23.1. Light the Bunsen burner. To the reaction tube containing the 2 g of Na_2SO_3, carefully add 2 mol L^{-1} H_2SO_4 to a depth of about 2 cm. Replace the stopper assembly. Some SO_2 will be evolved at this stage. Place a piece of moist red and blue litmus at the exposed end of the gas delivery tube. Record your observations. Move quickly to procedure 6.

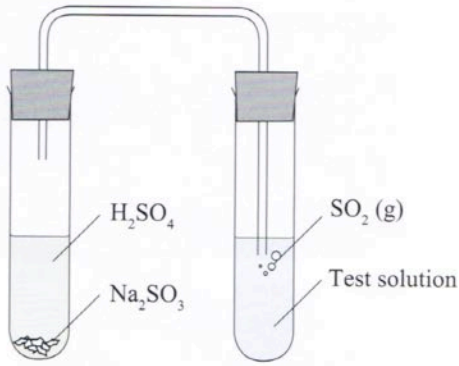


Figure 23.1

6. Gently heat the reaction tube with a Bunsen burner and pass the SO_2 into the test tube labeled "$K_2Cr_2O_7$". To stop water from being sucked into the reaction tube, remove the delivery tube from the $K_2Cr_2O_7$ solution **before** removing the heat from the reaction tube. Record your observations.

7. In the same way, pass SO_2 through the 0.01 mol L^{-1} $KMnO_4$ and 0.1 mol L^{-1} Na_2S and record your observations.

8. Dispose of the contents of the reaction tube down the sink in the fume hood and the permanganate, dichromate and sulfide solutions into the liquid waste container provided by your teacher.

9. Freshly cut two identical sections from an apple so that they will fit into a test tube. Place each piece into a different test tube as shown in Figure 23.2. Fill one of the test tubes with SO_2 gas. Label each test tube, stopper lightly and leave overnight.

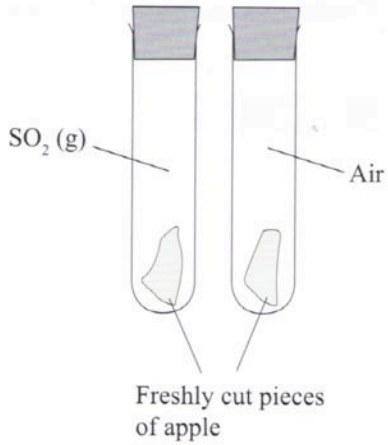


Figure 23.2

Processing of results and questions

1. Write an equation for the preparation of sulfur dioxide.

2. Write equations for the reactions of SO_2 with acidified $Cr_2O_7^{2-}$. Is SO_2 acting as an oxidising agent or reducing agent?

3. Write equations for the reactions of SO_2 with acidified MnO_4^-. Is SO_2 acting as an oxidising agent or reducing agent?

4. Write equations for the reactions of SO_2 with S^{2-}. Is SO_2 acting as an oxidising agent or reducing agent?

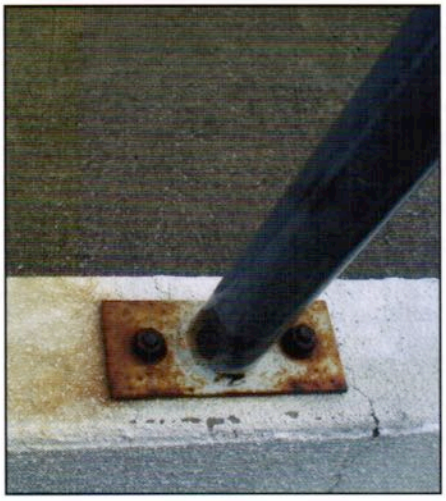
5. What observations made in this experiment would add value to the claim that sulfur dioxide is a major contributor to acid rain in industrial areas?

6. (a) Write an hypothesis for the experiment set up in step 9.
   (b) Identify the different variables: test, dependent, independent and controlled variables.
   (c) Was this a fair test? Explain.
   (d) How could you improve this experiment?

7. Describe and explain your results from the experiment set up in step 9. Do they confirm SO_2 as a useful food preservative?

Notes

Experiment 24: Factors affecting the corrosion of iron



Rusting iron

In 2009 Curtin University suggested that corrosion of metals costs Australia about $30 billion annually.

Corrosion is the process by which metals are converted to oxides or other compounds. This causes the metals to gradually deteriorate as illustrated by the rusting of iron and steel and the corrosion of aluminium fittings in salty ocean environments. Corrosion is an expensive problem in our society and quite extensive industries have developed that specialise in minimising the corrosion of metal structures.

In this experiment you will investigate the corrosion of iron and various factors that can accelerate or inhibit the rate of this process. In the rusting process iron is oxidised initially to iron(II), the ferrous ion and then to iron(III), the ferric ion as shown in the half equations:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^- \text{ then, } Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Oxygen from the air is reduced to hydroxide ions in the cathode half reaction. The reduction half equation involved in the corrosion of iron can be represented as:

$$O_2(g) + 2\,H_2O(\ell) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

The iron(II) and iron(III) ions can both combine with the hydroxide ions formed in the reduction process. The green iron(II) hydroxide slowly oxidises further to brown iron(III) hydroxide. The iron(III) hydroxide may partially dehydrate to form rust. Rust consists of hydrated iron(III) oxides $Fe_2O_3 \cdot xH_2O$ and iron(III) oxide-hydroxide ($FeO(OH)$, $Fe(OH)_3$).

Notes

Observing Corrosion

Normally we observe the end product of iron corrosion (rust) forming over a long period of time, but cannot see how it is formed. In this experiment it is possible to look at oxidation and reduction processes separately. An agar jelly containing water, phenolphthalein and potassium ferricyanide $K_3[Fe(CN)_6]$ will be used to observe corrosion under various conditions.

Anodic regions where the iron corrodes will appear blue. The Fe^{2+} from the oxidising metal, bonds with ferricyanide ion producing a blue complex ion, ferrous ferricyanide (also called "Prussian Blue"):

$$Fe \rightarrow Fe^{2+}(aq) + 2\,e^-$$

$$Fe^{2+}(aq) + Fe(CN)_6^{3-}(aq) \rightarrow Fe[Fe(CN)_6]^-(aq) \qquad \text{(blue)}$$

Cathodic regions where reduction of oxygen occurs will become pink due to the phenolphthalein indicator which changes colour in the presence of hydroxide ions:

$$O_2(g) + 2\,H_2O(\ell) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

$$HInd(aq) + OH^-(aq) \rightarrow H_2O(\ell) + Ind^-(aq) \qquad \text{(pink)}$$

Please note that the absence of blue regions does not mean there is no oxidation occuring, only that there is no corrosion of iron metal.

Equipment

test tubes (six)
clean iron nails (ten)
pliers
beaker (250 mL)
Bunsen burner
tripod and gauze mat
petri dishes (two small)
copper wire (10 cm)
zinc strip (10 cm)
stirring rod
distilled water

Vaseline ™
phenolphthalein solution 0.1 % (1 mL)
agar powder (2 g)
10 mL of:
- hydrochloric acid solution [$HC\ell$] 0.1 mol L^{-1}
- sodium hydroxide solution [NaOH] 0.1 mol L^{-1}
- sodium chloride solution [$NaC\ell$] 0.1 mol L^{-1}

potassium hexacyanoferrate(III) solution
[$K_3Fe(CN)_6$] 0.1 mol L^{-1} (2 mL)

Notes

Procedure

Part A: Rusting of iron in various aqueous solutions

Corrosion is dependent on oxygen and water. We would expect that varying concentrations of oxygen will have an effect on corrosion. You might have noticed that when there are water droplets on a metal structure, the metal tends to corrode more in those places where the water droplets are present.

In this part of the experiment you will observe the corrosion of iron nails in various aqueous solutions.

1. Place a clean, bright nail into each of five test tubes. Nails are usually covered in oil when manufactured so they will need cleaning with warm water and detergent.
2. Partly fill the test tubes with one of the following reagents so that the nail is just covered by the solution: 0.1 mol L^{-1} $HC\ell$, 0.1 mol L^{-1} NaOH, 0.1 mol L^{-1} $NaC\ell$, and distilled water.
3. Fill a sixth test tube with distilled water to a depth that will completely cover a nail. Boil the water vigorously for about 3 minutes to drive out dissolved air. While the water is still hot drop in a clean nail and add 1 mL of Vaseline ™ to cover the surface of the water. The Vaseline ™ melts, forming a layer between the air and the water.
4. Allow the nails to stand in the solutions for 24 hours.
5. After 24 hours observe the nails and solutions carefully and record any evidence of rusting.
6. To those solutions in which there is no evidence of rusting, add 2 drops of 0.1 mol L^{-1} $K_3[Fe(CN)_6]$ solution. The formation of a blue precipitate is indicative of the presence of iron(II) ions and, therefore, corrosion.

SAFETY NOTE:
CAUTION!
- **potassium hexacyanoferrate(III) solution [$K_3Fe(CN)_6$] should NEVER be mixed with acids, due to formation of toxic hydrogen cyanide gas.**

Experiment 24: Factors affecting the corrosion of iron

Corroding iron

Procedure

Part B: Stress and contact with other metals

History of manufacture and stress help to explain why the same metal-type structures placed in the same environments corrode at different rates or end up corroding in different places along the structure.

Dissimilar metal corrosion occurs when two different metals are in contact with each other and form an electrochemical cell, where one metal accelerates the oxidation (corrosion) of the other. This is a big problem for engineers, who must be very careful when designing metal constructions where different metals are used. One very famous example of dissimlar metal corrosion occurred in the structure of the Statue of Liberty in the USA. The statue was built in 1886, but in 1980 it needed serious repairs due to dissimilar metal corrosion between the copper skin and iron frame, weakening the structure. The table of reduction potentials can be used to predict which of the two metals in contact will corrode first. The metal lower in the table is the stronger reducing agent and will be preferentially oxidised. In the case of the Statue of Liberty, the wrought iron frame was oxidised.

Notes

In this part of the experiment you will investigate the effect of history and stress on the corrosion of iron nails and the effect of placing iron in contact with copper and zinc.

1. Collect two clean, non-painted, non-galvanised iron nails. Place a clean nail to one side of a petri dish and another, which has been sharply bent, to the other side of the petri dish as shown in Figure 24.1.

2. Prepare two clean, non-painted, non-galvanised iron nails by tightly wrapping a clean piece of:
   - copper wire around one of the nails
   - zinc strip around a second nail

   Place the two nails in a petri dish as shown in Figure 24.1. Ensure that the nails do not touch each other.

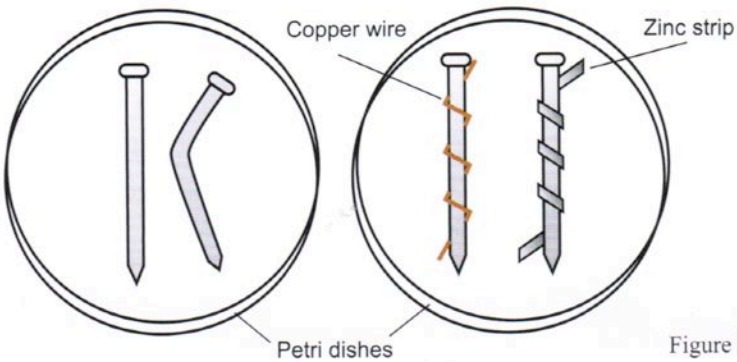


Figure 24.1

Notes

3. The agar jelly may already be prepared for you. If not you can prepare an agar mixture by bringing 200 mL of distilled water gently to the boil and adding, while stirring, 2 g of agar powder. Continue heating and stirring until the agar is evenly dispersed.

4. Add 10 drops of 0.1% phenolphthalein indicator and 10 drops of 0.1 mol L^{-1} $K_3[Fe(CN)_6]$ to the agar mixture and stir thoroughly. Allow the agar mixture to cool.

5. While the agar mixture is still warm, and before it sets, carefully pour some into both petri dishes until the nails are covered to a depth of about 0.5 cm.

6. Set the dishes aside in a suitable location in the laboratory. Examine them at the end of the laboratory period and again after they have stood for 24 hours.

Processing of results and questions

1. In part A, list the solutions in which there was evidence of corrosion. Give some indication of the relative amounts of corrosion in each case. Separately list those solutions in which there was no evidence of corrosion.

2. List the substances that must be present for rusting to occur. Is there any evidence from this experiment that supports this list?

3. Explain the different amounts of rusting in the $NaC\ell$, $HC\ell$, and NaOH solutions when compared with the distilled water.

4. What substances used in this experiment might be used as rust inhibitors?

5. In part B what indicates the sites of the oxidation and reduction reactions?

6. Did oxidation tend to occur at any particular part of the two isolated nails? If so, suggest reasons why this might be so.

7. For the two metal couples studied, in which case was the iron corroded? Explain why corrosion of the iron occurred readily in one case but was absent in the other.

8. Explain why a nail can stand for many days on the shelf and not rust but will rust rapidly if placed in tap water.

9. What is the white precipitate formed around the zinc strip in part B, where no corrosion of the iron occurred? Describe how the zinc coating in galvanised iron protects the iron from corrosion.

10. Define the term 'sacrificial anode'. Which of the metals in part B could be used as a sacraficial anode for iron?

Experiment 25: Galvanic cells

Notes

An important application of redox reactions is in the manufacture of galvanic cells or "batteries". These cells utilise spontaneous exothermic redox reactions and are designed so that the electrons are transferred through an external circuit rather than by contact of the reactants. This flow of electrons can be used to do useful work.

In galvanic cells the reactants are physically separated. The oxidation half-reaction takes place in the anode half-cell and the reduction half-reaction takes place in the cathode half-cell. A complete circuit is constructed by joining the electrodes of each half-cell with a wire and by connecting the solutions with a salt bridge.

In this experiment you will construct galvanic cells based on the following reactions and measure the potential difference of each cell.

1. Reaction of zinc with copper(II) ions
   $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
2. Reaction of lead with copper(II) ions
   $Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$
3. Reaction of zinc with lead(II) ions
   $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

Equipment

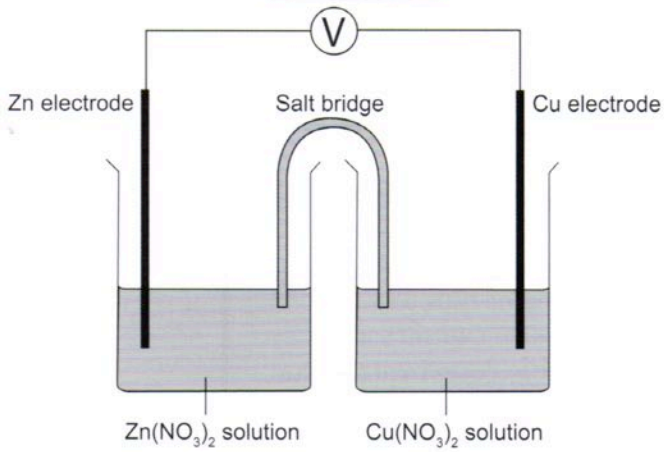


Figure 25.1

beakers (four 100 mL)
filter paper (four pieces)
electrical leads (two)
voltmeter
strips of copper [Cu], zinc [Zn] and lead [Pb] (approximately 8 cm × 1 cm)
30 mL of 0.1 mol L^{-1}:
- copper(II) nitrate solution [$Cu(NO_3)_2$]
- zinc nitrate solution [$Zn(NO_3)_2$]
- lead(II) nitrate solution [$Pb(NO_3)_2$]

2 mol L^{-1} sodium sulfide solution [Na_2S] (5 mL)
25 mL saturated ammonium nitrate solution [NH_4NO_3]

Procedure

1. In one 100 mL beaker place 30 mL of 0.1 mol L^{-1} $Cu(NO_3)_2$ solution and a freshly cleaned strip of copper. In another beaker place 30 mL of 0.1 mol L^{-1} $Zn(NO_3)_2$ solution and a freshly cleaned strip of zinc.

2. Connect the copper electrode to the positive terminal of a voltmeter and the zinc electrode to the negative terminal. Is there any reading on the voltmeter?

3. Soak a folded filter paper in saturated NH_4NO_3 solution and use the wet paper to bridge the solutions in the two beakers as shown in Figure 25.1. Make sure that the ends of the paper dip into the two solutions but are not touching the metal electrodes.

Notes

4. Measure and record the voltmeter reading.

5. Repeat the procedure for reaction 2, using a clean piece of lead dipping into a 0.1 mol L^{-1} $Pb(NO_3)_2$ solution for the Pb/Pb^{2+} half-cell instead of the Zn/Zn^{2+} half-cell. Use a fresh salt bridge.

6. Repeat the procedure for reaction 3, using Zn/Zn^{2+} and Pb/Pb^{2+} half-cells and a fresh salt bridge.

7. In a fume hood, set-up the $Zn/Zn^{2+}//Cu^{2+}/Cu$ cell again. To the $Cu(NO_3)_2$ solution add about 5 mL of 2 mol L^{-1} Na_2S. Note the voltmeter reading and the appearance of the solution.

SAFETY NOTE:

- **The addition of Na_2S to the zinc//copper cell should be conducted in a fume hood as the Na_2S will release $H_2S(g)$ which is foul-smelling and poisonous.**

Processing of results and questions

1. For each cell constructed, draw a diagram similar to that shown in Figure 25.1. On the diagram:
   (a) Write the half-equation for the reaction occurring in each half-cell.
   (b) Write an equation for the total reaction.
   (c) Label the anode and the cathode.
   (d) Mark the direction of electron flow through the wire.
   (e) Show the direction of movement of positive and negative ions through the salt bridge.
   (f) Calculate the cell potential from a list of standard reduction potentials and compare this with your observed value.

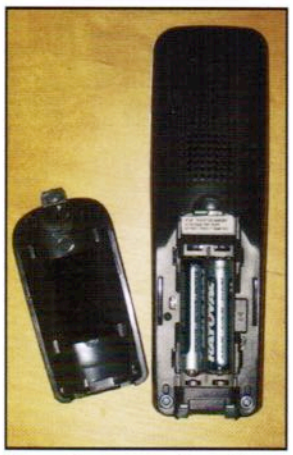
2. (a) What is the function of the salt bridge?
   (b) Why was no voltage observed before the salt bridge was used to connect the two solutions?
   (c) If the salt bridge were removed would the half-cell reactions continue to occur?
   (d) Would sodium carbonate be a suitable salt bridge?

3. Account for your observations when Na_2S solution was added to the $Cu(NO_3)_2$ solution in the $Zn/Zn^{2+}//Cu^{2+}/Cu$ cell.

4. (a) From the measured cell voltages and your knowledge of the reactions taking place, arrange the half-cells in order of decreasing ease of reduction, that is, with the most easily reduced metal ion at the top.
   (b) Which metal is the strongest reducing agent?

Investigation 26: Constructing a commercial galvanic cell

Notes



Dry cells in a cordless phone

The Leclanché or dry cell is commonly used to provide energy for everyday appliances such as torches, transistor radios, electric clocks and many other electrical devices. It produces electricity spontaneously and is called a PRIMARY CELL.

The lead-acid accumulator or `car battery' is commonly used in motor vehicles. It is rechargeable. This means the electrode reactions can be reversed using some source of electrical energy such as a car alternator or a battery charger. This galvanic cell needs charging before it will provide power. It is called a SECONDARY CELL.

The task

Construct and test one of the two commercial cells, the Leclanché dry cell or the lead-acid accumulator.

Equipment

Research the materials used in the commercial cell that you have chosen to construct. Write a list of equipment and materials you will require to build your model.

Planning the investigation

1. Draw a labeled diagram of the model of the cell you intend to build. Make sure you label the positive (+) and negative (-) electrodes.
2. Write a clear set of steps you will use to construct your cell. Include a risk assessment, a description of the precautions and safety procedures you will follow to ensure that you carry out the investigation safely.
3. Write a clear set of steps you will use to test that your cell works and how you will measure the voltage produced by your cell.

Conducting the investigation

Construct and test your cell, collecting and recording observations and results as you proceed.

Processing the data

1. On your diagram show the direction of the electron movement in the external circuit.
2. Using a suitable reference write equations for the cell you plan to construct:
   - the reactions that occur in the Leclanche cell at each electrode or
   - both electrode reactions in the lead-acid accumulator when it is discharging.
3. Compare the measured cell potential of your cell model with that of a commercial cell. Explain any differences in cell voltages.

Evaluating the investigation

Identify and describe any changes that you could make to the design of your cell that could improve its output voltage and usefullness as a cell or battery.

Experiment 27: Investigating electrolysis

Notes

One application of electrolysis is electroplating. In the 19th century electroplating was introduced as a method that could provide a cheaper imitation of expensive pure silver and gold items. Electroplating usually involves a cheaper metal being coated with a thin layer of the more expensive metal, such as silver or gold, both giving the illusion of value and preventing corrosion.

Oxidation and reduction processes like electroplating, involve electron transfer reactions. This means that we have electrons moving from one location to another. When an electric current is passed through a liquid (solution or molten) electrolyte, chemical reactions take place at the two electrodes. At the positive electrode, the anode, oxidation takes place. At the negative electrode, the cathode, reduction occurs. The products formed at each electrode depend on the ions present in the liquid electrolyte and how easily they are oxidised or reduced.

In this experiment you will electrolyse an aqueous copper(II) sulfate solution to copper-plate an object of your choice.

Equipment

100 mL beaker
DC power supply (0-12 V)
a copper electrode (at least 4 cm long)
pair of electrical leads with alligator clips
50 mL 0.5 mol L^{-1} copper(II) sulfate solution
emery paper or steel wool
a carbon electrode or metal object to be copper plated (at least 4 cm long)

Procedure

1. Fill the beaker with the 50 mL 0.5 mol L^{-1} $CuSO_4$ solution.
2. Weigh both the copper and carbon (or your object) electrodes.
3. Connect the carbon electrode or object to the negative terminal of the 12 V DC power supply using electrical leads with alligator clips as shown in figure 27.1. Connect the copper electrode to the positive terminal. Lower the electrodes into the solution.
4. Electrolyse the solution for between 5 and 20 minutes. Note any reaction such as gas evolution, deposition of solid or colour change that takes place at the electrodes. Record your observations.
5. After the electrolysis remove the electrodes and note the appearance of the two electrodes. Dry the electrodes thoroughly, then re-weigh.
6. With your teacher's permission replace the electrodes and continue the electrolysis for as long as you can, all day if possible.
7. Re-examine and re-weigh the two electrodes.

Processing of results and questions

1. Redraw figure 27.1 and include labels for the anode, cathode, electrolyte and the direction of movement of the electrolyte cations and anions and the flow of electrons in the external circuit.

2. For the electrolysis (electroplating) process:
   (a) State the products formed at the anode (+ve) and cathode (-ve).
   (b) Write equations for the electrode reactions and the overall reaction.
   (c) Do your observations support the equations written in b?

3. Draw up a table that identifies industries and their products that depend upon the application of electrolysis.

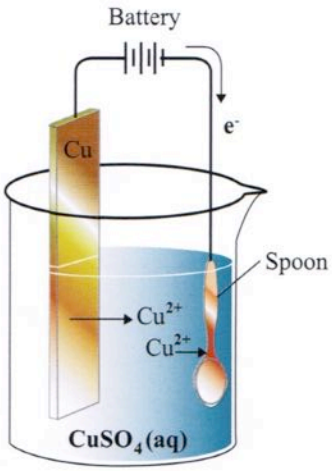


Figure 27.1: Electroplating with copper

Investigation 28: Electrolysis of potassium iodide

Notes

The tasks

1. Design and carry out an investigation of the electrolysis of an aqueous solution of potassium iodide, KI (aq).
2. Predict the products of the electrolysis of molten potassium iodide, KI(ℓ). Describe a procedure that could be used to test your predictions.

SAFETY NOTE:
- **Do not carry out Task 2 as an experiment. Potassium is extremely dangerous**

Planning the investigation

Task 1: aqueous potassium iodide

1. Predict the products formed at each electrode during the electrolysis of KI(aq).
2. Plan an investigation to determine the products of the electrolysis of KI(aq).
   Hint:
   Modify the procedure used for Experiment 27. You will need about 15 mL of 0.5 mol L^{-1} KI(aq) *and Universal Indicator™ solution*
3. Write out a proposed procedure for the investigation including any equipment and chemicals you need. Identify any safety requirements.
4. Check the proposed procedure with your teacher.

Conducting the investigation

1. Conduct the investigation.
2. If time allows replicate the experiment.

Processing the data

1. Does your investigation confirm your predictions for the products in task 1? Justify your answer by referring to the data you have collected.
2. Write balanced half equations for the observed electrode reactions.
3. Write an overall redox equation for the electrolysis process observed.

Evaluating the investigation

Evaluate the effectiveness of your procedure and describe any modifications you would make to improve the accuracy of the results and your organisation of the investigation.

Conclusion

Describe the electrolysis of potassium iodide solution used in task 1.

Planning the investigation

Task 2: molten potassium iodide

1. Predict the products formed at each electrode during the electrolysis of KI (ℓ). Write balanced half equations and an overall redox equation for the electrolysis process.
2. Plan an investigation to determine the products of the electrolysis of KI (ℓ).
3. Write out a proposed procedure for the investigation including any equipment and chemicals you need. Identify any safety requirements.

Conclusion

Describe what you would expect to observe during the electrolysis of molten potassium iodide in task 2. Include balanced half equations and an overall redox equation for the electrolysis of molten potassium iodide.

Organic Materials

The enormous range of organic compounds, with their diverse properties and applications has contributed greatly to the affluent consumerism of our modern society. The physical and chemical properties of these compounds are determined by the functional groups attached to an organic molecule. Alcohols, for example, all have a hydroxyl (OH) functional group. Such functional groups can be identified and named, and reactions involving them understood. Investigating the relationships between the properties of an organic molecule and its characteristic functional group leads to a deeper understanding of the chemistry of common organic substances. The function of a protein, for example, is closely linked to its structure. Scientists share their knowledge as exemplified by the Protein Data Bank (PDB), an international repostitory of structural data for proteins.

Modern living

Good Health

Chemistry, and in particular organic chemistry, has a huge impact on modern lifestyles. As lifestyles often depend on good health, food, dwellings and consumer goods, the chemistry of materials and products involved in these is of vital importance. Much of this chemistry is carbon based.

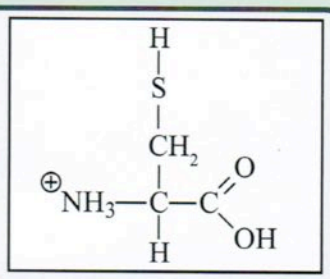
Good health often starts with the food we eat. Sugars, carbohydrates, proteins, vitamins, fats and oils are all carbon based. There have been many studies related to the effects on health of many carbon based compounds consumed as food. The effects of alcohol (ethanol) on liver and brain function, not to mention the intoxicating effects and the subsequent social issues of road trauma and domestic violence are all well documented. On the positive side we hear that a Mediterranean diet, based on olive oil, fruit, vegetables and fish tends to prolong life and reduce health issues. Eating oats tends to reduce cholesterol, while aspirin, apart from easing pain, actually tends to reduce heart disease and stroke.

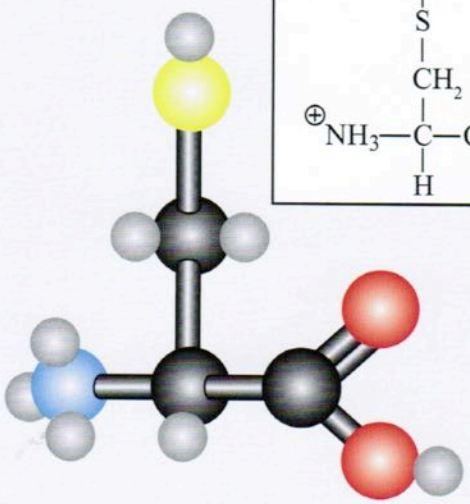
Good health also makes use of pharmaceuticals. Products that include antibiotics, drugs that cure or control life-threatening diseases, anaesthetics and painkillers and dietary supplements are all based on carbon compounds. Currently some of the greatest advances in science have come in the field of molecular biology and gene technology, again very much involved with carbon compounds. Genetically modified organisms for the production of food, pharmaceuticals and materials are something that is likely to have a significant impact on our health in the not-too-distant future. To further develop this field, an intimate knowledge and understanding of the structure and chemistry of α-amino acids is vital. Their diverse structures, the formation of peptide bonds that lead to the formation of peptides and polypeptides, including proteins, and finally the formation of DNA all hinge on the interaction of carboxylic acids and amine functional groups. There is ongoing research and discussion in relation to the use of these modified organisms.

Hair Chemistry

You may already know that hair is made of the protein keratin. A chemist explains, "Proteins are chains of amino acids. Keratin contains lots of the amino acid cysteine. Cysteine is special because it contains a sulfur atom (see diagram). When the sulfur atoms from two cysteine molecules join together, they form a disulfide bond that strengthens your hair."

Amino Acid Cysteine

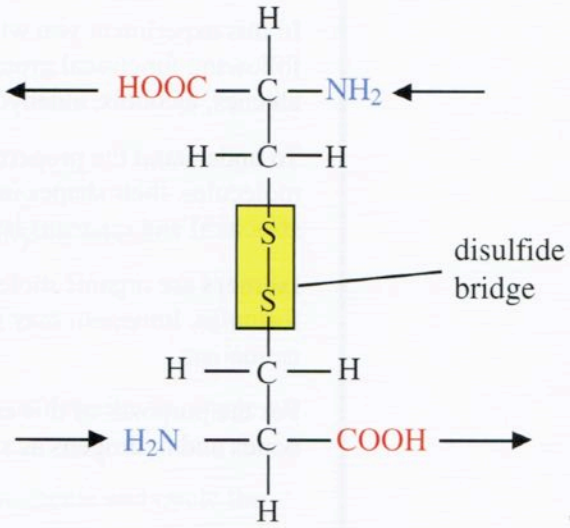




Career profiles 4: Pharmacist and Biochemist

Hair Chemistry (continued)
The ion OH^- can react with and split disulfide bonds. This removes the cross-links between keratin molecules and weakens the hair. H^+ does not disrupt the disulfide bonds, so the hair will remain strong in acid solutions. Thus, pH is important when it comes to shampoo. When deciding on which product to buy, would you choose a low or high pH brand? Do such shampoos actually strengthen hair?

Using a good shampoo can certainly reduce your chances of having a 'bad hair day'.



Profile of a Pharmacist

Pharmacists are involved in the development, testing, manufacture and distribution of medicines and the monitoring of drug therapy. Compounds used as medicines are mainly organic. Medicines can be small organic molecules or biopolymers, polymers produced by living organisms. Cellulose, proteins and DNA are all examples of biopolymers. The monomeric units, respectively, are sugars, amino acids, and nucleotides. As you can see form this, a pharmacist, in their study of pharmacy needs to be trained in Chemistry. In fact by definition pharmacy is the health profession that links the chemical sciences with the health sciences. Pharmacists are also responsible for ensuring the safe and effective use of medications and are fast becoming the first medical professional consulted on health issues by the community. This is forcing the expansion of their role in the pharmaceutical and health care industries.

Profile of a Biochemist

If you have a good understanding of the principles of organic and inorganic chemistry and have a general interest in living organisms, then a career in biochemistry could be for you.

Biochemists deal with chemistry at the molecular level and often pursue research roles within academia or within a laboratory environment.
In the laboratory, they would be responsible for analysing specimens to look for possible abnormalities and maintaining laboratory equipment.

Reliable and functioning laboratory equipment means precise and accurate results. Working in biochemistry could also involve developing biochemical products and processes. This would involve identifying the chemical and physical properties of the compounds in a biological system by conducting various types of analyses.

Experiment 29: Functional groups and isomers

Notes

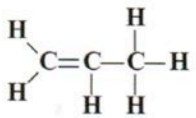
Functional groups are groups of atoms or bonds within molecules that are responsible for the molecule's characteristic chemical properties.

In this experiment you will construct molecular models of organic compounds with the following functional groups:
alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides.

To understand the properties of these molecules you should consider the bonding in these molecules, their shapes in relation to the functional group, and the possible existence of structural and *cis-trans* isomers.

Isomers are organic molecules with the same molecular formulas but different structural formulas. Iomerism may include chain and position structural isomerism and cis-trans isomerism.

For the purposes of this experiment, when asked to draw structural formulas, include all bonds and hydrogens as shown in the example for propene:



Equipment

A set of molecular models, or polystyrene balls and toothpicks

Procedure

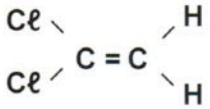
Part A: Alkenes

An alkene is a hydrocarbon containing at least one C=C double bond functional group and is represented by the general formula R=R'. The symbol R is used to represent an alkyl group such as methyl, $-CH_3$. The C-H bonds attached to the double bonded carbon atoms are planar with the double bond, and form bond angles of 120° to the double bond and to each other.

Ethene [C_2H_4, $H_2C{=}CH_2$]

1. Construct a model of the ethene molecule. If you are using polystyrene balls and toothpicks, join the two carbon atoms with two toothpicks spaced somewhat apart.
2. Try to rotate the two ends of the molecule. Does the carbon-carbon double bond rotate?
3. Draw a three-dimensional representation and a structural formula of your model.

Dichloroethene [$C_2H_2C\ell_2$]



1,1-dichloroethene

4. Remove two hydrogen atoms from your model of the ethene molecule and replace them with chlorine atoms to construct a model of 1,1-dichloroethene
5. Make a different model, an isomer of 1,1-dichloroethene.
6. Construct a third isomer of $C_2H_2C\ell_2$. The three isomers of $C_2H_2C\ell_2$ are called 1,1-dichloroethene, *cis*-1,2-dichloroethene, and *trans*-1,2-dichloroethene.
7. Draw structural formulas of the three isomers and label them appropriately.

Notes

Part B: Alcohols

The alcohol functional group is the hydroxy group (-OH). Alcohols are represented by the general formula ROH.

Methanol [CH_3OH]

1. Construct a model of the methanol molecule.
2. Observe the molecule and describe its shape.
3. Draw the structural formula and three-dimensional diagram of your model.

Ethanol [C_2H_5OH]

4. Construct a model of ethanol CH_3CH_2OH.
5. Does ethanol have a similar shape to methanol? How would you describe the shape of the molecule?
6. Using your model, draw a structural formula for the ethanol molecule and circle the alcohol functional group.

Propanol [C_3H_7OH]

7. To construct a model of propanol remove one hydrogen atom from one of the carbon atoms in your model of the ethanol molecule and replace it with a methyl (CH_3) group to give $CH_3CH_2CH_2OH$.
8. Draw a structural formula of your model.
9. Build a model of a different isomer of propanol by changing the position of the alcohol (OH) functional group with one of the hydrogen atoms attached to one of the carbon atom that does not contain the OH group.
10. Draw the structural formula and name this isomer and any other isomers of ethanol that you can construct.

Part C: Aldehydes

The aldehyde functional group is the CHO group. Aldehydes are represented by the general formula $RC\begin{matrix}\diagup\!\!\!

Experiment 29: Functional groups and isomers

Notes

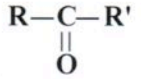
Propanal [C_3H_6O]

15 . Construct a model of the propanal molecule **CH_3CH_2CHO**.

16. Draw the structural formula of the model of the propanal molecule and circle the aldehyde functional group.

Part D: Ketones

The ketone functional group, like the aldehyde funtional group, contains the carbonyl group, C=O. Unlike aldehydes, ketones do not have the C=O group on an end carbon. Hence the smallest ketone is propanone. Ketones are represented by the general formula



R and **R'** may be the same OR different hydrocarbon chains

Propanone [C_3H_6O]

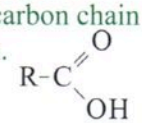
17. Rearrange the atoms in your model of propanal to build the isomer with structural formula: CH_3COCH_3. This new construction is a model of the propanone molecule.

18. Draw a structural formula of the model of the propanone molecule.

19. Distinguish between the propanal and propanone isomers by describing the position of the carbonyl, C=O, group.

Part E: Carboxylic Acids

The carboxylic acid functional group is the COOH group. Carboxylic acids are represented by the general formula RCOOH. The carboxylic acid functional group is always at the end of a carbon chain because the O and OH take up three bonds and so must be at the end of a chain.



Ethanoic (acetic) acid [$C_2H_5O_2$]

20. Build a model of the ethanoic acid molecule, CH_3COOH

21. Draw a structural formula of the model of the ethanoic acid molecule you constructed.

22. Circle the carboxylic acid functional group on your structural formula.

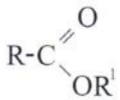
Methanoic acid [CH_2O_2]

23. Use your model of ethanoic acid to build a model of the methanoic acid molecule. To do this remove the CH_3 group and replace it with a single hydrogen atom. Keep your model for part F: Esters.

24. Draw the structural formula of the methanoic acid molecule you constructed.

Part F: Esters

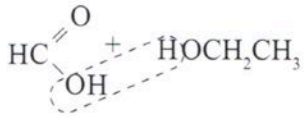
Esters have the general formula $RCOOR^1$. They have two-word names. The first part is the name of the alkyl group R^1, while the second part of the ester's name is derived from the carboxylic acid used to make it. The acid suffix '-oic acid' is changed to '-oate' in the ester.



Ethyl methanoate [$C_3H_6O_2$]

25. Construct a model of methanol, CH_3OH.

26. Join your model of ethanol with your model of methanoic acid from step 23 in the following way. This joining process is modeled on the reaction, **synthesis of an ester.** Align your models so that the two OH groups align. Remove the H from the ethanol(alcohol) OH group, and the OH group from the methanoic acid. Join the O from the,alcohol with the carbon on the methanoic acid to produce your ester, methyl methanoate. Join the H and the OH atoms that were removed, in such a way that you make water, H_2O, a byproduct of this condensation reaction.



27. Draw a structural formula of your model of the ethyl methanoate molecule.

28. Write an equation for the synthesis of ethyl methanoate described in step 26 using structural formulas of the molecules.

Notes

Methyl ethanoate [$C_3H_6O_2$]

29. Construct a model of the methyl ethanoate molecule (CH_3COOCH_3)

30. Draw a structural formula of the model of the methyl ethanoate molecule. Circle the part of the molecule derived from the alcohol, methanol.

Part G: Amines

The amine functional group is the $-NH_2$ group. Amines are represented by the general formula RNH_2.

Methanamine [CH_3NH_2]

31. Construct a model of methanamine, CH_3NH_2.

32. Draw a structural formula of the model of the methanamine molecule.

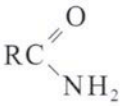
Ethanamine [$C_2H_5NH_2$]

33. Use your model of the methanamine molecule, remove a hydrogen atom attached to the carbon and replace this hydrogen atom with a CH_3 group.

34. Circle the amine functional group

Part H: Amides

Amides are represented by the general formula $RCONH_2$. They are derived from carboxylic acids where the –OH group from the acid is replaced by an amine ($-NH_2$) group.



Experiment 29: Functional groups and isomers

Notes

Ethanamide (acetamide) [CH_3CONH_2]

35. Construct a model of ethanamide, CH_3CONH_2.

36. Draw the structural formula of the model of the ethanamide molecule. Circle the amide functional group

Propanamide [$CH_3CH_2CONH_2$]

37. Use your model of the ethanamide molecule. Remove a hydrogen atom attached to the methyl group, CH_3, and replace it with an additional CH_3 group.

38. Draw the structural formula of the model of the propanamide molecule.

Processing of results and questions

1. Using examples from this activity distinguish between chain and position structural isomerism and cis-trans isomerism.

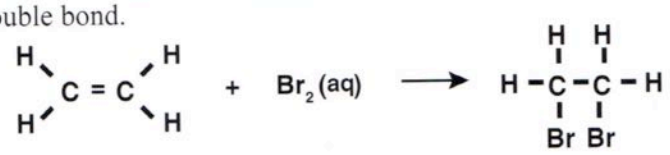
2. Draw a table to summarize the organic compounds based on the functional groups described in this experiment. Research a use for either the example you have chosen or a general use of the organic compound. Use the following headings for each column (the alkenes have been done for you):

Organic compound	Functional group	General formula	Name of example	Structural formula of example	Use
alkene	C = C	C_nH_{2n}	Ethene	$H_2C = CH_2$	Making polymers (plastics) such as polyethylene

Investigation 30: Saturated or unsaturated hydrocarbon

Notes

Alkanes are saturated hydrocarbons containing only single C-C bonds. Alkenes are unsaturated hydrocarbons containing at least one C=C double bond. When a halogen such as bromine reacts with an alkene an addition reaction occurs. The halogen atoms are added across the double bond.



Ethene **Bromine** **1,2 - dibromoethane**

Of all the halogens, bromine is most often used as it is relatively safe and has a pronounced colour change. A water solution of bromine has an orange colour, when mixed with an unsaturated hydrocarbon the colour fades as the bromine is added across the double bond. This distinctive colour change, makes the addition of bromine a useful test to distinguish between saturated and unsaturated hydrocarbons.

In this experiment you will investigate the reaction of bromine with a saturated and an unsaturated hydrocarbon. You will then use bromine as a test to distinguish between two saturated and unsaturated hydrocarbon samples.

Equipment

test tubes (four) | dropper | bromine water [Br_2] (3 mL)
hexane [C_6H_{14}] (1 mL) | hexene [C_6H_{12}] (1 mL)
1 mL of each unknown: Unknown 1 and Unknown 2:
either cyclohexane [C_6H_{12}] or cyclohexene [C_6H_{10}]

SAFETY NOTE:

- **Safety glasses are essential.**
- **Keep away from naked flames, the hydrocarbons are flammable.**
- **Hexane, hexene, cyclohexane and cyclohexene are poisonous.**
- **Bromine water is poisonous and corrosive, handle with care.**
- **Do not let the liquids come in contact with your skin or eyes. Wash the affected area with copious quantities of water.**
- **Carry out the experiment in a fumehood.**

Procedure

1. Into two separate, labelled test tubes place 1 mL of hexane and hexene.
2. Add 1 mL of bromine water to each of the test tubes containing the hydrocarbons. Shake each test tube gently and record any colour change.
3. Test the unknowns: Into two separate, labelled test tubes place 1 mL of each unknown.
4. Add 1 mL of bromine water to each of the test tubes containing the unknowns. Shake each test tube gently and record any colour change.

Processing of results and questions

1 Using your results, identify unknown 1 and unknown 2 as either cyclohexane or cyclohexene.

2 Write equations for any observed reactions of bromine water with the hydrocarbons.

Experiment 31: Reactivity of alcohols

Alcoholic drinks contain the alcohol, ethanol. It is water soluble. It enters the bloodstream and with excessive consumption affects liver and brain function. Alcohols are organic molecules that contain the hydroxyl, (OH), functional group.

In this experiment you will investigate the alcohols, ethanol (C_2H_5OH) and three isomeric alcohols with formula C_4H_9OH, for their reactivity with the acidified solutions of oxidising agents potassium permanganate and sodium dichromate and the reducing agent sodium metal (optional).The structures of these alcohols are set out below.

ethanol	*butan-1-ol*	*butan-2-ol*	*2-methylpropan-2-ol*
CH_3CH_2OH	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH(OH)CH_3$	$CH_3-C(OH)(CH_3)-CH_3$

Ethanol and butan-1-ol are primary alcohols because in both molecules the carbon atom bonded to the alcohol group has only one alkyl group bonded to it. Butan-2-ol is a secondary alcohol as the carbon atom bonded to the alcohol group has two alkyl groups bonded to it. 2-methylpropan-2-ol is a tertiary alcohol because it has three alkyl groups attached to the carbon atom to which the alcohol group is attached.

Notes

Equipment

beaker (250 mL)
thermometer (-10 to 110 °C)
14 large test tubes
Bunsen burner, tripod and gauze mat
dropper
metal tongs
graduated cylinder (10 mL)
sodium dichromate solution [$Na_2Cr_2O_7$] 0.1 mol L^{-1} (5 mL)
sulfuric acid [H_2SO_4] 6 mol L^{-1} (5 mL)
potassium permanganate solution [$KMnO_4$] 0.01 mol L^{-1} (2 mL)
sodium metal (four pieces each of rice grain size)
6 mL of each alcohol:
ethanol [CH_3CH_2OH]
2-methylpropan-2-ol [$(CH_3)_3COH$]
butan-1-ol [$CH_3CH_2CH_2CH_2OH$]
butan-2-ol [$CH_3CH_2CHOHCH_3$]

Procedure

Part A: Reaction of alcohols with oxidising agents

Reaction with dichromate ion

1. Prepare a hot water bath by heating 100 mL of hot tap water in a 250 mL beaker to 80 °C. Turn the bunsen off.

SAFETY NOTE:

- **Alcohols are flammable liquids and must be kept clear of naked flames. Make sure your Bunsen and all nearby Bunsens are turned off before you start using the alcohols.**

Notes

2. Into four, separate, labelled test tubes place 2 mL of ethanol, butan-1-ol, butan-2-ol and 2-methylpropan-2-ol respectively.

SAFETY NOTE:

- **6 mol L^{-1} sulfuric acid is corrosive and must be handled with care. If any H_2SO_4 comes in contact with your skin, immediately wash the affected area with plenty of water.**

3. In another test tube mix 4 mL of 0.1 mol L^{-1} $Na_2Cr_2O_7$ and 2 mL of 6 mol L^{-1} H_2SO_4.
4. Pour 1 mL of the acidified $Na_2Cr_2O_7$ solution into each of the test tubes containing the alcohols and heat them in the hot water bath for about 5 minutes. If the aqueous and alcoholic phases do not mix, shake the mixture occasionally.
5. Observe carefully for any evidence of reaction and note the relative rate of the reaction of each alcohol. Where a reaction has taken place carefully smell the contents of the tube. Write your observations in a suitable table.

Reaction with Permanganate Ion

6. Into four separate test tubes place 2 mL of ethanol, butan-1-ol, butan-2-ol and 2-methylpropan-2-ol respectively.
7. In another test tube mix 2 mL of 0.1 mol L^{-1} $KMnO_4$ and 1 mL of 6 mol L^{-1} H_2SO_4.
8. Add 3-5 drops of the acidified $KMnO_4$ to each of the test tubes containing the alcohols and shake gently.
9. Observe carefully for any evidence of reaction and note the relative rate of the reaction of each alcohol. Where a reaction has taken place, carefully smell the contents of the tube. Write your observations in a suitable table.

Procedure

Part B: Reaction of alcohols with sodium (optional)

SAFETY NOTE:

- **Sodium is a very reactive metal, particularly when it comes in contact with water. It must be handled with great care.**
  Wear safety glasses. Use a spatula, plastic spoon or tweezers to handle the sodium.
  At the end of the experiment the residual sodium must be disposed of carefully by pouring the alcohol-sodium mixture into the beaker provided by your teacher.

1. Into four, separate, dry test tubes place 2 mL of ethanol, butan-1-ol, butan-2-ol and 2-methylpropan-2-ol respectively.
2. Obtain from your teacher four small, freshly cut pieces of sodium.
3. Add one piece of sodium to each of the test tubes containing the alcohols. Observe carefully for any evidence of reaction and note the relative rate of the reaction of each alcohol.

Experiment 31: Reactivity of alcohols

Notes

Processing of results, and questions

1. Which alcohols were oxidised by acidified $Cr_2O_7^{2-}$ solution and acidified MnO_4^- solution?

2. Write formulas for the products formed in the oxidation of the alcohols used.

3. Write balanced half equations then total equations for the oxidation of ethanol by acidified $Cr_2O_7^{2-}$ and acidified MnO_4^- solutions.

4. Write balanced half equations then total equations for the reaction of solutions of acidified $Cr_2O_7^{2-}$ and acidified MnO_4^- with primary, secondary and tertiary alcohols.

5. What was the observed order of reactivity of the C_4H_9OH isomeric alcohols with sodium?

6. Write a general equation that represents the reaction of sodium with alcohols.

7. Write balanced half equations then a total equation for the reaction of sodium with alcohols.

8. There is a fourth isomeric alcohol with formula C_4H_9OH. Draw a structural formula for this isomer and write its systematic name. Predict how you would expect this isomer to react with
   (a) acidified $Na_2Cr_2O_7$ solution
   (b) metallic sodium.

9. A chemical plant involved in the production of solvents has received an order for a polar, water soluble solvent to be used in a commercial cleaning agent. The client has specified that the solvent should have low reactivity with a variety of common substances. As the plant chemist you are required to conduct preliminary tests to determine the relative reactivity of a number of polar, water soluble organic compounds. You decide that alcohols might fit the required criteria as they are able to hydrogen bond to water and generally make good solvents.
   Which of the alcohols tested in this experiment could be used in a commercial cleaning agent? Support your choice with evidence from this experiment.

Experiment 32: Esters

Notes

The chemistry of pleasant aromas and flavours is very often associated with the chemistry of esters. Natural aromas from fruits and herbs are due to the production of esters by plants.

Many fruit essences used in the food industry contain the same esters found in fruit. Examples of these include esters responsible for the characteristic odours and flavours associated with fruits such as bananas, oranges and pineapples.

In addition to the fruit esters, many other esters are commonly encountered in our everyday lives. Aspirin (acetyl salicylic acid), oil of wintergreen (methyl salicylate) and ethyl ethanoate (a common solvent used, for example, in nail polish remover) are all examples of esters.

Esters are formed by the reaction of carboxylic acids with alcohols, usually in the presence of a catalyst such as sulfuric acid. This reaction is called esterification. For example ethyl ethanoate is formed by the reaction between acetic acid and ethanol.

In this experiment you will prepare several esters and attempt to identify some you may have encountered previously.

Equipment

Bunsen burner, tripod and gauze mat
beakers (100 mL (6) and 1 L)
test tubes (six)
stoppers to fit test tubes
graduated cylinder (10 mL)
dropper
ethanol [CH_3CH_2OH] (2 mL)
methanol [CH_3OH] (5 mL)
butan-1-ol [$CH_3CH_2CH_2CH_2OH$] (2 mL)
pentan-1-ol [$CH_3(CH_2)_4OH$] (2 mL)
octan-1-ol [$CH_3(CH_2)_7OH$] (2 mL)
3-methylbutan-l-ol (isoamyl alcohol) [$CH_3CH(CH_3)CH_2CH_2OH$] (2 mL)
salicylic acid (2 g)
ethanoic acid (glacial acetic acid) [CH_3COOH] (10 mL)
concentrated sulfuric acid [H_2SO_4] (2 mL)

Procedure

SAFETY NOTE:

- **Concentrated ethanoic and sulfuric acids are very corrosive and must be handled with extreme care.**
- **If any of the concentrated ethanoic or sulfuric acids comes in contact with your skin immediately wash the affected area with large quantities of water.**

1. Label six test tubes A, B, C, D, E and F and place the following reagents in each.

   Tube A: 2 mL of ethanol, 2 mL of ethanoic acid and 5 drops of concentrated H_2SO_4.
   Tube B: 2 mL of butan-1-ol, 2 mL of ethanoic acid, and 5 drops of concentrated H_2SO_4.

Notes

Tube C: 2 mL of pentan-1-ol, 2 mL of ethanoic acid, and 5 drops of concentrated H_2SO_4.
Tube D: 2 mL of octan-1-ol, 2 mL of ethanoic acid, and 5 drops of concentrated H_2SO_4.
Tube E: 2 mL of 3-methylbutan-l-ol, 2 mL of ethanoic acid, and 5 drops of concentrated H_2SO_4.
Tube F: Salicylic acid crystals to a depth of about 1 cm, just enough methanol to dissolve the acid (about 2-3 mL), and 5 drops of concentrated H_2SO_4.

2. Stopper each test tube and set aside.

SAFETY NOTE:
- **Most organic substances are flammable and should be kept clear of naked flames.**
- **Turn off the Bunsen before heating the mixtures in a hot water bath to make the esters.**

3. Prepare a hot water bath by heating to boiling about 400 mL of hot tap water in a 1 L beaker.
4. When the water has boiled, turn off the Bunsen burner.
5. Remove the stoppers from the test tubes and place the test tubes in the water bath for 15 minutes.
6. Remove one of the test tubes from the water bath and pour the contents into a 100 mL beaker containing about 10 mL of tap water. Cautiously attempt to identify the odour of the ester floating on the water. Record your observations.
7. Pour the contents of each of the remaining test tubes, in turn, into a clean 100 mL beaker containing 10 mL of fresh tap water and note the odour. Use fresh water for each test.

Processing of results, and questions

1. Write equations for the formation of the esters you made
2. Write a general equation for the esterification reaction.
3. Write the names of each of the esters produced in this activity.
4. From the odours of the esters, identify where you have encountered any of them previously.
5. What is the role of the sulfuric acid in the esterification reactions?
6. What starting materials would you use to prepare ethyl butanoate, butyl ethanoate and methyl benzoate?
7. Why did the experiment call for glacial acetic acid?
8. Why did the experiment require you to pour the reactants and products into a beaker of water in step 7?

Investigation 33: Clothes, stains and cleaning

Notes

Many inventions have been the result of an accident. Dry cleaning is one such invention. It is said that one day in 1855, a maid accidentally knocked over a kerosene lamp onto the tablecloth of her employer, Jean Baptiste Jolly. He noticed that the tablecloth became cleaner. As the owner of a French dye-works company, Jolly was very familiar with the properties of fabrics. As a result he turned this minor accident into a major new service and called his invention and new enterprise "dry cleaning".

The chemistry underpinning the success of dry cleaning is based on the nature of the molecules (their functional groups) and their solvent properties. Water, a polar molecule, is capable of forming hydrogen bonds, the strongest of the intermolecular forces. Dirty clothing and many stains contain non-polar materials that have little to no affinity for water. Detergents and soaps help water remove most grime from clothing but some fabrics need special care. This is when solvents such as 'perc' have an advantage. The non-polar dry cleaning solvents can dissolve some of the non-polar grime, oils and grease, that water is unable to lift. This investigation requires you to test and compare the cleaning properties of different solvents on either different materials or on different stains and to apply your understanding of bonding and intermolecular forces to analyse the results.

Solvents

The task

Test and compare the cleaning properties of different solvents on either different materials or on different stains and apply your understanding of bonding and intermolecular forces to analyze the results.

Equipment

large test tubes and stoppers (5)
test tube rack
balance
graduated cylinder (50 ml)
beaker
distilled water
scissors
thermometer (-10 to 100 °C)

Investigation 33: Clothes, stains and cleaning

Notes

Cleaning solvent

The dry cleaning solvent 'perc' is classified as carcinogenic and is not permitted to be used in a school laboratory. For this investigation the solvents can be selected from the following list:

- Water detergent mixture
- Salt water
- Kerosene
- Dichloromethane
- Methylated spirits or ethanol

Fibres

- Cotton: 91% cellulose
- Wool: Keratin proteins composed of long chains of amino acids, which coil up on themselves due to hydrogen bonding and other intermolecular forces.
- Polyester: A manufactured fibre in which the fibre forming substance is a long-chain synthetic polymer.

Stains

- Red wine: Tannin molecules containing benzene rings with adjacent hydroxyl groups
- Vegetable oil or animal fat: triglycerides
- Mineral oil: petroleum derived long chain hydrocarbons

Planning the investigation

1. Pre-laboratory: Research properties of the fibre, stain and cleaning solvent molecules
   - Collect images of, or draw structural formulas, of representative molecules of each set of molecules (fibre, stain, solvent)
   - Identify the functional group or groups for each molecule
   - Identify the type of intermolecular force or forces that can be exhibited by each molecule.
   - Within each set (fibre, stain, solvent) rank the molecules by the strength of intermolecular forces and/or polarity that they can exhibit. Strongest / most polar first.
   - Tabulate the above information.

2. Predict the best cleaning solvent for each stain on each material. Explain your predictions.

3. Decide what you will investigate and write a hypothesis.

Notes

4. List the factors (variables) that could be investigated and record details in a table, like the one below.

	Variable/s	Unit/s	How the variable will be measured
Independent variable			
Dependent variable			
Factors kept constant (controlled variables)			

5. Outline your plan. Remember that you may need to modify your plan after any preliminary trials that you decide to conduct. List the chemicals and equipment you need and identify the safety requirements.

SAFETY NOTE:
- **Check your plan with your teacher before you commence.**

Conducting the investigation

1. Conduct some preliminary trials. You may need to clarify how the independent and dependent variables will be measured.

2. Describe what you learned from these initial trials and modifications that you made to your original plan.

3. Conduct the investigation properly, collecting and recording the data in a table as you proceed. If time allows, replicate the data collection.

Processing the data

Analyse your data and relate your conclusions to the hypothesis.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure and describe any modifications you would make to improve it. You may discuss factors that would improve the accuracy of your results such as sample size and selection, measurement errors and the control of variables. As well, you may address more general organisational factors such as the allocation of tasks among group members and the nature of the apparatus and how it was set up.

2. Discuss your confidence in the findings of the investigation.

Experiment 34: Condensation polymerisation of nylon

Notes

Nylon

Polymers are very large molecules usually containing hundreds of linked, relatively small, repeating sequences of atoms. They include many naturally occurring substances such as proteins (e.g. egg albumin, casein in milk, silk, collagen and keratin), polysaccharides (e.g. cellulose and starch), and rubber.

In this experiment you will prepare nylon. Synthetic nylons are versatile polymers used as fibres in clothing and in a wide variety of moulded objects such as gears and home fittings. Nylons are polyamides formed by the reaction of diamines and dicarboxylic acids or their derivatives. In this experiment a nylon is prepared by the reaction of sebacoyl chloride ($C\ell OC(CH_2)_8COC\ell$) and hexan-1,6-diamine ($H_2N(CH_2)_6NH_2$):

$$\underset{\text{sebacoyl chloride}}{n\ C\ell OC(CH_2)_8COC\ell} + \underset{\text{hexan-1,6-diamine}}{n\ H_2N(CH_2)_6NH_2} \rightarrow \underset{\text{nylon}}{(OC(CH_2)_8CONH(CH_2)_6NH)n} + 2n\ HC\ell$$

Equipment

sebacoyl chloride 5% solution in dichloromethane (20 mL)
hexan-1,6-diamine 5% aqueous solution (20 mL)
sodium hydroxide pellets four (about 0.4 g)
beakers (two 100 mL) stirring rod paper clips paper towels

Procedure **Part A: Preparation of nylon**

SAFETY NOTE:

- **Sodium hydroxide is corrosive and must be handled carefully.**
- **The solutions used in the preparation of nylon are poisonous.**
- **Handle the solutions carefully and avoid breathing the vapours.**
- **Do not pour the used liquids down the sink.**
- **Pour the used liquids into the container provided by your teacher.**

1. Place about 20 mL of the 5% sebacoyl chloride solution in a 100 mL beaker.
2. Place about 20 ml of 5% aqueous hexan-1,6-diamine in another 100 mL beaker and dissolve in it four pellets of sodium hydroxide.
3. Carefully add the hexan-1,6-diamine solution to the sebacoyl chloride solution by pouring slowly down the side of the beaker. A film forms immediately at the interface of the two solutions.
4. Use a paper clip as a hook to carefully lift the centre of the film and wind it onto a stirring rod. Continue to wind the thread onto the glass rod until the solutions are used up.
5. Wash the nylon thread thoroughly with water and dry using paper towels.
6. Note the appearance and physical properties of the product.

Processing of results, and questions

1. Write equations for
   (a) the general reaction between a dicarboxylic acid and a diamine
   (b) the general reaction between substituted ethenes.
2. Why is this production of nylon described as a condensation polymerisation reaction?
3. Identify some possible uses of nylon and relate these to the physical properties you observed.

Experiment 35: Protein modelling

Notes

Proteins are biomolecules found in every living organism. They are natural polymers formed when α-amino acids join together in a series of condensation reactions. A protein is therefore an example of a polyamide.

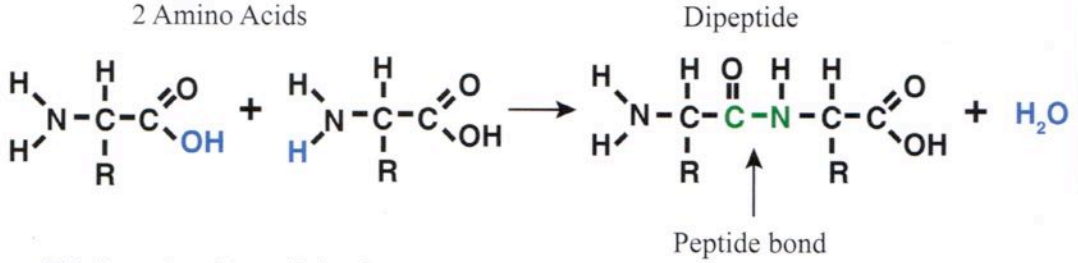


Figure 35.1: Formation of a peptide bond

Every protein has a uniquely folded 3 dimensional structure that is dependent on the primary structure and the nature and position of the side chains on the amino acids.

In this experiment you will model the formation of secondary structures and join these together to model a tertiary structure.

Primary, Secondary and Tertiary structure of proteins.

Primary structure
The primary structure of a protein refers to the number and order of amino acids in the polypeptide chain. For example when two amino acids join together they form a dipeptide. They can do so in two possible ways. When glycine and alanine join the primary structure could be Gly-Ala or Ala-Gly.

Secondary structure
The secondary structure of a protein is the folding of the polypeptide into strands running parallel to each other called beta pleated sheets (β-pleated), Figure 35.2, or a twisted structure known as alpha helix (α-helix), Figure 35.3.

Some amino acids (Methionine, leucine, glutamic acid, lysine, alanine) are more likely to form an α-helix while others (Trypotophan, tyrosine, phenylalanine, valine, isoleucine, threonine) are more likely to form a β-sheet.

In forming β-sheets some proteins, proline, glycine for example, are turn inducers. These allow the 'straight' chain to bend 180° to form the sheet.

Cystine is a cross linking amino acid binding chains by covalent bonds of sulfur, S-S bonding

Tertiary structure
The overall shape of the polypeptide chain is called the tertiary structure. Tertiary structures can contain both α-helix and β-pleated sheet structures depending on the protein.

In this experiment you will be using a molecular modelling kit ,Part A, to help your understanding of the process of folding a protein by building a primary protein structure and modelling the formation of a secondary structure. Pipe cleaners, Part B, are then used to demonstrate tertiary structure formation.

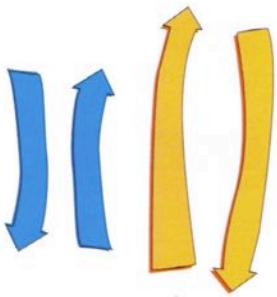


Figure 35.2: The flat arrow shapes represent β-pleated sheets. A typical β-pleated sheet has, on average, six strands bonding together.

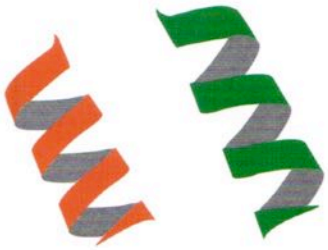


Figure 35.3: The coiled ribbons represent α-helix structures. A typical α-helix is about eleven amino acids long.

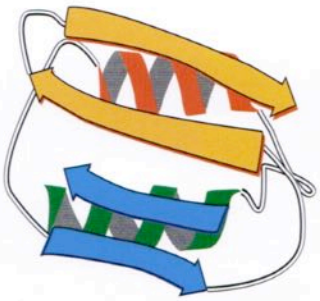


Figure 35.4: Tertiary protein structure

Experiment 35: Protein modelling

Notes

In this experiment you will be using a molecular modelling kit to help your understanding of the process of folding in a protein by building a primary protein structure and modelling the formation of a secondary structure. Pipe cleaners are then used to demonstrate tertiary structure formation.

Equipment

Part A
Three MolyMod kits per group
String and scissors or elastic bands

Part B
2 colours of pipecleaners
25 mL measuring cylinder

Procedure

Part A: Protein Primary and Secondary structures

1. Construct as many alanine molecules as possible given the number of kits that are available. Figure 35.4 shows a molecule of alanine.
2. Remove the OH from the carboxyl end of one alanine and a single H from the amino end of another alanine. Connect the two alanine molecules. The formation of the dipeptide results in a water molecule being produced as shown in Figure 35.5
3. Repeat step 2 to make one long protein chain using all the alanine molecules you have made. This has created a very simple alanine based protein in its primary structure as shown in the photograph Figure 35.6.

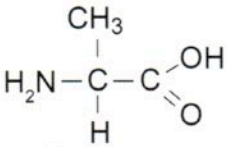


Figure 35.4

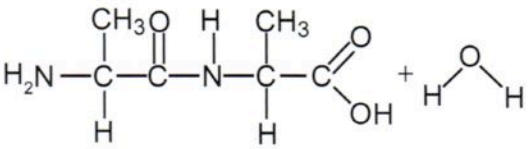


Figure 35.5

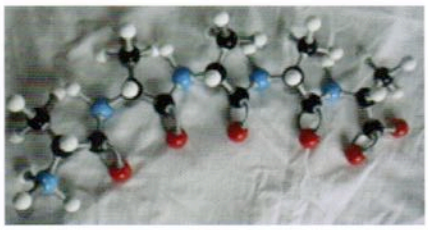


Figure 35.6

4. Adjust your protein model to show its zwitterion form. The two ends of the protein should look like those in figure 35.7.

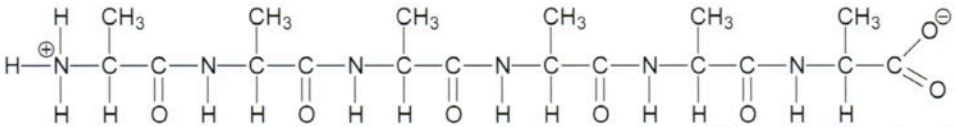


Figure 35.7: zwitterion

5. By using a piece of string (or elastic band) as shown in the figure 35.8, take your model and "lock" a H atom from the NH end of the molecule to the O atom in the C=O group located four carbon atoms down the chain. In real α-helices it locks on the eighth but our chain is too small for this to work.

   In an aqueous environment the protein molecule is colliding with huge numbers of water molecules and in this process the primary structure is repeatedly bent and deformed.

   The hydrogen atom in the NH part of the amino group is highly positive due to the high electronegativity of N and is capable of donating a hydrogen bond. The oxygen atom in the C=O part of the carboxyl group has two lone pairs of electrons capable of accepting hydrogen bonds. In the water colliding process one of these H atoms might pass by the C=O group located four CARBON atoms down the chain and will "lock" in place with a hydrogen bond.

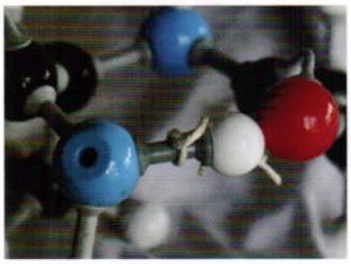


Figure 35.8: hydrogen bonding

6. Continue down the chain inserting these hydrogen bonds. You will note you have to bend and force the long molecule to enable these hydrogen bonds to form. The bending and forcing is called folding. You will see that the folding is totally dependent on the location of the NH and C=O parts of the chain which ends up much smaller than when it was in a primary structure. See figure 35.9, this helix is only part of a long protein chain that might include α-helices and β-sheets as well as some of the protein in the primary structure.

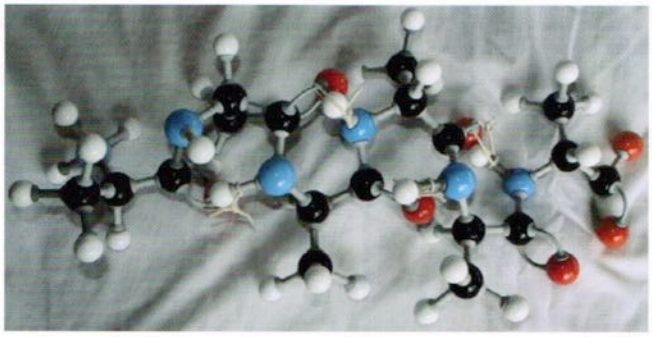


Figure 35.9: Protein secondary structure (an α–helix)

7. Look at the outside of your secondary structure protein. Note the large numbers of CH3 groups pointing outwards. These will be the key to forming the tertiary structure, where the long protein chain curls back on itself. If two compatible side groups meet they will bond, using dispersion forces, in the case of hydrophobic amino acids and hydrogen bonds, dipole-dipole bonds or ionic bonds, in hydrophilic amino acids.

   In this experiment the CH_3 groups will form dispersion forces and hold the tertiary structure in the protein. Tertiary structure interactions are described in Set 29.

Notes

Procedure

Part B: Modelling the Tertiary protein structure

1. The pipecleaners represent the primary structure of the protein. Join together pipecleaners to make different coloured lengths of about 20 cm.
2. To make an alpha helix wind the pipecleaners of one colour around a 25 mL measuring cylinder. Figure 35.10.
3. To make a beta pleated sheet fold another different coloured length of pipe cleaner into a zigzag. Figure 35.11.
4. Join together combinations of alpha helices and beta pleated sheets to give an overall tertiary structure. Figure 35.12.
5. Some polypeptide chains may be stabilised by disulphide bridges between cysteines. These form strong covalent bonds that allow the proteins to maintain shape. Add some sticky tape to your model to show the covalent bond. Figure 35.13.

Figure 35.10

Figure 35.11

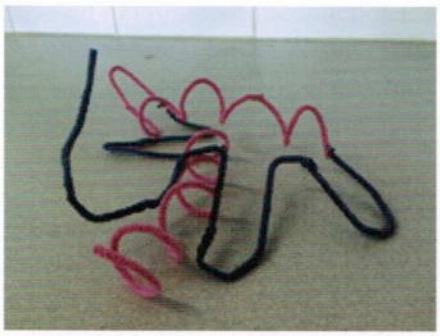


Figure 35.12

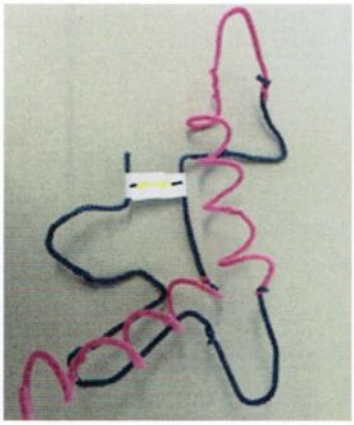


Figure 35.13

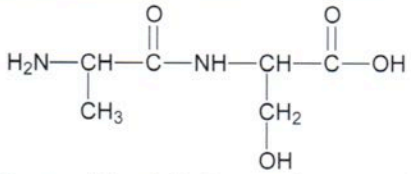
Experiment 35: Protein modelling

Notes

Processing of results, and questions

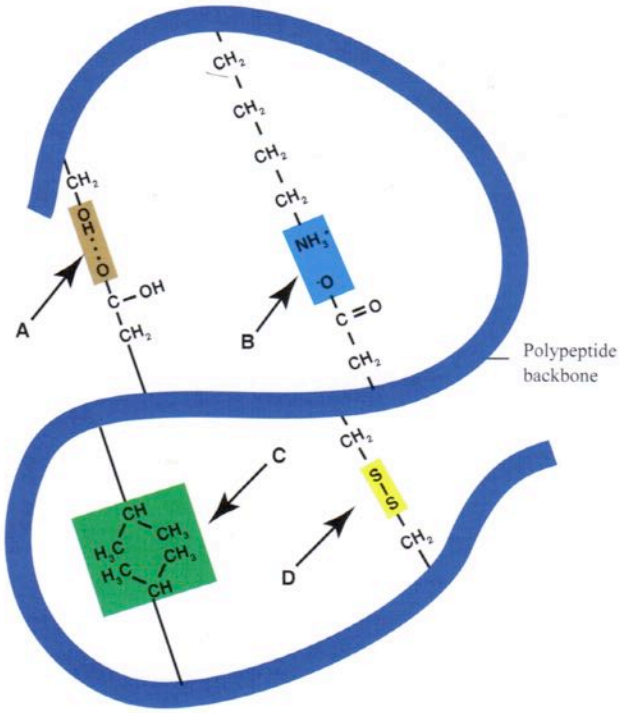
1. Using structural formulas, write the equation for the reaction of the two amino acids glycine and alanine to form a dipeptide.

2. Draw the structures of the amino acids from which the dipeptide shown was made.



3. There are four different side-chain interactions possible that can affect the tertiary structure:
   1. Hydrophobic – between non-polar side-chains
   2. Hydrogen bonds – between polar side-chains
   3. Ionic bonds – between side-chains with charges
   4. Disulfide bridges – covalent bonds between sulfur atoms

   Identify the different interections labeled A, B, C and D in the diagram.



4. Different polypeptide chains can interact. When there is more than one polypeptide chain involved for the function of a protein it is described as having quaternary structure. Haemoglobin has a quaternary structure characteristic. Most of the amino acids in haemoglobin form alpha helices, connected by short non-helical segments. Hydrogen bonds stabilise the helical sections inside this protein, causing attractions within the molecule, folding each polypeptide chain into a specific shape. Hemoglobin's quaternary structure comes from its four subunits in roughly a tetrahedral arrangement. The heme group in hemoglobin contains iron, which is required for the function of binding oxygen. Draw a diagram of a haeme unit.

Investigation 36: The Protein Data Bank

Notes

Scientists need to know the structure of proteins so that they can design and understand drugs and medicines. Vast numbers of protein data and structures are stored on the web in a Protein Data Bank. One of the earliest and most famous is the Brookhaven Protein Data Bank, named after the Brookhaven laboratory where much of the early x-ray crystallography experiments were performed that revealed the structure of proteins. This work was an extension to the work that won the Australian scientists William Lawrence Bragg and his father the 1915 Nobel Prize for Physics. The Brookhaven Data Bank is now housed at Rutgers University, and is now known as the Rutgers Protein Data Bank.

Task

Examine a protein data bank (pdb) and investigate the file of a protein.
The structure of the plant storage protein crambin has been used as an example. It is recommended that you complete Experiment 35 and Problem Set 30 before doing this investigation.

Pre-lab

In preparation for this experiment download appropriate software if you are using a device other than a computer:

Apple Mac users: Install iMol onto your device. iMol is a free molecular visualization application for Mac OS X operating system and can be downloaded from:
http://www.pirx.com/iMol/index.shtml
Use the Chemagic website: http://chemagic.com/JSmolVMK2.htm

Android / Windows users: Install JMol onto your device. JMol is an open-source Java viewer for chemical structures in 3D and can be downloaded from:
http://jmol.sourceforge.net/download/
Use the RCSB protein databank: http://www.rcsb.org/pdb/home/home.do

The following sample procedure works for devices that use HTML5 and javascript (ie iOS / Apple devices), and those devices that may have restrictions on executing java programs.

Sample procedure

1. Open the website: http://chemagic.com/JSmolVMK2.htm

2. **Examine amino acids**
   - Click on the **load** button (shown in green in Figure 36.1)
   - Type the name of the amino acid, glycine, into the textbox and click the **Load Model** button directly underneath
   - Draw a structural formula of the model produced highlighting the functional groups
   - Check your answers to Set 30 question 1 (a) for the amino acids: alanine, valine and leucine

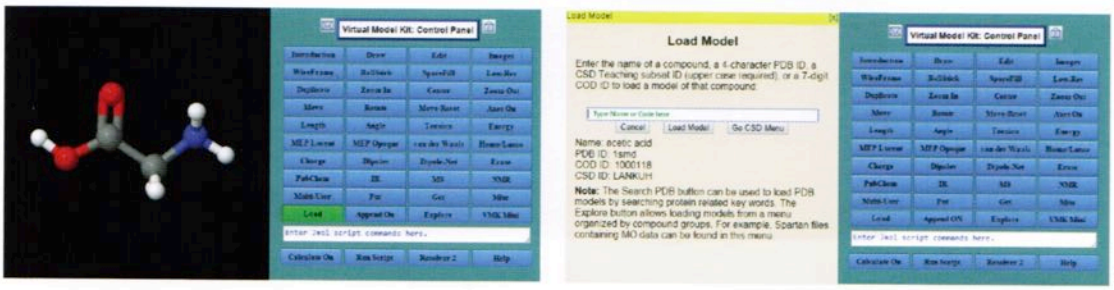


Figure 36.1

Notes

3. **Examine the peptide bond**
   - Click on the **load** button
   - Type the name of the amino acid, "alanine" into the textbox and click the **Load Model** button directly underneath
   - Draw two structural formulas of the model side by side separated by a + like in a reaction equation
   - Click the **load** button again and type "dialanine" into the textbox, click the **Load Model** button.
   - Draw an arrow after the 2 alanine structures then draw a structural formula of the dialanine model to complete the reaction equation for the production of the dipeptide.
   - Highlight the peptide bond in the dialanine structure
   - Repeat to form the tripeptide, triglycine.
   - Check your answers to Set 30 question 5.

4. **Examine a protein**

4.1 **Load a model of the plant storage protein, crambin**
   - Click on the **load** button
   - Type '1CRN' - the code of the plant storage protein crambin - into the textbox and click the **Load Model** button.
   - A cartoon of the plant storage protein crambin will appear, showing two alpha helixes and two beta sheets. If your device allows, capture an image of the cartoon model of the protein and record it as part of your report.
   - Rotate the molecule in the viewer by clicking on it and dragging your mouse or touch screen. Zoom in and out by clicking and dragging the mouse while holding the shift key down, or by pulling two fingers apart in iOS tablet devices. Observe and manipulate the model.

4.2 **Identify the alpha helix parts of the protein**
   - Type the word **console** in the textbox (shown by the green arrow in Figure 36.2) and hit the <enter> key. A new window will open.
   - Identify the alpha helix parts of the protein by typing in the following commands in the bottom text box, hitting the <Enter> key after each command.
     select all <Enter>**cartoon off**<Enter>**select helix**<Enter>**cartoon on**<Enter>
   - On completing these commands you should be able to see two helices. Label the two helices (alpha helix) on the image you captured in 4.1 above. Also label the beta sheets.

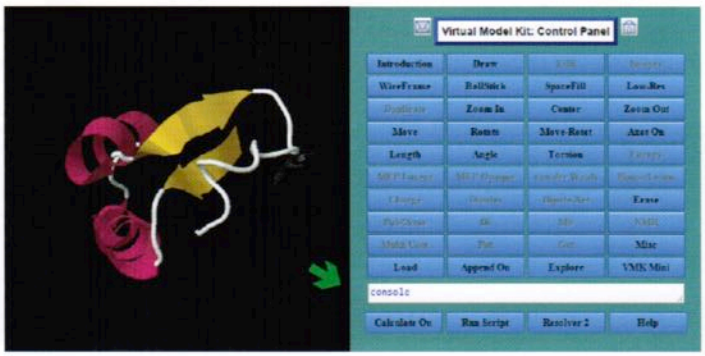


Figure 36.2

Notes

4.3 **Examine the hydrogen bonds that hold a protein's alpha helices together**

- Type in the following commands, each separated by the <enter> key
  calculate hbonds<enter>**wireframe on**<enter>**spacefill 23%**<enter>**color cpk**<enter>
- In the cpk color scheme, nitrogen is blue, the oxygen is red, the carbon is grey, and the sulfur is yellow. Hydrogen bonds are represented by a dashed line.
- Rotate the molecule in the viewer by clicking on it and dragging your mouse or touch screen. Zoom in and out by clicking and dragging the mouse while holding the shift key down, or by pulling two fingers apart in iOS tablet devices. Observe and manipulate the model.
- Capture / copy the cartoon image for your records as you did in 4.1 and call it alpha helix h-bonds.
- Using your colour codes what two elements are involved in the hydrogen bonds?

4.4 **Interpreting an atoms console display**

[TYR]29:A.N #201 1.621 13.19 6.511
Where:
[TYR]29 is the amino acid Tyr the 29th amino acid in the molecule
A.N indicates that the atom clicked on is Nitrogen

- Click on a blue nitrogen atom at the end of a hydrogen bond, dashed line. Record the details of the nitrogen atom that appears in the console.
- Click on the oxygen atom at the other end of the hydrogen bond in the model linked to the nitrogen atom. Record details of the atom that appears in the console.

Questions

a) The nitrogen and oxygen atoms involved in the hydrogen bond that you examined in 4.4 are from different amino acids. For example: [LEU]18:A.N and [VAL]15:A.O are 18-15 = 3 residuals apart. How many residues apart are the amino acid residuals involved in the hydrogen bond in each helix?

b) Observe the two yellow sulfur atoms that form a disulphide bond and hold the two alpha helixes together. What number amino acid residues do they belong to?

4.5 **Examine the beta sheet structures in this protein**

- Reload the protein crambin as per procedure 4.1.
- Type the word **console** into the textbox and hit the <enter> key.
- Type in the following commands, each separated by the <enter> key
  select all<enter>**cartoon off**<enter>**select sheet**<enter>**cartoon on**<enter>
  wireframe on<enter>**spacefill 23%**<enter>**calculate hbonds**<enter>
  color cpk<enter>
- Rotate the molecule in the viewer by clicking on it and dragging your mouse or touch screen. Observe and manipulate the model.

- There are three hydrogen bonds between the sheets.
  - o Click on a blue nitrogen atom at the end of a hydrogen bond, dashed line. Record the details of the nitrogen atom that appears in the console. Do the same for the oxygen atom in this hydrogen bond.
  - o Repeat for the other 2 hydrogen bonds.

Notes

Questions

c) How many amino acids are involved in hydrogen bonds in the beta sheets?
d) What are their names?
e) Examine the side chains of these amino acids. Use the table of the 20 amino acids at the back of this book. What do they have in common?

4.6 Examine the convention for numbering amino acids in proteins.

- Reload the protein crambin as per procedure 4.1.
- Make a mental note of where the end of the protein is.
- Type the word console into the textbox and hit the <enter> key.
- Type these commands, separated by the <enter> **keywireframe on**<enter> **spacefill23%**<enter>**color cpk**<enter>
- Locate the end, last amino acid in the protein, number 46. Clicking on atoms at the start of the arrows until you locate the number 1, starting protein. What is the name of the last, number 46, amino acid in this protein?
- Rotate and move the protein until you find amino acid number 1. Click on atoms at the start of the arrows until you locate the number 1, starting protein. What is the name of the first amino acid?

Questions

f) Look at amino acid number 1. What functional group is still visible at the start of the sheet/arrow? This functional group marks the start of the amino acid and protein.
g) Look at the highest numbered amino acid, 46. What functional group can you see that is still visible at the end of the protein? This functional group marks the end of the protein and amino acid, 46.
h) Protein chemists refer to the two ends of a protein as an amino terminus and a carboxy terminus. Using your answers to the last two questions, describe how amino acid residues are numbered in a protein.

Further Research

1. **The hormone insulin**: Use some of the procedures learned in this activity to investigate insulin. Download the file containing the protein insulin:
   - Click on the load button
   - Type in the code for human insulin: 2hiu

   Insulin is described as a tiny protein. How many amino acids does it contain? How many α-helices and β-sheets? Describe the function of insulin.

2. **The flu enzyme neuramidase**
   Australia has a history of excellence in protein chemistry and modelling. The 1996 Australia Prize was awarded to Peter Coleman, then of CSIRO, for his ground breaking research into the structure of the influenza virus that lead to the development of the commercial flu drug "Relenza". This drug inhibits (stops from working) the flu enzyme neuramidase, which is essential to the flu virus being able to leave an infected cell. You can read more about this discovery at: http://www.csiropedia.csiro.au/pages/viewpage.action?pageId=426541.

   Download the file containing the flu neuramidase:
   - Click on the **load** button
   - Type in its code: 3b7e

     Try some of the tricks you learned in this activity to discover more about this protein. In particular, see if you can find where the Relenza (called ZMR in the model) binds to the protein.

Experiment 37: Measuring Protein

Notes

Many situations, some life threatening, require the accurate measurement of protein:

> In China in 2008, 6 babies were killed and 294,000 were poisoned by milk that was contaminated by melamine, a substance used to illegally make milk appear to have higher protein content than it actually has. Melamine contains nitrogen and analysts tested milk protein by measuring nitrogen content. Hence adding melamine made the milk appear to have more protein.
>
> Currently in Australia, there are approximately 120,000 insulin-dependent diabetics, whose lives depend upon access to accurate doses of synthetic insulin.
>
> Early diagnosis of kidney failure, particularly among remote indigenous populations, which are especially at risk, can save lives. As 1.5 million Australians are estimated to have some form of chronic kidney disease, a good early diagnosis is essential for saving lives and cutting the cost of this devastating disease on our economy.

All of these situations require accurate measurement of protein. In this practical, you will learn one of the oldest and most accurate methods of protein determination, the Biuret reaction.

The Biuret Reaction

All proteins consist of amino acids linked together by peptide bonds. A peptide bond occurs when the amino group of an amino acid reacts with the carboxyl group of another amino acid to produce water and joins the two amino acid residues together. This is shown in the following equation:

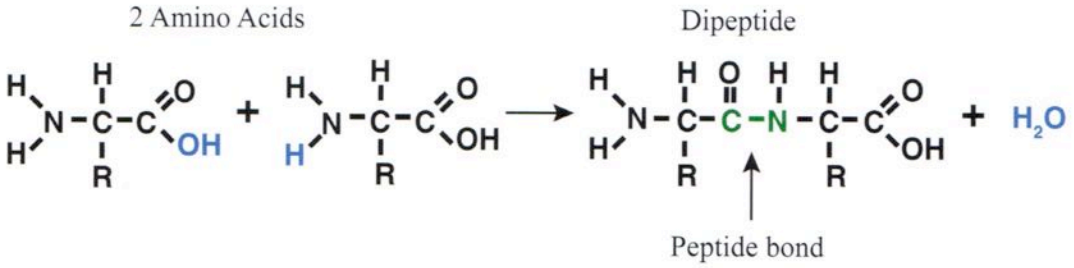


Figure 37.1 Formation of a peptide bond from two amino acids. The symbol R represents side chains of the amino acids (there are 21 possibilities that are naturally coded for in DNA).

The common factor in all proteins is the presence of peptide bonds. This means that *if you can measure the number of peptide bonds present in a mixture, you can tell how much protein is present in that mixture.* Chemists use a reaction call the Biuret Reaction to measure the amount of protein present in a sample. To measure the concentration of a protein, it is reacted with an alkaline solution of copper(II) ions. Under these conditions, the lone pair of electrons on the nitrogen atoms in the peptide bonds are attracted to the positively charged copper ion, and the colour of the copper ion changes from deep blue to a lilac colour, see figure 37.2. The amount of this colour formed can be compared to the amount formed by a known standard, and from this the amount of protein in an unknown sample can be measured.

Experiment 37: Measuring Protein

Notes

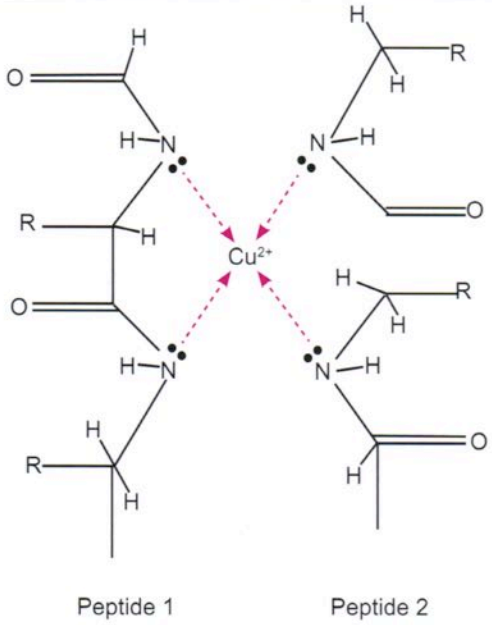


Figure 37.2: Formation of the coloured species in the Biuret Reaction for proteins. Lone pair electrons on nitrogen atoms present in the peptide bonds are bondedto copper(II) ions. The colour of copper ions is affected by the atoms surrounding them. The nitrogens displace the water that is weakly bnded to copper(II) ions in solution (blue) and the colour changes to a lilac-purple.

Equipment

1 g of unflavoured gelatine (used to prepare the 10 mg mL^{-1} standard)
1 g of egg white; 1 g of instant milk powder (used to prepare the protein sample unknowns)
0.75 g copper sulfate ($CuSO_4 \cdot 5H_2O$),
3.0 g Rochelle Salt, (potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$)
2.5 mol L^{-1} sodium hydroxide solution (approx. 200 mL)
100 mL, 250 mL and 500 mL beakers
500 mL volumetric flask
2 × test tube rack
12 test tubes
0-1 mL variable pipette (eg Gilson/Rainin P1000. Or other reliable method for measuring small volumes, you could even use a 1mL syringe, if washed between samples.).
5mL glass pipette with bulb. (You may substitute another device to reliably measure 4 mL such as a 5 mL syringe)
1.00 L volumetric flask
250 mL measuring cylinder

Procedure

Part 1: Preparation of solutions for whole of class use

(Your teacher may assign each of these preparations to different groups or your laboratory technician may have prepared them earlier for you)

1. Prepare a 10 mg mL^{-1} protein standard:
   To a 250 mL beaker add 1 g of unflavoured gelatine and dissolve in 100 mL of warmed (microwaved) distilled water. Store in the fridge. It can be kept for up to 5 days. If the gelatine sets, heat it in a microwave oven or hot water bath until liquid again, then cool to room temperature before use.

Notes

2. Prepare the unknown protein sample: The sample will contain between 1 and 10 mg of protein in 1mL of water.
   To a 100 mL beaker add 1 g of egg white and gently mix in 25 mL of water. OR
   To a 500 mL beaker dissolve 1 g of instant milk powder in 250 mL of water.

3. Prepare the **Biuret solution**:
   Please note that the order in which these chemicals is added is important.
   In a 250 mL beaker dissolve 0.75 g copper sulfate ($CuSO_4 \cdot 5H_2O$) together with 3.0 g Rochelle Salt, (potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$) using around 200 mL of distilled water. Transfer to a 500 mL volumetric flask and, using a measuring cylinder, add 150 mL of 2.5 mol L^{-1} sodium hydroxide solution. Using a wash bottle of distilled water, add water carefully to make up the solution to a final volume of 500 mL.

Part 2: The Biuret Reaction

1. Prepare the following test tubes:

Test tube	1	2	3	4	5	6	7	8	9	10	11
Protein Standard (mL)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Water (mL)	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0

2. Prepare a twelfth test tube and add 1 mL of your unknown sample to it.

3. Add 4 mL of Biuret reagent to each of the 12 test tubes. Mix by tapping the test tube against your finger hard enough to make a small vortex form then wait for 10 minutes.

4. After 10 minutes, take your unknown sample and compare its colour to those of the known (standard) concentrations. Hold your test tubes up against a piece of white paper to help you compare the colours. Which concentration of protein does its colour most closely resemble? This is the estimated concentration of protein in your unknown sample.

Processing of results, and questions

1. From the concentration of the diluted egg white, determine the concentration of protein in the original egg white.

2. How does the value you calculated in Question 1 compare to the expected value of protein in egg white (you will need to research this value)?

3. There are more than 20 proteins in egg white. The most common protein, ovalbumin, represents around 55-65% of the total protein content. If you assume that all of the protein present in the egg white is ovalbumin and the molar mass is 44 500 g mol^{-1}, calculate the percentage by mass of protein in 1 g of egg white.

4. Name and describe the two main proteins in powdered milk.

5. List at least four ways in which the experimental errors could be reduced. Identify an instrumental technique that would make the colour comparison of the samples more accurate.

Experiment 38: Conditions affecting protein structure

Notes

In the last decade, some major and groundbreaking medicines have come on the market. These are protein-based drugs, particularly those that contain specialized antibodies. Consider the drug Herceptin, which is capable of halting the spread of certain types of untreatable breast cancer. A year of treatment with Herceptin costs around $50,000. Given that a yearly dose contains around 10 grams of the active protein, Herceptin is worth approximately $5,000 per gram. Gold, by comparison, is worth approximately $36 per gram, in 2015. It is important to know the factors that damage such expensive materials. For example, nurses have traditionally shaken drugs prior to injection, would this practice harm a precious protein-based medicine? In this practical, you are going to examine some of the factors that influence the secondary and tertiary structure of proteins.

The white of an egg is composed of about 90 % water and 10 % protein by mass. It contains many different kinds of globular proteins. Globular proteins are roughly spherical in shape and when their tertiary structure is altered it changes the appearance of the egg white. This makes egg white liquid, suitable for studying the effects of changing environmental conditions on the secondary and tertiary structure of proteins.

Equipment

1 large hen's egg (this will be more than enough for 2 groups).
flour sieve
kettle to boil water
beaker tongs
2 × 100ml beaker
1 mol L^{-1} $HC\ell$ (10 mL)
1 mol L^{-1} NaOH (10 mL)
ethanol (30 mL 90% or better)
10 mL pipette and bulb
6 × test tubes and rack
stoppers for test tubes

SAFETY NOTE:

- **Wear safety glasses, NaOH and $HC\ell$ are corrosive and can cause blindness if splashed on eyes. Wash off any spills from affected areas immediately.**
- **Take care with boiling water; use tongs or an oven mitt to hold and pour from the hot container.**

Procedure

1. Crack open a chicken's egg and separate the white from the yolk into a 100 mL beaker. A large egg will give about 30 mL of egg white.

2. Gently massage the egg white through the sieve so as to break up any membrane structure. Repeat a couple of times to get a near homogenous mixture, so that equal portions can be transferred.

Notes

3. Draw a table (similar to that shown in processing of results and questions point 1) to record your observations. Including a photograph of the results is useful.

4. Pipette about 1-2 mL of the egg white into 6 test tubes, labeled (A-F).

5. Add approximately 10 mL of:
   - 1 mol L^{-1} $HC\ell$ to test tube B
   - Boiling water to test tube C
   - 1 mol L^{-1} NaOH to test tube D
   - 90-100% ethanol to test tube E

6. Place a stopper on test tube F and shake vigorously for 2 minutes.

Processing of results, and questions

1. Complete the following table considering the intra-molecular interactions in secondary and tertiary structures for your reasoning.

Test Tube	Treatment	Appearance	Explanation
A	raw egg		
B	raw egg + 1 mol L^{-1} $HC\ell$		
C	raw egg + boiling water		
D	raw egg + 1 mol L^{-1} NaOH		
E	raw egg + 97 % ethanol		
F	raw egg + vigorous shaking		

2. Based on your observations, make 2 practical recommendations for the handling of protein-based drugs.

3. Why do you think that the early explorers of Australia often preserved animal specimens in rum?

4. After looking at tubes D and E, give 2 reasons why ammonia is more likely to denature proteins than the ammonium ion at the same concentration.

Properties, reactions and chemical synthesis

Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts, this is called green chemistry. Chemical synthesis processes in this section include the production of ethanol, biodiesel, soap and polyethene. You can carry out these synthesis processes and explore the structure and function of many of these materials.

Green chemistry

Twelve Principles of Green Chemistry

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. Use renewable feedstocks: Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

From Paul Anastas and John Warner's - Green Chemistry: Theory and Practice (Oxford University Press: New York, 1998)

Green chemistry shifts dry cleaning to clean technology

Dry cleaning uses a solvent other than water to remove dirt and stains from fabrics. Early forms of dry cleaning used petroleum based solvents, flammable hydrocarbons like petrol and kerosene that were later replaced by the synthetic solvents carbon tetrachloride and trichlorethene. After the late 1930s, chemical manufacturers introduced tetrachloroethene, often called perchloroethylene, abbreviated, perc. Perc is a chlorocarbon and a carcinogen with a less than desirable environmental record. Nevertheless perc continues to dominate the industry as the preferred solvent.

The demand for environmentally safe products has led to recent developments that have introduced alternative solvents including carbon dioxide. Replacing perc with supercritical carbon dioxide, as the solvent in dry cleaning is an example of 'Green Chemistry.'

Career profiles 5: Chemist and Chemical Engineer

Profile of a Chemical Engineer

Chemical engineers work in the chemical industry, as you would expect. They work to change raw materials into products with responsibilities for the design and operation of plant and equipment needed to make the changes happen.

Check out the sample job description. This type of advertisement can be found in the job sections of newspapers, chemical journals and the internet.

Does this type of work interest you?

Peake Petrochemical

Petrochemical company seeks Chemical Engineers.

Jobs involve engineering design and fabrication. Participate in multiple projects from inception to completion. Some experience in combustion related equipment in the Petroleum, Petrochemical or Chemical industries preferred. Engineering Degree or equivalent experience is required, Chemical or Mechanical Engineering is preferred

Job Title: Chemical Engineer for the Petrochemical or Refining Industry
Primary Skills: Burners, Flares, Combustion Equipment, Pressure Vessels, Heat Exchangers, Chemical, Refining, Petrochemical, Gas Processing, H_2, Air Separation, Auto-CAD, 3-D, Pro-E.

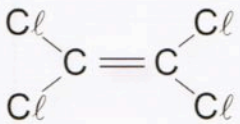
Profile of a Chemist

Chemists are interested in observing the small-scale properties of matter and can do so by observing reactions in the laboratory. This also enables them to learn the composition, structure, reactivity and properties of substances. Another significant role of the Chemist is to reproduce and synthesise naturally occurring substances as well as creating new artificial substances and processes.

Fields of chemistry include analytical, inorganic, forensics and biochemistry to name a few.

Employment is mainly within the chemical or pharmaceutical industries and academia. Working as a Chemist, you may see overlap within fields of chemistry and across other fields of science including biology, physics, and the new science of nanotechnology.

Supercritical carbon dioxide is carbon dioxide that has been heated slightly above room temperature (above 31 °C) at a pressure of above 73 atmospheres, so that it enters a phase somewhere between a liquid and a gas. The cleaning process needs to be done in a pressure vessel. The idea of using carbon dioxide in dry cleaning is similar to using a detergent when cleaning with water as the solvent. The lipophilic end of a detergent molecule dissolves in the oil and the hydrophilic end dissolves in water. You cannot use a water-based detergent with carbon dioxide though, as the hydrophilic end will not dissolve in carbon dioxide. What is needed is a molecule that can form a bridge between oil and carbon dioxide, a molecule with a 'carbon dioxide-philic' end so that it can dissolve in the carbon dioxide. University of North Carolina chemist Dr Joseph DeSimone made such a molecule. In 1996 he founded the dry-cleaning franchise Hangers Cleaners, which uses his green chemistry technology.



Perchloroethylene (Perc)

Investigation 39: Determining the limiting reagent

Notes

Quantitative gravimetric analysis methods can be used to determine the limiting reagent in many types of chemical reactions. If only an indication of the completion of a reaction is needed then qualitative methods could be used.

The limiting reagent is the reactant that determines how far the reaction will go or how much product is made. It is the chemical that gets "used up", causing the reaction to stop. Any reactant that is left over is said to be in excess.

The task

Devise a qualitative test that could be used to determine the limiting reagent in each of the reactions.

Reaction A: 20 mL of 0.1 mol L^{-1} solutions of hydrochloric acid and sodium hydroxide.
Reaction B: 20 mL of 0.1 mol L^{-1} solutions of barium nitrate and sulfuric acid
Reaction C: 20 mL of 0.1 mol L^{-1} solutions of barium nitrate and copper(II) sulfate

Planning the investigation

1. Plan an investigation to determine the limiting reagent in each of the reactions listed in the task.
2. Write out the proposed procedure for the investigation including any equipment and chemicals you require. Identify any safety requirements.
3. Check the proposed procedure with your teacher.

SAFETY NOTE:
- **Check your plan with your teacher before you commence.**

Conducting the investigation

Conduct the investigation.

Processing the data

From your observations explain the results of your tests for each reaction. Include balanced equations for the reactions and for any chemical test that you used to identify the limiting reagent.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure by considering the following:
   - What were the potential sources of error in the experiment?
   - What other method/s could have been used to determine the limiting reagent in reactions B and C?
   - What problems, if any, did you encounter with your procedure?
2. What modifications would you make to the procedure?
3. Collect class results. You all used the same solutions. Explain any differences in the limiting reagents identified in each reaction.

Experiment 40: Percentage purity of magnesium ribbon

Notes

The percentage purity of metal ores is an important quantity to know for economic viability in mining an ore body. It is often necessary to know the percentage purity of a refined metal. If the metals will react with acid (as zinc and magnesium do) we can use a simple experiment to collect the hydrogen produced in this reaction. The Ideal Gas Law (PV=nRT) can then be used to determine the number of moles of hydrogen. The number of moles of hydrogen can then be used to determine the number of moles of metal, then its mass and finally its percentage purity.

In this experiment you will be using the Ideal Gas Law to determine the percentage purity of a sample of magnesium.

Equipment

coil of copper wire (about 10 cm)

hydrochloric acid [HCℓ] 3 mol L^{-1} (15 mL)

gas measuring tube or burette (50 mL). If a burette is used in place of a gas measuring tube you will need to determine the volume between the 50 mL mark and the tap.

one-holed stopper to fit the gas measuring tube

magnesium ribbon, [Mg] (about 4 cm)

stand and clamp

graduated cylinder (250 mL)

thermometer (-10 to 110 °C)

barometer

beaker (500 mL)

rule

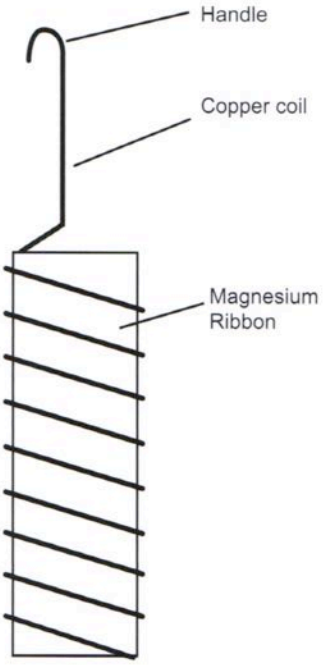


Figure 40.1

Procedure

1. Obtain some clean magnesium and carefully measure its length, recording the value to the nearest 0.05 cm. Your teacher will give you the mass of 50.00 cm of clean ribbon so that you can calculate the mass of your magnesium. If you have a balance that measures to 0.001 g, it is more accurate to measure the mass of the magnesium used.

2. Fold the magnesium ribbon and place it in the coil as shown in Figure 40.1.

3. Set up a retort stand and clamp to hold the gas measuring tube fitted with a one hole rubber stopper. Pour about 400 mL of tap water into a 500 mL beaker.

4. Pour 15 mL of 3 mol L^{-1} hydrochloric acid into the gas measuring tube. Carefully fill the tube with tap water from the beaker so that the acid layer remains at the bottom of the tube as shown in Figure 40.2.

5. Hold the copper coil by the handle and insert it into the tube. Place the hook in the handle over the edge of the gas measuring tube and fix it in position by inserting the one-hole rubber stopper as shown in Figure 40.2. The tube should contain no air bubbles and water should fill the hole in the stopper.

Experiment 40: Percentage purity of magnesium ribbon

Notes

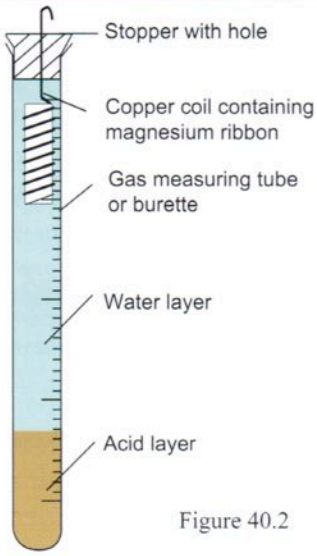


Figure 40.2

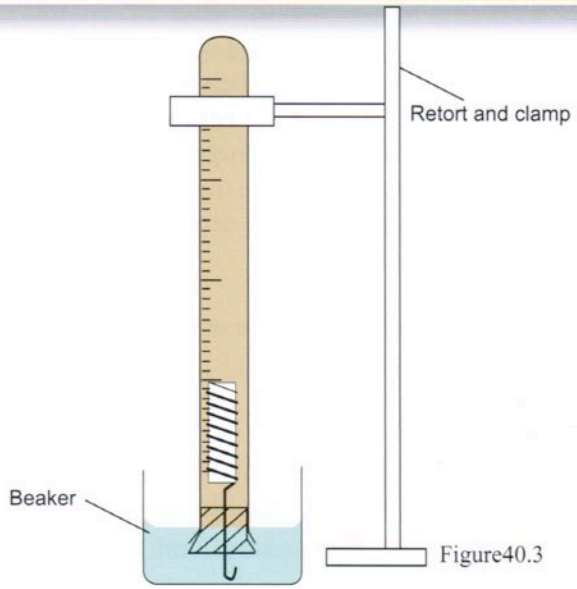


Figure40.3

6. Cover the hole with a finger, invert the gas measuring tube and place it in the beaker as shown in Figure 40.3. Clamp the tube in place. The acid, being more dense than water, will move down through the water and start to react with the magnesium.

7. When the reaction is complete, as shown in Figure 40.4, allow a few minutes for the solution and hydrogen to come to room temperature. Tap the tube gently to dislodge any gas bubbles that are still attached to the coil or to the sides of the gas measuring tube.

8. Cover the hole in the stopper with your finger and transfer the gas measuring tube to a 250 mL graduated cylinder which must be almost filled with tap water as shown in Figure 40.5. Adjust the position of the tube until the level of the acid solution inside the tube is the same as that of the water in the cylinder. Read the volume of hydrogen gas, taking care to observe the calibration marks on the tube. Record the volume to the nearest 0.1 mL.

9. Record the temperature of the laboratory, and obtain the barometric pressure.

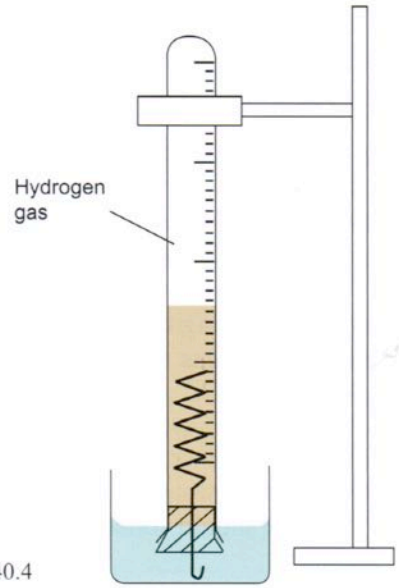


Figure 40.4

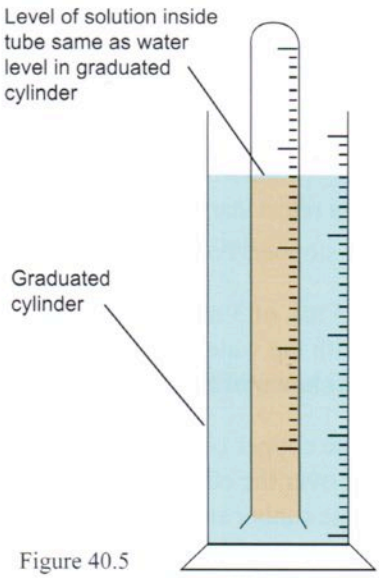


Figure 40.5

Processing of results and questions

Notes

1. The pressure in the burette (which is the same as the atmospheric pressure in the laboratory) is due to that of the hydrogen and water vapour. In order to calculate the number of moles of hydrogen gas, the pressure due to water vapour must be taken away from the total pressure. The pressure due to water vapour is a known value for a given temperature and can be obtained from table 40.1. Use the following equation to calculate the pressure due to hydrogen:

$$P_{H_2} = P_{total} - P_{H_2O}$$

Table 40.1 Vapour pressure of water at various temperatures

Temperature (°C)	Pressure (kPa)	Temperature (°C)	Pressure (kPa)
0	0.61	23	2.81
5	0.87	24	2.98
10	1.23	25	3.17
11	1.31	26	3.36
12	1.40	27	3.56
13	1.50	28	3.78
14	1.60	29	4.00
15	1.70	30	4.24
16	1.82	31	4.49
17	1.94	32	4.75
18	2.06	33	5.03
19	2.20	34	5.32
20	2.34	35	5.62
21	2.49	36	5.94
22	2.64	40	7.37

2. Using the Ideal Gas Equation, calculate the number of moles of hydrogen gas produced.

3. Write an equation for the reaction between hydrochloric acid and magnesium. From your answer to the previous question, calculate the number of moles and therefore the mass of magnesium.

4. Using the mass you calculated or measured in step 1 of the procedure and the mass calculated in the previous question, calculate the percentage purity of the magnesium.

5. The magnesium you used should have had a high purity. If your value from the previous question does not support this, identify the possible sources of error and suggest ways to reduce those errors.

6. A group of students conducted this experiment using a sample of zinc metal with a mass of 0.223 g. Gas having a volume of 45.6 mL at 104.3 kPa and 25 °C was collected. The P_{H_2O} = 3.17 kPa at this temperature. Calculate the percentage purity of the zinc.

Experiment 41: Percentage purity of iron wire

Notes

The purpose of this experiment is to analyse a sample of iron wire to determine its iron content. The iron is converted to iron(II) ions by dissolving in sulfuric acid. The acidified iron(II) is then oxidised to iron(III) using standard potassium permanganate solution. From the equation for this reaction, the volume of the iron(II) solution used, and the concentration and volume of permanganate solution, the mass of iron present in the original sample can be calculated. This enables the determination the percentage of iron in the iron wire.

The procedure is set out schematically below.

Weighed mass of iron wire (Fe)	→ *Dissolved in H_2SO_4 solution*	Iron present as iron(II), acidified (Fe^{2+}) ions	→ *Oxidation using standard $KMnO_4$ solution*	Iron(III), (Fe^{3+}) ions

In the course of this experiment iron(II) sulfate solution is prepared. The iron(II) ions in this solution are easily oxidised to iron(III) ions by air ($Fe^{2+} \rightarrow Fe^{3+} + e^-$). To prevent this happening, water used in the experiment should be distilled water that has been boiled to remove any dissolved oxygen, and then cooled.

Equipment

iron wire (about 1 g), other sources of iron such as steel wool, nails and iron filings could also be used.
conical flask (250 mL)
filter funnel and stand
filter paper
beakers (two 100 mL, one 250 mL)
volumetric flask (250 mL)
boiled distilled water (350 mL)
pipette (20 mL)
pipette filler
burette and stand
Bunsen burner, tripod and gauze mat
sulfuric acid [H_2SO_4] 2 mol L^{-1} (100 mL)
standardised potassium permanganate solution [$KMnO_4$] 0.02 mol L^{-1} (150 mL)

Procedure

1. Weigh out accurately about one gram of iron wire and place it in a conical flask. Add enough dilute H_2SO_4 to cover the sample and heat gently until the reaction starts.

SAFETY NOTE:

- **Sulfur dioxide is produced while dissolving the iron. It is a poisonous gas which must be handled with care.**
- **Do not breathe the SO_2.**
- **The reaction of the iron should be carried out in a fumehood.**

Notes

2. When all the iron has reacted, filter the solution into a 250 mL volumetric flask. Rinse the conical flask with boiled distilled water, pour the washings through the filter paper and finally wash the filter paper thoroughly with boiled distilled water.

3. Make the solution up to the mark on the 250 mL volumetric flask.

4. Pipette a 20 mL aliquot of the iron(II) sulfate solution into a conical flask, add about 10 mL of dilute H_2SO_4, and titrate immediately with the standardised $KMnO_4$ solution. Repeat the titration and record your results in a table.

Processing of results and questions

1. Write an equation for the reaction of permanganate (MnO_4^-) with acidified iron(II) (Fe^{2+}).

2. Calculate the average number of moles of MnO_4^- used in your titrations.

3. From the equation calculate the number of moles of Fe^{2+} in the 20 mL aliquots of iron(II) sulfate.

4. Calculate the number of moles of Fe^{2+} in the 250 mL flask and hence in the mass of iron dissolved.

5. Determine the percentage of iron in the iron wire.

6. Suggest possible impurities in iron wire.

7. Write an equation for the reaction of iron with sulfuric acid to form a solution of iron(II) ions.

Investigation 42: Ethyl ethanoate synthesis and percentage yield

Nail polish remover needs to be a good organic solvent to successfully remove hardened nail polish. An important component in many nail polish removers is the ester, ethyl ethanoate (ethyl acetate).

You are employed by a nail polish company to investigate the process of making and extracting the ester, ethyl acetate, for use in their product. To do this you must investigate the process of making the ester with a view to maximising the yield. This can be conducted in two parts. The first part is the making of the ester and the second part is extracting the ester from the reaction mixture.

The task

1. Make the ester, ethyl acetate.
2. Extract the ester from the reaction mixture and determine its percentage yield.

Designing the investigation

Notes

SAFETY NOTE:

- **Concentrated acids are very corrosive and must be handled with extreme care.**
- **If any of the concentrated acids come in contact with your skin immediately wash the affected area with large quantities of water.**
- **Most organic substances are flammable and should be kept clear of naked flames.**
- **Should you require any heating you should choose a method that does not involve a naked flame.**

1. In the design of the investigation you should consider the appropriate reagents including the relative quantities that need to be mixed, the reaction conditions and the method of maintaining those conditions without losing the reagents.
2. For the separation process you will need to determine the method of separation based on a significant difference in the properties of the ester and any remaining reagents. You should consider methods of maximising the separation and the purity of the ester.

Equipment

Write a list of equipment you will require.

Procedure

1. Write an outline of the procedure you would use to carry out this investigation. Some consideration should be given to
   (a) how you would determine the appropriate reaction time.
   (b) the safety issues that arise from the use of flammable organic compounds.
2. Conduct the investigation and calculate the percentage yield of the ester.

Processing of results, and questions

1. Write a report for your company management on the effectiveness of the processes you investigated.
2. Comment on the effectiveness of the procedures you used and make suggestions where improvements could be made to obtain a better yield.

Investigation 43: Empirical formula

Determining the empirical formula of a compound is an elemental analysis process and a part of analytical chemistry. Analytical chemists have made major contributions to pure science in the development of concepts and theories and to the practice of science, such as forensic science techniques, biomedical applications, monitoring the environment and quality control of industrial manufacturing.

In this investigation you will determine the empirical formula of an inorganic compound. The process involves several steps.

A hydrated copper chloride has the general formula $CuC\ell_a \cdot bH_2O$. The copper content could be determined by precipitation or displacement reactions.

A hydrated copper chloride sample

The task

Your task is to determine the values of a and b and hence the empirical formula of the compound, $CuC\ell_a \cdot bH_2O$.

Equipment

hydrated copper chloride
electronic balance
any other equipment as determined by the procedure

Planning the investigation

1. Plan an investigation to determine the empirical formula of a hydrated copper chloride.

2. Write out the proposed procedure for the investigation including any equipment and chemicals you require. Identify any safety requirements.

3. Check the proposed procedure with your teacher.

Conducting the investigation

Conduct the investigation. Include at least one replication of the experiment.

Processing the data

From the data you obtained, calculate the empirical formula of the hydrated copper chloride.

Evaluating the investigation

1. Evaluate the effectiveness of your procedure by considering the following:
   - What were the potential sources of error in the experiment?
   - What other method/s could have been used to determine the empirical formula of the compound?
   - What problems, if any, did you encounter with your procedure?

2. What modifications would you make to the procedure?

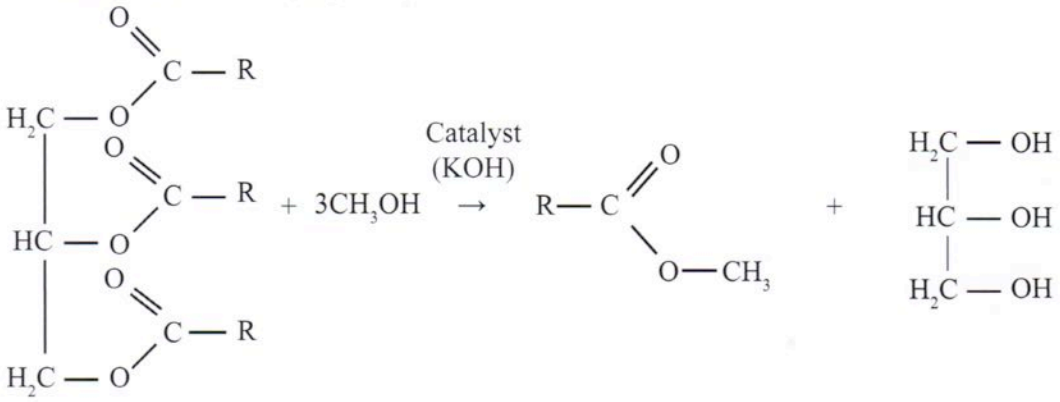
Notes

Experiment 44: Making bio-diesel

Biodiesel pump

Notes

Diesel refers to a particular petroleum fraction containing hydrocarbons with 12 to 16 carbon atoms. As such it is a non-renewable fuel. It is the fuel used in most trucks and large stationary engines such as those used to drive generators in remote towns. A fuel that has similar characteristics is known as bio-diesel. It contains esters with up to 18 carbon atoms and can be made from almost any vegetable oil or animal fat using a reaction called transesterification. This reaction converts the triglycerides in the oil or fat into esters which are used as the bio-diesel. The most common esters produced are methyl esters as indicated in the following equation.



Bio-diesel is therefore a renewable fuel and more environmentally friendly as it is easily bio-degradable.

In this experiment you will prepare a small batch of bio-diesel from cooking oil.

SAFETY NOTE:
Safety glasses must be worn at all times during this experiment.

Equipment

conical flask (100 mL) with stopper
conical flask (250 mL) with a two hole stopper
graduated cylinder (50 mL)
graduated cylinder (100 mL)
methanol [CH_3OH] (20 mL)
potassium hydroxide [KOH] (0.35 g)
cooking oil (100 mL)
hot plate
separating funnel (250 mL) (optional)
thermometer (0 to 110 °C)
safety glasses

Procedure

1. Measure accurately 0.35 g of potassium hydroxide in the 100 mL conical flask. Stopper immediately.

SAFETY NOTE:
- **Potassium hydroxide is corrosive to your skin and must not be handled with your fingers. Use a spatula or plastic spoon to transfer it to the conical flask.**
- **Potassium hydroxide absorbs water rapidly. Make the transfer quickly and replace the lid on the container immediately after use.**

Notes

2. Measure accurately 20 mL of methanol and place it into the 100 mL conical flask and stopper immediately. Swirl the methanol gently until the solid potassium hydroxide has all dissolved.

3. Measure exactly 100 mL of cooking oil with a measuring cylinder and pour the oil into the 250 mL conical flask. Very carefully add the potassium hydroxide solution to the oil by pouring it slowly down the inside of the flask. Stopper immediately with the two hole stopper. Insert the thermometer into one of the holes so that the thermometer bulb is in the liquid.

SAFETY NOTE:

- **Methanol is poisonous and highly flammable and must be handled with extreme care**
- **Do not use near naked flames nor breathe its vapours.**
- **The solution produced by mixing potassium hydroxide with methanol (potassium methoxide) is highly corrosive and must not be allowed to contact the skin.**
- **If any of the methanol or potassium methoxide comes in contact with your skin immediately wash the affected area with large quantities of water for 20 minutes.**

4. Warm the flask on the hot plate swirling the contents about every 1 minute. Maintain the temperature at about 45 °C. Do not allow the temperature to exceed 50 °C. Do this for 20 minutes.

5. Allow the mixture to cool then pour into the separating funnel (see Figure 44.1). Allow to stand overnight.

6. Drain off the glycerol (bottom layer).

Figure 44.1: Separating funnel

Processing of results, and questions

1. Write a general equation for the breaking up of esters into an acid and an alcohol.

2. Write a general equation for the formation of esters.

3. Research the identity of a triglyceride likely to be found in cooking oil and write an equation for the formation of bio-diesel from this triglyceride.

4. Why is it important to keep all reagents in this process dry?

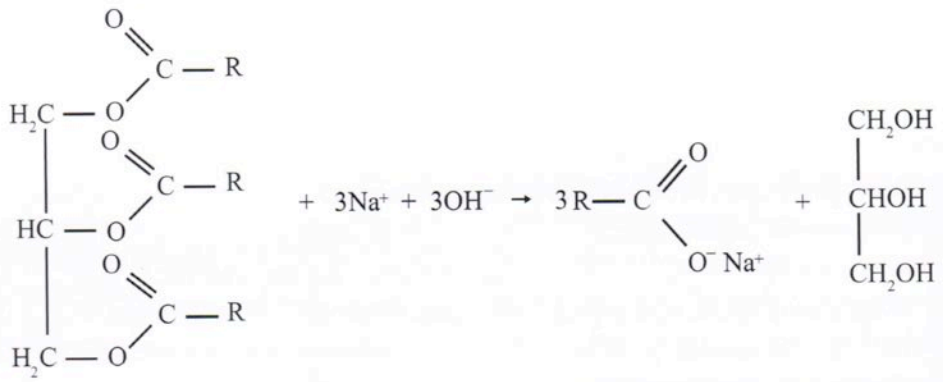
5. Many recipes for the making of bio-diesel include a step that requires the bio-diesel to be *washed* to improve its quality. Why do you think it is necessary to *wash* bio-diesel?

Experiment 45: Making and testing soap

Notes

Soap

Soap has been used for washing for thousands of years. It was produced from animal fat or vegetable oils and lye, contained in the alkaline ash left from the burning of wood. Soap is still used for washing although the use of detergents has replaced soaps for many applications. Boiling the fat or oil with ash produced the soap. The process is called saponification. Saponification can be represented by the following equation where R represents a long carbon chain.



In this experiment you will use the readily available and relatively cheap, castor oil and sodium hydroxide to make soap then test its behaviour when used in waters of different quality.

Equipment

Bunsen burner, tripod and gauze mat
test tubes (6)
graduated cylinder (10 mL)
beaker (100 mL)
balance
stirring rod (glass)
sodium hydroxide [NaOH] (6 g)
sodium chloride [NaCℓ] (10 g)
castor oil (6 mL)
distilled water
tap water (5 mL)
sea water (5 mL)
5 mL 1 g L^{-1} solutions of :
calcium chloride [$CaC\ell_2$],
magnesium chloride [$MgC\ell_2$],
potassium chloride [KCℓ]

Procedure **Part A: Making the soap**

SAFETY NOTE:

- **Sodium hydroxide pellets are very corrosive and must not be allowed to come into contact with your skin.**
- **Use a spatula or plastic spoon to transfer the sodium hydroxide pellets.**

Notes

1. Weigh out about 6 g of sodium hydroxide in a 100 mL beaker and dissolve it in 30 mL of distilled water.
2. Add 6 mL of castor oil to the solution.
3. Gently boil the solution for about 10 minutes stirring constantly. Occasionally add a little distilled water to maintain the volume. After this heating the castor oil should no longer be visible as a separate layer.
4. Cool the solution by placing the beaker in a larger beaker of tap water at room temperature and stir while adding 10 g of sodium chloride.
5. While stirring, heat the solution and boil for a further 2 minutes. Take care not to let it boil over. Again cool the solution and the soap should separate out as a solid.

SAFETY NOTE:

- **The soap you have produced should not be used on your skin as it may still contain traces of sodium hydroxide.**

6. Decant the liquid from the mixture. Rinse the soap twice with distilled water, decanting the liquid both times. Collect the soap on a filter paper.

Procedure

Part B: Behaviour of the soap

1. Place a little of the soap in a 100 mL beaker, add 20 mL of distilled water. Stir until the soap has mixed with the water. Keep the rest of the soap for use in the investigation of detergents.
2. Place about 3 mL of the soap solution into a test tube.
3. Add 3 mL of distilled water, shake it vigorously and record your observations.
4. Repeat step 3 with tap water, sea water, and the three chloride solutions. Again record your observations.

Processing of results, and questions

1. The major component of castor oil is the triglyceride made from glycerol and 3 molecules of ricinoleic acid. The formula of this triglyceride is

   $CH_2OCO(CH_2)_7CH{=}CHCH_2CH(OH)(CH_2)_5CH_3$
   |
   $CHOCO(CH_2)_7CH{=}CHCH_2CH(OH)(CH_2)_5CH_3$
   |
   $CH_2OCO(CH_2)_7CH{=}CHCH_2CH(OH)(CH_2)_5CH_3$

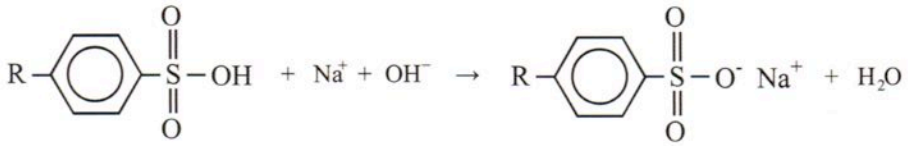
   Write a balanced equation for the reaction between this triglyceride and sodium hydroxide.
2. Write an equation for the soap you made, dissolving in water.
3. Explain your observation for the mixing of the soap with the calcium and magnesium chlorides. Write an equation for the changes observed.
4. Using an equation explain your observation for the mixing of soap with sea water.
5. Carboxylic acids are weak acids. Write an equation to show what would happen if hydrochloric acid is added to your soap solution.

Investigation 46: Making and comparing detergents with soap

Notes

Dishwashing detergent

The development of synthetic detergents or, more correctly, surfactants (surface active agents) was due to a combination of factors including the lack of raw materials and the limitations of soap in some applications. The composition of modern detergents varies depending on its use, but most are the sodium salt of an alkyl benzyl sulfonic acid. Detergents are made by the neutralisation of the sulfonic acids with a sodium hydroxide solution. This occurs quite rapidly at room temperature. The following equation represents the formation of a typical detergent where R is a long hydrocarbon chain.



Sulfonic acid

Sodium salt of sulfonic acid (detergent)

The task

Make a detergent from the sulfonic acid dodecylbenzenesulfonic acid, and compare its behaviour with the soap you made in Experiment 45: Making and testing soap.

Note: You should only attempt this investigation after you have completed Experiment 45: Making and testing soap

Designing the investigation

1. Devise a procedure for making a small amount of detergent from stoichiometric amounts of the reagents. Include any calculations that you may require to determine the amounts of reagents to use. In addition you should outline any safety procedures that are required to conduct this procedure.
2. Devise a procedure for testing the behaviour of the detergent in various solutions and then compare this with the behaviour of a soap solution made from the soap you made in Experiment 45: Making and Testing Soap.

Equipment

Write a list of equipment you will require for making and testing the detergent.

Procedure

1. Write a description of the procedure you will use to make and test the detergent.
2. Check this procedure with your teacher, then make the detergent.
3. Write a description of the observations or measurements.

Processing of results, and questions

1. Write an equation for the reaction between dodecylbenzenesulfonic acid and sodium hydroxide solution.
2. Describe how you could check that the reaction has finished.
3. Write a description of any difficulties you encountered during the making or testing of the detergent.
4. Describe how you could change your procedure to improve the production or testing processes.

Investigation 47: Fabric cleaning using soaps and detergents

With the increased use of synthetic fibers in the manufacture of fabrics for clothing, linen and upholstery it has become increasingly important to choose the appropriate surfactant for cleaning them. The issue has been compounded by the practice of blending synthetic and natural fibers to make fabrics that have more desirable properties. For some fabrics it is important to choose the type of cleaning agent to avoid issues related to shrinkage, colour fastness and texture after washing.

The task

Examine the effectiveness of a soap and a detergent as a cleaning agent on a variety of fabrics that have been soiled by different types of dirt or stains.

Designing the investigation

1. You will have to devise a measure of cleaning effectiveness.
2. Devise a procedure to clean a number of fabrics with soap and detergent.
3. Use your measure of cleaning effectiveness to rate each test you make.
4. Outline any safety procedures that are required to conduct these procedures.

Equipment

Write a list of equipment you will require for the testing process.

Procedure

1. Write a description of the procedure you will use to test the effectiveness of the cleaning process. Check the procedure with your teacher.
2. Conduct the investigation and write a description of the observations or measurements regarding the cleaning of the fabrics.

Processing of results, and questions

1. Write a report on your findings, and outline any significant trends.
2. Describe and explain how soaps and detergents remove dirt from fabrics.
3. Write a description of any difficulties you encountered during the testing of the fabrics with the soap and the detergent.
4. Describe how you could change your procedure to improve the testing process.

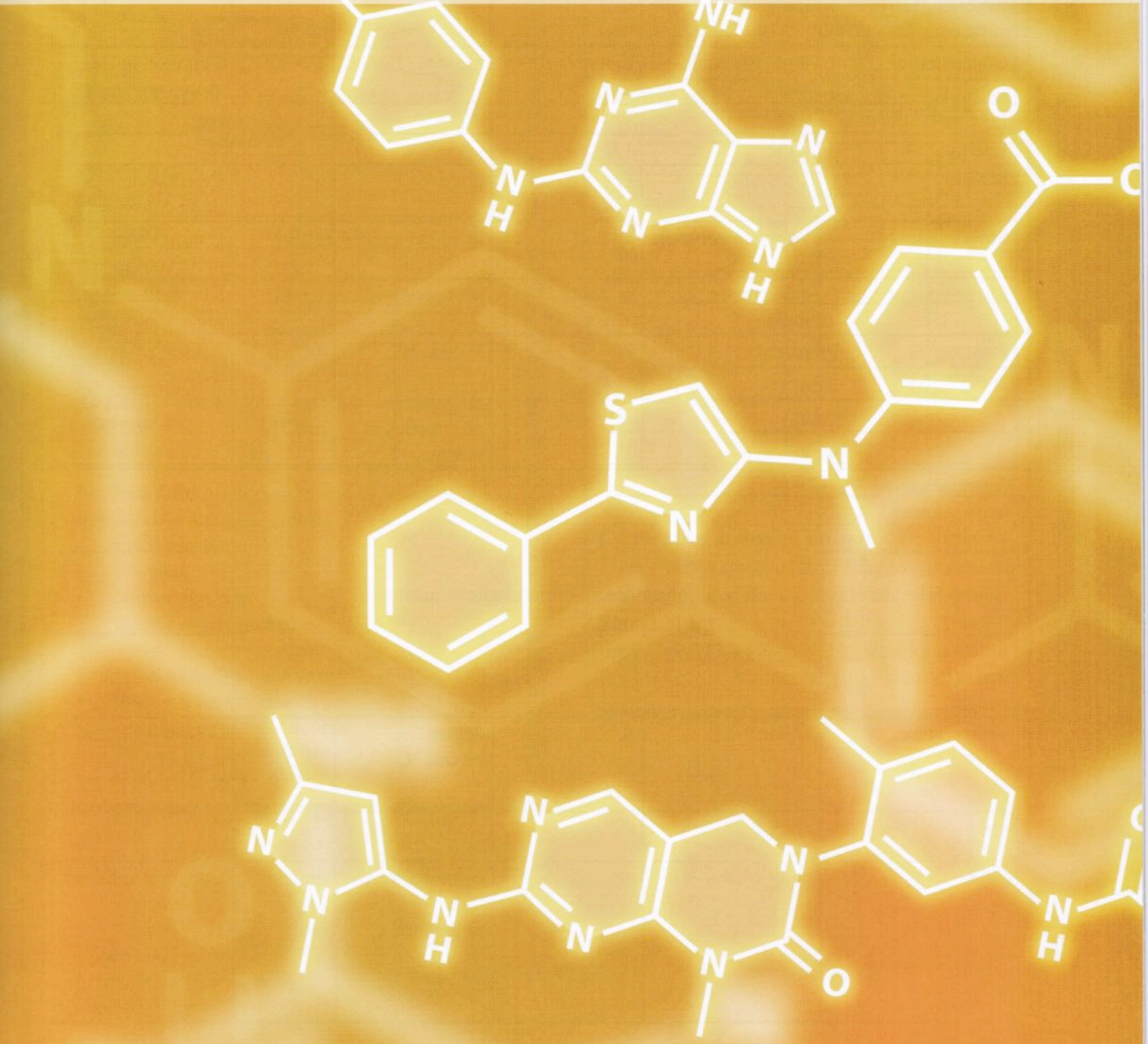
Notes

Laundry detergents

Section 2: Chemical understanding and problem solving

Exploring Chemistry Year 12: Experiments, Investigations and Problems **provides opportunities for students to continue developing their chemical understanding and problem solving skills in chemistry.**

Section 2: Chemical understanding and problem solving involves applying chemical knowledge and understanding of chemical concepts to situations, questions and problems, with a focus on the quantitative aspects of chemistry.



Measurment in chemistry

Commonly encountered quantities and units used in chemistry

Quantity	SI Unit	SI Symbol	Common unit	Common symbol	Comments
Amount of substance	mole	mol			
Concentration	mole per cubic metre	mol m^{-3}	mole per litre	mol L^{-1}	Common unit is more convenient
Potential difference	volt	V			
Energy	joule	J			
Mass	kilogram	kg	gram	g	Common unit is more convenient
Molar mass	kilogram per mole	kg mol^{-1}	gram per mole	g mol^{-1}	Common unit is more convenient
Molar volume	cubic metre per mole	m^3 mol^{-1}	litre per mole	L mol^{-1}	Common unit is more convenient
Pressure	pascal	Pa	kilopascal atmosphere millimetres of mercury	kPa atm mm Hg	All sets of units are useful 1 atm = 101.3 kPa = 760 mm Hg
Relative atomic mass (atomic weight)	These are all dimensionless quantities				
Relative molecular mass (molecular weight)					
Relative formula mass (formula weight)					
Temperature	kelvin	K	degree celsius °C		Both sets of units are useful K = °C + 273.15
Time	second	s			
Volume	cubic metre	m^3	cubic decimetre litre millimetre	dm^3 L mL	Common units are convenient 1L = 1dm^3 = 1000 mL = 1000 cm^3 = 1×10^{-3} m^3

Quantities and units In chemistry

Every measurement consists of two essential parts:

- a number, and
- a unit

Number

Byron measured 1.8 m tall with a mass of 67 kg.

Unit

The six **base units** relevant to chemistry problem solving are shown below:

Quantity	SI base unit	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Absolute temperature	kelvin	K
Amount of substance	mole	mol

Derived units are those defined by various operations with units, such as

- multiplication,
- division,
- conversion, and
- raising to any power.

Examples of derived units are:

- dm^3 or L for volume
- $g\ cm^{-3}$ or $g\ mL^{-1}$ for density
- $mol\ L^{-1}$ for concentration
- $g\ mol^{-1}$ for molar mass

Metric prefixes

Decimal multiples and decimal fractions of SI units are represented by standard prefixes, and each prefix has the standard symbol as shown in the table.

Power of 10	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deca	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Converting between units:

To convert a mass of 9.213 kg to a mass in g we can replace the kg unit with $\times 10^3$ g.

Since: $1\ kg = 1 \times 10^3\ g$

then: $9.213\ kg = 9.213 \times 10^3\ g$

$= 9213\ g$

Set 1: Significant figures and unit conversions

Exponential notation

This notation, also known as scientific notation, is used for convenience when writing very large or very small numbers.
To express a number using experimental notation, it is written as a number between 1 and 10 multiplied by the appropriate power of 10.
For examples 0.056 expressed in exponential notation is written as 5.6×10^{-2} while 167,000 would be written as 1.67×10^{5}.

Arithmetic using exponential notation is governed by the following rules:

Addition and subtraction Before adding or subtracting, numbers must be expressed to the same powers of 10.	**Multiplication** When multiplying powers of 10 add their indices algebraically.	**Division** When dividing powers of 10 by each other, subtract the index of the denominator from that of the numerator.
Example: $(2.04 \times 10^5) + (4.7 \times 10^4)$ $= (2.04 \times 10^5) + (0.47 \times 10^5)$ $= (2.04 + 0.47) \times 10^5$ $= 2.51 \times 10^5$	Example: $(5 \times 10^5) \times (4 \times 10^2)$ $= (5 \times 4) \times 10^{5+2}$ $= 20 \times 10^7$ $= 2 \times 10^8$	Examples: $\frac{1.8 \times 10^8}{6 \times 10^5} = \frac{1.8}{6} \times 10^{8-5}$ $= 0.3 \times 10^3$ $= 3 \times 10^2$

Notes

Set 1: Exercises

1. How many significant figures are there in the following?

   (a) 123
   (b) 1.23
   (c) 1.23×10^5
   (d) 1.23×10^{-59}
   (e) 123 000
   (f) 120 300
   (g) 102 003
   (h) 0.00000123

2. Express each of the following in scientific notation.

   (a) 6 409
   (b) 0.032
   (c) 891 000
   (d) 53.8
   (e) 0.0000061

3. Complete the following:

   (a) 8×10^{-4} m = mm
   (b) 4.5×10^3 g = kg
   (c) 9.0×10^{-2} kg = g
   (d) 7.03×10^5 mL = L
   (e) 0.05×10^4 L = mL
   (f) 2.59 nm = m

4. A mixture is prepared using 3.104 g of substance A, 0.72 g of B, 16.2 g of D, and 0.002 g of E. What is the total mass of the mixture, to the correct number of significant figures, assuming no losses occur?

Notes

5. An atom of sodium weighs 3.819×10^{-23} g. How many sodium atoms are there in 20 kg of sodium?

6. Complete the following conversion table for pressure using scientific notation:

	pressure/mmHg	pressure/atm	pressure/Pa
a	760	1.00	1.01×10^5
b	750		
c		2.05	
d	100		
e			7.31×10^3

7. A synthetic mixture was prepared from compounds abundant in nature. The constituents were 0.103 g of $CaCO_3$, 11.45 g of Fe_2O_3, 0.01 g of $NaC\ell$, 0.001 g of $KC\ell$, 68.53 g of SiO_2. What would be the total mass, to the correct number of significant figures, of the mixture?

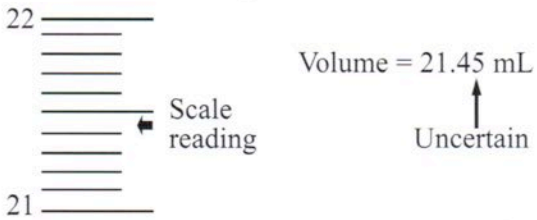
Set 2: Errors

Uncertainty and significant figures in measurement

When handling experimental data it is important to consider the appropriate number of significant figures to use and not be tempted to record values with large numbers of significant figures that may be produced by your calculator when processing data. Significant figures in a number are those digits that are known with certainty plus the first digit that is uncertain. All measurements have some level of uncertainty. These arise from the quality of the equipment used, the type of scale and the skill of the experimenter. Some apparatus will have a manufacturers' uncertainty assigned; however, there are cases where you will make a judgement.

Burettes are used in titration experiments to accurately measure the volume of a reactant added to another. A typical 50 mL burette has an analogue scale with a smallest scale division of 0.1 mL. A manufacturer's uncertainty of +/- 0.05 mL (representing half the smallest scale division) is often assigned. Depending on your skill level you may judge that you can read the scale on the burette to the nearest 0.02 mL and so reduce the range of uncertainty for each measurement to + /- 0.02 mL.

The burette reading in the diagram of 21.45 mL is estimated to the nearest 0.05 mL. The true value lies in a range from 21.40-21.50 mL.



Significant figures in a number are those digits that are known with certainty plus the first digit that is uncertain. In the reading of 21.45 mL the 2,1 and 4 are known with certainty and the 5 is uncertain. This value has 4 significant figures.

	Number	Number of significant figures
1.	713	3
2.	7.03×10^3	3
3.	11.05	4
4.	0.027	2
5.	9.9643×10^{-7}	5

Whole numbers ending with one or more zeros such as 430 and 500 are ambiguous with respect to the number of significant figures because it is unclear whether the terminating zeros are significant or merely serve to locate the decimal point.

The use of scientific notation avoids ambiguity as shown by the following examples:

1. If 430 has 3 significant figures it is written as 4.30×10^2

2. If 430 has 2 significant figures it is written as 4.3×10^2

3. If 500 has 1 significant figure it is written as 5×10^2

Rounding off

Rounding is used to reduce the complexity of a number when it is written with more digits than are wanted or justified. The last digit written should give the best approximation of the number as it was before rounding.If the number before rounding is as close to one number as another, the one ending with an even digit is chosen, zero being regarded as even (example 6).

The following examples illustrate rounding to **three significant figures**.

1.	1.294	rounds to	1.29
2.	8.12349	rounds to	8.12
3.	0.01249	rounds to	0.0125
4.	18.951	rounds to	19.0
5.	7.1451	rounds to	7.15
6.	7.145	rounds to	7.14

Rounding in multi-step calculations

When performing calculations requiring several steps, only round to the appropriate number of significant figures after the final step. This avoids possible errors that can accumulate during a calculation if rounding to the strict number of significant figures is carried out at each step.

Set 2: Exercises

1. An analyst is asked to find the iron content in a waste water sample. She chooses to use a four step method.
   1. weigh a sample of waste water
   2. precipitate the soluble iron by using hydroxide ions,
   3. filter the sample and then heat the filtrate until all the iron hydroxide is converted to iron (III) oxide and the ash-less filter paper burns away.
   4. weigh the iron (III) oxide sample

   Steps 1 and 4 involve two uses of a balance - finding before and after weights. Her balance is capable of an accuracy of ±1 mg. The mass of her original sample was 12.363 g and that of her iron (III) oxide residue was 0.834 g.

   (a) What was the percentage uncertainty of each of the two masses recorded?
   (b) What is the percentage uncertainty of the final result?

2. An investigator reported the volume of liquid escaping from a factory as 36 671 ± 153 L. What is the percentage uncertainty of this result?

3. A balance indicates masses correct to ±0.2 mg. What is the minimum mass of a sample which must be taken if the weighing error is not to exceed

   (a) 1 part in 3000?
   (b) 0.01%?

4. A piece of plastic has a mass, which may be as little as 80.1 g or as much as 80.5 g. If it is cut into two pieces, one of which weighs 40.0±0.2 g.
   (a) What is the smallest mass that the other piece could have?
   (b) What is the mass of this piece, expressed in a plus or minus notation?

Set 2: Errors

Notes

5. Divide 6.8245 by 1.13, expressing your answer to the correct number of significant figures.

6. In processing the results of an experiment a student's final calculation is this

$$\frac{0.574862 \times 100}{156.0 \times 16.1}$$

What answer should he write down?

7. Convert the following Fahrenheit temperatures to Celsius readings:(To convert Fahrenheit to Celsius use the formula °C = (°F - 32) × 5/9)

   (a) 332°
   (b) 1°

8. These data show the first ionisation energies of various atoms measured in the unit electronvolt. Convert these values to kJ mol^{-1} (1 eV = 96.485 kJ mol^{-1}).

   (a) H:13.6
   (b) He:24.6
   (c) Be:9.32

9. Using the radioactive dating method, the linen wrapping of one of the Dead Sea Scrolls was found to be 1920 ± 350 years old. What is the percentage uncertainty of this result?

10. In solving a chemistry problem, a student has to evaluate the expression

$$\frac{4.00 \times 0.011 \times 273.16}{0.166 \times 299}$$

What figure should she quote as her answer?

Set 3: Random and systematic errors

Notes

All measurements have a degree of uncertainty resulting in experimental error. The experimental error in a result is the difference between the experimental value and the literature or theoretical value. There are two types of experimental error: random error and systematic error. Both should be considered when evaluating any quantitative investigation.

Random errors come from measurements that have an equal chance of being above or below the actual value.

Systematic errors are a result of flaws in the experimental method or apparatus that lead to a result that is always either above or below the true value.

Errors are discussed in detail on pages 16 and 17.

Set 3: Exercises

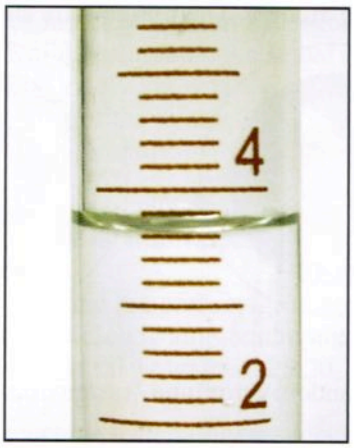
1. To perform a titration a student will require the use of a balance, a pipette, a burette and a volumetric flask.

   List each of the following under the correct heading

Random error	Systematic error

   (a) incorrect etching of "the mark" on the volumetric flask
   (b) careless reading of the liquid levels in the burette
   (c) a fault in the balance such that it read 100 mg too heavy
   (d) allowing the pipette to drain for only 5 seconds instead of the recommended draining time of 30 seconds, following delivery of a volume of solution

2. Four students were asked to read this measuring cylinder volume. John said 4.3 mL, Mary said 2.85 mL, Barry 4.15 mL and Kathy said 3.75 mL. Are any of them correct?



Set 3: Random and systematic errors

Notes

3. A student records a temperature as 17.00 °C involving an error of 0.12 °C. He assumes that 0 °C is exactly 273 K thereby making another error of 0.16 K. He uses his temperature value in a gas equation calculation. What is his maximum percentage error due to temperature?

4. A rectangular piece of domestic aluminium foil measuring 51 cm × 3 cm has a mass of 3.0 g. What is the thickness of the foil if the density of aluminium is 2.70 g cm^{-3}? ($\rho = m/v$)

5. Lyndon and Jenny were working as a team to complete a titration experiment. They obtained the following titre results

Final Reading (mL)	14.45	16.82	12.43	21.56	20.05
Initial Reading (mL	34.57	37.34	32.98	42.01	40.59
Titre	20.12	20.52	20.55	20.45	20.54

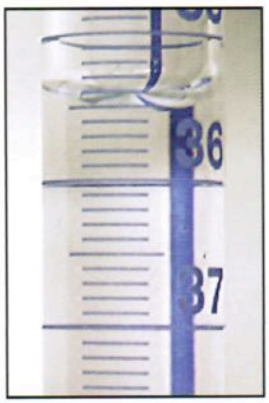
Their teacher said the correct titre for the experiment was 22.54 mL.

(a) Lyndon suggests they have a random error while Jenny suggests a systematic error. Who do you think is right?

(b) Jenny suggests repeating the experiment and averaging all the results. Do you agree?

(c) They cannot agree so they decide to abandon the experiment and start it all again. What changes would you suggest they make to achieve a successful result?

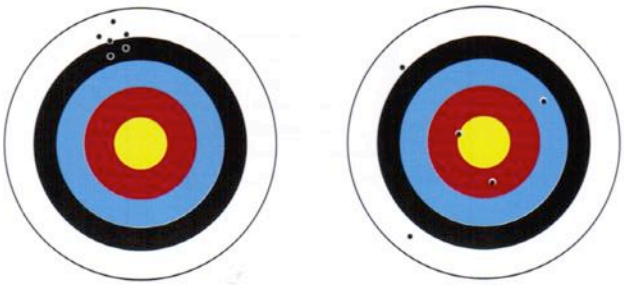
6. If the titration of 20.0 mL of 0.105 M NaOH with 0.098 M HCℓ yields an average titre of 20.9 mL calculate:
(a) the actual error
(b) the percentage error.



Question 7

7. If a student observed a burette in this manner (left) would he be able to accurately take a reading? What is this mistake called? How do you know the reading will be inaccurate?

8. Two people are practicing archery. Their targets are shown below.


Jenny Lyndon

(a) Explain the terms 'random error' and 'systematic error' using the targets above.

(b) Using the terms 'accurate' and 'precise' describe the results.

(c) How could each person improve their result?

Notes

Use the following uncertainties for glassware information to complete questions 9 to 13:

Glassware	B grade tolerance	A grade tolerance
Burette (50 mL)	50 ± 0.10 mL	50 ± 0.05 mL
Pipette (20 mL)	20 ± 0.060 mL	20 ± 0.030 mL
Pipette (25 mL)	25 ± 0.060 mL	25 ± 0.030 mL
Volumetric flask (100 mL)	100 ± 0.20 mL	100 ± 0.10 mL
Volumetric flask (250 mL)	250 ± 0.30 mL	250 ± 0.15 mL
Volumetric flask (500 mL)	500 ± 0.50 mL	500 ± 0.25 mL

9. An analysis method consistently produces an absolute error of 0.6 mg. Calculate the percentage relative error caused by this uncertainty for the following sample masses.
   (a) 600 mg
   (b) 250 mg
   (c) 30 mg

10. When titrating it is found that an over-titration of 0.05 mL is required to produce a visible colour change. Calculate the relative percentage error of this over titration if the titre is:
   (a) 10.5 mL
   (b) 25.3 mL
   (c) 37.2 mL

11. 2.445 g of anhydrous sodium hydrogencarbonate is dissolved in distilled water, transferred to a 250.0 mL B grade volumetric flask and water is added to the mark. Calculate the concentration of the standard sodium hydrogencarbonate solution and the percentage and absolute uncertainties. (Assume the mass is accurate)

12. All glassware used was A grade. 20.00 mL aliquots of a 0.0446 mol L^{-1} sodium hydrogencarbonate solution were titrated against a hydrochloric acid solution and the following titres obtained (in mL) 23.15, 22.45, 22.55, 22.60:
   (a) Calculate the average titre and the percentage uncertainty based on the tolerance of the glassware from these results.
   (b) Calculate the percentage uncertainty based on the range of the titres.
   (c) Calculate the number of moles of sodium hydrogencarbonate and the percentage uncertainly in the conical flask (assume the initial concentration of sodium hydrogencarbonate is accurately known).
   (d) Calculate the concentration of the hydrochloric acid solution and the percentage and absolute uncertainly.

13. Using B grade glassware, a sample of cloudy ammonia was titrated with 0.100 mol L^{-1} hydrochloric acid. The titre values were found to be 5.44 mL, 5.60 mL, 6.00 mL and 5.55 mL.
   (a) Calculate the average titre and the percentage uncertainty.
   (b) In a second experiment, the cloudy ammonium was diluted by a factor of 5 and the following titres (in mL) obtained: 25.20, 24.50, 24.45 and 24.30.
      (i) Calculate the average titre
      (ii) Calculate the percentage uncertainty associated with the glassware.
   (c) Using your answers to (a) and (b), explain why diluting the cloudy ammonia produces a more accurate result.

Chemical Equilibrium

The problem sets in the chemical equilibrium section of Exploring Chemistry Year 12: Experiments, Investigations and Problems, provides opportunities for students to explore:

- reaction rates and energy
- the effects of concentration, temperature, pressure, the presence of catalysts and surface area on the rate of chemical reactions
- equilibrium constant expresions
- using Le Châtelier's Principle to predict the effect of changes to reaction conditions on a system at equilibrium

Set 4: Reaction Rates and Energy

Notes

The rate of a chemical reaction is the speed at which the reactants are changed to products. Reaction rates can therefore be determined by measuring the rate of disappearance of reactants or the rate of appearance of products.

Factors that affect the rate of a reaction are:

- The nature of reactants,
- State of subdivision of the reactants
- Concentration or pressure of the reactants,
- Temperature of the reaction system and
- The presence of a catalyst.

These factors can be explained and their effects on the rate of a reaction predicted using the collision theory. The collision theory of reactions uses the idea that particles must first collide before a reaction can occur. A successful collision is one where products are formed. For a collision to be successful it must have sufficient energy (activation energy) and an appropriate orientation so that reactant bonds can be broken and new bonds formed to make products.

Observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level. An energy profile diagram for example can be used to represent the energy changes that occur in a chemical reaction (see Figure 4.1).

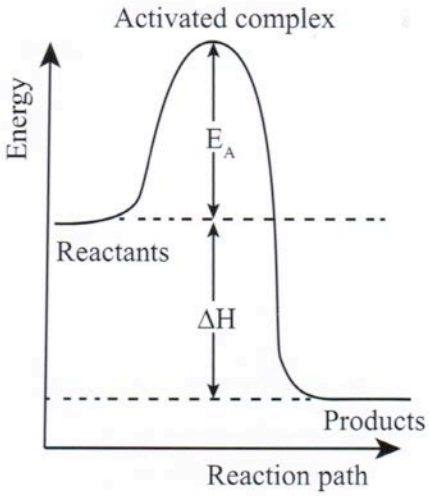


Figure 4.1: Energy profile diagram for an exothermic reaction.

Set 4: Exercises

Notes

1. Describe two ways that could be used to measure the rate of the following reaction.
   $Zn\ (s) + 2\ H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2\ (g)$

2. Suggest reasons why the precipitation of lead iodide at room temperature is a faster reaction than the metabolism of glucose during respiration, which is slow at room temperature.
   $Pb^{2+}\ (aq) + 2\ I^-\ (aq) \rightarrow PbI_2\ (s)$
   $C_6H_{12}O_6\ (aq) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (\ell)$

3. Predict the effect of increasing the concentration of the reactant (in bold type) on the rates of the following reactions. Explain your prediction using the collision theory.

   (a) $\mathbf{Ba^{2+}}\ (aq) + SO_4^{2-}\ (aq) \rightarrow BaSO_4\ (s)$

   (b) $Mg\ (s) + \mathbf{2\ H^+}\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2\ (g)$

4. Predict the effect of increasing the pressure of the reaction system on the rates of the following reactions. Explain your prediction using the collision theory.

   (a) $H_2\ (g) + I_2\ (g) \rightarrow 2\ HI\ (g)$

   (b) $Pb^{2+}\ (aq) + 2\ I^-\ (aq) \rightarrow PbI_2\ (s)$

5. In the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. Some catalytic convertors in motor vehicles have a honeycomb structure, while many metal catalysts are used in the form of fine wire mesh.
   Explain the purpose of a catalyst. What property of reactants and reactions is being exploited to make them more effective in the examples described? Use the collision theory to help with your explanation.

6. Draw energy profile diagrams for the following reactions. Draw the profiles on the same axes and assume that the reactants start with the same energy, 20 kJ:

	Reaction A	Reaction B
Activation Energy (kJ)	100	120
Heat of Reaction - ΔH (kJ)	-50	50

   (a) Label the reactions as Endothermic or Exothermic.
   (b) Explain the difference between the endothermic and exothermic reactions in term of their heat of reaction and what you would expect to observe.
   (c) Assuming all the other factors affecting rates of these two reactions are the same identify the faster:
      I. forward reaction.
      II. reverse reaction and give its activation energy.

7. Using the collision theory and energy profile diagrams explain at a molecular level how increasing the temperature of the reactants can affect the rate of a reaction.

Set 5: Equilibrium constant expressions

Notes

Chemical systems include physical changes and chemical reactions and may be open or closed. An open system allows matter and energy to be exchanged with the surroundings. A closed system allows energy but not matter to be exchanged with the surroundings. Over time in a closed system, reversible physical and chemical changes may reach a state of dynamic equilibrium, with the relative concentration of products and reactants define the position of equilibrium. A reversible reaction is represented by the use of double arrows in the chemical equation:

$$CH_3COOH(aq) + OH^-(aq) \leftrightarrows CH_3COO^-(aq) + H_2O(\ell)$$

Equilibrium constant expressions are mathematic representations of the relationship between the concentrations of the products and reactants in a system at equilibrium. They are based on the equation for the reaction taking place. The value of the expression, the equilibrium constant, is constant for a given temperature.

Haber used equilibrium constant expressions to predict the concentration conditions that would give the greatest yield of ammonia when he investigated a method for producing it at a commercial level.

Consider the following general equation for a system of gases in equilibrium:

$$aA(g) + bB(g) \leftrightarrows cC(g) + dD(g)$$

Where A, B, C and D are substances involved and a, b, c and d are the relative number of moles of each substance. The equilibrium constant expression for this reaction is written as:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K = \frac{[\text{Products}]}{[\text{Reactants}]}$$

As the equilibrium constant expression uses concentrations (shown by using [ ]), we do not include solids and liquids in the expression.

Example

Write the equilibrium constant expression for the ionisation of oxalic acid in water given the following equation:

$$H_2C_2O_4\,(g) + H_2O\,(\ell) \leftrightarrows HC_2O_4^-(aq) + H_3O^+\,(aq)$$

As water is a liquid, it will not be included in the expression, so K will be:

$$K = \frac{[HC_2O_4^-][H_3O^+]}{[H_2C_2O_4]}$$

Set 5: Exercises

Notes

Write equilibrium constant expressions for the following equations.

1. $2\ H_2(g) + O_2(g) \leftrightarrows 2\ H_2O(g)$
2. $2\ N_2O(g) \leftrightarrows 2\ N_2(g) + O_2(g)$
3. $CO(g) + 2\ H_2(g) \leftrightarrows CH_3OH(g)$
4. $Ag_2CrO_4(s) \leftrightarrows 2\ Ag^+(aq) + CrO_4^{2-}(aq)$
5. $CO_2(aq) + H_2O(\ell) \leftrightarrows HCO_3^-(aq) + H^+(aq)$
6. $HSO_4^-(aq) + H_2O(\ell) \leftrightarrows SO_4^{2-}(aq) + H_3O^+(aq)$
7. $Cr_2O_7^{2-}(aq) + H_2O(\ell) \leftrightarrows 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$
8. $CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$
9. $HCO_3^-(aq) + NH_3(aq) \leftrightarrows CO_3^{2-}(aq) + NH_4^+(aq)$
10. $CaO(s) + SO_3(g) \leftrightarrows CaSO_4(s)$
11. $2\ NaHCO_3(s) \leftrightarrows Na_2CO_3(s) + H_2O(g) + CO_2(g)$
12. $2\ Hg(\ell) + C\ell_2(g) \leftrightarrows Hg_2C\ell_2(s)$
13. $CaCO_3(s) + H_2O(\ell) + CO_2(aq) \leftrightarrows Ca^{2+}(aq) + 2\ HCO_3^-(aq)$
14. $CaC\ell_2(s) + H_2O(g) + CO_2(g) \leftrightarrows CaCO_3(s) + 2\ HC\ell(g)$

Set 6: Equilibrium systems

Notes

Le Châtelier was a French industrial chemist who spent a great deal of his life investigating equilibrium systems. He found that in many cases, a system at equilibrium would react in a predictable way when a change was imposed on the system. This ability to predict the impact of a change imposed on a system is called Le Châtelier's Principle:
When a change is imposed on a system at equilibrium, the system will move in such a way as to partially counteract that change.
You may have met similar ideas in biology as 'homostasis' and in physics as Lenz's Law.

Le Châtelier's Principle can be used to predict the effect of changing temperature, pressure and concentration on a system at equilibrium. Adding a catalyst has no effect on equilibrium yield as it increases the rate of the forward and reverse reactions equally.

Example

A reaction that is significant in the formation of smog is one between ozone and nitrogen monoxide. It can be represented by the following equation.

$$O_3(g) + NO(g) \leftrightarrows O_2(g) + NO_2(g) + 57.5 \text{ kJ mol}^{-1}$$

colourless brown

(a) Write the equilibrium constant expression for this equation.

(b) Predict the effect on the yield of NO_2 due to the following changes being made to the system at equilibrium.
(i) More O_3 is added to the system (a by-product of the combustion of petrol)
(ii) NO_2 is removed from the system.
(iii) The volume of the system is increased.
(iv) The temperature of the system is decreased.

Answer:

(a) $K = \frac{[O_2][NO_2]}{[O_3][NO]}$

(b)(i) Increase in yield, $[NO_2]$
(ii) Increase in yield, $[NO_2]$
(iii) no change (the number of gas particles is the same on both sides of the equation)
(iv) increase in yield, $[NO_2]$ (the forward reaction is exothermic)

Set 6: Exercises

1. The industrial production of ammonia involves a reaction between nitrogen and hydrogen in the presence of an iron/iron oxide catalyst and can be represented by the following equation:

$$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g) \quad \Delta H = -92 \text{ kJ}$$

(a) Write an equilibrium constant expression for the equation.
(b) Predict the effect on the concentration of ammonia due to the following changes being made to the above reaction at equilibrium.
(i) Increase the temperature,
(ii) Inject more $N_2(g)$ into the system,
(iii) Reduce the volume of the system,
(iv) Remove the catalyst.

Notes

2. When water is chlorinated the following equilibrium is established:

$$C\ell_2(g) + 2\ H_2O(\ell) \leftrightarrows 2\ OC\ell^-(aq) + 4\ H^+(aq) \qquad \Delta H = +ve$$

(a) Write an equilibrium constant expression for the equation.

(b) Predict the effect on the concentration of $OC\ell^-(aq)$ due to the following changes:

(i) More $C\ell_2(g)$ is added to the system,

(ii) The temperature is decreased,

(iii) A small amount of concentrated NaOH solution is added to the system,

(iv) A small amount of concentrated $HC\ell$ solution is added to the system.

3. Ag_2CrO_4 is a slightly soluble salt and forms a saturated solution. This can be represented by the following equation:

$$2\ Ag^+(aq) + CrO_4^{2-}(aq) \leftrightarrows Ag_2CrO_4(s) \qquad \Delta H = -ve$$

(a) Predict the initial effect on the rate of the forward reaction when the equilibrium is re-established after the following changes have been applied:

(i) A few drops of concentrated $NaC\ell$ solution is added to the system.

(ii) The solution is diluted by the addition of a small amount of water.

(iii) The temperature is increased.

(b) Predict the effect on the concentration of Ag^+ when equilibrium is re-established after the following changes have been applied:

(i) A few drops of concentrated $NaC\ell$ solution is added to the system.

(ii) Some solid Ag_2CrO_4 is added to the system.

(iii) The temperature is increased.

4. Dinitrogen trioxide decomposes to form nitrogen monoxide and nitrogen dioxide.

$$N_2O_3(g) \leftrightarrows NO\ (g) + NO_2\ (g) \qquad \Delta H = 40.5\ kJ$$

a) Predict the effect on the rate of the forward reaction due to the following changes.

(i) Extra N_2O_3 is pumped into the system at constant volume.

(ii) The temperature is increased.

(iii) The volume of the system is doubled.

b) Predict the effect on the concentration of products when equilibrium is re-established when the following changes are applied.

(i) Extra N_2O_3 is pumped into the system at constant volume.

(ii) The temperature is decreased.

(iii) The volume of the system is doubled.

5. When barium carbonate is heated it decomposes into barium oxide and carbon dioxide.

$$BaCO_3(s) \leftrightarrows BaO(s) + CO_2(g) \qquad \Delta H = +ve$$

a) Predict the effect on the rate of the forward reaction due to the following changes.

(i) The $BaCO_3$ is ground up more finely.

(ii) The system is cooled.

(iii) CO_2 is removed.

b) Predict the effect on the concentration of carbon dioxide when equilibrium is re-established due to the following changes.

(i) More $BaCO_3$ is added.

(ii) The volume is doubled.

(iii) The temperature is increased.

Set 7: Equilibrium

Notes

Research

1. An ice cube is placed in a beaker of water at 25.0 °C. The temperature of the water is lowered to 0 °C to match that of the ice and no changes are apparent.
   (a) Is the system at equilibrium?

   (b) Describe what is happening at the molecular level.

   (c) Suggest an experiment that could be used to test that your description is valid.

2. Hyperventilation (breathing quickly and with shallow breaths) can cause a condition known as acidosis. Explain with the use of equations how this condition affects the oxygen content in blood and why breathing into a paper bag is used to counteract the condition.

3. Glasses that change their level of shading with different light conditions often contain silver chloride in the lenses. With reference to Le Châtelier's Principle, explain how these glasses work.

Light sensitive glasses

4. Synthetic EPO (erythropoietin) was originally developed to improve the red blood cell count in people where it was low, usually due to illness or disease. During the 1980s elite athletes began using it as a performance-enhancing drug. With reference to your understanding of equilibrium and rates of reactions, explain why EPO could be considered a performance-enhancing drug. Also, briefly discuss the negative side effects of using this drug.

Extended answer questions

To answer the following extended answer questions, where applicable, use equations, diagrams and illustrative examples of the chemistry you are describing. Your answer should focus on the relevant chemical content specific to the situations described. Be sure your answer is presented in a logical and coherent manner.

1. Research the industrial production of sulfuric acid and phosphoric acid. Discuss the similarities and differences in their production with particular reference to equilibrium and rates of reactions.

2. Choose two chemicals from the list provided. Research the conditions under which these chemicals are produced at the industrial level. Compare and contrast those conditions with reference to equilibrium and rates of reaction.
   (i) Methanol
   (ii) Acetic acid
   (iii) Ammonia
   (iv) Sulfuric acid

Acids and Bases

The problem sets in the acids and bases section of Exploring Chemistry Year 12: Experiments, Investigations and Problems, provides opportunities for students to explore:

- the Arrhenius model and the Brønsted – Lowry theory to explain the behaviour of strong and weak acids and bases in aqueous solutions
- acid and base strength; hydrolysis and the ionisation constant for water
- indicators and their use, the pH scale and buffers
- acid – base titrations and the types of calculations that accompany titrations

Set 8: Acids and bases

Notes

A brief history of acids and bases

Ancient Greeks BC - a time of vinegar and soap: Originally, acidity came from the ancient Greeks who defined "sour-tasting" substances as acids. Additional properties were discovered as acids were found to change the colour of red wine and corrode metals. Bases or alkaline substances were typically defined and studied by their ability to counteract the effects of acids. Consequently our chemical understanding of bases trailed that of the acids.

18th century: French chemist Antoine Laurent Lavoisier (1743–1796) worked on the idea that all acids contained a particular "essence" that was responsible for their acidity. They contained more or less of this 'essence' and were not uniquely different. He wrongly thought that oxygen was the common 'essence' of all acids.

English chemist **Humphry Davy** (1778–1829) in the early 19th century demonstrated that oxygen could not be responsible for acidity. He identified many acids that did not contain oxygen. He identified that acids contain 'replacable hydrogen'. This referred to the fact that active metals would react with acids and yield hydrogen.

19th century: German chemist Justus von Liebig (1803–1873) proposed the idea that acidity was associated with the presence of hydrogen.

Svante August Arrhenius (1859–1927) in 1887 defined acids as "*substances that produced hydrogen ions in solution and bases as substances that contained hydroxyl ions in solution*".

Strong acid (complete ionisation) $HC\ell\,(g) \rightarrow H^+\,(aq) + C\ell^-\,(aq)$

Weak acid (partial ionisation) $CH_3COOH\,(aq) \leftrightarrows H^+\,(aq) + CH_3COO^-\,(aq)$

The hydrogen ions produced in aqueous solutions can be represented as H^+ or H_3O^+ (hydronium ion)

Strong base (complete dissociation) $NaOH\,(s) \rightarrow Na^+\,(aq) + OH^-\,(aq)$

Weak base (partial dissociation) $NH_3\,(aq) + H_2O\,(\ell) \leftrightarrows NH_4^+\,(aq) + OH^-\,(aq)$

The ionisation of strong and weak acids, and the dissociation of strong and weak bases can be represented diagrammatically as shown in Figure 8.1.

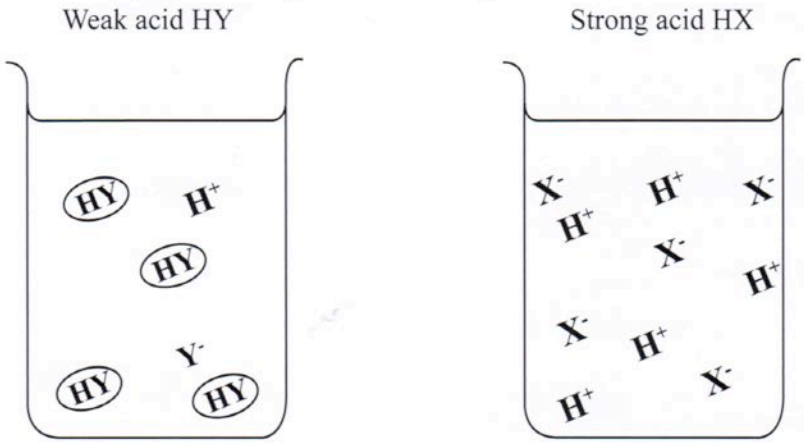


Figure 8.1: Aqueous solutions of a strong acid are virtually completely ionised but a weak acid is only partially ionised in water.

Notes

Arrhenius also proposed the neutralization reaction:

Acid + Base → Salt + Water

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (\ell)$

20th century: Danish chemist Johannes Brønsted and English chemist Thomas Lowry in 1923 independently proposed a modification of the Arrhenius model. In the Brønsted - Lowry theory an acid-base reaction is one that involves the transfer of a proton from one species to another. The acids are proton donors, while bases are proton acceptors. As a result of this new model, measurements of the hydrogen ion concentration became the key to defining the level of acidity.

The Brønsted – Lowry theory

In the Brønsted – Lowry theory the ionisation of $HC\ell$ is represented by the following equation:

$HC\ell (g) + H_2O (\ell) \rightarrow H_3O^+ (aq) + C\ell^- (aq)$

The $HC\ell$ is donating a proton (H^+) and acting as an acid. The water (H_2O) is accepting a proton and is classified as a base.

In the reaction of ammonia with water:

$NH_3 (aq) + H_2O (\ell) \leftrightarrows NH_4^+ (aq) + OH^- (aq)$

The ammonia accepts a proton and is acting as a base, while the water, donating a proton, is acting as an acid.

In the Brønsted – Lowry theory every acid once it has donated a proton has the potential to act as a base. It has formed its conjugate base. The same is true for a base that has accepted a proton, forming its conjugate acid, now has the potential to act as an acid.

$CH_3COOH (aq) + OH^- (aq) \leftrightarrows H_2O (\ell) + CH_3COO^- (aq)$

acid base conjugate acid conjugate base

The conjugate acid-base pairs in the reaction are shown by the matching colours.

The stronger an acid is, the weaker its conjugate base.

Acid-base reactions tend to occur in the direction in which a stronger acid and stronger base react to form a weaker acid and weaker base. For example, in the equation above for the reaction of acetic acid and the hydroxide ion, the reaction favours the forward direction. CH_3COOH is a stronger acid than H_2O and OH^- is a stronger base than CH_3COO^-.

The extent to which an acid ionises in aqueous solution can be determined from the equilibrium constant or the ionisation process. This equilibrium constant (K_a) is called the acid ionisation constant or the acid dissociation constant. In the ionisation of ethanoic acid the acid ionisation constant (K_a) is given by:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The K_a for ethanoic acid at 25 °C is 1.8×10^{-5}. This value indicates that the reaction only proceeds to a very limited extent. In a 0.1 mol L^{-1} solution only a little more than 1% of ethanoic acid molecules are ionised. See Table 8.1

Set 8: Acids and bases

Notes

Name	Formula	K_a
hydrochloric acid	$HC\ell$	large
sulfuric acid	H_2SO_4	large
nitric acid	HNO_3	large
sulfurous acid	H_2SO_3	1.7×10^{-2}
hydrogensulfate ion	HSO_4^-	1.2×10^{-2}
phosphoric acid	H_3PO_4	7.5×10^{-3}
hydrofluoric acid	HF	7.2×10^{-4}
ethanoic acid	CH_3COOH	1.8×10^{-5}
carbonic acid	H_2CO_3	4.2×10^{-7}
dihydrogenphosphate ion	$H_2PO_4^-$	6.2×10^{-8}
hydrogen sulfide	H_2S	1.0×10^{-7}
ammonium ion	NH^+	5.6×10^{-10}
hydrogencarbonate ion	HCO^3	4.8×10^{-11}
hydrogenphosphate ion	HPO^{4-}	3.6×10^{-13}
hydrogensulfideion	HS^-	1.3×10^{-13}

Set 8: Exercises

1. Identify the conjugate acid of F^-, CO_3^{2-}, $C\ell O_4^-$, SO_3^{2-}, NH_3

2. Identify the conjugate base of HBr, HSO_4^-, $H_2PO_4^-$, HS^-, HNO_3, H_2O

3. Write equations for the reactions of the following substances when dissolved in water.

   a. The strong acid H_2SO_4
   b. The weak acid H_2S
   c. The strong base KOH
   d. The weak base N_2H_4

4. Explain the difference between strong and weak, and concentrated and dilute, acid solutions. Draw diagrams (similar to Figure 8.1) that represent the following acid solutions to support your explanations:
   a. A concentrated solution of a strong acid
   b. A concentrated solution of a weak acid
   c. A dilute solution of a strong acid
   d. A dilute solution of a weak acid

5. For the following reactions:
   I. Identify the conjugate acid-base pairs
   II. Predict whether the reaction favours the formation or products or reactants as written.

   a. $HF\ (aq) + H_2O\ (\ell) \leftrightarrows F^-\ (aq) + H_3O^+\ (aq)$
   b. $HSO_4\text{-}(aq) + NH_3(aq) \leftrightarrows SO_4^{2-}\ (aq) + NH_4^+\ (aq)$
   c. $H_2CO_3\ (aq) + F^-(aq) \leftrightarrows HCO_3^-\ (aq) + HF\ (aq)$
   d. $HCO_3\text{-}\ (aq) + H_2O\ (\ell) \leftrightarrows H_3O^+\ (aq) + CO_3^{2-}\ (aq)$

Set 9: Acid and base strength

Notes

Strength of acids and bases refers to the degree of ion formation that occurs when an acid or base is dissolved in water as a proportion of the solute actually dissolved.

A **strong** acid: When hydrogen chloride dissolves in water it ionises completely to form ions (hydrochloric acid). The ionisation process is represented by the equation:

$$HC\ell(aq) \rightarrow H^+(aq) + C\ell^-(aq)$$

A **weak** acid: When the very soluble hydrogen fluoride dissolves in water there is little ionisation. The ionisation process is represented by the equation:

$$HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$$

Concentration is a description or measure of the proportion of solute in a solution. It can refer to the original form of the solute or to the resulting species formed as a result of the solution process. For example a 6 mol L^{-1} solution is concentrated while a 0.1 mol L^{-1} solution is dilute.

Set 9: Exercises

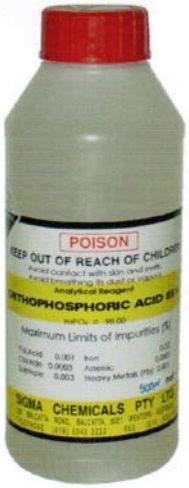
1. People often talk about strong or weak solutions when they actually mean concentrated or dilute solutions. With the aid of diagrams and equations distinguish between the properties of 'concentration' and 'strength' when applied to solutions of acids and bases.

2. The uses of acids and bases are to a large extent determined by their strength. Write three examples of:
   (a) strong acids
   (b) weak acids
   (c) strong bases
   (d) weak bases

3. Classify each of the following solutions on the basis of concentration and strength.
   (a) 10.0 mol L^{-1} hydrofluoric acid solution used in etching glass.
   (b) 0.0100 mol L^{-1} hydrochloric acid solution used in the analysis of basic solutions.
   (c) 10.0 mol L^{-1} sodium hydroxide solution used in the purification of alumina.
   (d) 0.100 mol L^{-1} ammonia solution used as a component of some floor cleaners.

4. (a) Write an equation or equations to illustrate the process that occurs when 0.1 mol of each of the following are mixed with 1.0 L of water.
   (b) In each case indicate whether the process is ionisation or dissociation.
   (c) In each case write the formula of all the species present in order of increasing concentration.
      (i) hydrogen bromide
      (ii) acetic acid
      (iii) sulfuric acid
      (iv) ammonia
      (v) barium hydroxide

Set 9: Acid and base strength



Question 7: Concentrated phosphoric acid

Question 9: Washing Powder

Notes

5. Consider the equation:

$$HC\ell O_4(aq) + H_2O(\ell) \leftrightarrows H_3O^+(aq) + C\ell O_4^-(aq)$$

It represents the reaction of perchloric acid with water to produce hydronium and perchlorate ions . Salts that contain the perchlorate ions are increasingly used to make explosive mixtures used in fireworks. It was found that such a solution contained only a very small number of perchloric acid molecules. Which is the stronger acid and which is the weaker base present in the solution?

6. Hydrogen sulfide is produced by certain anaerobic organisms that use sulfur compounds for respiration instead of oxygen. It is readily soluble in water.
   (a) Write equations to represent the process that occurs when hydrogen sulfide has dissolved in water.
   (b) Write the formulas of the strongest acid and the strongest base present in the resulting solution.

7. Concentrated phosphoric acid is used to convert phosphate rock into a fertiliser known as triple superphosphate.
   (a) Write equations to show what happens when about 10 mL of phosphoric acid is dissolved in 1.0 L of water.
   (b) Identify all the molecules and ions present in the solution and write them in order of decreasing concentration.

8. With precautions, concentrated sulfuric acid (99 %) can be safely stored in iron tanks but a 2 mol L^{-1} sulfuric acid solution readily dissolves steel wool. Account for these observations.

9. Hydroxide ions in solution readily react with fats and oils to produce salts that are relatively water soluble. Both sodium carbonate and sodium hydroxide produce hydroxide ions when dissolved in water. Washing powders used to wash clothing contains amongst other things sodium carbonate. Why is sodium carbonate preferred to sodium hydroxide for this use?

10. One of the uses of boric acid, H_3BO_3 is as an antiseptic and to treat certain yeast infections in humans. Small amounts are used in eye wash solutions. Based on these uses, comment on the likely strength of this acid. Why would it not be appropriate to use hydrochloric acid for these purposes?

Set 10: Hydrolysis

Notes

Hydrolysis means reaction with water. When ions associated with weak acids or bases are dissolved in water they undergo hydrolysis, they react with water. It is a chemical reaction where one or more water molecules are split into hydrogen ions and hydroxide ions, which may participate in further reactions. Dissolved salts in soils can make the soil either acidic or basic.

Table 10.1: Acid and base properties of common aqueous anions and cations

Acidic	Neutral	Basic
Anions from polyprotic acids: HSO_4^-, $H_2PO_4^-$	Anions from strong acids: NO_3^-, $C\ell^-$, Br^-, I^-	Anions from weak acids: CH_3COO^-, CO_3^{2-}, HCO_3^-, PO_4^{3-}, HPO_4^{2-}, $C\ell O^-$, F^-, S^{2-}, SO_4^{2-}
Acidic cations : NH_4^+, $A\ell^{3+}$, Fe^{3+}	Cations from strong bases: Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}	

Example

When the strong acid $HC\ell$ reacts with the weak base NH_3 the acidic salt $NH_4C\ell$ is formed.

$$HC\ell\,(aq) + NH_3\,(aq) \leftrightarrows NH_4^+\,(aq) + C\ell^-\,(aq) + H_2O\,(\ell)$$

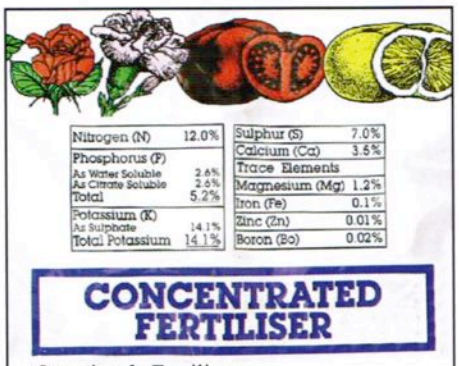
The ammonium ion, NH_4^+, hydrolyses in water according to the equation:

$$NH_4^+\,(aq) + H_2O\,(\ell) \leftrightarrows NH_3\,(aq) + H_3O^+\,(aq)$$

$NH_4C\ell$ is an acidic salt because the NH_4^+ ion reacts with water to produce hydronium ions, H_3O^+. The $C\ell^-$ does not hydrolyse.

Set 10: Exercises

1. Classify the following salts as acidic, basic or neutral.
   (a) sodium chloride
   (b) potassium phosphate
   (c) calcium hydrogencarbonate
   (d) ammonium nitrate
   (e) sodium acetate
2. Write hydrolysis equations for the acidic and basic salts identified in question 1.
3. Many salts that contain essential elements for plant growth are used as fertilisers. In common use are salts such as ammonium nitrate, sodium nitrate, calcium hydrogenphosphate, potassium chloride, potassium sulfate and ammonium chloride.
   (a) Which of these salts have the potential to change the pH of the soils in which they are used?
   (b) Explain how you decided which of these would change the soil's pH?
   (c) Write equations that show how the soil's pH would be increased or decreased by these salts.
   (d) Why do some salts used as fertilisers not change the soil's pH?



Question 3: Fertiliser

Notes

4. Calcium dihydrogenphosphate, which is sparingly soluble, is the main compound in the fertiliser superphosphate. It is a source of the element phosphorus, essential for plant growth. Write an equation to show what happens when calcium dihydrogenphosphate dissolves in water.

5. Washing soda (sodium carbonate decahydrate) is a major component of washing powders.

INGREDIENTS

DRIVE contains ingredients to lift dirt from clothes (anionic and nonionic surfacants); soften water (sodium polyphosphate and zeolite); break up fatty soils (sodium carbonate, sodium silicate) and remove stains (enzymes). Small amounts of fluorescer, soil responding agent, colcur and perfume are also included.

   (a) When dissolved in water, does the washing soda change the pH of the water? If so, does the solution become acidic or basic?
   (b) Write an equation to represent the solution process and any other equations that may be required to explain your answer to part (a).

6. Used wine barrels can sometimes end up with acid forming in them as the alcohol in any residual wine is converted to acetic acid. Before they can be used to store wine again, this acetic acid must be removed. This can be achieved by washing the barrel with a dilute solution of sodium hydroxide.
   (a) Write an ionic equation for the reaction between the acetic acid and sodium hydroxide solutions.
   (b) If the salt formed from this reaction was recovered, dried then dissolved in distilled water would the pH of the solution formed be greater than 7, equal to 7 or less than 7?
   (c) Write an equation to justify your answer to part (b).

Question 6: Wine barrel

7. Sodium fluoride is added in very small amounts (0.7 to 1.2 ppm) to some drinking water to reduce tooth decay as the tooth enamel that contains some fluorine atoms seems to be much more resistant to attack from acids produced by mouth bacteria than normal enamel. Does the addition of sodium fluoride to water change its pH? Write an equation or equations to support your answer.

8. Ammonium acetate could be used as a fertiliser as it contains the element nitrogen that is important for plant growth. Would you expect a solution of ammonium acetate to be acidic, neutral or basic? Write equations to support your answer.

Set 11: Water equilibrium

Notes

Ionisation Constant of Water (K_w)

Water is a weak electrolyte and dissociates to a very small extent according to the equation.

$$H_2O(\ell) \leftrightarrows H^+(aq) + OH^-(aq)$$

The equilibrium constant for this reaction at 25 °C is:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

where $[H^+]$ is the concentration of hydrogen ions in mol L^{-1}, and $[OH^-]$ is the concentration of hydroxide ions in mol L^{-1}.

Examples

1. Hydrobromic acid is a strong acid and is used for making brominated hydrocarbons. Calculate the hydrogen and hydroxide ion concentration of a 2.50×10^{-3} mol L^{-1} aqueous solution of hydrobromic acid.

   (a) Write an ionisation equation:

   $$HBr(aq) \rightarrow H^+(aq) + Br^-(aq)$$

   (b) Calculate the hydrogen ion concentration:
   As HBr is a strong acid, it is fully ionised.
   So the:

   $$[H^+] = [HBr] = 2.50 \times 10^{-3} \text{ mol L}^{-1}$$

   (c) Calculate the hydroxide ion concentration:
   Since:

   $$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

   $$[OH^-] = \frac{1.00\times10^{-14}}{[H^+]} = \frac{1.00\times10^{-14}}{2.50\times10^{-3}} = 4.00\times10^{-12} \text{ mol L}^{-1}$$

2. Calcium hydroxide is sparingly soluble in water and at 25°C its concentration is around 0.0158 mol L^{-1}. Calculate the concentration of the hydroxide and hydrogen ion for this solution.

   Step 1: Write a dissociation equation:

   $$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$$

   As $Ca(OH)_2$ is ionic it is fully dissociated.

Notes

Step 2: Calculate the hydroxide ion concentration:

$$[OH^-] = 2 \times [Ca(OH)_2] = (2)\,(0.0158) = 0.0316 \text{ mol L}^{-1}$$

Since:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

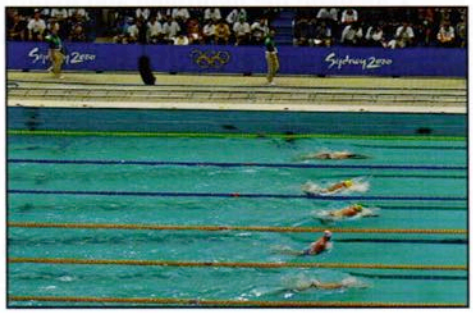
$$[H^+] = \frac{1.00\times10^{-14}}{[OH^-]} = \frac{1.00\times10^{-14}}{0.0316} = 3.16\times10^{-13} \text{ mol L}^{-1}$$

Set 11: Exercises

In all of the following questions the temperature is assumed to be 25 °C

1. Write an equation to represent the ionisation of water according to the Brønsted-Lowry theory of acids and bases.

2. The concentration of acid and base in a swimming pool is critical to maintaining an adequate level of chlorine in the water. The concentration of hydrogen ions in the water of an Olympic swimming pool was measured to be 1.48×10^{-7} mol L^{-1}.
   (a) Calculate the concentration of hydroxide ions.
   (b) Is the swimming pool water basic or acidic?



Question 2: Swimming pool

3. Water in the tailings dam of a gold processing plant was found to have a hydroxide ion concentration of 1.58×10^{-6} mol L^{-1}. Calculate the $[H^+]$.

4. Calculate the hydrogen ion concentration in the following solutions.
   (a) A standard 1.55×10^{-4} mol L^{-1} sodium hydroxide solution used for analysing the acid content of wine.
   (b) A 3.90×10^{-2} mol L^{-1} barium hydroxide solution used to make soap.

5. Calculate the hydroxide ion concentration in the following solutions.
   (a) A standard 0.104 mol L^{-1} hydrochloric acid used to analyse floor cleaning solutions
   (b) A 0.125 mol L^{-1} sulfuric acid solution used to dissolve samples of malachite (copper ore containing mostly copper carbonate). Assume the first hydrogen is fully ionised and the second is 10.0% ionised.

6. The ionisation constant for water is usually taken to be 1.00×10^{-14} at 25 °C.
   (a) Why is a temperature stated?
   (b) Would the equilibrium constant increase or decrease if the temperature of pure water was decreased? Use Le Châtelier's Principle in your discussion.
   (c) What would be the effect on the hydrogen ion concentration in pure water if the temperature was increased above 25 °C?
   (d) Explain this effect in terms of changes in reaction rates.

7. Rain water collected near a nickel smelter where nickel sulfide ore is heated in air was found to have a hydrogen ion concentration of 1.55×10^{-5} mol L^{-1}.
   (a) Calculate the $[OH^-]$.
   (b) What could have caused the rain water to have such a high $[H^+]$?
   (c) Write an equation or equations to show how the $[H^+]$ in the rain water could become greater than 1.00×10^{-7} mol L^{-1}.

8. Lemon juice with a $[H^+]$ of 1.60×10^{-4} mol L^{-1} was mixed with an equal volume of orange juice with a $[H^+]$ of 1.30×10^{-6} mol L^{-1} to make a citrus juice drink. Calculate the hydrogen and hydroxide ion concentration of the citrus juice drink.

Question 8: Lemons and oranges

9. When you suffer from an acid stomach, the fluid in your stomach can contain hydrochloric acid at a concentration of 2.50×10^{-4} mol L^{-1}.
   (a) To reduce the amount of acid in your stomach you are advised to take an antacid tablet that contains 5.00 mg of aluminium hydroxide and 5.00 mg of magnesium hydroxide. If at this time you have 1.50 L of fluid in your stomach, calculate the concentration of hydrogen ions and hydroxide ions in your stomach after you have taken the tablet.
   (b) If you took a second antacid tablet what would the hydrogen and hydroxide ion concentration be now?

10. Your friend complains to you of a burning sensation in their stomach just before a chemistry test. You both suspect that this is caused by hyperacidity, an unusually high amount of acid in the stomach, so your friend decides to seek medication from the resident nurse. The nurse decides to use milk of magnesia, an 80 g L^{-1} slurry of solid magnesium hydroxide suspended in water, to reduce the amount of acid in your friend's stomach. The nurse estimated that your friend's stomach contained 2.00×10^{-2} moles of hydrochloric acid.
    (a) Calculate the volume of milk of magnesia the nurse should administer to reduce the hydrogen ion concentration in your friend's stomach to one third of the original value.
    (b) Calculate the hydrogen ion and hydroxide ion concentration in your friend's stomach after he took the medication if the volume of the fluid in his stomach was estimated to be 800 mL.

Notes

Set 12: Indicators and their use

Notes

Acid-base indicators are dyes with colours that depend upon the hydrogen ion concentration in solution. Each indicator changes colour at a unique $[H^+]$.

The neutralisation reaction of an acid base indicator can be represented by the equation:

$$\underset{\text{Colour 1}}{HInd} + OH^- \leftrightarrows \underset{\text{Colour 2}}{Ind^-} + H_2O$$

The colour of the indicator in a solution depends on the relative concentration of HInd (acid) and Ind^- (conjugate base). The colour change for different indicators occurs at different pH values. Using the equation as an example, colour 1 would be observed at a lower pH value than colour 2. If the pH were to be increased the indicator, over a specific pH range, would change to colour 2. Table 12.1 shows some acid-base indicators and their colours at different pH values.

Table 12.1 Acid-base indicators and their colour change

Indicator	Colour on acid side	pH range of colour change	Colour on base side
Methyl violet	yellow	0.0 – 1.6	violet
Bromophenol blue	yellow	3.0 – 4.6	blue
Methyl orange	red	3.1 – 4.4	yellow
Methyl red	red	4.4 – 6.2	yellow
Litmus	red	5.0 – 8.0	blue
Bromothymol blue	yellow	6.0 – 7.6	blue
Phenolphthalein	colourless	8.3 – 10.0	pink
Alizarin yellow	yellow	10.1 – 12.0	red
Indigo carmine	blue	11.4 – 13.0	yellow

Indicators are chosen and used to show the pH of aqueous solutions such as swimming pool water and most importantly in volumetric analysis **titrations**. Indicators are selected so that their colour change occurs over the pH range that is important for the task that they are being used for.

Titrations

The process of adding one solution to another until reaction between them is complete is known as titration. One solution, the standard, contains a known quantity of one reactant and a titration can be used to find out information about the other solution from knowledge of the reaction involved. When chemically equivalent amounts of acid and base have been added the equivalence point has been reached. Indicators are used to determine the equivalence point of a reaction. It does this by changing colour indicating the end point. The indicator is chosen so that its colour change, that is the end point, (measured in pH units) matches as closely as possible the equivalence point (measured in mL of titrate) of the titration reaction.

Example

Which indicator would you use in the titration of a cloudy ammonia solution (NH_3) and hydrochloric acid solution.

Reaction: $NH_3(aq) + H^+(aq) \leftrightarrows NH_4^+(aq)$

At the equivalence point of the reaction the acidic cation NH_4^+ and the neutral anion $C\ell^-$ are present (see table 10.1). I would choose an indicator that changes colour at an acidic pH such as methyl red (see table 12.1).

Set 12: Exercises

1. Knowledge of the acidity or alkalinity of swimming pool water is vital for proper maintenance of the pool and associated equipment and for the comfort of swimmers. Use of acid – base indicators is a relatively simple method of checking the pH of the water.
   (a) What type of compound is usually used as an acid – base indicator?
   (b) Describe the essential properties that a compound must possess to be a useful indicator.

Question 1: pH test kit

2. (a) Write an equation to show what happens when an indicator is dissolved in water.
   (b) Describe how the addition of an acid results in a change of colour of the solution.
   (c) Describe how the addition of a base results in a change of colour of the solution.
   (d) Explain in terms of changes in reaction rates why these colour changes occur.

3. Indicators are often used to detect the end point during the analysis of acids or bases. During the analysis of fruit juice the end point is known to occur when the reaction mixture is alkaline.
   (a) By referring to table 12.1, give an example of an indicator that will change colour in an alkaline solution.
   (b) What are the colours that this indicator can have at various levels of acidity?
   (c) What is the pH range where the indicator changes colour?

Question 3: Titration equipment

4. During the analysis of formalin solutions that contain the weak base methanal, the end point is known to occur when the reaction mixture is acidic.
   (a) By referring to table 12.1, give an example of an indicator that will change colour in an acid solution.
   (b) What are the colours that this indicator can have at various levels of acidity?
   (c) What is the pH range where the indicator changes colour?

5. The active ingredient of vinegar is the organic acid, acetic acid. A Consumer Affairs agency was investigating complaints that a particular brand of vinegar was not the advertised concentration. A chemist was commissioned to determine its concentration. Volumetric analysis using standard sodium hydroxide solution was the method chosen by the chemist. Determine the following for the chemist.
   (a) What species are present in the reaction mixture at the equivalence point? List them in order of decreasing concentration.
   (b) Sketch a graph of the change in pH that occurs in the reaction mixture as the acetic acid is added to the sodium hydroxide solution. Continue the graph until a significant excess of the vinegar has been added to the base in the flask.
   (c) At equivalence point is the solution acidic, neutral or basic? Write an equation to justify your answer.
   (d) By referring to table 12.1, choose an appropriate indicator to determine the end point. Explain your choice.

Notes

Set 12: Indicators and their use

Notes

6. One of the components of floor cleaners is ammonia. To make sure that the floor cleaner contains the correct concentration of ammonia the quality control chemist conducted an analysis of a sample of floor cleaner. Volumetric analysis using standard hydrochloric acid solution was the method used. Determine the following for the chemist.

   (a) What species are present in the reaction mixture at the equivalence point? List them in order of decreasing concentration.
   (b) Sketch a graph of the change in pH that occurs in the reaction mixture as the hydrochloric acid is added to the floor cleaner solution. Continue the graph until a significant excess of the acid has been added to the base in the flask.
   (c) At equivalence point is the solution acidic, neutral or basic? Write an equation to justify your answer.
   (d) Choose an appropriate indicator to determine the end point. Explain your choice.

7. Builders' lime is often supplied as a thick slurry of calcium hydroxide suspended in water. When left in a container for some time, some of the solid settles leaving a clear saturated calcium hydroxide solution above the solid. You were asked to determine the concentration of this solution using volumetric analysis. Standard hydrochloric acid solution was the suggested reagent for the analysis. Determine the following.

   (a) What species are present in the reaction mixture at the equivalence point? List them in order of decreasing concentration.
   (b) Sketch a graph of the change in pH that occurs in the reaction mixture as the hydrochloric acid is added to the calcium hydroxide solution. Continue the graph until a significant excess of the acid has been added to the base in the flask.
   (c) At equivalence point is the solution acidic, neutral or basic? If possible write an equation to justify your answer.
   (d) Choose an appropriate indicator to determine the end point. Explain your choice.

8. Oxalic acid is a constituent of edible plants such as rhubarb and spinach. You are asked to analyse the oxalic acid content of these plants by titration. During the analysis the oxalic acid solution is added to a standard sodium hydroxide solution. Methyl orange and phenolphthalein are the only two indicators available to you.

   (a) Which indicator should you use to obtain an accurate analysis?
   (b) If you chose the other indicator, would you use more or less oxalic acid solution to reach the end point?
   (c) How would using the wrong indicator affect the value you obtained for the oxalic acid content of the plants you measured?

Question 8: Rhubarb

Set 13: The pH scale

Notes

The pH scale is a convenient way of expressing concentrations of hydrogen ions, $[H^+]$ in aqueous solutions. The definition of pH is expressed by the equation:

$$pH = -\log_{10} [H^+] \text{ where pH is a number without units.}$$

The pH scale has a usual range of 0 to 14 as illustrated in the diagram below:

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[H^+]$	$1=10^0$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
Acidic pH < 7								Neutral pH = 7	Basic pH > 7						

Examples

1. Hydrochloric acid is one of the most common acids with many uses. It is produced in Western Australia in large quantities as a by product of the refining of titanium dioxide from the mineral sand ilmenite. Low concentration solutions of the acid can be standardised and used in analysis of basic solutions. Calculate the $[OH^-]$, $[H^+]$ and pH of a 0.0200 mol L^{-1} $HC\ell$ solution

   (a) Write an ionisation equation:

   $$HC\ell(aq) \rightarrow H^+(aq) + C\ell^-(aq)$$

   (b) Calculate the hydrogen ion concentration:
   As $HC\ell$ is a strong acid, it is fully ionised.
   So the $[H^+] = 0.0200$ mol L^{-1}

   (c) Calculate the hydroxide ion concentration:
   Since:

   $$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

   $$[OH^-] = \frac{1.00\times10^{-14}}{[H^+]} = \frac{1.00\times10^{-14}}{0.0200} = 5.00\times10^{-13} \text{ mol L}^{-1}$$

   (d) Calculate the pH of the solution:

   $$pH = -\log_{10} [H^+] = \log_{10} (0.0200) = 1.70$$

2. Barium hydroxide is one of the few soluble metal hydroxides. It can be used in the analysis of acidic solutions. Calculate the $[H^+]$, $[OH^-]$ and pH of a 3.00×10^{-3} mol L^{-1} $Ba(OH)_2$ solution.

   (a) Write a dissociation equation:

   $$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$$

Notes

(b) Calculate the hydroxide ion concentration:
As $Ba(OH)_2$ is ionic it is fully dissociated.

$$[OH^-] = 2 \times [Ba(OH)_2] = (2)\,(3.00 \times 10^{-3}) = 6.00 \times 10^{-3} \text{ mol L}^{-1}$$

(c) Calculate the hydrogen ion concentration:
Since:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

$$[H^+] = \frac{1.00\times10^{-14}}{[OH^-]} = \frac{1.00\times10^{-14}}{6.00\times10^{-3}} = 1.67\times10^{-12} \text{ mol L}^{-1}$$

(d) Calculate the pH of the solution:

$$pH = -\log_{10}[H^+] = \log_{10}(1.67 \times 10^{-12}) = 11.8$$

3. Orange juice has a pH of 4.50. What are the $[H^+]$ and $[OH^-]$ concentrations in orange juice?

(a) Calculate the hydrogen ion concentration:

$$pH = -\log_{10}[H^+]$$
$$-4.50 = \log_{10}[H^+]$$
$$[H^+] = 10^{-4.50} = 3.16 \times 10^{-5} \text{ mol L}^{-1}$$

(b) Calculate the hydroxide ion concentration:
Since:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

$$[OH^-] = \frac{1.00\times10^{-14}}{[H^+]} = \frac{1.00\times10^{-14}}{3.16\times10^{-5}} = 3.16\times10^{-10} \text{ mol L}^{-1}$$

Set 13: Exercises

In all of the following questions the temperature is assumed to be 25 °C

1. Calculate the $[H^+]$, $[OH^-]$ and pH of the following solutions.

   (a) A 0.100 mol L^{-1} standard $HC\ell$ solution used to analyse ammonia-based floor cleaners.
   (b) A 0.00500 mol L^{-1} HNO_3 solution used to reduce the pH of nutrient solutions used for hydroponics.
   (c) A 0.0100 mol L^{-1} standard NaOH solution used to analyse vinegar solutions.
   (d) A 2.00 mol L^{-1} $HC\ell$ solution used to dissolve limestone prior to analysis.
   (e) A 2.45 mol L^{-1} $NaC\ell$ solution used to preserve olives.

2. Calculate the $[H^+]$ and $[OH^-]$ of solutions with the following pH:
   (a) Lemon juice of pH 3.00
   (b) Dishwashing solution of pH 11.0 made from dishwashing powder used in a dishwasher.
   (c) Pool acid of pH -1.00
   (d) Orange juice of pH 4.56
   (e) Swimming pool water of pH 7.60

Question 2: Dishwasher solution

3. Before disposal, a hydrochloric acid solution of pH 4.00 used to remove rust from iron parts prior to galvanising, needs to be neutralised. Base is added until the pH is 7.00. By what factor has the hydrogen ion concentration changed?

4. A brick cleaner needs to replenish a hydrochloric acid solution. Using a pH meter he measures the pH of his depleted solution to be 2.00. He decides to add 3.00 L of 3.00 mol L^{-1} $HC\ell$ solution to 2.00 L of his solution. Calculate the final hydrogen ion concentration of the new solution.

Question 7: Concrete batching plant

5. A laboratory chemist wants a low concentration hydrochloric acid solution with a pH of 5.00, for calibrating a conductivity meter. What volume of water must be added to a 25.0 mL sample of hydrochloric acid solution of pH 3.60 to produce the required solution?

6. A researcher studying the extraction of alumina from bauxite requires 100 mL of a sodium hydroxide solution of pH 12.0. When the stock solution was checked it was found to have a pH of 11.7. What mass of sodium hydroxide must be added to increase the pH of 100 mL of this solution to 12.0? Assume the volume of the solution does not change with the addition of the solid.

Notes

7. An environmental chemist is conducting research into highly alkaline solutions found in a drain near a concrete batching plant. The concentration of the solution was found to be 0.236 mol L^{-1} hydroxide ion and the runoff from the plant was found to have a concentration of hydroxide ion of 0.156 mol L^{-1}. The chemist mixed 200 mL of the solution from the drain with 300 mL of the runoff from the plant.
   (a) Calculate the pH of the resulting solution.
   (b) What volume of 1.00 mol L^{-1} hydrochloric acid solution does the chemist need to add per litre of the mixed solution to neutralise it?
   For both (a) and (b) Assume the volumes are additive.

8. A water tank contains 15 000 L of bore water of pH 5.50. In an effort to increase the pH, 10.0 g of sodium hydroxide was added to the water in the tank. Determine the pH of the resulting solution. Assume the volume does not change on adding the solid.

9. A swimming pool contains 2.00 ML of water at a pH of 7.80 making swimming in it unpleasant. The caretaker needs to reduce the pH to 7.20. What volume of 12.0 mol L^{-1} hydrochloric acid does he need to add? Assume the volume of acid is insignificant compared to the volume of the pool.

Set 13: The pH scale

Notes

10. (a) In an experiment to determine the effect of acid rain on the pH of a small lake near a lead smelter a researcher mixed equal volumes of water, one from the lake having a pH of 6.75 and the other from rain water collected during ,a winter downpour having a pH of 5.1. Calculate the pH of the resulting mixture. Assume that the solution volumes are additive.

(b) In a different experiment designed to investigate methods of increasing the pH of the lake water the researcher mixed equal volumes of lake water and water of pH 8.00. Calculate the pH of the resulting solution. Again assume that the solution volumes are additive.

Question 10: Lake water

Set 14: Buffers

Notes

A buffer solution is one that resists changes in pH when small quantities of an acid or a base are added to it. They work by removing most of the added hydrogen ions or hydroxide ions that would otherwise change the pH. Acidic and alkaline buffer solutions achieve this in different ways.

Buffer solution

An acidic buffer solution has a pH less than 7. They are commonly made from a weak acid and one of its salts, a mixture of acetic acid and sodium acetate in solution for example. Solutions of the same concentration, mixed in equal molar proportions, will give the buffer a pH of around 4.76.

$$CH_3COOH\,(aq) \leftrightarrows CH_3COO^-(aq) + H^+\,(aq)$$

The acetic acid and sodium acetate buffer solution contains the following active ingredients:

- a relatively high concentration of un-ionised acetic acid
- a relatively high concentration of acetate ions from the sodium acetate.
- a sufficient concentration of hydrogen ions to make the solution acidic.

Example

How will the acid buffer solution, acetic acid and sodium acetate, maintain its pH balance if
(a) extra acid (H^+) is added?
(b) extra alkali (OH^-) is added?

(a) To avoid the pH from dropping by the addition of extra hydrogen ions the buffer solution must remove them. It does this by combining the hydrogen ions with the acetate ions to make acetic acid. An equilibrium exists in the buffer solution, as illustrated by the equation.

$$CH_3COOH\,(aq) \leftrightarrows CH_3COO^-(aq) + H^+\,(aq)$$

On the addition of extra H^+ the concentration of H^+ increases causing the equilibrium to shift towards the acetic acid and so using up most of the H^+ added. As a result the extra hydrogen ions are removed, so the pH does not change very much.

(b) To avoid the pH increasing by the addition of extra hydroxide ions the buffer solution must counter the change. When the extra hydroxide ions are added they react with the hydrogen ions of the buffer solution as illustrated by the equation.

$$H^+\,(aq) + OH^-(aq) \leftrightarrows H_2O\,(\ell)$$

Removal of H^+ from the buffer on the addition of extra OH^- reduces the concentration of H^+ which in turn results in the equilibrium shifting towards the products replacing most of the H^+ used up by the added OH^- ions.

$$CH_3COOH\,(aq) \leftrightarrows CH_3COO^-(aq) + H^+\,(aq)$$

Set 14: Buffers

Notes

An alkaline buffer solution has a pH greater than 7. They are commonly made from a weak base and one of its salts. A mixture of ammonia solution and ammonium chloride solution is an example of an alkaline buffer. Solutions of the same concentration, mixed in equal molar proportions, will give the buffer a pH of 9.25.

$$NH_3\,(aq) + H_2O\,(\ell) \leftrightarrows NH_4^+\,(aq) + OH^-\,(aq)$$

The ammonia solution and ammonium chloride solution mixture gives a buffer with the following active ingredients:

- a relatively high concentration of unreacted ammonia.
- a relatively high concentration of ammonium ions from the ammonium chloride.
- a sufficient concentration of hydroxide ions to make the solution basic.

Set 14: Exercises

1. Describe the function of buffer solutions and comment on their importance in biological systems.

2. Explain how the alkaline buffer, ammonia solution and ammonium chloride solution mixture works to buffer against
   (a) an increase in pH (addition of OH^-)
   (b) a decrease in pH (addition of H^+)

Question 3: pH meter

3. A pH meter is a convenient tool for the measurement of the pH of a solution. It must however be calibrated regularly. Buffer solutions are used for the calibration process. Explain why buffer solutions are used for calibration of pH meters.

4. (a) Why does a buffer need to be used in swimming pool water?
   (b) Sodium hydrogencarbonate is added to swimming pool water for its buffering effect. Write an equation to help explain how it works.

5. Carbon dioxide dissolved in the blood helps to maintain a pH of 7.4.
   (a) What other species need to be present for this process to work?
   (b) Write equations to show how carbon dioxide is involved in maintaining this constant pH.

6. (a) Starting with a 1 mol L^{-1} acetic acid solution, describe two methods of preparing a buffer solution.
   (b) Write equations for any reactions that may occur.

7. (a) Starting with sodium citrate ($Na_3C_6H_5O_7$) describe how you could prepare a buffer solution.
   (b) Write equations for any reactions that may occur.

8. Commercial buffer solutions are usually supplied with temperature-pH charts that give the pH of the solution at various temperatures. Explain why the pH of a buffer solution varies with temperature.

Set 15: Acid-base titrations 1

Notes

Analysis of acids and bases often requires the determination of an accurate concentration of a solution. Volumetric techniques rely on accurate measurement of quantities. Mass and volume are the usual quantities measured. Knowledge of the stoichiometry of the reaction involved is essential for the calculation of concentrations.

Experiments and investigations 12 to 18 used volumetric analysis techniques. Acid-base titrations were conducted and the results used to determine the quantities of substances present in solutions. Set 15 will focus on the types of calculations that accompany titrations.

The reaction in many acid-base titrations can be represented by the equation:

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (\ell)$$

The H^+ may be supplied by acids such as hydrochloric acid ($HC\ell$) or sulfuric acid (H_2SO_4) and OH^- by bases such as sodium hydroxide (NaOH).

Examples

1. 1.36 g of pure anhydrous sodium carbonate was dissolved in distilled water and made up to 250.0 mL. If 20.0 mL of this solution required 19.6 mL of a hydrochloric acid solution for complete neutralisation, calculate the concentration of the hydrochloric acid solution.

   (a) Write the equation for the reaction:

   $$CO_3^{2-} (aq) + 2\ H^+ (aq) \rightarrow H_2O (\ell) + CO_2 (g)$$

   (b) Calculate the number of moles of Na_2CO_3 in 250.0 mL

   $$n = \frac{m}{M} \qquad M(Na_2CO_3) = 105.99 \text{ g mol}^{-1}$$

   $$n = \frac{1.36}{105.99}$$

   $$= 0.0128 \text{ mol of } Na_2CO_3$$

   (c) Calculate the number of moles of Na_2CO_3 in 20.0 mL

   $$n(Na_2CO_3) = \frac{20.0}{250.0} \times 0.01283$$

   $$= 1.03 \times 10^{-3} \text{ mol } Na_2CO_3$$

   (d) Calculate the number of moles of H^+ needed to neutralise the Na_2CO_3

   1 mol of Na_2CO_3 reacts with 2 mol of H^+

   $$n(H^+) = 2 \times n(Na_2CO_3)$$
   $$= 2 \times (1.026 \times 10^{-3})$$
   $$= 2.05 \times 10^{-3} \text{ mol of } H^+$$

   (e) Calculate the concentration of $HC\ell$

   $$c = \frac{n}{V}$$

   $$c = \frac{2.053 \times 10^{-3}}{0.01960}$$

   $$= 0.105 \text{ mol L}^{-1}$$

Notes

2. What volume of 0.200 mol L^{-1} sulfuric acid solution is needed to neutralise 25.0 mL of 0.150 mol L^{-1} sodium hydroxide solution?
   (a) Write the equation for the reaction:
   $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

   (b) Calculate the number of moles of NaOH
   $n(NaOH) = cV$
   $= 0.150 \times 0.0250$
   $= 3.750 \times 10^{-3}$ mol of NaOH
   (c) Calculate the number of moles of H^+
   1 mol of H^+ reacts with 1 mol of OH^-
   $n(H^+) = n(OH^-)$
   $= 3.750 \times 10^{-3}$ mol
   (d) Calculate the number of moles of H_2SO_4
   1 mol H_2SO_4 contains 2 mol H^+
   $n(H_2SO_4) = \frac{1}{2} n(H^+)$
   $= \frac{1}{2} \times 3.750 \times 10^{-3}$
   $= 1.875 \times 10^{-3}$ mol
   (e) Calculate the volume of H_2SO_4
   $n(H_2SO_4) = cV$
   $1.875 \times 10^{-3} = 0.200 \times V$

$$V = \frac{1.875 \times 10^{-3}}{0.200}$$

$$= 9.38 \times 10^{-3} \text{ L (9.38 mL)}$$

Set 15: Exercises

1. Write equations for each reaction and calculate the volume of 0.500 mol L^{-1} sodium hydroxide solution required to neutralise
   (a) 100.0 mL of 2.00 mol L^{-1} hydrochloric acid
   (b) 150.0 mL of 1.50 mol L^{-1} acetic acid
   (c) 20.0 mL of 0.250 mol L^{-1} sulfuric acid
   (d) 75.0 mL of 0.800 mol L^{-1} phosphoric acid

2. Write equations for each reaction and calculate the volume of 0.200 mol L^{-1} sulfuric acid required to neutralise
   (a) 200.0 mL of 0.600 mol L^{-1} sodium hydroxide solution.
   (b) 50.0 mL of 0.100 mol L^{-1} barium hydroxide solution.

3. In a titration, 0.105 mol L^{-1} hydrochloric acid is used to standardise a potassium hydroxide solution using phenolphthalein as an indicator. If 21.1 mL of the hydrochloric acid is needed to neutralise 25.0 mL of potassium hydroxide solution. What is the concentration of the potassium hydroxide solution?

4. A 5.00 mL sample of sulfuric acid from a lead-acid accumulator or car battery required 22.2 mL of 2.00 mol L^{-1} sodium hydroxide for complete neutralisation. Calculate the concentration of the sulfuric acid in the battery.

Notes

5. Calculate the concentration of an unknown sodium carbonate solution using the following titration results. 3.50 mL of 1.00 mol L^{-1} nitric acid added to 25.0 mL of sodium carbonate solution gave a colour change of methyl orange indicator from yellow to red at the end-point of the titration.

6. A tablet of antacid contains 0.450 g of magnesium hydroxide, $Mg(OH)_2$. Calculate the volume of stomach fluid (0.150 mol L^{-1} hydrochloric acid) that reacts with one tablet.

7. Calculate the mass of quicklime (calcium oxide), which will react completely with 250.0 mL of 1.50 mol L^{-1} hydrochloric acid.

8. A fire extinguisher produces carbon dioxide by the reaction between sodium hydrogencarbonate and sulfuric acid. If a fire extinguisher is designed to hold 600.0 g of sodium hydrogencarbonate, calculate
   (a) the mass of sulfuric acid required to react with the sodium hydrogencarbonate.
   (b) the volume of 12.0 mol L^{-1} sulfuric acid required to react with the sodium hydrogencarbonate.

9. If 24.4 mL of hydrochloric acid is needed to neutralise 25.0 mL of 0.104 mol L^{-1} sodium hydroxide solution. Calculate
   (a) the concentration of hydrochloric acid in
      (i) mol L^{-1} (ii) g L^{-1}
   (b) the volume of the original acid solution needed to make 1.00 L of 0.100 mol L^{-1} of hydrochloric acid solution.
   (c) the volume of water which must be added to 2.00 L of the original acid solution to make it's concentration 0.100 mol L^{-1}.

10. A 20.0 mL sample of 2.00 mol L^{-1} sodium hydroxide solution was diluted to 500.0 mL in a volumetric flask. A 20.0 mL aliquot of the dilute solution was neutralised by 21.8 mL of nitric acid solution. Calculate the concentration of the acid solution.

11. A sample of vinegar has a density of 1.01 g mL^{-1} and contains 3.00% by mass acetic acid. What volume of 0.500 mol L^{-1} potassium hydroxide is required to neutralise 25.0 mL of the vinegar?

12. A 9.32 g sample of 'cloudy ammonia' was dissolved in distilled water and made up to 250.0 mL in a volumetric flask. 20.0 mL portions of this solution were titrated with 0.980 mol L^{-1} hydrochloric acid. An average of 25.8 mL hydrochloric acid was required for neutralisation using methyl orange indicator. Calculate the percentage by mass of ammonia in the 'cloudy ammonia'.

13. A 2.00 g sample of an acid was dissolved in water and made up to 250.0 mL of solution in a volumetric flask. 20.0 mL of this acid solution required 24.3 mL of 0.103 mol L^{-1} sodium hydroxide solution for complete neutralisation. If one mole of the acid can release three moles of hydrogen ions, determine the relative molecular mass of the acid.

14. You are provided with 200.0 mL of 0.500 mol L^{-1} hydrochloric acid in which has been dissolved a small quantity of anhydrous sodium carbonate. When titrated, 25.0 mL of this solution requires 20.5 mL of 0.500 mol L^{-1} sodium hydroxide solution for complete neutralisation. Calculate the mass of anhydrous sodium carbonate added to the hydrochloric acid solution.

Set 16: Acid-base titrations 2

Notes

Volumetric Analysis has many industrial and commercial applications where accurate concentrations of solutions are required to be known.

This set provides some more challenging investigative types of titration calculations.

Example

1. A standard sodium hydroxide solution is often used to determine the acid content of wine. As sodium hydroxide cannot be used as a primary standard a solution of approximately the required concentration must be standardised. Such a sodium hydroxide solution was standardised using a standard oxalic acid solution prepared by accurately measuring 1.575 g of oxalic acid-2-water ($H_2C_2O_4 \cdot 2H_2O$), dissolving this in water and making the solution up to exactly 250.0 mL in a volumetric flask. 20.0 mL of the sodium hydroxide solution required an average of 12.43 mL of the acid solution for complete reaction. Calculate the concentration of the sodium hydroxide solution.

   (a) Calculate the number of moles of the solid oxalic acid-2-water.
   $M(H_2C_2O_4 \cdot 2H_2O) = 126.068 \text{ g mol}^{-1}$

   $$n(H_2C_2O_4 \cdot 2H_2O) = \frac{m}{M} = \frac{1.575}{126.068} = 0.0125 \text{ mol}$$

   (b) Calculate the concentration of the standard oxalic acid solution.

   $$[H_2C_2O_4] = \frac{n}{V} = \frac{0.0125}{0.250} = 0.0500 \text{ mol L}^{-1}$$

   (c) Write an equation for the reaction.
   $H_2C_2O_4(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2O_4^{2-}(aq)$

   (d) Calculate the number of moles of standard oxalic acid used for complete neutralisation.
   $n(H_2C_2O_4) = cV = 0.0500 \times 0.01234 = 6.17 \times 10^{-4}$ mol

   (e) Calculate the number of moles of sodium hydroxide in 20.0 mL of the solution.
   $n(NaOH) = 2 \times n(H_2C_2O_4) = 2 \times 6.17 \times 10^{-4} = 1.23 \times 10^{-3}$ mol

   (f) Calculate the concentration of the sodium hydroxide solution.

   $$[NaOH] = \frac{n}{V} = \frac{1.23 \times 10^{-3}}{0.0200} = 0.0167 \text{ mol L}^{-1}$$

Set 16: Exercises

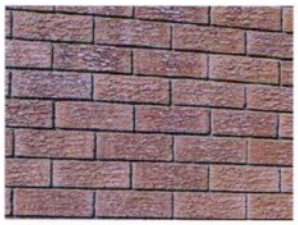
Notes

1. Prior to fermentation in wine making, the acid content of the 'must' (the grape juice) is usually tested and adjusted if required. Such an analysis was conducted by titrating the must with 20.00 mL standard 1.50×10^{-4} mol L^{-1} sodium hydroxide solution using phenolphthalein as an indicator. An average of 109.0 mL of must was required for complete reaction. Assuming all the acid present is the diprotic tartaric acid, calculate the concentration of the acid in the must.

2. A new vineyard was being established in a paddock formerly used for pasture and treated with superphosphate on a yearly basis. There was reason to suspect that the soil may have been acidic. To check that the soil's acidity was suitable for growing grape vines a sample of the soil from the paddock was tested as follows. A 150.0 g sample of soil was mixed with an equal volume of water, stirred thoroughly, allowed to stand for about one hour then the mixture filtered. The resulting solution was then titrated with 20.0 mL samples of standard sodium hydroxide solution of concentration 6.06×10^{-5} mol L^{-1}. An average of 48.0 mL of the solution was required for complete reaction. Assuming all the acids present were monoprotic, calculate the acid concentration of the soil.

3. Water from a domestic bore that sprayed onto a nearby wall was observed to leave white deposits on its surface. This led to the suspicion that the water may have been significantly alkaline due to the presence of hydrogencarbonate ions. This was confirmed by testing with red litmus which turned blue when placed into the water. To determine the actual pH, 20.0 mL samples of the water were titrated with standard 3.76×10^{-6} mol L^{-1} hydrochloric acid solution. An average of 33.6 mL of the standard acid solution was required for complete reaction. If the only substance in the bore water that reacts with the acid is the hydrogencarbonate ion, calculate its concentration.

Question 2: Vinyard



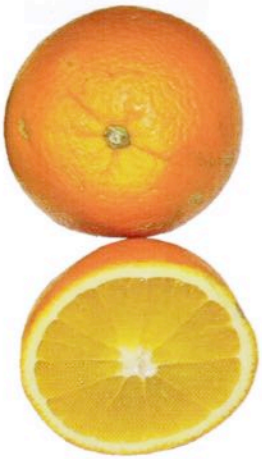
Question 3: Wall

4. The pH of swimming pool water needs to be in the range of around 7.2 to 7.6 for the comfort and safety of swimmers. With the addition of sodium hypochlorite to control bacterial and algal growth the water tends to become alkaline. The water of the local swimming pool was tested by titration to determine the concentration of titratable base it contains. An average of 47.23 mL of standard 6.72×10^{-7} mol L^{-1} hydrochloric acid solution was required to neutralise 20.0 mL samples of the pool water. Calculate the concentration of titratable base in of the water.

5. The pH of fresh milk is between 6.4 and 6.8. Over a period of four or five days the pH can drop to below 5 as lactose is converted to the diprotic lactic acid. A sample of five day old milk was analysed as follows. The milk was centrifuged to remove fats and other insoluble materials. The remaining, almost clear solution was titrated with 20.0 mL samples of standard 3.41×10^{-5} mol L^{-1} sodium hydroxide solution. If 34.2 mL of the milk solution was required for complete reaction, calculate the concentration of the lactic acid in the milk.

Question 5: Milk

Set 16: Acid-base titrations 2



Question 7: Oranges

NOTES

6. Concentrated 12 mol L^{-1} hydrochloric acid solution used to decrease the pH of swimming pool water tends to become diluted over time as hydrogen chloride gas leaves the solution. The actual concentration of the acid was determined by titration. as follows. A 5.00 mL sample of the concentrated acid was placed into a 1.00 L volumetric flask and distilled water added to the mark. An average of 38.2 mL of the dilute acid solution was required to neutralise 20.0 mL samples of standardised 0.107 mol L^{-1} sodium hydroxide solution. Calculate the concentration and the pH of the concentrated acid.

7. Orange juice is acidic mostly because it contains citric acid ($H_3C_6H_5O_7$), a triprotic acid. A sample of orange juice was filtered then analysed for its acid content by titration. A 50.0 mL sample of juice was titrated with a standardised 0.00120 mol L^{-1} solution of NaOH, using phenolphthalein as an indicator. An average of 21.5 mL of the NaOH solution was required for complete neutralisation. If all the acidity of the orange juice was due to the citric acid calculate the concentration of citric acid in the juice measured in parts per million. The density of the filtered juice was measured to be 1.05 g mL^{-1}.

8. A medical chemist working in a hospital laboratory was required to determine the pH of a sample of gastric fluid from the stomach of a patient. Gastric fluid contains hydrochloric acid. She was able to obtain about 12 mL of the gastric fluid of which she used exactly 10.0 mL for the analysis. The procedure she used was as follows.

   She placed the measured 10.0 mL of the gastric fluid into a 250.0 mL volumetric flask and filled the flask to the mark with distilled water, thoroughly mixing the solution. She then titrated the diluted gastric fluid with 20.0 mL amounts of the only suitable standard solution she had available. This was a 0.000671 mol L^{-1} of standardised ammonia solution. The results she obtained are summerised in the table.

	Rough Trial	Trial 1	Trial 2	Trial 3	Trial 4
Initial Reading (mL)	0.31	0.87	1.69	1.01	0.76
Final Reading (mL)	38.86	39.24	40.39	39.44	39.16
Amount used (mL)					

   (a) Write an equation for the reaction that occurs during the titration.
   (b) Calculate the pH of the gastric fluid.
   (c) (i) Sketch a graph of the pH (vertical axis) verses the volume of dilute gastric fluid added for one of the titrations. Continue the graph until at least an excess of 20 mL of the dilute gastric fluid is added.
   (ii) Referring to Table 12.1 on page 178, name a suitable indicator that the chemist can use for this titration?
   (iii) Justify your choice of indicator by referring to the graph you sketched.

Notes

9. Water from another domestic bore that sprayed onto a nearby fence was observed to leave orange-brown deposits on its surface. This indicated that the water contained iron compounds. The water was analysed for iron by titration in the following way. Air was bubbled through a 250.0 mL sample of the water for several hours to convert all the dissolved iron into Fe^{3+} then boiled to precipitate all the calcium ions as calcium carbonate. The solid was removed by filtration then 10.0 mL of standard 0.103 mol L^{-1} sodium hydroxide was added to the bore water which precipitated all the iron in the sample and left some excess sodium hydroxide in the solution. After the mixture was filtered it required 27.34 mL of standard 0.0277 mol L^{-1} hydrochloric acid for neutralisation. If the density of the bore water was 1.01 g mL^{-1} calculate the concentration of iron in the bore water measured in parts per million.

10. A 9.87 g sample of lead ore, composed mostly of Cerussite (lead(II) carbonate) was analysed as follows. The sample was ground to a fine powder then placed into 50.0 mL of 2.00 mol L^{-1} nitric acid until no further reaction occurred. The solution was boiled to drive off all the carbon dioxide then 20.0 mL samples were titrated with standard 0.156 mol L^{-1} sodium hydroxide solution. An average of 35.76 mL of the standard solution was required for complete neutralisation. Calculate the percentage by mass of lead in the sample.

Question 10: Lead ore

Set 17: Acids and bases in action

Notes

Acid and base reactions

Write ionic equations and give appropriate observations and reasons for the following reactions.

1. Brick cleaning acid is used to wash a limestone mortar from a wall.
2. The antacid, Milk of Magnesia, is mixed with lemon juice.
3. Alka-Seltzer (sodium hydrogencarbonate) is dropped into a glass of soft drink.
4. Vinegar is mixed with household ammonia solution.
5. A ZINCALUME® (an alloy of Zn and Aℓ) gutter has had brick cleaning acid pooled in one corner.
6. A plumber has used vinegar to distinguish between a small sample of lead and magnesium.
7. Brick cleaning acid has not been rinsed from a wall and a nickel-coated light fitting is bolted to the wall.
8. Car battery acid is spilt onto the steel (iron) tray that supports it in the car.
9. A geologist uses a few drops of car battery acid to help distinguish between two rock samples, thought to be $CaCO_3$, marble and SiO_2, quartz.

Research

Question 3: Hydrangea

Question 6: The acidity of wine

1. Research the ionisation and pH of water at a variety of temperatures. Use your knowledge of equilibrium to explain your findings.

2. Research the use of salts to change the pH of soil.

3. Alum, a double salt of potassium and aluminium sulfate ($KA\ell(SO_4)_2$) is added to soil near a flowering plant called hydrangea. Addition of the salt to the soil changes the colour of the flowers produced by the plant. Find out why the flowers are a different colour if this salt is added.

4. Swimming pool water should be maintained at a pH of between 7.2 and 7.6. Find out how large changes in the pool water's pH are prevented.

5. Acid-base indicators can be obtained from many plants or their parts such roots, flowers and leaves. Research sources of such indicators, their colours in acid and base and the pH at which their colour changes.

6. The acidity of wine:
   (a) Wines contain a number of weak acids that ionise with water. Write equations for the ionisation of the following acids found in wines:
      (i) tartaric acid
      (ii) lactic acid
      (iii) malic acid
      (iv) acetic acid
   (b) What is the relationship between pH and grape ripeness?
   (c) How are adjustments made to the pH of the must (grape juice) prior to fermentation?
   (d) Describe the effect of pH on the ultimate quality of a wine.

7. Research the use of captured carbon dioxide to treat alkaline residues from the refining of alumina.

8. Buffers are used to maintain the pH of solutions for a variety of uses including the calibration of pH meters. A convenient way to make buffer solutions is to use commercially available buffer tablets. Find out the range of buffer solutions that can be made using buffer tablets.

9. Some low concentration metal ores can be concentrated or even extracted in situ by a process called acid leaching. Research the use of this process for the in situ extraction of uranium oxide.

10. Research the process for the purification of titanium dioxide (titanium(IV) oxide) with particular emphasis on the production of concentrated hydrochloric acid as a waste product.

11. Research the use of buffer solutions in agriculture.

12. Research methods of determining the pH of wine.

13. Research the use of the electrical conductivity of the reaction solution to determine the end point of a titration.

14. Human blood must maintain a pH of 7.4. Find out what can cause the pH of blood in the body to change and what processes in the blood, work to maintain a relatively constant pH.

Notes

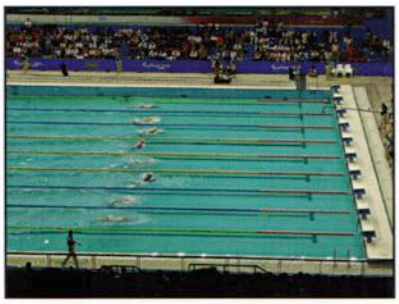
Question 10: Titanium dioxide

Extended answer questions

To answer the following extended answer questions, where applicable, use equations, diagrams and illustrative examples of the chemistry you are describing. Your answer should focus on the relevant chemical content specific to the situations described. Be sure your answer is presented in a logical and coherent manner.

1. Swimming Pool Maintenance

As a consultant to a swimming pool maintenance company you are required to advise the maintenance team on the best strategy for the regular maintenance of a large aquatic complex incorporating an Olympic size 50 m pool, a diving pool and a wading pool. The swimmers have been complaining of stinging eyes, excessive chlorine smell and bleaching of hair and bathing suits. You are required to investigate the cause of these problems and suggest to the maintenance team how they can correct these problems.



Notes

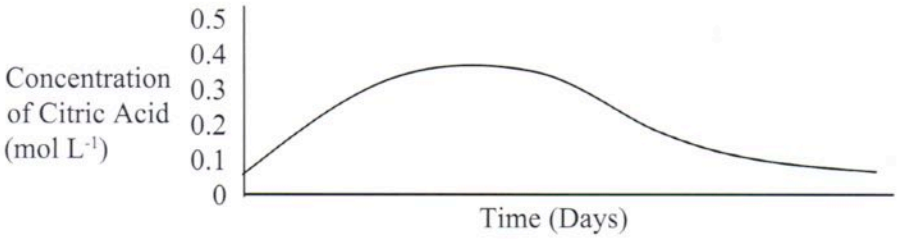
Copper ore

2. In situ acid leaching

A mining company has discovered a very large but low grade copper ore deposit. The copper is mostly in the form of oxides, hydroxides and carbonates. The company management, acting on the advice of their chemical engineer believes that the most economical method of extraction is the use of acid leaching of bulk stock piles of the crushed ore. In this process sulfuric acid solution is sprayed onto the top of the ore stock piles, allowed to seep through the ore and collected as it seeps out of the bottom of the stock pile. After conducting a pilot project the company employees encountered two significant problems. Firstly the rate at which the acid percolated through the stock pile was extremely slow and became even slower with time and secondly the amount of copper leached from the ore was only about 20% of the total copper content. As a consulting chemical engineer you are engaged to investigate these problems and suggest possible solutions.

3. Acid concentration in citrus fruits

Citrus fruits such as mandarins contain citric acid, a triprotic acid with a formula $H_3C_6H_5O_7$. The amount of citric acid in the fruit changes as the fruit grows and ripens. A researcher was interested in investigating how the amount of citric acid in mandarins changes during the ripening process. He designed an experiment that produced the results in the graph.



Mandarins at various stages of ripening

Describe a possible experiment the researcher could have used to obtain the results he used to plot the graph. Your answer should explain in detail how the concentration of citric acid was determined. It should include the names and concentration, where appropriate, of substances used, details of equipment used and samples of calculations employed.

Oxidation and Reduction

The problem sets in the oxidation and reduction section of Exploring Chemistry Year 12: Experiments, Investigations and Problems, provides opportunities for students to explore:

- oxidation number, writing and balancing half equations and full redox equations
- galvanic cells, standard reduction potentials and the calculations of cell voltage and predicting cell reactions
- electrolytic cells, their construction and the identification and prediction of electrode reactions and products together with the calculation of cell voltage

Set 18: Oxidation number

Notes

The oxidation number of an atom in a molecule or ion is a number which indicates qualitatively its state of oxidation. The number is determined by applying the following rules:

	Rule	Example
1	For elements in the free form, the oxidation number is 0.	Cu, Fe, C, O_2, N_2
2	For monatomic ions, the oxidation number is the charge on the ion. (The oxidation number of Group 1 elements is +1)	Na^+, K^+, H^+, O^{2-}, F^-
3	For combined oxygen, the oxidation number is -2, except in peroxides such as H_2O_2 and Na_2O_2 where it is -1 and OF_2 where it is +2	O.N. of oxygen is -2 in each of H_2O, SO_4^{2-}, H_3PO_4
4	For combined hydrogen, the oxidation number is +1, except in metal hydrides, such as LiH, where it is -1.	O.N. of hydrogen is +1 in each of H_2O, OH^-, H_3PO_4
5	For a molecule the sum of the oxidation numbers of the constituent atoms is zero.	H_2O 2xO.N.(H) + O.N.(O) = 0 2x(+1) + (-2) = 0
6	For an ion, the sum of the oxidation numbers of the constituent atoms is equal to the charge on the ion.	OH^- O.N.(H) + O.N.(O) = -1 (+1) + (-2) = -1

Example

1. What is the oxidation number of chlorine in potassium perchlorate ($KC\ell O_4$)?

	K		Cℓ		O	
Oxidation number (O.N.)	(+1)		?		(-2)	
Since	(+1)	+	(?)	+	4(-2)	= 0
Then			O.N.(Cℓ)			= +7

2. Determine the oxidation number of sulfur in the hydrogen sulfite ion (HSO_3^-)

	H		S		O	
Oxidation number (O.N.)	(+1)		?		(-2)	
Since	(+1)	+	(?)	+	3(-2)	= -1
Then			O.N.(S)			= +4

Changes in oxidation number

Oxidation involves an increase in oxidation number, while reduction involves a decrease in oxidation number. In an oxidation-reduction reaction oxidation and reduction occur simultaneously. One element must undergo an increase in oxidation number, while another undergoes a decrease in oxidation number. If none of the oxidation numbers change, then the reaction is not an oxidation-reduction reaction.

To identify which elements have changed oxidation number the following rules are applied:

1. Ignore the coefficients of substances in the equation;
2. Identify the oxidation numbers of each of the elements;
3. Determine which elements have changed their oxidation number.

Example

Determine which elements have undergone oxidation and reduction in the reaction represented by the equation: $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

Step 1: Assign oxidation numbers for each element

NH_3		O_2	NO		H_2O	
Nitrogen (-3)	Hydrogen (+1)	Oxygen (0)	Nitrogen (+2)	Oxygen (-2)	Hydrogen (+1)	Oxygen (-2)

Step 2: Identify any changes to oxidation numbers for each element

Nitrogen (-3)	Oxygen (0)	Nitrogen (+2)	Oxygen (-2)	Oxygen (-2)

Step 3: An increase in oxidation number shows oxidation of an element

Nitrogen (-3)	Nitrogen (+2)

An decrease in oxidation number shows reduction of an element

Oxygen (0)	Oxygen (-2)	Oxygen (-2)

Step 4: State your answer: Nitrogen in the ammonia has been oxidised. Oxygen gas has been reduced.

Set 18: Exercises

1. Determine the oxidation number of the element in **bold** type in each of the following:

(a) $\mathbf{S}O_2$	(h) $[\mathbf{Cu}(NH_3)_4]^{2+}$	(o) H**C**OOH	(v) **Sn**O
(b) $H_2\mathbf{S}$	(i) $H_3\mathbf{P}O_4$	(p) $\mathbf{N}O_2$	(w) $\mathbf{Cu}_2O$
(c) $H_2\mathbf{S}O_4$	(j) $Mg_2\mathbf{P}_2O_7$	(q) $\mathbf{N}_2O$	(x) **Cu**S
(d) $Na_2\mathbf{S}_2O_3$	(k) $\mathbf{C}H_4$	(r) $\mathbf{N}H_4C\ell$	(y) $\mathbf{Fe}C\ell_2$
(e) $\mathbf{S}F_6$	(l) $\mathbf{C}O_2$	(s) Na$\mathbf{N}O_3$	(z) $\mathbf{Fe}_2O_3$
(f) $\mathbf{P}_2O_5$	(m) $\mathbf{C}H_3OH$	(t) $\mathbf{N}_2H_4$	
(g) $\mathbf{P}H_3$	(n) H**C**HO	(u) $\mathbf{Sn}C\ell_4$	

2. For each of the following reactions determine whether any elements have undergone a change in oxidation number and note whether they have been oxidised or reduced.
   (a) $Mg + O_2 \rightarrow 2\ MgO$
   (b) $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$
   (c) $C\ell_2 + 2\ I^- \rightarrow I_2 + 2\ C\ell^-$
   (d) $3\ H_2S + 2\ HNO_3 \rightarrow 3\ S + 2\ NO + 4\ H_2O$
   (e) $2\ MnO_4^- + 5\ H_2S + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ S + 8\ H_2O$
   (f) $2\ SnC\ell_2 + 4\ HC\ell + O_2 \rightarrow 2\ SnC\ell_4 + 2\ H_2O$
   (g) $H_2SO_4 + 2\ HBr \rightarrow SO_2 + Br_2 + 2\ H_2O$
   (h) $Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$
   (i) $2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$
   (j) $NH_4NO_2 \rightarrow N_2 + 2\ H_2O$
   (k) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$
   (l) $Na_2CO_3 + 2\ HC\ell \rightarrow 2\ NaC\ell + CO_2 + H_2O$
   (m) $HC\ell + NaOH \rightarrow NaC\ell + H_2O$
   (n) $H_2S + CuC\ell_2 \rightarrow CuS + 2\ HC\ell$

Notes

Set 19: Balancing half equations

Notes

Redox equations are often complex and a special method, the half equation method, can be used to balance them.

To balance a half equation the following procedure can be used.

1. Set out the reactant and product, together with the respective oxidation numbers, in equation form.
2. Balance the number of atoms of the element that is oxidised or reduced.
3. Balance oxygen atoms in aqueous solutions by adding water, H_2O, to the appropriate side of the half equation.
4. Balance hydrogen atoms in aqueous solutions by adding H^+ to the appropriate side of the half equation.
5. Add electrons to the side of the equation that will balance charge.
   You can check this using oxidation numbers, in the following way.
   Calculate the change in oxidation number of the element from reactant to product. If there is an increase in oxidation number, add an equal number of electrons to the right-hand side of the equation. If there is a decrease in oxidation number add the electrons to the left-hand side of the equation. If more than one atom is oxidised or reduced, the number of electrons added to the half equation equals the number of atoms of the element multiplied by the change in oxidation number.

Examples

1. Balance the half equation for Fe^{2+} being oxidised to Fe^{3+}

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

2. Balance the half equation for the reduction of Br_2 to Br^-

Br_2	$\rightarrow$	Br^-
(0)		(-1)
Br_2	$\rightarrow$	$2Br^-$
(0)		2 x (-1)
$Br_2 + 2e^-$	$\rightarrow$	$2Br^-$

Set 19: Exercises

Balance the following half equations and state whether they are reduction or oxidation.

1. $Mg \rightarrow Mg^{2+}$
2. $S \rightarrow S^{2-}$
3. $C\ell^- \rightarrow C\ell_2$
4. $Ca \rightarrow Ca^{2+}$
5. $I_2 \rightarrow I^-$
6. $Zn \rightarrow Zn^{2+}$
7. $Cu^+ \rightarrow Cu^{2+}$
8. $Au^+ \rightarrow Au$
9. $H^+ \rightarrow H_2$
10. $Cu^{2+} \rightarrow Cu$

Extra for experts: Unless stated otherwise, assume acidic conditions.

11. $AsO_3^{3-} \rightarrow AsO_4^{3-}$
12. $S_2O_3^{2-} \rightarrow SO_4^{2-}$
13. $NO_3^- \rightarrow NH_4^+$
14. $MnO_4^- \rightarrow Mn^{2+}$

Set 20: Balancing redox equations

Notes

To write a balanced redox equation the following procedure is used:

1. Break the overall equation into two half equations, one which represents the oxidation half reaction, the other the reduction half reaction.
2. Balance the separate half equations.
3. Multiply each half equation by a number chosen so that the number of electrons lost in the oxidation half equation equals the number gained in the reduction half equation.
4. Add the two half equations resulting from the multiplications and cancel out the electrons and any other species that appear on both sides of the equation in equal numbers.

Example

Write a balanced equation for the reaction

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

1. MnO_4^- (+7) $\rightarrow$ Mn^{2+} (+2) and H_2O_2 (-1) $\rightarrow$ O_2 (0)

2. $(MnO_4^- + 5\,e^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O) \times 2$

   $(H_2O_2 \rightarrow O_2 + 2\,H^+ + 2\,e^-) \times 5$

3. $2\,MnO_4^- + 10\,e^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 8\,H_2O$

   $5\,H_2O_2 \rightarrow 5\,O_2 + 10\,H^+ + 10\,e^-$

4. $2\,MnO_4 + H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$

Set 20 Exercises

Write balanced equations for the following redox reactions:

1. $Br_2 + I^- \rightarrow Br + I_2$
2. $Cu + Ag^+ \rightarrow Cu^{2+} + Ag$
3. $Mg + Pb^{2+} \rightarrow Mg^{2+} + Pb$
4. $Mg + H^+ \rightarrow Mg^{2+} + H_2$
5. $A\ell + H^+ \rightarrow A\ell^{3+} + H_2$
6. $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
7. $A\ell + Zn^{2+} \rightarrow A\ell^{3+} + Zn$
8. $Cu + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$
9. $Zn + Ag^+ \rightarrow Zn^{2+} + Ag$
10. $C\ell_2 + I^- \rightarrow C\ell^- + I_2$

Extras for experts: write balanced equations for the following.

11. $Li + H_2O \rightarrow Li^+ + OH^- + H_2$
12. $Cu + NO_3^- + H^+ \rightarrow Cu^{2+} + NO_2$
13. $Cu + SO_4^{2-} + H^+ \rightarrow Cu^{2+} + SO_2$
14. $H_2O_2 \rightarrow H_2O + O_2$
15. $Cr_2O_7^{2-} + C_2H_5OH \rightarrow Cr^{3+} + CH_3CHO$
16. $Mg + H_2O \rightarrow Mg^{2+} + H_2$
17. $Cu_2O \rightarrow Cu + Cu^{2+}$
18. $Au + CN^- + O_2 \rightarrow [Au(CN)_4]^- + H_2O$

Set 20: Balancing redox equations

Notes

19. The degree of unsaturation of a fat can be determined by reacting the fat with a known quantity of iodine, I_2. The iodine that does not react with oil is titrated against a sodium thiosulfate solution of known concentration. From this information, the food chemist can determine how much iodine reacted with the fat, and how unsaturated it is.
    (a) Write a balanced half-equation for the conversion of iodide ions to iodine molecules.
    (b) Write a balanced half-equation for thiosulfate ions ($S_2O_3^{2-}$) becoming sulfate ions.
    (c) Combine the two equations to give an overall balanced equation.

20. Ethanol (CH_3CH_2OH) is the alcohol component of wines, beer and spirits. When a bottle of wine is opened, the ethanol is exposed to oxygen in the atmosphere. If the wine is left open for a long period of time, the wine will acquire a strong taste of vinegar. This is because the ethanol becomes oxidised to acetic acid.
    (a) Write a balanced half-equation for the oxidation of ethanol to acetic acid (CH_3COOH).
    (b) Write a balanced half-equation for the reduction of oxygen gas to hydroxide ions.
    (c) Combine the two half-equations to produce a balanced equation.

21. Photosynthesis and respiration are oxidation-reduction processes essential for plants and animals. Photosynthesis is the formation of glucose ($C_6H_{12}O_6$) and oxygen gas from carbon dioxide and water. Respiration is the reverse process.
    (a) Write a balanced equation for the respiration process. You do not need to write half-equations first.
    (b) Using oxidation numbers, identify what is oxidised and what is reduced.
    (c) What is the oxidising agent and what is the reducing agent?

22. Titanium metal is used for making artificial hip joints and for plating together badly broken bones because it is resistant to oxidation and does not appear to interact with any bodily processes. However, titanium metal is very difficult to produce. Titanium tetrachloride vapour at 900 °C is mixed with molten magnesium metal to form solid titanium metal and molten magnesium chloride.
    (a) Write a balanced equation for this reaction starting with two half-equations.
    (b) What is being oxidised? What is the oxidising agent?
    (c) What is being reduced? What is the reducing agent?

23. Nitrogen dioxide is one of the gaseous pollutants given off by cars in their exhaust. Nitrogen dioxide is able to cause acid rain because it will dissolve in water in rain clouds to produce nitric acid and nitric oxide (NO).
    (a) Write a balanced overall equation for the reaction.
    (b) Identify the oxidising agent and the reducing agent.
    (c) What is the special term given to this type of oxidation-reduction reaction where a substance reacts with itself?

Set 21: Galvanic cells

Notes

Galvanic cells

A galvanic cell is a device in which an oxidation-reduction reaction is used to generate an electric current.

Standard reduction potential

The standard reduction potential of a half-cell is a measure of its tendency to accept electrons with reference to the standard hydrogen electrode.

Cell emf

The cell potential for a redox reaction is the voltage generated when two half-cells are combined to form a galvanic cell. A table of standard reduction potentials is included on the page opposite the inside back cover of this book.

Examples

1. (a) Calculate the standard cell voltage for a cell which consists of the Ag^+ / Ag half-cell and the Br_2 / Br^- half-cell.

   (i) List half-cell reactions and reduction potentials.

   $Ag^+ + e^- \rightarrow Ag \quad E° = +0.80\ V$
   $Br_2 + 2\ e^- \rightarrow 2\ Br^- \quad E° = +1.08\ V$

   (ii) Select the most positive half-cell potential. This half-reaction goes as written.

   (iii) Reverse the direction of the other half-cell reaction and change the sign of the half-cell potential.

   $Ag \rightarrow Ag^+ + e^- \quad E° = -0.80\ V$
   $Br_2 + 2\ e^- \rightarrow 2\ Br^- \quad E° = +1.08\ V$

   (iv) Calculate cell voltage by adding half-cell potentials

   Cell voltage $= +1.08 - 0.80$
   $= +0.28\ V$

   (b) Write a balance equation that represents the overall reaction.
   To determine the overall cell reaction, multiply the half-cell equations by numbers, which balance the electrons in the two equations and add the resulting equations.

$$(Ag \rightarrow Ag^+ + e^-) \times 2$$
$$Br_2 + 2\ e^- \rightarrow 2\ Br^-$$
$$2\ Ag \rightarrow 2\ Ag^+ + 2\ e^-$$
$$Br_2 + 2\ e^- \rightarrow 2\ Br^-$$
$$2\ Ag + Br_2 \rightarrow 2\ Ag^+ + 2\ Br^-$$

Notes

2. Predict whether the reaction below would occur in aqueous solution. All concentrations are 1 mol L^{-1}.

$$2\ Fe^{3+} + 2\ Br^- \rightarrow 2\ Fe^{2+} + Br_2$$

(a) Identify half-reactions involved

$Fe^{3+} \rightarrow Fe^{2+}$
$Br^- \rightarrow Br_2$

(b) Write half-cell equations and reduction potentials

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\quad E° = +0.77$ V
$2\ Br^- \rightarrow Br_2 + 2\ e^-$ $\quad E° = -1.08$ V

(c) Calculate cell voltage

Cell voltage = +0.77 - 1.09
= - 0.32 V

(d) Since cell voltage is negative the reaction is not expected to occur spontaneously. If a reaction has a positive cell voltage it could occur as written.

Set 21 Exercises

1. For each of the following electrochemical cells
(i) $Zn / Zn^{2+} // Sn^{2+} / Sn$ (ii) $Fe / Fe^{2+} // Ag^+ / Ag$

(a) draw a diagram similar to that shown in Figure 23.1.
(b) Write the half-equation for the reaction occurring in each half-cell.
(c) Write an equation for the total reaction.
(d) Label the anode and the cathode.
(e) Mark the direction of electron flow through the wire.
(f) Show the direction of movement of positive and negative ions through the salt bridge.
(g) Calculate the cell potential, from a list of standard reduction potentials.

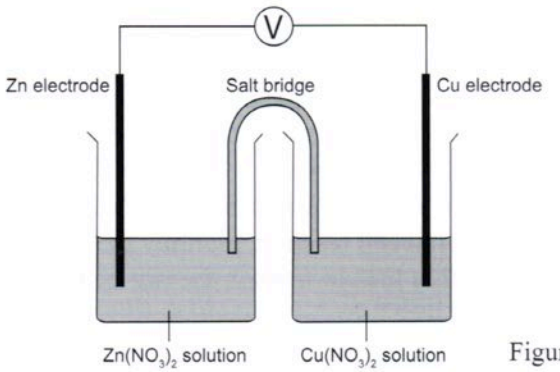


Figure 23.1

2. Calculate the standard cell voltages and write the overall chemical reactions for cells that consist of the following half-cells
(a) Cr^{3+} / Cr and Ag^+ / Ag
(b) Mg^{2+} / Mg and Cu^{2+} / Cu
(c) Mg^{2+} / Mg and Ag^+ / Ag
(d) Fe^{3+} / Fe^{2+} and $Cr_2O_7^{2-} / Cr^{3+}$ ($Cr_2O_7^{2-}$ is acidified)
(e) $C\ell_2 / C\ell^-$ and I_2 / I^-

Notes

3. Predict whether the following reactions could occur under standard conditions. Show your reasoning as demonstrated in example 2
   (a) $2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2\ Mn^{2+} + 5\ I_2 + 8\ H_2O$
   (b) $Sn^{2+} + H_2O_2 \rightarrow Sn + 2\ H^+ + O_2$
   (c) $Cr_2O_7^{2-} + 6\ F^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ F_2 + 7\ H_2O$
   (d) $Cu + 2\ H^+ \rightarrow Cu^{2+} + H_2$

4. (a) Which of the following species could react with 1 mol L^{-1} $HC\ell$ to form hydrogen gas? Show your reasoning.
   (i) Cu
   (ii) Mg
   (iii) Sn
   (iv) Ag
   (v) Sr
   (vi) Zn

   (b) From the table of reduction potentials (inside back cover), identify
   (i) a reducing agent which could convert Pb^{2+} to Pb, but not Co^{2+} to Co.
   (ii) an oxidising agent which could convert $C\ell^-$ to $C\ell_2$, but not F^- to F_2.
   (iii) a reductant which could convert H^+ to H_2, but not H_2O to H_2.
   (iv) an oxidant which could convert Ag to Ag^+, but not Au to Au^{3+}.
   (v) a reductant which could convert acidified MnO_4^- to Mn^{2+}, but not acidified $Cr_2O_7^{2-}$ to Cr^{3+}.

5. A disproportionation reaction involves a substance reacting with itself in a redox process. Predict whether the following disproportionation reactions could occur in aqueous solution. Show your reasoning.
   (a) Iron(II) ion to iron(III) ion and iron metal
   (b) hydrogen peroxide to water and oxygen gas
   (c) chlorine to hypochlorous acid and chloride ion

6. Predict whether reactions could occur in each of the following. Assume standard conditions. Show your reasoning.
   (a) Chlorine gas is bubbled through potassium bromide solution.
   (b) Iron(II) nitrate is mixed with sodium iodide.
   (c) Aluminium is added to hydrochloric acid.
   (d) An iron nail is placed in a tin(II) chloride solution.
   (e) An iron(II) sulfate solution is placed in a nickel container.
   (f) Hydrogen sulfide is bubbled through an acidified potassium dichromate solution.
   (g) Chlorine gas is bubbled through an acidified solution of barium nitrate.
   (h) Chlorine gas is bubbled through an acidified solution of iron(II) bromide.

Set 22: Electrolytic cells

Notes

Electrolysis is a process that uses electrical energy to produce a chemical change. Electrolysis occurs in an electrolytic cell. As with galvanic cells oxidation occurs at the anode and reduction occurs at the cathode. But unlike galvanic cells in an electrolytic cell the cathode is labelled negative and the anode is positive and the two electrodes are usually immersed in a common electrolyte.

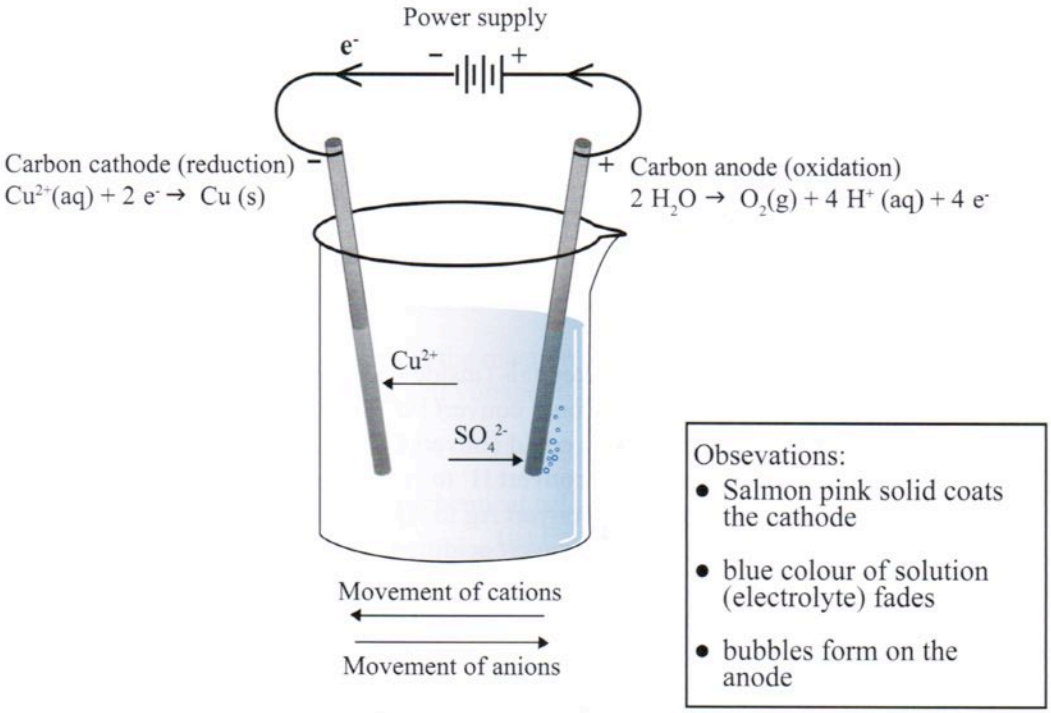


Figure 24.1: Electrolysis of copper sulfate

The products of electrolysis depend on the nature of the electrolyte and electrode material. In the electrolysis of a molten metalic salt using inert electrodes the metalallic cations are reduced at the cathode and the anions are oxidised at the anode. This is shown in as in Figure 24.1. Inert electrodes like carbon and platinum are rarely involved in electrolysis reactions. However, if a reactive metal is used at the anode, it may undergo oxidation in preference to other reactions. The products of electrolysis in aqueous electrolyte solutions also depend on the relative E^o values of the possible half reactions at the electrodes (see example 2), and the concentration of reactants.

The concentration of ions in an aqueous electrolyte can influence the products formed at the anode and cathode of an electrolytic cell. For example by increasing the concentration of chloride ions can favour the formation of chlorine gas at the anode, while increasing the concentration of hydrogen ions (acidity) will favour the formation of hydrogen gas.

Examples

1. In the electrolysis of 1 mol L^{-1} KI solution with inert electrodes, predict

   (a) the products formed at each electrode,
   (b) the overall reaction, and
   (c) the minimum voltage which must be applied to produce the overall reaction.

Notes

(a) (i) List possible reactions at each electrode and their potentials. Cathode:

$K^+(aq) + e^- \rightarrow K(s)$ $E° = -2.93$ V
$2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^- (10^{-7} \text{ mol } L^{-1})$ $E = -0.41$ V

Anode:
$2 I^-(aq) \rightarrow I_2(s) + 2 e^-$ $E° = -0.54$ V $E° = -0.54$ V
$2 H_2O(\ell) \rightarrow O_2(g) + 4 e^- + 4 H^+(aq) (10_{-7} \text{ mol } L^{-1})$ $E = -0.82$ V

(ii) Select the reaction, at each electrode, with the more positive potential as the probable reaction.

Cathode:
$2 H_2O(\ell) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$

Anode:
$2 I^-(aq) \rightarrow I_2(s) + 2 e^-$

(b) Determine the overall reaction.

$2 I^-(aq) + 2 H_2O(\ell) \rightarrow H_2(g) + I_2(s) + 2 OH^-(aq)$

(c) To determine the minimum applied voltage, add the half reaction potentials and change the sign.

$E = -0.41 + (-0.54)$
$= -0.95$ V

Therefore the minimum applied voltage required is + 0.95 V

2. For the electrolysis of a 1 mol L^{-1} $CuSO_4$ solution with copper electrodes, indicate

(a) the products formed at each electrode,
(b) the overall reaction, and
(c) the minimum voltage which must be applied to produce the overall reaction.

(a) (i) Cathode:
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ $E° = +0.34$ V $E° = +0.34$ V
$2 H_2O(\ell) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq) (10^{-7} \text{ mol } L^{-1})$ $E = -0.41$ V

Anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2 e^-$ $E° = -0.34$ V $E° = 0.34$ V
$2 H_2O(\ell) \rightarrow O_2(g) + 4 e^- + 4 H^+(aq) (10^{-7} \text{ mol } L^{-1})$ $E = -0.82$ V

(ii) Cathode:
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$

Anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2 e^-$

(b) No net equation but copper deposited at the cathode and dissolved at the anode.

(c) $E° = +0.34 + (-0.34)$
$= 0.00$ V

Therefore the minimum applied voltage is 0.00 V

Set 22: Electrolytic cells

Notes

Set 22 Exercises

1. A 1.0 mol L^{-1} aqueous solution of copper (II) Iodide, CuI_2, is electrolysed using inert carbon electrodes.
   (a) Draw a diagram of the electrolytic cell, identifying the anode and cathode, and the direction of current flow in the external circuit and through the electrolyte.
   (b) Write half-equations for reactions at the electrodes (anode and cathode).
   (c) Using standard reduction potential (E^o values) calculate the minimum e.m.f needed to electrolyse the solution under standard conditions.
   (d) Describe what you would expect to obseve (colour changes, bubles of gas etc) during this electrolysis.

2. In the electrolysis of each of the following predict

   (i) the products formed at each electrode,
   (ii) the equations for the cathode and anode reactions,
   (iii) the overall reaction,
   (iv) the minimum voltage which must be applied to produce the overall reaction, and
   (v) what you would expect to observe at each of the electrodes. Assume inert electrodes.

   (a) 1.0 mol L^{-1} aqueous solution of HBr
   (b) 1.0 mol L^{-1} aqueous solution of NiI_2
   (c) Molten $KC\ell$
   (d) Molten $PbBr_2$
   (e) Molten $CoC\ell_2$

3. (a) Using inert electrodes predict the product for the electrolysis of Molten $AlC\ell_3$
   (b) When Aqueous $AlC\ell_3$ is electrolysed, hydrogen is produced at the cathode and oxygen is produced at the anode.
   Explain why different products are formed from those in (a).

4. Electrolytic cells are used in a range of industrial situations.
   Draw a labelled diagram of the electrolytic cell, and write half-equations for reactions at the electrodes, for each of the industrial processes:
   (a) The electrorefining of copper metal.
   (b) Electroplating of silver metal onto an item of jewelry.
   (c) The electrolytic reduction of alumina to aluminium metal by the Hall-Héroult process.

Set 23: Oxidation and reduction

Set 23 Exercises

1. Fuel cells are a serious alternative to the combustion engine found in most cars. The reacting materials are stored in tanks and are fed through pipes into the fuel cell for reaction.
   a) One well-known fuel cell consists of hydrogen gas reacting with oxygen gas to produce water. This is the type of fuel cell used on the space shuttle. Write balanced half-equations and an overall equation for the hydrogen fuel cell.
   b) Another fuel cell gaining attention from car manufacturers is the methanol fuel cell. Methanol (CH_3OH) is a by-product of breweries and can also be made by fermenting vegetation. In the fuel cell, methanol is oxidised to carbon dioxide gas while oxygen gas is reduced to water vapour. Write balanced half-equations and an overall equation for the methanol fuel cell.
   c) Compare the two fuel cells in terms of their "environmental friendliness".

2. Before steel is chrome plated it is first electroplated with copper. If your chromium-plated steel bicycle gets scratched after you park it at the bike racks, will it rust faster or slower now because of the chrome plate damage?

3. Tarnished silver items are coated in a layer of silver sulfide. The tarnish can be removed by placing the silverware into an aluminium saucepan containing salt water. Explain the electrochemistry behind this cleaning technique.

Extended answer questions

To answer the following extended answer questions, where applicable, use equations, diagrams and illustrative examples of the chemistry you are describing. Your answer should focus on the relevant chemical content specific to the situations described. Be sure your answer is presented in a logical and coherent manner.

1. A research chemist has been supplied with a piece of the hull of the Titanic and asked to determine the percentage of iron in the sample. Describe how the chemist would go about using volumetric analysis to test the hull sample. Describe the procedures and equipment required. In your answer include an outline of the calculations that would also be required.

2. Corrosion of iron is dependent upon the oxygen and water contacting the metal surface, therefore the easiest way to prevent corrosion is to place a physical barrier (eg. paint, grease or another metal) on the metal surface. Other ways of preventing oxidation of the metal are to supply it with an electric current, modify the environment around the metal, modify the structure of the metal, connect the metal to a sacrificial metal and use chemical corrosion inhibitors.

   Unfortunately, in most practical situations corrosion cannot be totally prevented, it can only be controlled so that a useful life is obtained from a structure.
   - Explain factors that affect corrosion of iron.
   - Explain measures that can be applied to reduce or possibly prevent corrosion.

Organic materials

The problem sets in the organic materials section of Exploring Chemistry Year 12: Experiments, Investigations and Problems, provides opportunities for students to explore:

- organic compounds, including alkanes, alkenes, amines, alcohols, aldehydes, ketones, carboxylic acids, esters and amino acids by making models
- molecular models show the arrangement of atoms and bonding in covalent molecular substances and help draw structural formulae and understand functional groups
- the characteristic reactions of hydrocarbons such as combustion, addition reactions for alkenes and reactions of alcohols, esterification and polymerisation reactions
- protein biochemistry
- calculations involving organic compounds including empirical, molecular and structural formula calculations and quantitatively using the mole concept as it relates mass, moles, molar mass and the combined gas equation

Set 24: Organic compounds

Notes

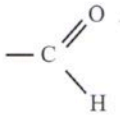
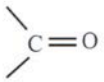
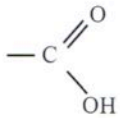
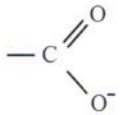
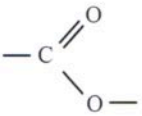
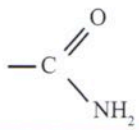
The names of simple organic compounds are based on their structure. It ensures that given the structure, a unique name can be constructed and given the name a particular structure can be drawn. The rules that govern this naming convention were adopted and first published by the Union of Pure and Applied Chemistry (IUPAC) in 1958. This set of rules has become known as the IUPAC System of Nomenclature for Organic Compounds. The rules used here include those revised in 1993.

Rules for naming and drawing carbon compounds

1. The prefix of the name is used to identify the number of carbon atoms in a continuous chain, that is, the longest chain length.

Number of carbon atoms	Prefix	Prefix for alkyl group
1	meth-	methyl
2	eth-	ethyl
3	prop-	propyl
4	but-	butyl
5	pent-	pentyl
6	hex-	hexyl
7	hept-	heptyl
8	oct-	octyl

2. Some functional groups are identified using a suffix. This includes the following groups.

Class of Compound	Functional group	Suffix
Amines	$-NH_2$	-anamine
Alcohols	-OH	-anol
Aldehyde		-anal
Ketones		-anone
Carboxylic Acids		-anoic acid
Carboxylate ions		-anoate ion
Esters		-anoate
Amides		-anamide

Set 24: Organic compounds

Notes

3. Some functional groups are identified using a prefix. This includes the following groups.

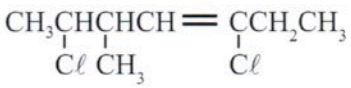
Class of compound	Functional group	Name of group
Amines	$-NH_2$	amino-
Fluorocarbon	-F	fluoro-
Chlorocarbon	$-C\ell$	chloro-
Bromocarbon	-Br	bromo-
Iodocarbon	-I	iodo-
Alkylated compounds	-R	alkyl-
Methylated compound	$-CH_3$	methyl-
Nitrated compounds	$-NO_2$	nitro-

4. The rules for naming hydrocarbons are applied as follows.
   (i) Identify the longest continuous carbon chain containing the functional group. This determines the prefix for the name.
   (ii) Assign a number to each carbon atom in the longest continuous chain starting at the end of the chain that results in the lowest possible number for the position of the functional group.
   (iii) The suffix of the name is determined by the presence of one of the functional groups in 2 above.
   (iv) Identify all groups from 3 above attached to the longest carbon chain.
   (v) Add the names of the groups from 3 above in front of the chain name, indicating the position of the group using the number of the carbon to which it is attached. If a group occurs more than once , use the prefix di-, tri-, tetra-, etc to indicate the number present and indicate the position of each as described above. A number for the location of groups is often used even though it may be redundant. The locating number is placed as close to the part of the name referring to the group as in propan-1-ol.
   (vi) Substituent groups are written alphabetically on the basis of the group name. Numbers are separated from each other by commas and numbers are separated from names by hyphens. Words are joined to make one word (tomakeoneword).

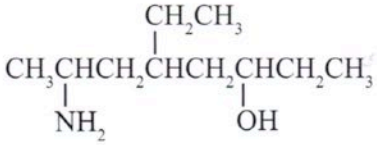
Examples

Aliphatic compounds

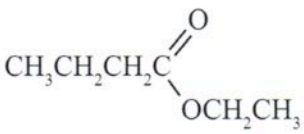
1. Write names for the following compounds

(a) 

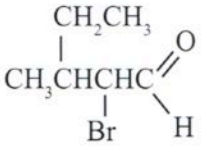
3,6-dichloro-5-methylhept-3-ene

(b) 

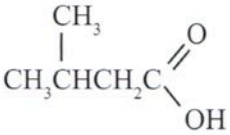
7-amino-5-ethyloctan-3-ol

(c) 

ethylbutanoate

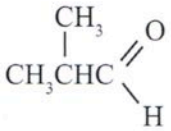
(d) 

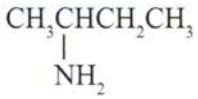
2-bromo-3-methylpentanal

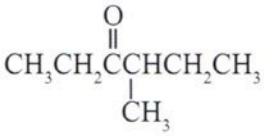
(e) 

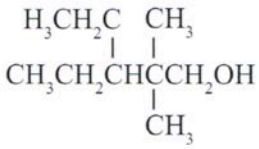
3-methylbutanoic acid

2. Draw structural formulae for the following.

(a) methylpropanal 

(b) butan-2-amine 

(c) 4-methylhexan-3-one 

(d) 3-ethyl-2,2-dimethylpentan-1-ol 

(e) butylmethanoate

Alicyclic compounds

These are ring structures formed when the ends of a carbon chain join.

The rules for naming alicyclic compounds are mostly the same as for those used to name aliphatic compounds.
There are some differences which include the following.

1. The prefix cyclo- is placed in front of the name indicating the number of carbon atoms.

2. The carbon atoms are numbered starting at the functional group and for double bonds the numbering is such that the carbon atoms either side of the multiple bond have the numbers 1 and 2.

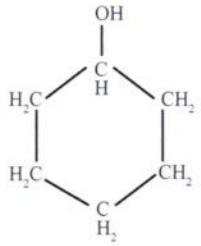
Set 24: Organic compounds

Notes

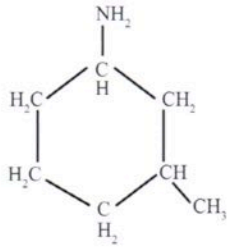
3. If more than one type of group is attached the numbering starts at the group that is first in alphabetical order.

Examples

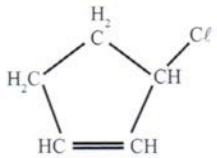
(a) Cyclohexanol ($C_6H_{11}OH$)



(b) 3-methylcyclohexanamine ($C_7H_{13}NH_2$)



(c) 3-chlorocyclopentene ($C_5H_7C\ell$)



Set 24 Exercises

1. Write the systematic names for the following structures

(a) $CH_3CH(OH)CH_3$

(b) $CH_3CH_2CH(CH_3)CH_2OH$

(c) $CH_3CH_2CH_2NH_2$

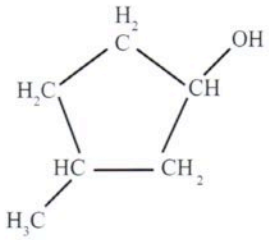
(d) $CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

(e) $CH_3CH_2CH(C\ell)CH(CH_3)CH_2CH(NH_2)CH_3$

(f) $CH_3C(CH_3)(OH)CH_2CH_3$

(g) $CH_3CH_2C(C\ell)(CH_3)CH_2CH_2CH_2OH$

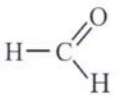
(h)



Notes

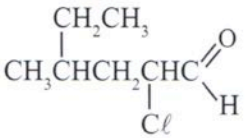
2. Draw structural formulae for the following.
   (a) pentan-1-ol
   (b) ethanamine
   (c) propan-1,2,3-triol (glycerol)
   (d) 3-bromopropan-1-ol
   (e) 1,2-dichloropropan-2-amine
   (f) 3-ethylpentan-1-amine
   (g) 4-chloro-4-methylhexan-1-ol
   (h) 5-chloro-3,4-dimethylpentan-2-amine
   (i) fluorocycloheptane

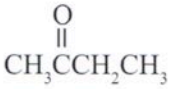
3. Write the systematic names for the following structures

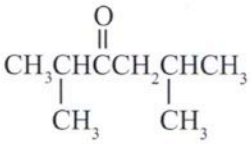
(a) 

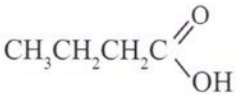
(b)

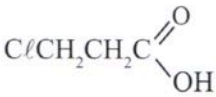
(c)

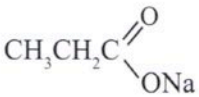
(d) 

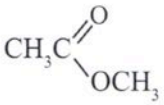
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

4. Draw structural formulae for the following.

   (a) butanal
   (b) propanone
   (c) 3-methylbutanal
   (d) 6-amino-7-bromoheptan-3-one
   (e) 2-bromobutanoic acid
   (f) ethandioic acid (oxalic acid)
   (g) methyl propanoate
   (h) propyl methanoate
   (i) potassium butanoate
   (j) cyclohexanone

5. Draw structural formulae and write systematic names for the following.

   (a) All isomeric alcohols with the formula C_4H_9OH.
   (b) one carboxylic acid and two esters with the formula $C_4H_8O_2$.
   (c) two aldehydes and one ketone with the formula C_4H_8O.
   (d) all isomers of compounds with the formula C_4H_8.
   (e) all isomers of compounds with the formula $C_5H_{10}O$.

Set 25: Reactions of organic compounds

Notes

Examples

1. Combustion of hydrocarbons as in the combustion of propane:

$$CH_3CH_2CH_3 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$$

2. Substitution in alkanes as in the chlorination of ethane:

$$CH_3CH_3 + C\ell_2 \xrightarrow{h\nu} CH_3CH_2C\ell + HC\ell$$

3. Addition in alkenes and alkynes as in the bromination of pent-2-ene:

$$CH_3CH_2CH{=}CHCH_3 + Br_2 \rightarrow CH_3CH_2CHBrCHBrCH_3$$

4. Oxidation of primary alcohols with MnO_4^- and $Cr_2O_7^{2-}$.
Example: oxidation of propan-1-ol with acidified potassium permanganate.

$$5\,CH_3CH_2CH_2OH + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CH_3CH_2C{=}O{-}H + 2\,Mn^{2+} + 8\,H_2O$$

propan-1-ol propanal

and

$$5\,CH_3CH_2C{=}O{-}H + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CH_3CH_2C{=}O{-}H + 2\,Mn^{2+} + 3\,H_2O$$

propanal propanoic acid

5. Oxidation of secondary alcohols with MnO_4^- and $Cr_2O_7^{2-}$.
Example: oxidation of propan-2-ol with acidified potassium permanganate.

$$CH_3CH(OH)CH_3 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CH_3C(=O)CH_3 + 2\,Mn^{2+} + 8\,H_2O$$

propan-2-ol propanone

6. Reaction of alcohols with carboxylic acids.
Example: ethanol with propanoic acid.

$$CH_3CH_2C{=}O{-}OH + 2\,CH_3CH_2OH \xrightarrow{H_2SO_4(conc.)} CH_3CH_2C{=}O{-}OCH_2CH_3 + H_2O$$

propanoic acid ethanol ethyl propanoate

7. Reaction of alcohols with sodium. (Optional)
Example: ethanol with sodium.

$$2\,CH_3CH_2OH + 2\,Na \rightarrow 2\,CH_3CH_2ONa + H_2$$

ethanol sodium ethoxide

Notes

Set 25 Exercises

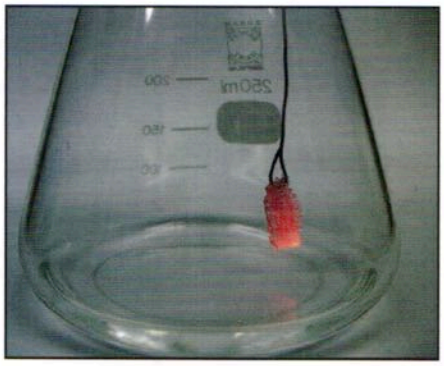
1. Hydrocarbons are mostly used as fuels as they all undergo combustion to produce heat. Write an equation for the reaction between propane and oxygen when used to heat, weld or cut metal.

2. Hydrocarbons are important starting materials for the production of many useful substances. Write equations for and name any organic products formed in the reactions between:
   (a) methane and chlorine in the presence of ultraviolet radiation.
   (b) ethene and bromine.
   (c) but-2-ene and water.
   (d) propene and hydrogen in the presence of a platinum catalyst.
   (e) cyclohexene and hydrogen bromide.

Burning propane and oxygen

3. As a research chemist you are employed to investigate the conditions that give the best yield of substituted hydrocarbons starting with simple hydrocarbons. You are required to make the following substances. If there is more than one type of reaction that could produce the product, use the reaction that occurs most readily.
Write equations for each step of the process, in each case draw the structure and name the starting hydrocarbon and name any other reagents required.
   (a) ethanol
   (b) chlorofluoromethane

4. Write balanced half equations for the following reactions.
   (a) catalytic oxidation of methanol to methanal
   (b) oxidation of ethanol to ethanoic acid
   (c) oxidation of ethanal to ethanoic acid
   (d) oxidation of propanal
   (e) oxidation of propan-2-ol
   (f) oxidation of butan-2-ol


Catalytic oxidation of methanol

Set 25: Reactions of organic compounds

Notes

5. Write balanced equations for the reactions between the following. Name any organic products formed.

   (a) pentanal with acidified potassium permanganate solution.
   (b) propan-1-ol with acidified potassium permanganate solution to produce propanoic acid.
   (c) propan-2-ol with acidified potassium permanganate solution.
   (d) butan-1-ol with acidified potassium dichromate solution to form butanal.
   (e) ethanal with acidified potassium dichromate solution.
   (f) methanol with acidified potassium dichromate solution to produce methanoic acid.
   (g) butan-2-ol with acidified potassium dichromate solution.
   (h) propan-1-ol with acidified potassium permanganate solution to form propanal.

6. Write balanced equations for the reactions between the following. Name any organic products formed.
   (a) methanol with sodium (optional).
   (b) propan-2-ol with sodium (optional).
   (c) heating propanoic acid with butan-1-ol in the presence of an acid catalyst.
   (d) heating methanoic acid with propan-2-ol in the presence of an acid catalyst.
   (e) propanoic acid with a sodium hydroxide solution.
   (f) sodium ethanoate with hydrochloric acid solution.

7. Write a balanced equation for the reactions. Write the names of the reactants required to produce the following and draw the structure for any organic reactant required.
   (a) butanone (butan-2-one but the 2 is not really required)
   (b) trichloromethane
   (c) pentanoic acid
   (d) propyl propanoate
   (e) cyclopentanol
   (f) 2,3-dibromohexane
   (g) 2-chloropropane
   (h) pentanal
   (i) ethyl methanoate
   (j) butan-2-ol

Heating a carboxilic acid with an alcohol

Set 26: Calculations involving carbon compounds

Notes

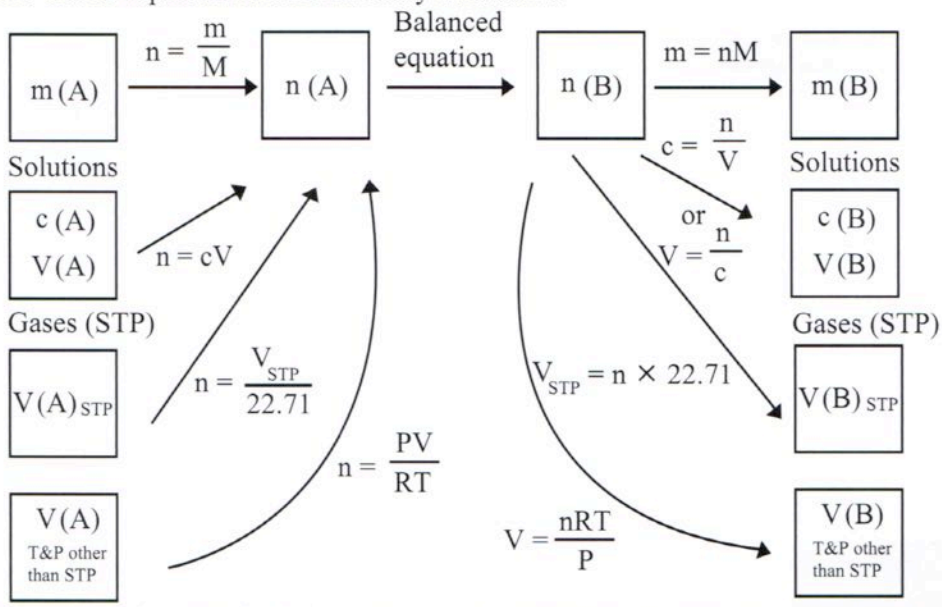
Reaction stoichiometry

A chemical equation shows the relationship between the numbers of moles of reactants and the products in a chemical reaction. For example the equation representing the burning of propane gas is:

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

This indicates that one mole of propane, C_3H_8 reacts with five moles of oxygen, O_2 to form three moles of carbon dioxide, CO_2 and four moles of water, H_2O.

Using the stoichiometric relationship between the numbers of moles of reactants and products in a chemical reaction, a range of calculations can be carried out involving the masses, gaseous volumes and solution volumes of reactants and products. These calculations can be represented schematically as follows:



A represents the substance for which you know the amount that reacts or is produced (known quantity)

B represents the substance for which you are required to calculate the amount that reacts or is produced (unknown quantity)

Example

Petrol or gasoline is a hydrocarboon fuel used in the majority of motorcars on the road today. The burning of petrol produces carbon dioxide and water. Calculate the mass and volume (at STP) of carbon dioxide produced from the burning of 55.00 kg (approximately 76 L) of fuel. Assume octane is the main hydrocarbon in petrol.

Step 1: Write a balanced equation for the reaction:

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$$

Step 2: Calculate the number of moles of the known quantity

$n(C_8H_{18}) = m/M$ $\quad$ $M\ (C_8H_{18}) = 8(12.01) + 18(1.008) = 114.224\ g\ mol^{-1}$

$= 55 \times 1000 / 114.224$

$= 481$ mol

Set 26: Calculations involving carbon compounds

Notes

Step 3: State the mole relationship between the known and unknown quantities

$n(CO_2) = 16/2\ n(C_8H_{18}) = 8\ n(C_8H_{18})$

Step 4: Calculate the number of moles of unknown quantities

$n(CO_2) = 8\ n(C_8H_{18}) = 8(481.51) = 3852.08$ mol

Step 5: Convert the number of moles of unknown quantities to the units asked in the question

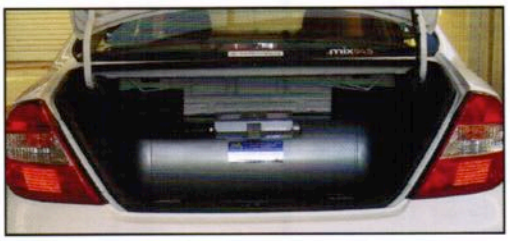
$m(CO_2) = n\ M = (3852.08) \times (44.01) = 169\ 530$ g $= 1.69 \times 10^2$ kg

$V(CO_2)_{STP} = n(22.71) = (3852.08) \times (22.71) = 86\ 325$ L $= 8.63 \times 10^4$ L

Set 26 Exercises

1. Propan-2-ol is used in a variety of cleaning products. One method of producing propan-2-ol is by the addition of water to propene. Calculate the mass of propene required to make 1.00 kg of propan-2-ol.

2. Sodium methoxide could be made by the reaction of methanol with sodium. To test the effectiveness and economics of this method of making sodium methoxide, excess sodium is reacted with 250 g of methanol.
   Calculate the
   (a) mass of sodium methoxide produced.
   (b) volume of gas produced measured at STP.
   (c) volume of gas produced measured at a temperature of 23.0 °C and a pressure of 102.4 kPa.



Question 3: Propane used as fuel

3. Propane is sometimes used as a fuel additive in vehicles powered by diesel engines. It is injected into the engine as a gas via the air intake. Calculate the volume of carbon dioxide produced per litre of propane burnt in the engine if all the volumes are measured at the same conditions of temperature and pressure.

Question 4: Detergent

4. Detergents can be produced by neutralisation of sulfonic acids with sodium hydroxide. A common monoprotic sulfonic acid used for this purpose is dodecylbenzenesulfonic acid. ($CH_3(CH_2)_{11}C_6H_4SO_3H$). To produce a batch of detergent a chemist mixed 64.0 kg of the sulfonic acid with a solution containing 8.50 kg of sodium hydroxide. Calculate the
   (a) mass of detergent produced
   (b) mass of reagent left after the reaction has stopped.

Notes

5. Naphthalene ($C_{10}H_8$) is sometimes used to prevent moths damaging clothing stored for long periods of time. It can be purified by crystallisation from a non-polar solvent such as hexane. To test the purification process a chemist dissolved 50.0 g of naphthalene in some hexane then made the solution up to a volume of 250 mL by adding more hexane.
   (a) Calculate the concentration of the naphthalene in mol L^{-1}.
   (b) To promote crystallisation of the naphthalene the chemist decided to increase the concentration of the solution to 2.80 mol L^{-1} by distilling some hexane from the solution at a reduced pressure. Calculate the volume of hexane that needs to be removed from the solution to achieve the new concentration.

6. A specially formulated surfactant for use with bore water was known to contain a mixture of detergent and soap. The soap used in the surfactant was sodium stearate ($CH_3(CH_2)_{16}COONa$). To check the composition of the surfactant, a researcher working for the consumer protection agency dissolved 10.0 g of the surfactant in distilled water then added excess calcium chloride solution. The resulting precipitate was filtered, dried and then found to have a mass of 1.25 g. Calculate the percentage by mass of the soap in the surfactant.

7. To produce better quality wine the pH of the 'must' (grape juice) is sometimes adjusted prior to fermentation by the addition of tartaric acid. To determine the amount of acid required the titratable acid content of the wine needs to be measured. In such a determination the winemaker found that 20.0 mL of the 'must' required 16.35 mL of a standard 1.506×10^{-5} mol L^{-1} sodium hydroxide solution for neutralisation. Assume that all the acids present are monoprotic.
   (a) Calculate the concentration of titratable acid in the 'must'.
   (b) The organic acids present in the 'must' are weak acids. Assuming that the acids are, on average, ionised to 2.00%, calculate the pH of the 'must'.

8. The alcohol (ethanol) content of wine can be analysed by titration with standard potassium permanganate solution. Analysis of dry white wine was conducted as follows.

   A 5.00 mL sample of the wine was diluted to 500 mL in a volumetric flask. 20.0 mL samples of the diluted wine was titrated against a standardised 0.0216 mol L^{-1} potassium permanganate solution the results are shown in the table below.

	Rough Trial	Trial 1	Trial 2	Trial 3
Initial Reading (mL)	0.80	0.35	0.28	0.42
Final Reading (mL)	24.36	23.73	23.40	23.47
Volume used (mL)				

Question 8: Wine

   Assuming that the only oxidisable compound in the wine is ethanol, and that it was oxidised to ethanoic acid, calculate the alcohol concentration in the wine in
   (a) moles per litre.
   (b) grams per litre.

Set 26: Calculations involving carbon compounds

Notes

9. An aqueous methanamine solution can be used as feedstock in the production of dyes and insecticides. Methanamine has properties that are similar to those of ammonia and over time the solution concentration decreases as the methanamine comes out of solution. To check that the solution was still suitable for use, a chemist analysed a sample by titration. A 25.0 mL sample of the filtered used solution was diluted to 250 mL in a volumetric flask. 20.0 mL samples of the diluted methanamine solution were titrated with standard 0.0507 mol L^{-1} hydrochloric acid solution. The results are shown in the table.

	Rough Trial	Trial 1	Trial 2	Trial 3	Trial 4
Initial Reading (mL)	0.15	0.36	0.22	0.50	0.42
Final Reading (mL)	25.23	25.22	25.35	25.29	25.30
Volume used (mL)					

(a) Calculate the concentration, in mol L^{-1}, of the methanamine in the feedstock solution.

(b) The density of the feedstock solution was measured to be 1.07 g mL^{-1}. Calculate the percentage by mass of methanamine in the feedstock solution.

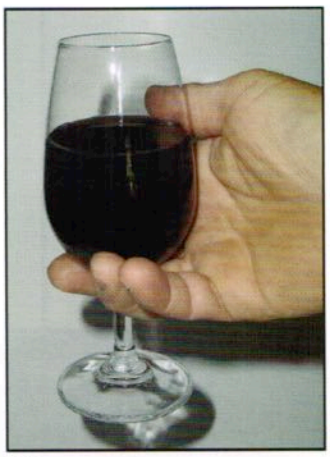
10. Some bathroom cleaners contain small amounts of propan-2-ol. Analysis of a bathroom cleaner was conducted using standardised 0.0203 mol L^{-1} potassium permanganate solution. A 5.00 mL sample of the cleaner was diluted with distilled water to 250 mL in a volumetric flask. 20.0 mL of the dilute solution required an average of 28.73 mL of the standard permanganate solution for complete reaction. Assuming the only oxidisable substance in the cleaner is propan-2-ol, calculate the concentration of the propan-2-ol in the cleaner measured in g L^{-1}.

Question 10: Bathroom cleaner

Set 27: Empirical, molecular and structural formula

Example

A barrel of wine that had been stored for some years was tested for quality before being bottled. It was found to be highly acidic and unpleasant to drink. Chemical analysis revealed that the compound responsible for the unpleasant taste contained only carbon, hydrogen and oxygen. A small amount of the compound was extracted and purified. When a 0.344 g sample of the compound was burnt in pure oxygen it produced 0.504 g of carbon dioxide and 0.206 g of water.



Wine

(a) Determine the empirical formula of the compound.

(b) A 1.876 g sample of the compound was vaporised and found to occupy 0.973 L at 120 °C and a pressure of 105 kPa.
   (i) Calculate the molecular mass of the compound.
   (ii) Determine the compound's molecular formula.

(c) Write a possible structural formula for the compound.

(a) $n(C) = n(CO_2) = \frac{m}{M} = \frac{0.504}{44.01} = 0.01145 \text{ mol}$ $\qquad M(CO_2) = 44.01 \text{ g mol}^{-1}$

$m(C) = nM = 0.01145 \times 12.01 = 0.1375 \text{ g}$

$n(H) = 2n(H_2O) = 2 \times \frac{m}{M} = 2 \times \frac{0.206}{18.016} = 0.02287 \text{ mol}$ $\qquad M(H_2O) = 18.016 \text{ g mol}^{-1}$

$m(H) = nM = 0.02287 \times 1.008 = 0.02305 \text{ g}$

$m(O) = m(\text{Compound}) - (m(C) + m(H))$

$= 0.344 - (0.1375 + 0.02305) = 0.1835 \text{ g}$

$n(O) = \frac{m}{M} = \frac{0.1835}{16.00} = 0.01147 \text{ mol}$

Elements	C	H	O
Number of moles	0.01145	0.02287	0.01147
Simplest ratio (Divide by smallest)	$\frac{0.01145}{0.01145}$	$\frac{0.02287}{0.01145}$	$\frac{0.01147}{0.01145}$
Simplest whole number ratio	1.00	1.997	1.002
	1	2	1

The empirical formula is therefore CH_2O

Notes

Notes

(b)(i) Calculate the volume of the gas at STP.

$V_1 = 0.973$ L $\quad V_2 = ?$

$P_1 = 105$ kPa $\quad P_2 = 101.3$ kPa

$T_1 = 120\ °C = 393$ K $\quad T_2 = 0\ °C = 273$ K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ so } V_2 = V_{STP} = \frac{P_1V_1T_2}{T_1P_2} = \frac{105 \times 0.973 \times 273}{393 \times 100} = 0.7097 \text{ L}$$

Calculate the number of moles of the gas.

$$n(\text{compound}) = n(\text{gas}) = \frac{V_{STP}}{22.71} = \frac{0.7097}{22.71} = 0.03125 \text{ mol}$$

OR Use PV = nRT that is:

$$n(\text{compound}) = n(\text{gas}) = \frac{PV}{RT} = \frac{105 \times 0.973}{8.315 \times 393} = 0.03125 \text{ mol}$$

Calculate the molar mass.

$$n = \frac{m}{M} \text{ so } M(\text{compound}) = \frac{m}{n} = \frac{1.876}{0.03125} = 60.013 \text{ g mol}^{-1}$$

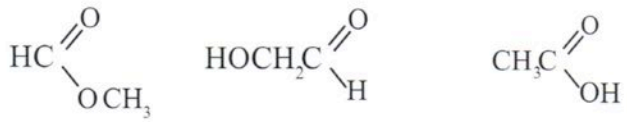
$$\text{so } M_r(\text{compound}) = 60.013$$

(ii) $M_r(CH_2O) = 12.01 + 2(1.008) + 16.00) = 30.026$

$$\frac{M_r(\text{compound})}{M_r(CH_2O)} = \frac{60.013}{30.026} = 1.9987 \approx 2$$

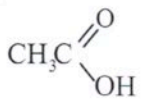
The molecular formula is 2 × the empirical formula = 2 × CH_2O = $C_2H_4O_2$

(c) There are a number of possible structures for a compound with this molecular formula.



are three of them.

However, as the compound caused the wine to become acidic the compound must be an acid. So the most likely structure is:



Set 27 Exercises

1. A hydrocarbon extracted from oil shale was analysed and found to contain 85.7% carbon and 14.3% hydrogen.
   (a) Determine the empirical formula of the hydrocarbon.
   (b) A 2.80 g sample of the hydrocarbon, in the gaseous state occupied 1.18 L at 25.0 °C and 105 kPa pressure. Calculate its relative molecular mass and determine the molecular formula.
   (c) Draw three possible structural formulas for the hydrocarbon.
   (d) When treated with bromine the hydrocarbon formed a 2,3-dibromohydrocarbon. Which one of the possible structures is it most likely to be.

2. Fuel from a local fuel station was reported to have been contaminated. On analysis, substantial amounts of an unidentified organic compound containing only carbon, hydrogen and oxygen was found. When 3.45 g of the purified compound was burnt in oxygen, 6.60 g of carbon dioxide and 4.05 g of water was produced.
   (a) Determine the empirical formula of the compound.
   (b) When 1.38 g of the compound was vaporised and the vapour heated to 100.0 °C it was found to occupy 0.950 L at a pressure of 98.0 kPa. Calculate its relative molecular mass and determine the molecular formula.
   (c) Draw possible structural formulas for the compound.

Question 2: Fuel station

3. Liquid, seen leaking from a car was analysed and was found to contain large amounts of an organic compound made up of only carbon, hydrogen and oxygen. When 0.682 g of the purified compound was burnt in oxygen, 0.968 g of carbon dioxide and 0.594 g of water were produced. Another 0.744 g of pure compound was vaporised. It was found the occupy 497 mL at a temperature of 200.0 °C and a pressure of 95.0 kPa.
   The compound was found to contain an OH group and analysis of its infrared spectrum indicated that the compound did not contain a carbonyl group.
   (a) Determine the empirical formula of the compound.
   (b) Calculate its relative molecular mass and determine the molecular formula.
   (c) Draw two possible structural formulas for the compound.

Question 3: Fluid leak

4. During the production of propan-2-ol a strong smelling by-product was detected in the reaction mixture. Contamination of the reaction mixture was suspected. To track down the contaminant the unknown compound was isolated, purified and when analysed found to contain carbon, hydrogen, nitrogen and possibly oxygen.
   When 1.180 g sample of the compound was burnt in oxygen it produced 1.758 g of carbon dioxide and 0.900 g of water. A second 1.180 g sample was decomposed to release 0.471 L of nitrogen gas measured at a temperature of 25.0 °C and a pressure of 105 kPa.
   Another sample of mass 0.5896 g was vaporised and was found to have a volume of 0.281 L at a temperature of 50.0 °C and a pressure of 95.5 kPa.
   (a) Determine the empirical formula of the compound.
   (b) Calculate its relative molecular mass and determine the molecular formula.
   (c) Draw a structural formula for the compound.

Notes

Set 27: Empirical, molecular and structural formula

Question 5: Toilet deoderant

Notes

5. During the routine analysis of coal tar, a by product of the production of coke from coal, a colourless, oily liquid was isolated. Analysis revealed that it contained only carbon, hydrogen and nitrogen. When a 0.620 g sample of the compound was burnt in oxygen it produced 1.76 g of carbon dioxide. A second sample of the compound of mass 0.232 g was decomposed. This produced 29.5 mL of nitrogen gas measured at 15.0 °C and 101.3 kPa pressure. Another sample of the compound was vaporised and at 100 °C and 101.3 kPa pressure was found to have a density of 3.04 g L^{-1}. Density is calculated by:

   Density = mass ÷ volume

   s $\quad p = \frac{m}{v}$

   The unknown compound was found to undergo substitution reactions with bromine and exhibit basic properties in aqueous solution.
   (a) Determine the empirical formula of the compound.
   (b) Determine the molecular formula.
   (c) Draw the structural formula for the compound.

6. An environmental chemist was asked to determine the identity of the solvent used in an insecticide preparation. Preliminary analysis revealed that the compound contained only carbon, hydrogen and oxygen. A 0.666 g sample of the compound when burnt in oxygen produced 1.584 g of carbon dioxide and 0.810 g of water. The unknown compound was vaporised and at a temperature of 200 °C and a pressure of 101.3 kPa its density was measured to be 1.91 g L^{-1}.
   (a) Determine the empirical formula of the compound.
   (b) Determine the molecular formula.
   (c) Draw three possible structural formulas for the compound.
   (d) The compound reacts slowly with sodium, but it is not oxidised by acidified potassium permanganate solution. Draw the structural formula for the compound.

7. An organic compound used in perfumes and flavours contains only carbon, hydrogen and oxygen. When 1.760 g of the compound was burnt in oxygen, it produced 3.52 g of carbon dioxide and 1.44 g of water. When vaporised, the compound has a density of 2.62 g L^{-1} at 150.0 °C and 105.0 kPa pressure. Determine:
   (a) the empirical formula
   (b) the molecular formula
   (c) the structural formula if the compound is an ester

Set 28: Amino acids

Notes

Proteins are biomolecules found in every living organism. They are natural polymers formed when α-amino acids join together in a series of condensation reactions. A protein is therefore an example of a polyamide. There are other large biomolecular polymers including carbohydrates and DNA, however, proteins are arguably the most interesting due to their amazing ability to perform a diverse range of functions. Proteins are essentially the molecular machinery that scaffolds, runs and controls cell function. What these molecules are capable of is staggering when you consider that at their simplest level they are just long chains of α-amino acids.

Name of protein	Function in the organism
Insulin	a hormone involved in controlling blood glucose levels
Keratin	a structural material in skin, hair and nails
Myosin	provides the contractile function in muscle
Pepsin	a digestive enzyme that breaks down proteins
Haemoglobin	transports oxygen in the bloodstream

Table 28.1: Some examples of proteins and their functions.

Chemists are most interested in the chemistry of enzymes and their application in industrial processes. This class of proteins acts as highly efficient biological catalysts. There are many applications and potential applications for the use of enzymes due to unique properties that distinguish them from inorganic catalysts. Scientists now have the capacity to engineer novel enzymes with properties designed to suit a particular process.

Small proteins can be made in the laboratory, however, in order to engineer a protein with novel function, genetic engineering is used. In this way the protein is synthesised using the machinery of the cell and following the instructions of the DNA code. Protein synthesis in cells can be regarded as a form of nanotechnology with the cellular machinery acting as a molecular factory.

When fewer than about 40 amino acids join together the molecule is referred to as a peptide rather than a protein. Two amino acids join together to form a dipeptide and three amino acids would form a tripepetide. Functional polymers generally range in size from tens to thousands of amino acids. The size of the proteins classified as nanoparticles are defined as 1-100 nm in size.

Generalised structure of an amino acid

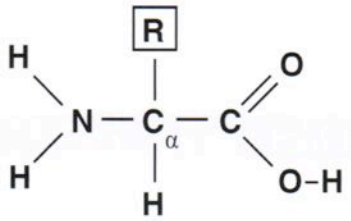
There are a huge variety of different proteins in all shapes and sizes, however, when they are initially made they are chains of α-amino acids joined by covalent bonds. As the name suggests amino acids contain a basic amino group and an acidic carboxylic acid group. The presence of these two groups on the same molecule gives amino acids their unique chemistry. In an amino acid there is a central carbon joined to an amino group (NH_2), a carboxylic acid group (COOH), a hydrogen atom (H) and one of 20 different side chains (called R groups).

Set 28: Amino acids

Notes

The presence of the different R groups means there are 20 different amino acid monomers used in making proteins.

α-amino acids can be represented in a generalised structure using R to represent the different side chains.



The last two pages of this book has a table that shows the names and the abbreviations of the 20 amino acids. The abbreviation is used for convenience.

Amino acid chemistry and zwitterions

As all α-amino acids contain a carboxylic acid group and a basic amino group they are capable of both accepting and donating protons. As pH changes the ionisation of the amino acid varies and the relative amounts of each form in solution changes

Low pH ⟷ **High pH**

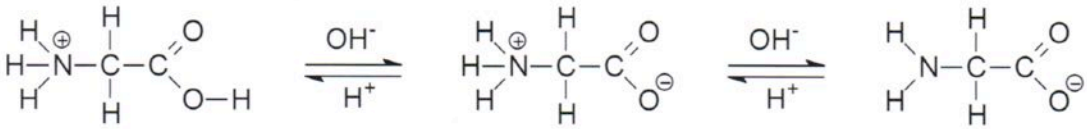


Figure 28.2: Ionisation of amino acids at varying pH

Amino acids can act as a buffer. As shown in figure 28.2, adding either H^+ and OH^- to a neutral amino acid results in a reaction that resists changes in pH.

At a particular pH for each amino acid a zwitterion exists. The word zwitter in German means hermaphrodite. A zwitterion contains both a positive and negative ionic charge. The zwitterion is the form of the amino acid where the COOH has lost a proton and the NH_2 has gained a proton. The zwitterion has no net charge as the negative charge of the COO^- is counterbalanced by the NH_3^+.

Although there is no net charge the amino acids effectively bond ionically due to the opposite charges present on the molecules. Zwitterion formation cause amino acids in the solid state to have high melting points due to the strong ionic bonds between the ions.

The crystalline solids of amino acids are highly soluble in water. The solubility varies depending on the nature of the side chain on the particular amino acid. This is due to the ion-dipole forces they form with water molecules. Water molecules are polar and so are strongly attracted to the charges on the amino acids.

Notes

For the amino acid, glycine, the zwitterion exists at pH 6. At this pH the positive charge on the amino group balances the negative charge on the carboxyl group.

Property of amino acid	Explanation
ability to act as buffer	have both acidic and basic properties due to the amino and carboxylic acid groups
high melting points	bond ionically to other zwitterions as they have opposite charges on the same molecule
solubility in water	can form ion-dipole interactions with polar water molecules

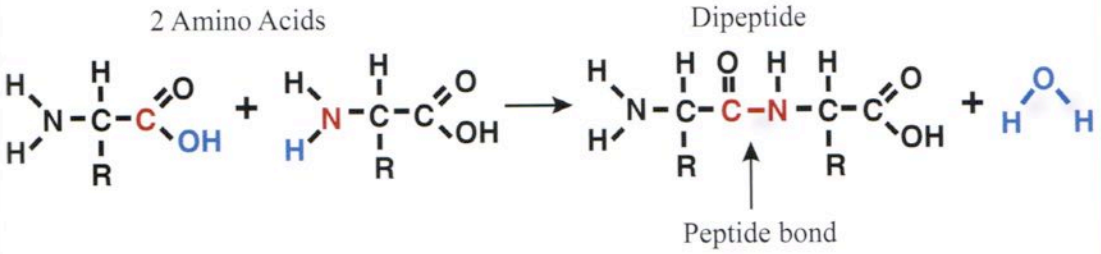
Table 2: Summary of amino acid properties.

Condensation reactions

In living cells, protein synthesis, also referred to as translation, involves a series of precisely controlled processes resulting in the formation of covalent bonds between α-amino acid monomers joined in a specific order. The groups that take part in the reaction are the amino and carboxyl groups on adjacent amino acids. A series of condensation reactions join the amino acids via covalent bonds called peptide bonds or amide linkages.

The information that determines the order of the 20 possible α-amino acids in any protein is encoded in the DNA sequence.

As each linkage is made, a water molecule is also produced.

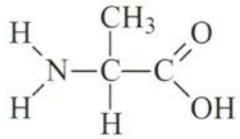


Set 28: Amino acids

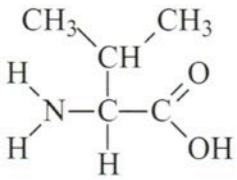
Notes

Set 28 Exercises

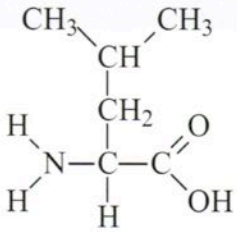
1. For the following three amino acids



Alanine



Valine



Leucine

(a) Draw the structure of each amino acid if it were in an environment of pH 3.

(b) Draw the zwitterion structure of each amino acid.

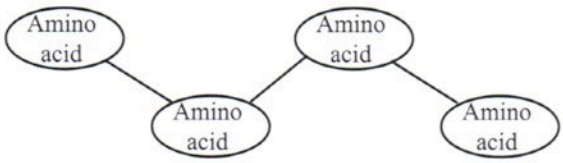
(c) Draw the structural formula of the protein Ala Val Leu that would form when these three amino acids are joined by peptide bonds. Label the peptide bonds in your diagram.

(d) Are the two ends of the dipeptide molecule identical? Biochemists often refer to the amino terminus (or end) and carboxy terminus. Label the amino terminus and carboxy terminus on your tripeptide. Try building the structure using the model kits to help you visualize the molecules.

(e) Draw the structural formula of the protein in an environment of pH 3.

2. The formation of peptide bonds requires the action of an enzyme. What is the chemical function of an enzyme? Suggest a reason why enzymes are essential in biological systems.

3. Small proteins may contain just a few hundred amino acids, whereas large proteins may contain thousands of amino acids. If a protein consisted of four amino acids and underwent hydrolysis, how many water molecules must be used in order to break apart this small protein?



4. If a protein were to be formed from 100 amino acids. How many water molecules will be created in the making of this small protein?

5. Draw the structures of glycine, aspartic acid, and lysine structures that would be predominant at pH = 14.

Set 29: Proteins

Notes

Primary, Secondary and Tertiary structure.

Primary structure

The primary structure of a protein refers to the number and order of amino acids in the polypeptide chain.

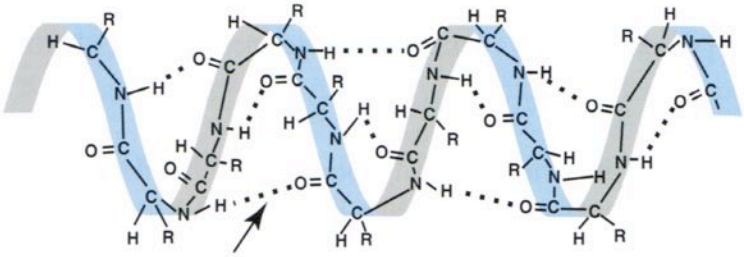
When two amino acids join together to form a dipeptide they can do so in 2 possible ways. For example when glycine and alanine join, the primary structure could be Gly-Ala or Ala-Gly.

Secondary structure

The secondary structure is the folding of the polypeptide into strands running parallel to each other called β-pleated sheets or twisted structures known as α-helices. These are shown in figure 29.1

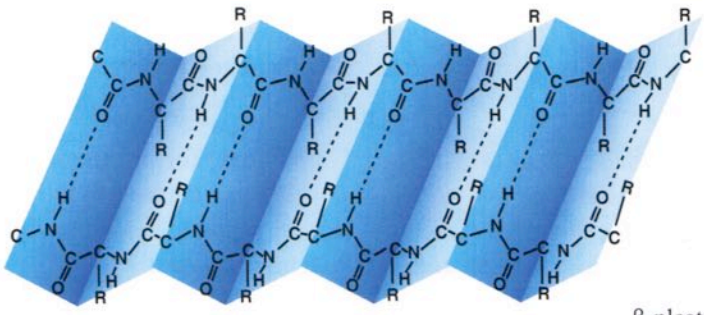
Figure 29.1: beta pleated sheets (β-pleated) and an alpha helix (α-helix).

The interactions that stabilise these folds in the polypeptide chain are hydrogen bonds between the oxygen on the carbonyl group and the nitrogen on the amide groups. See figure 29.2



Hydrogen bonds between amino acids
at different locations in polypeptde chain

α-helix



β-pleated sheet

Figure 29.2: An α-helix and β-pleated sheets showing hydrogen bonding.

Notes

Tertiary structures

The overall shape of the polypeptide chain is called the tertiary structure. Tertiary structures can contain both α-helix and β-pleated sheet structures depending on the protein.-see Figure 29.3.

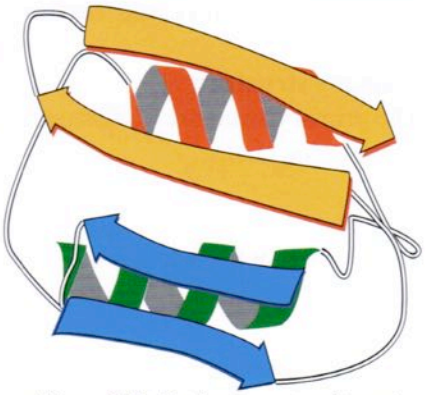


Figure 29.3: Tertiary structure formed by the arrangement of different secondary elements.

There are four different side-chain interactions possible that can affect the tertiary structure:

(a) Hydrophobic – between non-polar side chains
(b) Hydrogen bonds – between polar side-chains
(c) Ionic bonds – between side-chains with charges
(d) Disulfide bridges – covalent bonds between sulfur atoms

There is another level of structure when two or more polypeptide chains come together to function as a unit. This is called **quaternary structure**.

Sometimes other functional groups are also attached to the polypeptide chains, for example the haem group in haemoglobin contains iron which is required for the function of binding oxygen.

Denaturation of proteins: ***Temperature and pH effects***

When proteins are exposed to high temperatures or change in pH the interactions between amino acid side chains are disrupted. Raising the temperatures can weaken the dispersion forces between non polar side chains and as it increases other stronger attractions can be affected. Altering pH will change the ionisation of acidic and basic side chains of amino acids and therefore disrupts hydrogen bonds and ionic bonds. This means the tertiary structure of the protein changes. As the 3D structure of a protein is closely linked to its function, proteins generally require a narrow pH and temperature range in which to function.

Enzymes

Enzymes are biological catalysts. They are highly specific in the reactions they catalyse. This is because their tertiary structure includes an active site. The active site is often a crevice in the overall structure that creates an ideal environment to which the substrate (reactant) binds. In the active site specific side chains will be exposed and form interactions with the substrate. When the product is formed it will be released and the enzyme be available to be reused again and again. Alteration in the shape of the active site and ionisation of side chains involved will result in a non-functional enzyme. In effect the changes cause the precisely folded polypeptide chain to unravel and become random coils.

The Protein Data Bank

The Worldwide Protein Data Bank (PDB) acts as a global database for information supplied by a consortium of organisations around the world about proteins and their function. This information acts as a resource for the scientific community, it is freely available and allows comparison of protein structures for research and commercial purposes.

Notes

Databanks of gene sequences allow scientists to determine the primary structure of the proteins encoded from the sequence of bases in DNA. The data in the PDB was obtained from X-ray crystallography, NMR and other techniques and shows the three dimensional structure of the proteins. This allows scientists to identify the secondary, tertiary and quaternary structure of the protein.

The shape of an enzyme affects its catalytic efficiency and substrate specificity. Alteration of a single amino acid can result in changes in the folding and the ability of the enzyme to bind a particular substrate. Enzymes can be engineered to be more stable at high temperatures by adding cysteines that form disulfide bridges.

Enzymes that catalyse the same reactions, can be found in a variety of organisms. The primary sequence of the enzymes show degrees of similarity depending on how closely related the organisms are. As a result the tertiary structures also show similarity. If the tertiary structure of a protein from one species is established, then the 3 dimensional shape of a related protein can be deduced from its primary structure.

The relationship between the primary and tertiary structures can be used commercially. Proteins that share a high degree of similarity in primary structure can be predicted to have a similar tertiary structure. The information on tertiary structure aids scientists in the design of proteins with novel properties. The information provides opportunities for designing enzymes that can function better under particular conditions for industrial processes such as the production of biodiesel.

Set 29 Exercises

1. Using diagrams describe the following:
   - Primary structure
   - Secondary structure
   - Tertiary structure

2. List the bonding forces involved in primary, secondary and tertiary protein structures.

3. Haemoglobin is a globular protein made up of four polypeptide chains - 2 alpha and 2 beta.

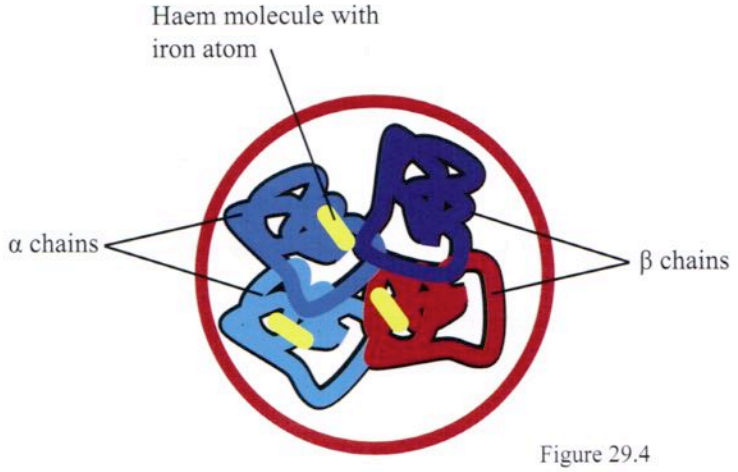


Figure 29.4

Notes

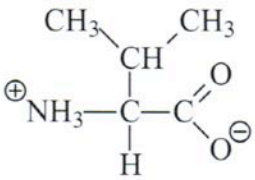
(a) Explain the terms α-helix and β-pleated sheet.

(b) Explain how we know this is a quaternary structure.

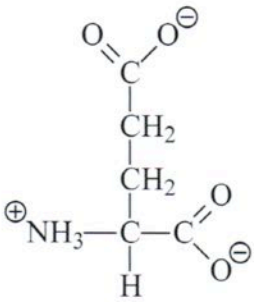
(c) Sickle Cell Disease is a genetic condition that results from the substitution of valine for glutamic acid in one of the hemoglobin polypeptides, as indicated below. Examine the structures of these two amino acids. Based on just their structures, do you expect this single amino acid substitution to have an effect on this protein's structure? Why or why not?

Normal Adult Haemoglobin
Amino acid Leu Thr Pro Glu Lys Ser

Sickle Cell Adult Haemoglobin
Amino acid Leu Thr Pro Val Lys Ser



Valine

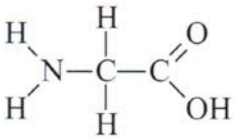


Glutamic acid

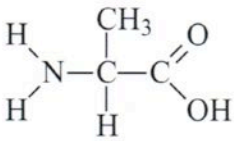
4. What makes different proteins unique?

5. Explain how a protein's shape is determined.

6. Examine the structures of glycine and alanine, two of the 20 amino acids we use to build our proteins.



Glycine



Alanine

(a) What do these two structures have in common? Draw a common structure for an amino acid.

(b) In what way are these structures different?

Notes

7. Once a series of amino acids have been linked together to form a polypeptide, that polypeptide (the protein's primary structure) is free to interact to form secondary structures. The two most common secondary structures are alpha helices and beta sheets. Using figure 29.2 to help answer the following questions.
   (a) What type of molecular interactions hold the alpha helices together?
   (b) Between which two atoms do these bonds form?
   (c) What type of molecular interactions hold the beta sheets together?
   (d) Between which two atoms do these bonds form?
   (e) Do you expect these secondary structures, alpha helices and beta sheets to hold their shape at high temperature? Why or why not?

8. Regions of a polypeptide, not involved in alpha helices or beta sheets, are also free to interact, forming a protein's tertiary structure. The primary force driving their interactions is the hydrophobic effect.

   The diagram right illustrates the various interactions that can stabilize a protein's tertiary structure. Which of these interactions do you expect to be most thermostable and why?

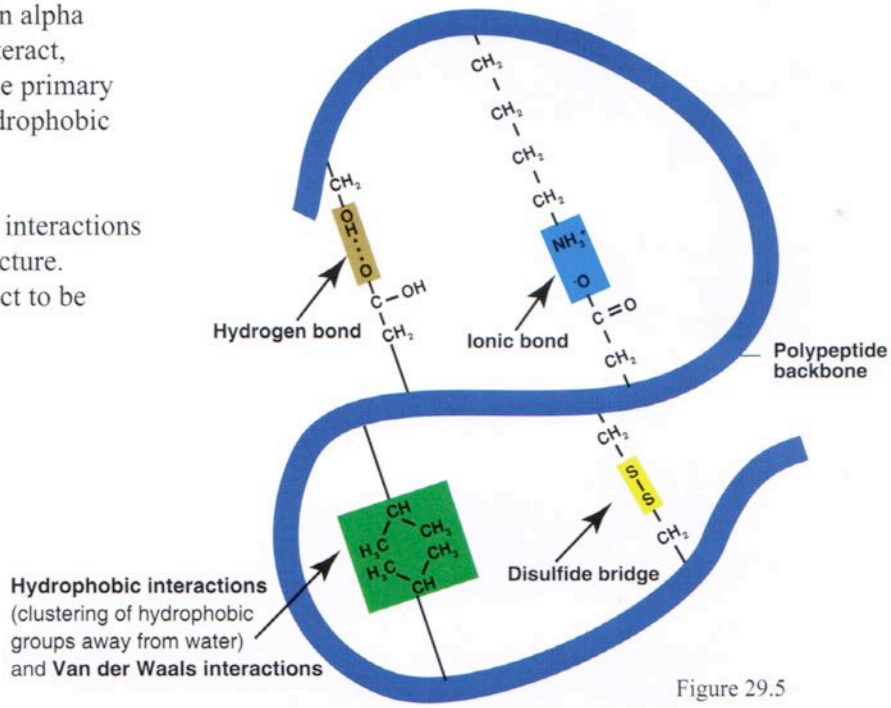


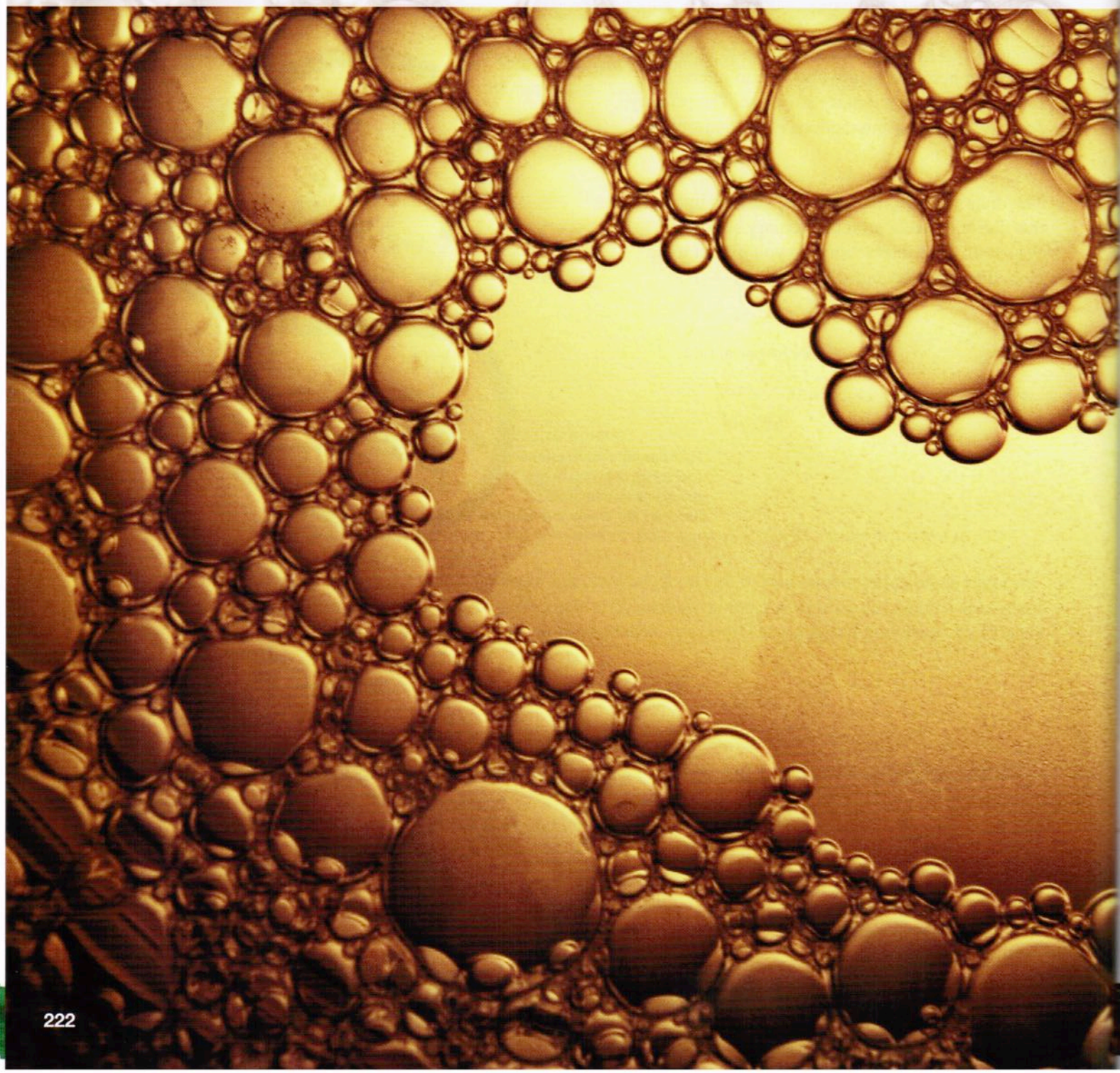
Figure 29.5

9. Throughout the experimental part of this book we included warnings about the danger of spilling sodium hydroxide solution on your skin. Sodium hydroxide is also called *caustic soda*. The word 'caustic' means capable of destroying living tissue. How does caustic soda destroy living tissue?

Properties, reactions and chemical synthesis

Chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product. In this section you will:

- explore quantities of products in a chemical synthesis reaction:
- calculate and compare stoichiometric quantities with actual quantities and determine the limiting reagent;
- calculate the percentage yield of a chemical synthesis reaction by comparing theoretical versus actual product quantities; and
- calculate empirical formula of compounds from experimental data.



Set 30: Reaction types

Set 30: Exercises

Notes

1. Write ionic equations for the following reactions.
   (a) Glacial acetic acid is added to water.
   (b) Ammonia gas is dissolved in water.
   (c) Sodium hydrogencarbonate solid is added to water.
   (d) Sodium hydrogensulfate solid is added to water.
   (e) Potassium carbonate solid is added to water.
   (f) Ammonium acetate solid is added to water.

2. Write ionic equations and give appropriate observations for the following reactions.
   (a) Sulfuric acid solution is added to sodium hydroxide solution.
   (b) Solid barium hydroxide is added to nitric acid solution.
   (c) Solid magnesium oxide is added to hydrochloric acid solution.
   (d) Acetic acid solution is added to ammonia solution.
   (e) Zinc is added to hydrochloric acid solution.
   (f) Acetic acid solution is added to magnesium.
   (g) Copper is added to concentrated nitric acid solution to produce nitrogen dioxide and copper nitrate solution.
   (h) Hydrochloric acid solution is added to nickel.
   (i) Sulfuric acid solution is added to iron.

3. Write ionic equations and give appropriate observations for the following reactions.
   (a) Liquid bromine is added to potassium iodide solution.
   (b) Magnesium is added to iron(II) chloride solution.
   (c) Copper is added to silver nitrate solution.
   (d) Zinc is added to nickel(II) nitrate solution.
   (e) Sodium is added to water.
   (f) Potassium is added to water.
   (g) Chlorine gas is bubbled through sodium bromide solution.

4. Write ionic equations and give appropriate observations for the following reactions. (Assume the concentrations of all solutions are 0.100 mol L^{-1}.)
   (a) Silver nitrate solution is added to sodium chloride solution.
   (b) Sodium bromide solution is added to silver nitrate solution.
   (c) Lead(II) nitrate solution is added to barium iodide solution.
   (d) Calcium nitrate solution is added to sodium sulfate solution.
   (e) Barium hydroxide solution is added to sulfuric acid solution.
   (f) Potassium carbonate solution is added to iron(II) nitrate solution.
   (g) Zinc chloride solution is added to sodium phosphate solution.
   (h) Copper(II) sulfate solution is added to sodium hydroxide solution.
   (i) Chromium nitrate solution is added to potassium carbonate solution.

Set 31: Percentage composition and yield

Notes

In the production of pharmaceuticals multiple steps are often required to produce the required drug. Many of these steps do not go to completion and so the yield of the required chemical can be low. Usually the more steps required, the lower the yield. As a result chemists are continually working through the manipulation of reaction conditions such as reactant concentrations, temperature and pressure to improve the yield while minimising the costs of production.

It is important, therefore, to be able to compare the actual yield to the theoretical yield. This is usually expressed as a percentage.

Examples

1. Magnetite, Fe_3O_4, is an important iron-bearing mineral. Calculate the percentage mass of iron in magnetite.

   $M(Fe_3O_4) = 3(55.85) + 4(16.00) = (167.55) + (48) = 215.55 \text{ g mol}^{-1}$

   $$\%Fe = \frac{m(Fe)}{M(Fe_3O_4)} \times 100 = \frac{167.55}{215.55} \times 100 = 77.7\%$$

2. Redox titrations involve the reaction of an oxidising agent such as permanganate ion (MnO_4^-) or dichromate ion ($Cr_2O_7^{2-}$) with a reducing agent such as iron(II) ion (Fe^{2+}) or oxalic acid ($H_2C_2O_4$).
   An approximately 0.02 mol L^{-1} potassium permanganate solution was standardised against 0.0502 mol L^{-1} oxalic acid solution. 20.0 mL of the oxalic acid solution, acidified with sulfuric acid, was oxidised by an average of 20.8 mL of the permanganate solution. Calculate the concentration of the potassium permanganate solution.

   (a) Write the equation for the reaction

   $$MnO_4^- + 5\,e^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O \quad \times 2$$
   $$H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,e^- + 2\,H^+ \quad \times 5$$
   $$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$
   2mol 5mol 6 mol 2 mol 10 mol 8 mol

   (b) Calculate the number of moles of $H_2C_2O_4$

   $$n(H_2C_2O_4) = cV = 0.0502 \times 0.0200 = 1.004 \times 10^{-3} \text{ mol of } H_2C_2O_4$$

   (c) Calculate the moles of MnO_4^-
   2 mol MnO_4^- reacts with 5 mol $H_2C_2O_4$

   $$n(MnO_4^-) = \frac{2}{5}\,n(H_2C_2O_4) = \frac{2}{5} \times 1.004 \times 10^{-3} = 4.016 \times 10^{-4} \text{ mol of } MnO_4^-$$

(d) Calculate the concentration of MnO_4^-

$$n = cV$$
$$4.016 \times 10^4 = c \times 0.0208$$
$$c = \frac{4.016 \times 10^{-4}}{0.0208}$$
$$= 0.0193 \text{ mol L}^{-1}$$

Notes

Set 31: Exercises

1. Hematite (Fe_2O_3) is a common mineral found in iron ore.
   (a) Calculate the percentage of iron in pure hematite.
   (b) If a sample of iron ore consists only of hematite and contains 65.0% iron, what is the percentage of hematite in the ore?

2. A 2.71 g alloy of zinc and copper was added to excess 2.00 mol L^{-1} hydrochloric acid solution. After the reaction was complete, the remaining solid was washed and dried. The mass of the dry solid was found to be 0.630 g. What was the percentage of zinc in the original sample?

3. When bromine (Br_2) is added to benzene (C_6H_6) a substitution reaction occurs and bromobenzene is formed. The reaction can be represented by the equation:

$$Br_2 + C_6H_6 \rightarrow C_6H_5Br + HBr$$

   (a) Calculate the theoretical yield of bromobenzene when 60.0 g of benzene reacts with 125 g of bromine.
   (b) If 93.2 g of bromobenzene is actually produced, what is the percentage yield of this reaction?

4. Quicklime (CaO) absorbs water from the atmosphere to form a mixture of calcium oxide and calcium hydroxide. The fully hydrated form of quicklime was historically used to plaster walls.
   (a) Write an equation for the decomposition of calcium hydroxide to calcium oxide and water.
   (b) A 5.67 g sample of partially hydrated quicklime was analysed by heating to 400 °C to drive off the water. The mass of the sample stabilised at 4.33 g. Calculate the percentage by mass of calcium oxide in the above sample.

5. A student was converting copper(II) sulfate-5-water to copper(II) chloride-2-water by adding barium chloride. The barium sulfate produced was removed by filtration and the filtrate evaporated to dryness to leave copper(II) chloride-2-water.
   (a) Write an equation for the reaction between copper(II) sulfate and barium chloride.
   (b) What mass of barium chloride would be required to completely react with 1.11 g of copper(II) sulfate-5-water.
   (c) If 0.345 g of copper(II) chloride-2-water was produced, what was the percentage yield of this reaction?

Question 5:
copper(II) sulfate-5-water

Notes

6. Sodium pyrosulfate ($Na_2S_2O_7$) is produced by the following series of reactions:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$
$$SO_3(g) + H_2O(\ell) \rightarrow H_2SO_4(aq)$$
$$2\ H_2SO_4(aq) + Na_2CO_3(s) \rightarrow 2\ NaHSO_4(aq) + H_2O(\ell) + CO_2(g)$$
$$2\ NaHSO_4(aq) \rightarrow Na_2S_2O_7(s) + H_2O(\ell)$$

In the commercial production of $Na_2S_2O_7$, 17.5 kg of sulfur is consumed in the production of 50.0 kg of $Na_2S_2O_7$. Calculate the percentage efficiency of the process.

7. A 1.00×10^2 g mixture of sodium carbonate and sodium hydrogencarbonate is heated at 110 °C until all the hydrogencarbonate has been converted to the carbonate according to the equation:

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

The residue, pure sodium carbonate, was found to have a mass of 90.7 g. Determine the mass of sodium hydrogencarbonate in the mixture and hence the percentage of sodium carbonate in the mixture.

8. 1.63 g of iron wire was dissolved in dilute sulfuric acid. The solution was filtered, transferred to a volumetric flask and made up to 250.0 mL with distilled water. 20.0 mL of this solution required 18.1 mL of 0.0209 mol L^{-1} potassium dichromate for complete reation. Find the percentage of iron in the iron wire.

9. The percentage by mass of chromium in a mineral is determined by converting a sample of known mass into sodium dichromate, and titrating an acidified solution of the sodium dichromate with a standard solution of iron(II) sulfate. Using this method, 1.27 g of a chromium-containing mineral was converted into an acidified solution of sodium dichromate, which required 37.5 mL of 0.400 mol L^{-1} iron(II) sulfate to reach the end-point. Calculate the percentage by mass of chromium in the mineral.

10. A 0.752 g sample of impure sodium sulfite was oxidised by titration with acidified 0.0993 mol L^{-1} $K_2Cr_2O_7$ solution. 17.2 mL of the dichromate solution was used in the titration. Calculate the percentage purity of the sodium sulfite.

11. A 3.08 g sample of haematite was dissolved in sulfuric acid, reduced to Fe^{2+} and diluted to 250.0 mL in a volumetric flask. A 25.0 mL sample of this solution was titrated with 0.0260 mol L^{-1} potassium permanganate solution. A volume of 28.7 mL of $KMnO_4$ was needed to reach the end-point. Calculate the percentage of Fe_2O_3 in the haematite.

12. A sample of iron ore consisting of a mixture of FeO and Fe_2O_3 was dissolved in dilute sulfuric acid. The resultant solution was divided into two equal aliquots. The first aliquot was titrated with a potassium permanganate solution containing 6.30 g of $KMnO_4$ per litre, and required 15.0 mL for complete reaction. The second aliquot was reduced with zinc and the solution then titrated with the permanganate solution. 25.1 mL was required for the second oxidation. Calculate the mass of each iron oxide in the original sample.

Set 32: Limiting reagents

Notes

In many chemical reactions one reactant is used up before the others. When this happens the amount of product formed is limited by that reactant. The other reactants are said to be in excess. In order to determine the amount of product formed, the limiting reagent (reactant) must be identified and used in the calculation.

Example

Hydrogen chloride can be produced by the reaction of concentrated sulfuric acid with sodium chloride to produce sodium sulfate and hydrogen chloride. If 4.90 g of sulfuric acid and 5.265 g of sodium chloride were mixed, calculate:

(a) the limiting reagent, and
(b) the mass of $HC\ell$ produced.

(a)(i) Write a balanced equation:

$$H_2SO_4(aq) + 2\ NaC\ell(s) \rightarrow Na_2SO_4(aq) + 2\ HC\ell(g)$$

(ii) Calculate the moles of each reactant:

$$n(H_2SO_4) = \frac{4.90}{98.067} \qquad M(H_2SO_4) = 98.067\ g\ mol^{-1}$$
$$= 5.00 \times 10^{-2}\ mol$$

$$n(NaC\ell) = \frac{5.265}{58.44} \qquad M(NaC\ell) = 58.44\ g\ mol^{-1}$$
$$= 9.01 \times 10^{-2}\ mol$$

(iii) Compare the actual mole ratio with the stoichiometric mole ratio:

Actual mole ratio: $\frac{n(NaC\ell)}{n(H_2SO_4)} = \frac{9.00 \times 10^{-2}}{5.00 \times 10^{-2}} = \frac{1.8}{1}$

Stoichiometric mole ratio: $\frac{n(NaC\ell)}{n(H_2SO_4)} = \frac{2}{1}$

(vi) Decide on the limiting reagent:
since the actual ratio is less than the stoichiometric ratio then $NaC\ell$ is the limiting reagent. This means that:
$n(NaC\ell)$ available/actual) < $n(NaC\ell$ required/stoichiometric) and the H_2SO_4 is in excess, while the $NaC\ell$ is the limiting reagent.

(b)(i) Identify the unknown and relate it to the limiting reactant:

$$n(HC\ell) = n(NaC\ell)$$
$$n(HC\ell) = 9.00 \times 10^{-2}\ mol$$

(ii) Convert the moles to mass:

$$n(HC\ell) = 9.00 \times 10^{-2}$$
$$m(HC\ell) = (9.00 \times 10^{-2})(36.458) \qquad M(HC\ell) = 36.458\ g\ mol^{-1}$$
$$m(HC\ell) = 3.28\ g$$

Set 32: Limiting reagents

Notes

Set 32: Exercises

1. The precipitation of lead(II) iodide can be represented by the following equation:

   $$Pb(NO_3)_2(aq) + 2\ KI(aq) \rightarrow PbI_2(s) + 2\ KNO_3(aq)$$

   If 0.300 moles of $Pb(NO_3)_2$ are added to 0.400 moles of KI.
   a) Determine the limiting reagent.
   b) What mass of lead(II) iodide is produced?

2. The neutralistion of sodium hydroxide by hydrochloric acid can be represented by the following equation:

   $$NaOH(aq) + HC\ell(aq) \rightarrow NaC\ell(aq) + H_2O(\ell)$$

   If 5.55 g of sodium hydroxide was added to a solution containing 4.88 g of hydrochloric acid.
   a) Determine the limiting reagent.
   b) What mass of sodium chloride is produced?

3. Vinegar can be used to dissolve calcium carbonate build up in kettles from hard water. This reaction can be represented by the following equation:

   $$CaCO_3(s) + 2\ CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2(aq) + CO_2(g) + H_2O(\ell)$$

   A solution containing 4.78 g of acetic acid was added to 2.22 g of calcium carbonate.
   (a) Identify the limiting reagent.
   (b) What mass of carbon dioxide is produced?
   (c) What mass of calcium acetate would be produced if the solution was evaporated to dryness?

4. Sulfuric acid solution containing 20.0 g of pure H_2SO_4 was added to 6.08 g of magnesium to produce hydrogen gas:

   $$Mg(s) + H_2SO_4(aq) + 7\ H_2O(\ell) \rightarrow H_2(g) + MgSO_4{\cdot}7H_2O(s)$$

   (a) Identify the limiting reactant.
   (b) What mass of hydrogen is produced?
   (c) What mass of magnesium sulfate crystals ($MgSO_4{\cdot}7H_2O$) would be obtained if the solution was evaporated to dryness?

5. 1.60 g of sodium hydroxide is added to a solution containing 1.472 g of H_2SO_4

   (a) Identify the limiting reactant.
   (b) Calculate the mass of sodium sulfate formed in solution.
   (c) Calculate the mass of unused reactant remaining in solution.

Notes

6. Silver does not react with dilute acids but will dissolve in concentrated acid.

$$3\ Ag(s) + 4\ HNO_3(aq) \rightarrow 3\ AgNO_3(aq) + NO(g) + 2\ H_2O(\ell)$$

If 16.3 g of silver metal is added to a solution containing 18.4 g of nitric acid.
(a) Identify the limiting reagent.
(b) What mass of NO is produced?
(c) What is the mass of the excess reactant at the end of the reaction?

7. Some self-contained breathing apparatus make use of the reaction between potassium superoxide (KO_2) and carbon dioxide to produce potassium carbonate and oxygen:

$$4\ KO_2(s) + 2\ CO_2(g) \rightarrow 2\ K_2CO_3(s) + 3\ O_2(g)$$

If 5.00 g of potassium superoxide is added to 9.00 g of carbon dioxide:
(a) what mass of potassium carbonate is produced?
(b) what mass of oxygen is produced?
(c) what is the mass of the excess reactant after the reaction is complete?

8. The overall reaction for the manufacture of triplesuperphosphate is:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow 3\ Ca(H_2PO_4)_2$$

If 25.0 tonnes of calcium phosphate ($Ca_3(PO_4)_2$) is heated with 30.0 tonnes of phosphoric acid (H_3PO_4). What mass of calcium dihydrogenphosphate $Ca(H_2PO_4)_2$ is formed?

9. When 7.20 g of impure anhydrous sodium carbonate was treated with 0.176 mol of dilute hydrochloric acid, 2.94 g of carbon dioxide was produced:

$$Na_2CO_3(s) + 2\ HC\ell(aq) \rightarrow 2\ NaC\ell(aq) + H_2O(\ell) + CO_2(g)$$
$$\text{or } Na_2CO_3(s) + 2\ H^+(aq) \rightarrow 2\ Na^+(aq) + H_2O(\ell) + CO_2(g)$$

Calculate the percentage purity of the sodium carbonate.

10. The equation for the reaction of manganese dioxide with hot concentrated hydrochloric acid is:

$$MnO_2(s) + 4\ HC\ell\ (aq) \rightarrow C\ell_2(g) + MnC\ell_2(aq) + 2\ H_2O(\ell)$$
$$\text{or } MnO_2(s) + 4\ H^+(aq) + 2\ C\ell^-(aq) \rightarrow C\ell_2(g) + Mn^{2+}\ (aq) + 2\ H_2O(\ell)$$

When 3.52 g of impure manganese dioxide was treated with 0.0800 mol of hydrochloric acid, 2.84 g of chlorine was evolved. Calculate the percentage purity of the manganese dioxide.

Set 33: Calculations involving gases

Notes

Many processes such as the Haber process involve the consumption and production of gases. The Ideal Gas Equation gives the relationship between pressure, temperature, volume and number of moles.

Temperature

The SI unit for temperature (T) is the kelvin (K). Temperatures used in gas calculations must be stated in kelvin. The relationship to convert Celsius temperature (°C) to kelvin is

$$T(K) = T(°C) + 273.15$$

Gas volume

The SI unit for volume is the cubic metre (m^3), but litre (L) is the most common unit used and the one we will use in our calculations.

Gas pressure

The SI unit for pressure is the pascal (Pa). Other units of pressure which are commonly used are the atmosphere (atm) and millimetres of mercury (mm Hg).

Note: 1 atm = 760 mm Hg = 101.3 kPa

The units that are used in the ideal gas equation are kPa.

STP

Standard Temperature and Pressure (STP) are 273.15 K (0 °C) and 100 kPa (1 atmosphere)

Molar volume of gases

The molar volume of a gas is the volume occupied by 1 mole of the gas. The molar volume for an ideal gas, and for some real gases, is 22.71 L at S.T.P.
The relationship between the number of moles (n) of a gas and its volume (V) in litres at S.T.P. is

$$n = \frac{V(\text{in litres at S.T.P.})}{22.71}$$

Ideal gas equation

The Ideal Gas Equation gives the relationship between pressure, volume, temperature and number of moles of a gas.

$$PV = nRT$$

Where pressure is in kPa, volume is in L, and temperature is in kelvin. The R is called the Universal Gas Constant and has the value 8.314 J K^{-1} mol^{-1} . This value is provided on data sheets and is not something you need to memorise.

Examples

Notes

1. In a blast furnace iron (III) oxide reacts with carbon monoxide to produce iron metal. Calculate the mass of iron metal produced for every 1.0 kL of carbon monoxide consumed in this reaction.

(i) Write an equation for the reaction

$Fe_2O_3 + 3\,CO\,(g) \rightarrow 2\,Fe\,(s) + 3\,CO_2\,(g)$

(ii) Calculate the number of moles of carbon monoxide

$n = V / 22.71 = 1.0 \times 10^3 / 22.71 = 44.03$ mol

(iii) From the equation determine the number of moles of Iron metal produced

$n(Fe) = 1/3\,n(CO) = 1/3 \times (44.03) = 14.68$ mol

(iv) Calculate the mass of Iron metal produced per 1.0 kL of CO consumed

$m(Fe) = nM = 14.68 \times 55.85 = 819$ g

2. What volume of carbon dioxide will be produced at 10^5 kPa and 25.0 °C when 120 mL of 2.00 mol L^{-1} hydrochloric acid solution is added to 10.2 g of solid calcium carbonate?

As this problem is also a limiting reagent problem, the first step is to find the limiting reagent.

$$CaCO_3(s) + 2\,H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2\,(g) + H_2O(\ell)$$

$$n(HC\ell) = cV = 0.120 \times 2 = 0.240 \text{ mol}$$

$$n(CaCO_3) = \frac{m}{M} = \frac{10.2}{100.02} = 0.102 \text{ mol}$$

$$n(H^+) \text{ to use all } CaCO_3 = 2n(CaCO_3) = 2 \times 0.102 = 0.204 \text{ mol}$$

$n(H^+ \text{ required}) < n(H^+ \text{ available})$

$CaCO_3$ is LR

Now use the ideal gas equation to calculate the volume of CO_2.

$$n(CO_2) = n(CaCO_3) = 0.102 \text{ mol}$$

$$PV = nRT$$

$$V(CO_2) = \frac{0.102 \times 8.314 \times (25 + 273)}{10^5} = 0.00253 \text{ L}$$

0.00

Set 33: Calculations involving gases

Notes

Set 33: Exercises

1. Calculate the number of moles in each of the following gas samples.

   (a) A sample of carbon dioxide occupies 0.450 L at 120.1 kPa and 299 K.
   (b) A sample of methane occupies 889 mL at 99.3 kPa and 41.0 °C.
   (c) A sample of nitrogen occupies 27.5 L at 145 kPa and 55.0 °C.

2. Calculate the molar mass of the following gases.

   (a) 2.22 g of a gas was found to occupy 559 mL at 105 kPa and 25.0 °C.
   (b) 0.456 g of a gas was found to occupy 1.22 L at 98.5 kPa and 75.0 °C.
   (c) 6.46 g of a gas was found to occupy 3.33 L at 68.4 kPa and 120 °C.

3. A gaseous hydrocarbon was isolated from a petrochemical process. 0.741 g of the gas occupied 668.4 mL at 25.0 °C and a pressure of 98.0 kPa. Determine

   (a) the relative molecular mass of the compound, and
   (b) the identity of the hydrocarbon.

4. A sample of calcium carbonate was reacted with excess hydrochloric acid. The carbon dioxide was captured and found to occupy 25.5 mL at 105 kPa and 25.0 °C. What was the mass of the calcium carbonate in the original sample?

5. More than 80% of the ammonia produced in the world is used to fertilize agricultural crops. Ammonia when reacted with sulfuric acid for example makes ammonium sulfate, $(NH_4)_2SO_4$, an important soil fertilizer.

   The following equation represents the making of ammonium sulfate from ammonia gas:

   $$2\ NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

   If 1.50 L of ammonia gas at STP is reacted with 50.0 mL of 2.54 mol L^{-1} sulfuric acid calculate:

   (a) the limiting reagent.
   (b) the mass of ammonium sulfate produced.
   (c) the moles of the excess reagent remaining at the end of the reaction.

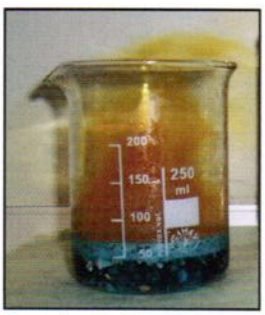
6. 0.273 g of sodium hydrogencarbonate was added to 50.0 mL of 2.50 mol L^{-1} hydrochloric acid solution.

   (a) Identify the limiting reagent.
   (b) What volume of carbon dioxide would be produced at 95.6 kPa and 28.0 °C?

7. 1.33 g of copper shavings were added to 25.0 mL of 6.00 mol L^{-1} nitric acid solution. This reaction can be represented by the following equation:

   $$Cu(s) + 4\ HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\ NO_2(g) + 2\ H_2O(\ell)$$

   (a) Identify the limiting reagent.
   (b) What volume of nitrogen dioxide was collected at 104 kPa and 33.0 °C?



Question 7: Copper metal reacts with nitric acid

Notes

8. Chlorine gas can be produced using the following reaction between manganese(IV) oxide and concentrated hydrochloric acid:

$$MnO_2(s) + 4\ H^+(aq) + 2\ C\ell^-(aq) \rightarrow Mn^{2+}(aq) + C\ell_2(g) + 2\ H_2O(\ell)$$

If 3.44 g of MnO_2 was added to 15.0 mL of 6.20 mol L^{-1} $HC\ell$ and the gas was collected in a rigid vessel with a volume of 250.0 mL at a temperature of 35.0 °C, what was the pressure of the gas?

9. A solution containing 30.0 g of ammonium sulfate and 34.0 g of potassium nitrate is heated and the following reaction occurs:

$$(NH_4)_2SO_4(aq) + 2\ KNO_3(aq) \rightarrow K_2SO_4(aq) + 4\ H_2O(\ell) + 2\ N_2(g)$$

(a) Which reactant is used up?
(b) What mass of the other reactant remains?
(c) What would be the pressure of nitrogen produced in a volume of 760.0 mL at 220 °C?

Set 34: Empirical formulas 1

Notes

Forensic science television programs routinely show chemists analysing small traces of material to identify their composition. There are a number of different techniques used. The most common are a variety of chromatographic and spectroscopic techniques. These techniques are used to identify what elements are present and can also determine bonding arrangements. If a compound contains carbon and hydrogen, combustion analysis can be performed to determine the amount of carbon present. From this information the empirical formula can be determined.

The empirical formula specifies the simplest whole-number ratio of atoms of each element in a compound.

The molecular formula specifies the number of atoms of each element in a molecule. A table of molecular and empirical formulae of some common substances is shown below:

Substance	Molecular formula	Empirical formula
water	H_2O	H_2O
hydrogen peroxide	H_2O_2	HO
methane	CH_4	CH_4
ethane	C_2H_6	CH_3
ethene	C_2H_4	CH_2
glucose	$C_6H_{12}O_6$	CH_2O
ammonia	NH_3	NH_3
phosphorus(V) oxide	P_4O_{10}	P_2O_5
sodium chloride	*	$NaC\ell$
calcium carbonate	*	$CaCO_3$
copper(II) sulfate-5-water	*	$CuSO_4{\cdot}5H_2O$
silicon dioxide	**	SiO_2

Note: 1. (*) exists as an ionic lattice under normal conditions
2. (**) exists as a covalent network solid under normal condition

Examples

1. A 7.86 g sample of a substance was found to consist of 1.59 g of aluminium and 6.27 g of chlorine. Calculate the empirical formula.

Elements	$A\ell$	$C\ell$	
Mass (g)	1.59	6.27	
Moles ($n = \frac{m}{M}$)	$\frac{1.59}{26.98}$	$\frac{6.27}{35.45}$	
	5.89×10^{-2}	1.77×10^{-1}	
Simplest ratio (divide by smallest)	$\frac{5.89 \times 10^{-2}}{5.89 \times 10^{-2}}$	$\frac{5.89 \times 10^{-2}}{5.89 \times 10^{-2}}$	1.77×10^{-1}
	1	3	
Empirical formula	$A\ell C\ell_3$		

Notes

2. A 2.50 g sample of an unknown compound was found, on analysis, to consist of 60.0% carbon, 8.00% hydrogen and 32.0% oxygen. The unknown compound had a relative molecular mass of 200.0. Calculate the empirical and molecular formulae of the compound.

Elements	C	H	O
Mass (g in 100 g)	60.0	8.0	32.0
Moles ($n = \frac{m}{M}$)	$\frac{60.0}{12.01}$	$\frac{8.0}{1.008}$	$\frac{32.0}{16.00}$
Simplest ratio	5	8	2

Empirical formula $C_5H_8O_2$

M (empirical formula) = 5(12.01) + 8(1.008) + 2(16.00)
= 100.114 g mol^{-1}

Given the molecular mass = 200.0 g mol^{-1}
Then the molecular formula = 2 x empirical formula
= $C_{10}H_{16}O_4$

3. An organic compound was known to contain carbon, hydrogen and oxygen. A 5.25 g sample was burnt completely in air. The products formed were water, 2.49 g, and carbon dioxide, 6.08 g. Determine:
(a) the empirical formula of the compound;
(b) the molecular formula knowing that the compound has a relative molecular mass of 228.

Note: When performing calculations requiring several steps, carry one figure more than the appropriate number of significant figures in each step and round to the appropriate number of significant figures after the final step. This avoids possible errors which can accumulate during a calculation if rounding to the strict number of significant figures is carried out at each step.

$$CxHyOz \rightarrow \times CO_2 + 2\ H_2O$$

Note: The number of moles of oxygen cannot be determined from H_2O or CO_2 as these species derive their oxygen content both from the organic compound itself and the O_2 used for combustion.

$$n(C) = n(CO_2) = \frac{6.08}{44.01} \qquad M(CO_2) = 44.01\ g\ mol^{-1}$$

$$= 1.382 \times 10^{-1}\ mol$$

$$n(H) = 2 \times n(H_2O) = \frac{2 \times 2.49}{18.016} \qquad M(H_2O) = 18.016\ g\ mol^{-1}$$

$$= 2.767 \times 10^{-1}\ mol$$

Notes

$$m(O) = m(\text{compound}) - [m(C) + m(H)]$$
$$= 5.25 - [1.382 \times 10^{-1}(12.01) + 2.767 \times 10^{-1}(1.008)]$$
$$= 3.315 \text{ g}$$

$$n(O) = \frac{3.315}{16.00}$$
$$= 2.072 \times 10^{-1} \text{ mol}$$

Elements	C	H	O
Moles	1.382×10^{-1}	2.767×10^{-1}	2.072×10^{-1}
Ratio (divide by smallest)	$\frac{1.382 \times 10^{-1}}{1.382 \times 10^{-1}}$	$\frac{2.767 \times 10^{-1}}{1.382 \times 10^{-1}}$	$\frac{2.072 \times 10^{-1}}{1.382 \times 10^{-1}}$
	1	2	1.5
	2	4	3

Empirical Formula $C_2H_4O_3$

$$M(\text{empirical formula}) = 2(12.0) + 4(1.0) + 3(16.0)$$
$$= 76.0 \text{ g mol}^{-1}$$

Given the molecular mass $= 228 \text{ g mol}^{-1}$
then the molecular formula $= 3 \times$ empirical formula
$= 3 \times C_2H_4O_3$
$= C_6H_{12}O_9$

Set 34: Exercises

1. Determine the empirical formula and molecular formula where asked, for the following compounds described below:
   (a) a sample of a compound that contains 2.76 g of iron and 3.51 g of chlorine produced when iron reacts with hydrogen chloride
   (b) a sample of a compound containing 2.06 g of carbon and 0.430 g of hydrogen, found in an arson investigation, had a molar mass of 58.12 g mol^{-1}
   (c) a sample of a disinfectant that contains 3.71 g of potassium, 5.21 g of manganese and 6.07 g of oxygen
   (d) a sample of a compound containing 7.72 g of sodium, 5.38 g of sulfur and 10.7 g of oxygen, found in a drain cleaner

2. A chemist has obtained the following data on three unknown compounds. Use this information to determine their empirical formulae.
   (a) A compound found in plaster:
   Ca, 54.1% : O, 43.2% : H, 2.70%
   (b) A soluble lead compound:
   Pb, 62.5% : N, 8.50% : O, 29.0%
   (c) A compound found in an organic solvent:
   C, 60.0% : H, 13.3% :O, 26.7%

Notes

3. A chemist is asked to analyse a sample of acid rain. The main contaminant contains 40.0% by mass of sulfur and 60.0% by mass of oxygen. What is the empirical formula of the contaminant?

4. An analyst conducts combustion analysis of 2.12 g of an unknown organic compound which was derived from a flowering plant and finds it contains 1.25 g of carbon. A separate analysis of a 1.64 g sample of the unknown compound contains 0.161 g of hydrogen. There is also oxygen present. Use the information given to first determine the percentage composition of the unknown organic compound. From the percentage composition determine the empirical formula of the compound.

5. Tellurium oxide is used to make glass with a high refractive index. A 5.00 g sample of tellurium oxide is found to contain 1.00 g of oxygen. What is the empirical formula of the oxide?

6. The residue of an unknown compound found in an old earthenware jar has the following composition by mass: carbon 52.0%: hydrogen 13.0% and the rest is oxygen. Find its empirical formula.

7. An oxide of iron was reduced to metallic iron by reaction with hydrogen gas. 11.2 g of iron oxide formed 7.83 g of metallic iron. Calculate the empirical formula of the iron oxide. Its molar mass was 159.6 g mol^{-1}, determine its molecular formula

8. Iron forms two chlorides which contain respectively 44.0% and 34.4% of iron. Calculate the empirical formulas of these compounds.

9. Nitrogen forms three oxides each containing respectively 63.6%, 46.7% and 30.4% of nitrogen. Calculate the empirical formulas of the three nitrogen oxides.

10. A 3.40 g sample of a titanium compound dissolves in water to produce titanium ions and chloride ions. All the chloride ions in the solution are precipitated by the addition of excess silver nitrate solution and after filtration and drying 9.47 g of the silver chloride was obtained. What is the empirical formula of this chloride of titanium?

11. An organic compound believed to be a preservative in animal feed is analysed by combustion and found to contain only carbon, hydrogen and oxygen. Complete combustion of 0.290 g of the compound gave 0.660 g of carbon dioxide and 0.270 g of water. Calculate the empirical formula of the compound.

12. A residue of an organic compound found in an ancient urn contains only carbon, hydrogen and oxygen. A 0.275 g sample of the compound was burned in excess oxygen to yield 0.403 g of carbon dioxide and 0.165 g of water. Calculate the empirical formula of the unknown compound.

13. Elementary analysis of an organic compound indicated that it contained only carbon, hydrogen, nitrogen and oxygen. A 1.279 g sample was burned completely in oxygen such that all the carbon was converted to carbon dioxide and the hydrogen to water. This resulted in 1.600 g of carbon dioxide and 0.770 g of water. A separate 1.279 g sample was shown by analysis to contain 0.1697 g of nitrogen. Calculate the empirical formula of the compound.

Set 35: Empirical formulas 2

Notes

Many empirical formula calculations involve organic compounds, but inorganic compounds, such as minerals, are also often determined through analysis and empirical formula calculations. This set includes a variety of compounds, both organic and inorganic.

Example

An organic herbicide was found to contain carbon, hydrogen, oxygen and chlorine. When a 2.66 g sample was combusted in excess oxygen, it produced 0.651 g of water and 4.24 g of carbon dioxide. A second sample of mass 1.73 g was treated with silver nitrate and 2.24 g of silver chloride was produced.

Calculate the empirical formula of the herbicide.

As the samples are of different sizes, the most appropriate method will be to calculate the percentage of each element present in the sample.

$$\%C: \quad \frac{4.24}{44.01} \times 12.01 \times \frac{100}{2.66} = 43.5\ \%$$

$$\%H: \quad \frac{0.651}{18.016} \times 2 \times 1.008 \times \frac{100}{2.66} = 2.74\ \%$$

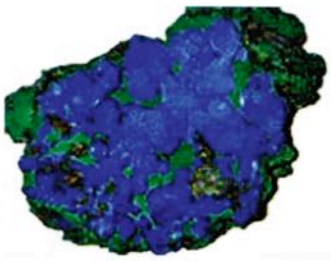
$$\%C\ell: \quad \frac{2.24}{(107.9 + 35.45)} \times 35.45 \times \frac{100}{1.73} = 32\ 1\ \%$$

$$\%O: \quad 100 - (43.5 + 2.74 + 32.1) = 21.7\ \%$$

	C	H	$C\ell$	O
m (g) in 100 g	43.5	2.74	32.1	21.7
Number of moles in 100 g (mol)	$\frac{43.5}{12.01}$ = 3.62	$\frac{2.74}{1.008}$ = 2.72	$\frac{32.1}{35.45}$ = 0.906	$\frac{21.7}{16.00}$ = 1.36
Simplest ratio (divide by smallest)	$\frac{3.62}{0.906}$ = 4	$\frac{2.72}{0.906}$ = 3	$\frac{0.906}{0.906}$ = 1	$\frac{1.36}{0.906}$ = 1.5
Simplest whole number ratio (× 2)	8	6	2	3

EF: $C_8H_6C\ell_2O_3$

Set 35: Exercises



Question 1: Azurite

1. Azurite is a copper mineral and has the empirical formula $Cu_a(CO_3)_b(OH)_c$. When azurite is heated it decomposes into carbon dioxide, water and copper(II) oxide. A 2.088 g sample of the pure ore was heated to produce 0.531 g of carbon dioxide and 0.109 g of water. Calculate the values of a, b and c in the empirical formula.

2. (a) An unknown hydrocarbon was found by analysis to consist of 85.7% carbon and 14.3% hydrogen. Determine the empirical formula.
   (b) A 2.80 g sample of the hydrocarbon, in the gaseous state, occupied 1.18 L at 25 °C, and 105 kPa pressure. Calculate the molar mass and determine the molecular formula.
   (c) Write three possible structural formulas for the unknown hydrocarbon.
   (d) When treated with bromine the unknown formed a 2,3-dibromo hydrocarbon substituted product. What is the actual structural formula?

3. Mendipite is a lead mineral that also contains oxygen and chlorine. A 3.41 g sample of the pure mineral was heated with hydrogen gas until all of the chlorine and oxygen were driven off and 2.93 g of lead metal remained. A second sample, with a mass of 2.93 g, was boiled in concentrated nitric acid. Excess silver nitrate solution was added and the precipitate isolated. 1.16 g of silver chloride was produced.

   Determine the empirical formula of the mendipite.

4. (a) A 3.45 g sample of an organic compound containing carbon, hydrogen and oxygen was burnt in oxygen to yield 6.60 g of carbon dioxide and 4.05 g of water. Determine the empirical formula of the compound.
   (b) When 1.38 g of the compound was heated to 100.0 °C it was gaseous and occupied 0.950 L at a pressure of 98.0 kPa. Calculate the molar mass and determine the molecular formula.
   (c) Write possible structural formulas for the unknown compound. The unknown compound reacts with sodium. What is its structural formula?

5. A compound was found to contain cobalt, carbon and oxygen.
   (a) A 1.22 g sample of the compound was treated with sodium carbonate and 0.849 g of cobalt carbonate was precipitated.
   A second sample, of mass 3.33 g, was burnt in excess oxygen and 3.43 g of carbon dioxide was produced.
   Determine the empirical formula of the compound.
   (b) If the molar mass of the compound was found to be 341.9 g mol^{-1}, determine the molecular formula of the compound.

Notes

Set 35: Empirical formulas 2

Notes

6. A 1.180 g sample of a gaseous organic compound produced, on combustion, 2.64g of carbon dioxide and 1.62 g of water. When 1.180 g of the same compound was decomposed, it released 0.236 L of nitrogen gas measured at 25 °C and 105 kPa pressure. Another sample of the gaseous compound at 19 °C and 95.5 kPa pressure was found to have a volume of 0.254 L and a mass of 0.5896 g. Determine:
   (a) the empirical formula
   (b) the molar mass and molecular formula

7. An unknown compound consists of carbon, hydrogen and chlorine. 1.324 g of the compound is divided into two equal samples. The first sample, when burnt in oxygen, produced 1.189 g of carbon dioxide. The second sample was oxidised with concentrated nitric acid and treated with silver nitrate solution to yield 1.292 g of silver chloride. The relative molecular mass of the unknown was found from freezing point depression measurements to be 147. Determine:
   (a) the empirical formula
   (b) the molecular formula
   (c) given that the compound is derived from benzene, draw three possible structural formulas for the compound

$$\text{Density} = \frac{\text{mass}}{\text{Volume}}$$

$$P = \frac{m}{v}$$

8. A 0.620 g sample of an organic compound produced, on combustion, 1.76 g of carbon dioxide and 0.420 g of water. When 0.232 g of the same compound was decomposed it released 29.5 mL of nitrogen gas measured at 15 °C and 101.3 kPa pressure. Another sample of the compound was gaseous at 100.0 °C and 101.3 kPa pressure. It was found to have a density of 3.04 g L^{-1}. Determine:
   (a) the empirical formula
   (b) the molecular formula

9. An oxalate compound with the general formula $K_xNi_y(C_2O_4)_z.aH_2O$. 5.43 g of the compound was heated to 150 °C to drive off the water. After a number of hours a constant mass of 4.88 g was obtained.

   2.00 g of the anhydrous sample was dissolved in water and H_2S was bubbled through the solution. 0.578 g of NiS was produced.

   The remaining 2.88 g of the anhydrous sample was oxidised and 1.62 g of carbon dioxide was produced.

   Determine the empirical formula of the compound.

10. An unknown compound contains sulfur, oxygen and chlorine. When mixed with water the compound yields a mixture of sulfuric and hydrochloric acids. A 0.5404 g sample of the compound was dissolved in water and split into two equal aliquots. The first aliquot, when treated with excess barium nitrate solution, yielded 0.4671 g of barium sulfate. The second aliquot was titrated with 0.250 mol L^{-1} NaOH solution, requiring 24.0 mL for complete neutralisation.

    Determine the empirical formula of the unknown compound.

Set 36: Chemical synthesis

Notes

Set 36 Exercises

1. Research the chemistry of methanol, its manufacture and its major uses.
2. Research the manufacture and uses of ethanol.
3. Research the chemistry of methanamine, its commercial manufacture and its uses.
4. Research the use of carboxylic acids and alcohols in the manufacture of polyesters.
5. Synthetic polymers are important materials used to make anything from plastic bags to car parts. Research the production and uses of two types of synthetic polymers. One type should be produced from one monomer and the other from two monomers.
6. Research the manufacture of soap and discuss its suitability for use in cleaning.
7. Research the manufacture of detergents and compare their structure and function as cleaning agents with those of soap.
8. Find out about the current manufacture of aspirin. Research the reactions required to produce aspirin and comment on its current use.

Extended answer questions

To answer the following extended answer questions, where applicable, use equations, diagrams and illustrative examples of the chemistry you are describing. Your answer should focus on the relevant chemical content specific to the situations described. Be sure your answer is presented in a logical and coherent manner.

9. **Analysis of wine**

Wine contains hundreds of compounds. The main components of wine are water, ethanol and various acids. Wine can be analysed for the ethanol and acid content. Whilst there are several acids present, it is assumed for the purpose of analysis that all acid is present in the form of tartaric acid, $C_4H_2(OH)_2(COOH)_2$, a weak diprotic acid. Most wines contain around 7 g L^{-1} of tartaric acid.

You have been given a bottle of white wine for analysis and have been asked to determine the acid content. You have a laboratory equipped to conduct accurate volumetric analyses of acids and bases including the primary standards anhydrous sodium carbonate and oxalic acid dihydrate, but no standard solutions have been prepared.

Give a detailed account of the laboratory procedures that you would use to determine the acid content of the wine.

You should include in your answer

i. A list of materials and equipment you will need.
ii. A description of the procedure you will use including the rinsing of the equipment prior to use.
iii. Quantities of materials you will use.
iv. A set of possible results you may obtain.
v. Relevant chemical equations and sample calculations for determining the amount of material to be used and for determining the concentration of acid in the wine from the results.
vi. Identify sources of error in the experiment and describe how you would minimise such errors

Question 9: Reagents used as primary standards

Measurement in Chemistry

Set 1: Measurement, Exponential Notation and Significant Figures

1 (a) 3 (b) 3 (c) 3 (d) 3 (e) 3
(f) 4 (g) 6 (h) 3

2 (a) 6.409×10^3 (b) 3.2×10^{-2} (c) 8.91×10^5 d) 5.38×10^1 (e) 6.1×10^{-6}

3. (a) 0.8 mm (b) 4.5 kg (c) 90 g (d) 703 L (e) 5×10^5 mL

4. 3.104 + 0.72 + 16.2 + 0.002 = 20.0 g

5. 2×10^4 g ÷ 3.819×10^{-23} = 5×10^{26} atoms

6.

	Pressure - mmHg	Pressure - atm	Pressure - Pa
(a)	760	1.00	1.01×10^5
(b)	750	9.87×10^{-1}	9.97×10^{-1}
(c)	1.56×10^3	2.05	2.07×10^5
(d)	100	1×10^{-1}	1×10^5
(e)	4.83×10^3	6.36×10^0	7.31×10^3

7. 0.103 + 11.45 + 0.01 + 0.001 + 68.53 = 80.09 g

Set 2: Errors

1. (a) first weighing = ±2 mg ∴ 0.002/12.363 × 100 = 0.02%; final weighing ± 2 mg ∴ 0.002/0.834 × 100 = 0.2%
(b) Total error ±4 mg = ±4 mg = 0.004/0.834 × 100 = 0.5 %

2. 153/36671 × 100 = 0.417 %

3. (a) 600 mg (b) 2 g

4. (a) 39.9 g (b) 40.3 ± 0.4 g

5. 6.04

6. 0.229

7. (a) 167 °C (b) -2×10^1 °C

8. (a) 0.141 kJ mol^{-1} (b) 0.255 kJ mol^{-1} (c) 0.966 kJ mol^{-1}

9. 18%

10. 0.24

Set 3: Random and Systematic and errors

1. Random Error: b and d Systematic Error: a and c

2. No one was correct. The instrument can only be read to half a graduation (3.7 mL)

3. 0.77 %

4. 0.007 cm

5. (a) Jenny (b) No (c) Obtain new glassware and solutions

6. (a) 0.0005 L (b) 2.39% .

7. parallax – note the view of the circles around the burette

8. (a) Lyndon random errors, Jenny has a close set of inaccurate results - systematic error
(b) Jenny has high precision and low accuracy, while Lyndon has low accuracy and low precision
(c) Jenny - adjust sights or obtain new equipment. Lyndon - needs coaching.

9. (a) 0.1% (b) 0.24% (c) 2 %

10. (a) 0.48% (b) 0.20% (c) 0.13%

11. $c(NaHCO_3)$ = 0.1164 mol L^{-1} ± 0.12 % $c(NaHCO_3)$ = 0.11642 ± 0.00014 mol L^{-1}

12. (a) 22.53 mL 1.33% (b) 0.67% (c) 8.92×10^{-4} mol 0.3 %
(d) 3.96×10^{-2} mol L^{-1} % uncertainty 1.63 % Absolute uncertainty 6.45×10^{-4}

13. (a) 5.53 11% (b) (i) 24.42 mL (ii) 2.5 % (c) Diluting ammonia increases average titre, reducing error.

Chemical equilibrium

Set 4: Reaction Rates and Energy

1. (a) Perform the experiment on a balance and observe the rate of loss of mass
(b) Capture the hydrogen by downward delivery of water and read the level of gas at regular intervals

2 Ions in solution need no activation energy, have an infinite surface area while the sugar requires large activation energy and has relatively small surface area

3 (a) increased concentration - more collisions higher rate of forward reaction
(b) increasing the concentration of the acid - more collisions and a higher rate of reaction

4 (a) increasing pressure decreases volume means concentration increases so the rate will increase
(b) no effect as reactants are in solutions

5 The catalyst provides a new pathway of lower activation energy. Offering a new pathway with lower activation energy means more particles can achieve activation and the rate will increase.

Set 5: Equilibrium constant expressions

1. $K = \frac{[H_2O]^2}{[H_2]^2[O_2]}$
2. $K = \frac{[N_2]^2[O_2]}{[N_2O]^2}$
3. $K = \frac{[CH_3OH]}{[H_2]^2[CO_2]}$
4. $K = [Ag^+]^2[CrO_4^{2-}]$
5. $K = \frac{[HCO_3^-][H^+]}{[CO_2]}$
6. $K = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]}$
7. $K = \frac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$
8. $K = [CO_2]$
9. $K = \frac{[CO_3^{2-}][NH_4^+]}{[HCO_3^-][NH_3]}$
10. $K = \frac{1}{[SO_3]}$
11. $K = [H_2O][CO_2]$
12. $K = \frac{1}{[C\ell_2]}$
13. $K = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]}$
14. $K = \frac{[HC\ell]^2}{[H_2O][CO_2]}$

Set 6 : Equilibrium Systems

1. (a) $K = \frac{[NH_3]^2}{[N_2][H_2]^2}$ (b) (i) decrease (ii) increase (iii) increase (iv) no change
2. (a) $K = \frac{[H^+]^4[OC\ell^-]^2}{[C\ell_2]}$ (b) (i) increase (ii) decrease (iii) increase (iv) decrease
3. (a) (i) decrease (ii) decrease (iii) increase
   (b) (i) decrease (ii) increase (iii) increase
4. (a) (i) increase (ii) increase (iii) decrease
   (b) (i) increase (ii) increase (iii) increase
5. (a) (i) increase (ii) decrease (iii) increase
   (b) (i) no effect (ii) same concentration (pressure) but more CO_2 is present (iii) increase

Set 7 Equilibrium: no answers provided

Acids and bases

Set 8 Acids and Bases

1. Conjugate acids: HF, HCO_3^-, $HC\ell O_4$, HSO_3^-, NH^{4+}
2. Conjugate bases: Br^-, SO_4^{2-}, HPO_4^{2-}, S^{2-}, NO_3^-, OH^-
3. (a) $H_2SO_4(aq)) + H_2O(\ell) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$ (b) $H_2S(aq)) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$
   (c) $KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$ (d) $N_2H_4(aq) + H_2O(\ell) \rightleftharpoons N_2H_5^+(aq) + OH^-(aq)$
4. A strong acid completely ionises in solution, while a weak acid only partially ionises in solution. Acid concentration refers to the amount of acid dissolved. A concentrated solution contains a high proportion of acid, while a dilute acid solution is mainly water with a very small proportion of acid.
5. I. conjugate acid–base pairs II. Reaction favours the formation of:
   a. $HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$
   acid base conjugate base conjugate acid — forward reaction
   b. $HSO_4^-(aq) + NH_3(aq) \rightleftharpoons SO_4^{2-}(aq) + NH_4^+(aq)$
   acid base conjugate base conjugate acid — forward
   c. $H_2CO_3(aq) + F^-(aq) \rightleftharpoons HCO_3^-(aq) + HF(aq)$
   acid base conjugate base conjugate acid — reverse reaction
   d. $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$
   acid base conjugate acid conjugate base — forward reaction

Set 9: Acid and Base strength

1. Concentration is a measure of the proportion of solute in a solution. Strength refers to the degree of ion formation when an acid or base is dissolved in water. Eg., hydrogen chloride a strong acid completely ionises: $HC\ell(aq) \rightarrow H^+(aq) + Cl(aq)$; hydrogen fluoride a weak acid - little ionisation: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

2. (a) $HC\ell$, HNO_3, H_2SO_4, HBr, HI, $HC\ell O_4$,
   (b) CH_3COOH, H_2S, HF, H_3PO_4, $H_2C_2O_4$, HSO_4^-, or any organic acid.
   (c) NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$, or any metal hydroxide or oxide.
   (d) NH_3, CO_3^{2-}, CH_3NH_2 or any organic amine.
3. (a) Concentrated and weak (b) Dilute and strong (c) Concentrated and strong (d) Dilute and weak
4. (i) (a) $HBr(g) \rightarrow H^+(aq) + Br^-(aq)$ (b) ionisation (c) HBr, OH^-, Br^-, H_3O^+, H_2O
   (ii) (a) $CH_3COOH(l) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ (b) ionisation
   (c) OH^-, CH_3COO^-, H_3O^+, CH_3COOH, H_2O
   (iii) (a) $H_2SO_4(\ell) \rightarrow H^+(aq) + HSO_4^-(aq)$ and $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$
   (b) ionisation (c) H_2SO_4, OH^-, SO_4^{2-}, HSO_4^-, H_3O^+, H_2O
   (iv) (a) $NH_3(g) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (b) ionisation
   (c) H_3O^+ or H^+, NH_4^+, OH^-, NH_3, H_2O (always use H_3O^+ when considering Bronsted-Lowry acids)
   (v) (a) $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$ (b) dissociation
   (c) $Ba(OH)_2$, H_3O^+, Ba^{2+}, OH^-, H_2O
5. Stronger acid is $HC\ell O_4$ and the weaker base is $C\ell O_4^-$
6. (a) $H_2S(g) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ and $HS^-(g) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$
   (b) Strongest acid is H_3O^+ and the strongest base is S^{2-}
7. (a) $H_3PO_4(\ell) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) > H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) > HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$
   (b) H_2O, H_3PO_4, H_3O^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, OH^-
8. 99% sulfuric acid consists mostly of H_2SO_4 molecules, little water so very few hydrogen ions to react with iron. 2 mol L^{-1} sulfuric acid a strong acid; full ionisation; a high concentration of hydrogen ions to react with the iron: $2\ H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$ Steel wool - high surface area, more collisions, higher rate of reaction.
9. For effective washing, large numbers of OH^- ions are required in the washing powder. Sodium hydroxide, strong base, high concentration of OH^- ions, but detrimental to fabrics and dangerous /corrosive to skin. Sodium carbonate, a weak base, lower concentrations of OH^- ions but as these are consumed, more are produced until all of the carbonate ions are used up: $CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
10. For this use $[H^+]$ must be very low but must be a process that replaces the H^+ used up - a weak acid. As hydrochloric acid is a strong acid the $[H^+]$, even in dilute solutions, is high and would damage human skin.

Set 10 : Hydrolysis

1 (a) neutral (b) basic (c) basic (d) acidic (e) basic
2. (b) $PO_4^{3-}(aq) + H_2O(\ell) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$
   (c) $HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
   (d) $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   (e) $CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
3. (a) Ammonium nitrate, calcium hydrogenphosphate, potassium sulfate, and ammonium chloride.
   (b) The salts contain either an anion of a weak acid or the cation of a weak base.
   (c) Ammonium nitrate (↓ pH) $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   calcium hydrogenphosphate (↑pH) $HPO_4^{2-}(aq) + H_2O(\ell) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$
   and $H_2PO_4^-(aq) + H_2O(\ell) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$
   potassium sulfate (↓pH) $SO_4^{2-}(aq) + H_2O(\ell) \rightleftharpoons HSO_4^-(aq) + OH^-(aq)$
   ammonium chloride (↓pH) $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   (d) These salts contain only ions derived from strong acids and strong bases so they do not react with water to produce the strong acid or strong base.
4. $Ca(H_2PO_4)_2(s) \rightleftharpoons 2\ H_2PO_4^-(aq) + Ca^{2+}(aq)$ and $H_2PO_4^-(aq) + H_2O(\ell) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$
5. (a) Yes, it becomes basic.
   (b) $Na_2CO_3(aq) \rightarrow 2\ Na^+(aq) + CO_3^{2-}(aq)$ and $CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
6. (a) $OH^-(aq) + CH_3COOH(aq) \rightleftharpoons H_2O(\ell) + CH_3COO^-(aq)$
   (b) The solution would be basic, pH > 7.
   (c) $CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
7. Yes it becomes basic as F^- is the anion of a weak acid. $F^-(aq) + H_2O(\ell) \rightleftharpoons HF(aq) + OH^-(aq)$
8. The pH of a solution of ammonium ethanoate depends on the relative strength of the weak base ammonia and the weak acid ethanoic acid. The hydrolysis process is represented by the equations:
   $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ and $CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
   Their ionisation constants are both close to 1.8×10^{-5} so the solution will be neutral.

Set 11: Water Equilibrium

1. $H_2O(\ell) + H_2O(\ell) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$
2. (a) $[OH^-] = 6.76 \times 10^{-8}$ mol L^{-1} (b) Acidic
3. $[H^+] = 6.33 \times 10^{-9}$ mol L^{-1} 4. (a) $[H^+] = 6.45 \times 10^{-11}$ mol L^{-1} (b) $[H^+] = 1.28 \times 10^{13}$ mol L^{-1}
5. (a) $[OH^-] = 9.62 \times 10^{-14}$ mol L^{-1}
   (b) $H_2SO_4(\ell) \rightarrow H^+(aq) + HSO_4^-(aq)$ and $HSO_4^-(aq) \rightarrow 0.9\ HSO_4^-(aq) + 0.1\ H^+(aq) + 0.1\ SO_4^{2-}(aq)$
   Overall $H_2SO_4(\ell) \rightarrow 0.9\ HSO_4^-(aq) + 1.1\ H^+(aq) + 0.1\ SO_4^{2-}(aq)$
   $[H^+] = 1.1\ [H_2SO_4] = 1.1 \times 0.125 = 0.1375$ mol L^{-1} $[OH^-] = 7.27 \times 10^{-14}$ mol L^{-1}
6. (a) Ionisation of water is endothermic: heat + $H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$ a change in temperature will change the proportion of reactants and products and so change the equilibrium constant.
   (b) K value decreases. A decreased in temperature causes the equilibrium position to move to restore some of the heat removed. H^+ and OH^- combine to produce water and heat, concentration become smaller.
   (c) If temperature is increased a greater concentration of hydrogen ions will result.
   (d) As the temperature is increased the rate of both the forward and reverse reactions will increase, but the endothermic forward reaction increases more than reverse reaction so hydrogen ion concentration increases.
7. (a) $[OH^-] = 6.45 \times 10^{-10}$ mol L^{-1}
   (b) Some release of SO_2 from the smelter with elevated levels of CO_2 dissolving in the rainwater.
   (c) $SO_2(aq) + H_2O(\ell) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$ and $CO_2(aq) + H_2O(\ell) + 4\ HCO_3^-(aq) + H^+(aq)$
8. $[H^+] = 8.07 \times 10^{-5}$ mol L^{-1} $[OH^-] = 1.24 \times 10^{-10}$ mol L^{-1}
9. (a) $[H^+] = 7.33 \times 10^{-6}$ mol L^{-1} $[OH^-] = 1.36 \times 10^{-9}$ mol L^{-1}
   (b) Excess $A\ell(OH)_3$ and $Mg(OH)_2$ would remain undissolved (both insoluble in water) and the concentration of both hydrogen and hydroxide ions would therefore be 1.00×10^{-7} mol L^{-1}.
10. (a) $V(Mg(OH)_2) = 4.86$ mL (b) $[H^+] = 8.34 \times 10^{-3}$ mol L^{-1} $[OH^-] = 1.20 \times 10^{-12}$ mol L^{-1}

Set 12 Indicators and their use

1. (a) An organic acid or base
   (b) The acid must be distinctly different in colour from its conjugate base.
   E.g.: H(Litmus) (aq) $\rightleftharpoons$ $H^+(aq)$ + (Litmus)$^-$(aq)
   Red Blue
2. (a) H(Indicator)(aq) $\rightleftharpoons$ $H^+(aq)$ + (indicator)$^-$(aq)
   (b) Addition of an acid increases $[H^+]$, causes more H(Indicator) to be produced and a reduction in the concentration of (Indicator)$^-$. The colour changes from the (Indicator)$^-$ colour to the H(Indicator) colour.
   (c) Addition of a base reduces $[H^+]$ as H^+ reacts with OH- to produce water. This causes the production of more (Indicator)$^-$ and less H(Indicator). The colour changes from H(Indicator) colour to (Indicator)$^-$ colour.
   (d) *Addition of Acid:* increase in the rate of the reaction producing H(Indicator) with no immediate change to the reaction producing (Indicator)$^-$ hence a colour change from (Indicator)" colour to H(Indicator) colour.
   Addition of Base: a reduction in $[H^+]$ causes a reduction in the rate of the reaction producing H(Indicator) with no immediate change in the rate of the reaction producing (Indicator)$^-$ hence a colour change from H(Indicator) colour to (Indicator)$^-$ colour.
3.

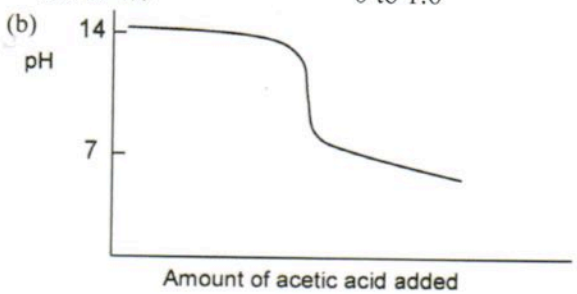
(a)	Phenolphthalein	Alizarin Yellow	Indigo Carmine
(b)	<pH=8.3 Colourless)	<pH = 10.1 (Yellow)	<pH = 11.4 (Blue)
	>pH = 10 (Pink)	>pH = 12.0 (Red)	>pH = 13.0 (Yellow)
(c)	8.3 to 10	|10.1 to 12.0	11.4 to 13.0

4.

(a)	Methyl red	Methyl orange	Bromophenol blue	Methyl violet
(b)	<pH = 4.4 (Red)	<pH = 3.1 (Red)	<pH = 3.0 (Yellow)	<pH = 0 (Yellow)
	>pH = 6.2 (Yellow)	>pH = 4.4 (Yellow)	>pH = 4.6 (blue)	>pH = 1.6 (Violet)
(c)	4.4 to 6.2	3.1 to 4.4	3.0 to 4.6	0 to 1.6

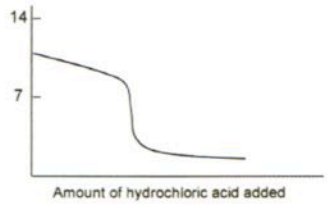
5. (a) H_2O, Na^+, CH_3COO^-, OH^-, CH_3COOH, H^+
   (c) The solution is basic.
   $CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
   (d) Phenolphthalein.
   The end point (the point where the colour changes) must occur at the equivalence point. As the equivalence point is basic use an indicator that changes colour within pH pH 7 and 11. Phenolphthalein changes in pH range 8.3 to 10.

(b)



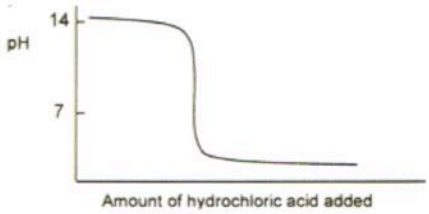
6. (a) H_2O, $C\ell^-$, NH_4^+, H_3O^+, NH_3, OH^-
   (c) The solution is acidic.
   $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   (d) methyl orange, methyl red or bromothymol blue.
   Acid equivalence point - use an indicator that changes colour (an end point) at a pH between about 3 and 7

   (b)



7. (a) H_2O, Ca^{2+} / $C\ell^-$, OH^- / H^+
   (c) The solution is neutral. Neither the calcium ion nor the chloride ion will react with water to undergo hydrolysis.
   (d) Most indicators will give the correct equivalence point, which is at pH = 7 as long as they change colour (have an end point) somewhere in the range of pH = about 3 to 11.

   (b)



8. (a) Phenolphthalein. (b) More acid will be used. (c) The concentration measured lower than it actually is.

Set 13 : The pH Scale

1. (a) $[H^+] = [HC\ell] = 0.100$ mol L^{-1} $[OH^-] = 1.00 \times 10^{-13}$ mol L^{-1}; pH = 1.00
   (b) $[H^+] = [HNO_3] = 0.00500$ mol L^{-1} $[OH^-] = 2.00 \times 10^{-12}$ mol L^{-1}; pH = 2.30
   (c) $[OH^-] = [NaOH] = 0.0100$ mol L^{-1} $[H^+] = 1.00 \times 10^{-12}$ mol L^{-1}; pH = 12.0
   (d) $[H^+] = [HC\ell] = 2.00$ mol L^{-1} $[OH^-] = 5.00 \times 10^{-15}$ mol L^{-1}; pH = 0.300
   (e) $[H^+] = [OH^-] = 1.00 \times 10^{-14}$ mol L^{-1} and the pH = 7.00. Neutral as solutions of Na^+ ions and $C\ell^-$ ions do not hydrolyse in water.
2. (a) $[H^+] = 1.00 \times 10^{-3}$ mol L^{-1} $[OH^-] = 1.00 \times 10^{-11}$ mol L^{-1}
   (b) $[H^+] = 1.00 \times 10^{-11}$ mol L^{-1} $[OH^-] = 1.00 \times 10^{-3}$ mol L^{-1}
   (c) $[H^+] = 10.0$ mol L^{-1} $[OH^-] = 1.00 \times 10^{-15}$ mol L^{-1}
   (d) $[H^+] = 2.75 \times 10^{-5}$ mol L^{-1} $[OH^-] = 3.63 \times 10^{-10}$ mol L^{-1}
   (e) $[H^+] = 2.51 \times 10^{-8}$ mol L^{-1} $[OH^-] = 3.98 \times 10^{-7}$ mol L-^{1}
3. Concentration changed by a factor of 1000
4. $[H^+] = 1.80$ mol L^{-1}
5. Water required = 630 - 25.0 = 605 mL
6. $m(NaOH)_{\text{to be added}} = 20.0$ mg
7. (a) pH = 13.3 (b) $V(HC\ell) = 188$ mL
8. pH = 9.13
9. $V(HC\ell) = 7.87$ mL
10. (a) pH = 5.39 (b) pH = 7.61

Set 14 : Buffers

1. Buffer solutions resist a change in pH even with the addition of substantial amounts of hydrogen or hydroxide ions. Many specific reactions that occur in biological systems occur only at specific pH values. Some reactions produce or use up hydrogen ions in these solutions. Buffers prevent large changes in the pH of solutions such as - blood, cell contents and lymph system allowing vital reactions to continue.
2. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell)$ $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$
   Thus a buffer can accept or donate a proton to approximately maintain pH
3. Buffer solutions can be produced that have specific and known pH value. The fixed pH values are use as standards to calibrate the meters.
4. (a) Hypochlorite ions added to pool water as sodium hypochlorite solution or calcium hypochlorite solid to kill micro organisms. Weak acid hypochlorous acid forms: $OC\ell^-(aq) + H_2O(\ell) \rightleftharpoons HOC\ell(aq) + OH^-(aq)$
   The buffer uses up some of these OH^- ions stopping the pool water becoming alkaline too quickly.
   (b) $OH^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2O(\ell) + CO_3^{2-}(aq)$ and $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ where the H^+ reacts with the OH^-. Both processes use up OH^- ions.
5. (a) H_2O and HCO_3^- ion (b) $CO_2(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$
   H^+ ion is used up by reacting with the HCO_3^- as indicated in the reverse reaction above and OH^- ions is used up by reacting with CO_2 directly, $OH^-(aq) + CO_2(aq) \rightleftharpoons HCO_3^-(aq)$ or with H^+ ions which results in more H^+ ions being produced. $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(\ell)$
6. Method 1: Add an equal volume of 1 mol L^{-1} sodium ethanoate solution
   Method 2: Add an equal volume of a 0.5 mol L^{-1} solution of sodium hydroxide. This reacts with half the acetic acid to produce acetate ion as in the equation: $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(\ell)$

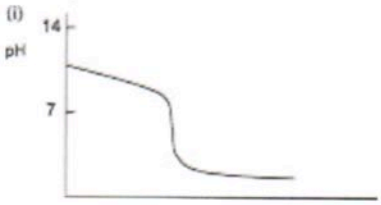
7. Method 1 Make a solution in water of the sodium citrate mixed with an equal number of moles of citric acid. Method 2 Make a solution in water of the sodium citrate add 1½ times that number of moles of hydrochloric acid. This reacts with half the citrate ion to produce citric acid: $C_6H_5O_7^{3-}(aq) + 3\ H^+(aq) \rightleftharpoons H_3C_6H_5O_7(aq)$
8. A change in temperature changes the equilibrium concentration of the species in equilibrium and as one of the species is always either H^+ or OH^- ions, changing their concentrations changes the pH.

Set 15: Acid-base titrations 1

1. a) $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ V = 0.400 L
   b) $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(\ell)$ V = 0.450 L
   c) $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ V = 0.0200 L
   d) $H_3PO_4(aq) + 3\ OH^-(aq) \rightarrow PO_4^{3-}(aq) + 3\ H_2O(1)$ V = 0.360 L
2. a) $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ V = 0.300 L
   b) $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ V = 0.0250 L
3. 8.86×10^{-2} mol L^{-1}
4. 4.44 mol L^{-1}
5. 7.00×10^{-2} mol L^{-1}
6. 0.103 L
7. 10.5 g
8. a) 223 g b) 0.189 L (189 mL)
9. a) i) 0.107 mol L^{-1} ii) 3.89 g L^{-1} b) 0.935 L (935 mL) c) 0.140 L (140 mL)
10. 7.34×10^{-2} mol L^{-1}
11. 25.2 mL of KOH
12. 57.5%
13. 192 g mol^{-1}
14. 0.954 g of Na_2CO_3

Set 16: Acid-bases titrations 2

1. [Acid] = 1.38×10^{-5} mol L^{-1}
2. [Acid] = 2.53 mol L^{-1}
3. $[HCO_3^-] = 6.32 \times 10^{-6}$ mol L^{-1}
4. [OH-] = 1.59×10^{-6} mol L-^{1}
5. [lactic acid] = 9.97×10^{-6} mol L^{-1}
6. pH = $-\log_{10}[H^+] = -\log_{10}(11.2) = -1.05$
7. $[H_3C_6H_5O_7]_{ppm}$ = 31.4 ppm
8. (a) $NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$ (b) pH = 2.06
   (c) (ii) Methyl orange, methyl red or bromothymol blue.
   (iii) As the equivalence point is acidic an indicator that changes colour at a pH between about 3 and 7 is required. Methyl orange (3.1 - 4.4), methyl red (4.4 - 6.2) and bromothymol blue (3.0 - 4.6) all change colour within this range.



Volume of diluted gaustric fluid added

9. [Fe] ppm = 20.1 ppm
10. %Pb = 90.4%

Set 17 Acids and Bases in Action: no answers provided

Oxidation and reduction

Set 18: Oxidation Number

1.(a)	+4	(b)	-2	(c)	+6	(d)	+2	(e)	+6	(f)	+5
(g)	-3	(h)	+2	(i)	+5	(j)	+5	(k)	-4	(l)	+4
(m)	-2	(n)	0	(o)	+2	(p)	+4	(q)	+1	(r)	-3
(s)	+5	(t)	-2	(u)	+4	(v)	+2	(w)	+1	(x)	+2
(y)	+2	(z)	+3								

2. (a) Mg (0 +2) O (0 -2)
   (b) Na (0 +1) H (+1 0)
   (c) I (-1 0) C(0 -1)
   (d) S (-2 0) N (+5 +2)
   (e) S (-2 0) Mn (+7 +2)
   (f) Sn (+2 +4) O (0 -2)
   (g) Br (-1 0) S (+6 +4)
   (h) Fe (+2 +3) Cr (+6 +3)
   (i) None (this is an acid/base reaction)
   (j) N (-3 0) N (+3 0)
   (k) None (this is a precipitation reaction)
   (l) None (this is an acid/carbonate equation)
   (m) None (this is an acid/base neutralisation equation)
   (n) None (this is a precipitation reaction)

Set 19: Balancing half equations

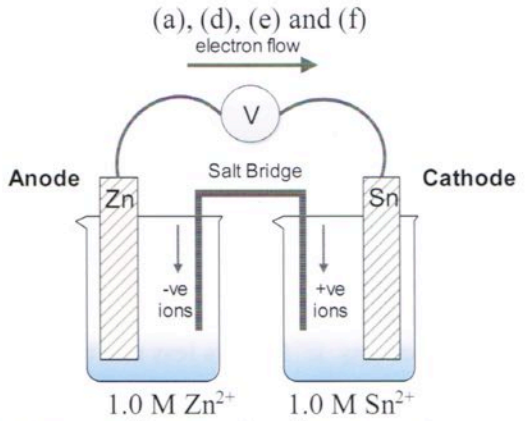
1. $Mg \rightarrow Mg^{2+} + 2\ e^-$ Oxidation
2. $S + 2\ e^- \rightarrow S^{2-}$ Reduction
3. $2\ C\ell^- \rightarrow C\ell_2 + 2\ e^-$ Oxidation
4. $Ca \rightarrow Ca^{2+} + 2\ e^-$ Oxidation
5. $I_2 + 2\ e^- \rightarrow 2\ I^-$ Reduction
6. $Zn \rightarrow Zn^{2+} + 2\ e^-$ Oxidation
7. $Cu^+ \rightarrow Cu^{2+} + e^-$ Oxidation
8. $Au^+ + e^- \rightarrow Au$ Reduction
9. $2\ H^+ + 2\ e^- \rightarrow H_2$ Reduction
10. $Cu^{2+} + 2\ e^- \rightarrow Cu$ Reduction
11. $AsO_3^{3-} + H_2O \rightarrow AsO_4^{3-} + 2\ H^+ + 2\ e^-$ Oxidation
12. $S_2O_3^{2-} + 5\ H_2O \rightarrow 2\ SO_4^{2-} + 10\ H^+ + 4\ e^-$ Oxidation
13. $NO_3^- + 10\ H^+ + 8\ e^- \rightarrow NH_4^+ + 3\ H_2O$ Reduction
14. $MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ Reduction

Set 20: Balancing Redox Equations I

1. $Br_2 + 2\ I^- \rightarrow 2\ Br^- + I_2$
2. $Cu + 2\ Ag^+ \rightarrow Cu^{2+} + 2\ Ag$
3. $Mg + Pb^{2+} \rightarrow Mg^{2+} + Pb$
4. $Mg + 2\ H^+ \rightarrow Mg^{2+} + H_2$
5. $2\ A\ell + 6\ H^+ \rightarrow 2\ A\ell^{3+} + 3\ H_2$
6. $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
7. $2\ A\ell + 3\ Zn^{2+} \rightarrow 2\ A\ell^{3+} + 3\ Zn$
8. $Cu + 2\ Fe^{3+} \rightarrow Cu^{2+} + 2\ Fe^{2+}$
9. $Zn + 2\ Ag^+ \rightarrow Zn^{2+} + 2\ Ag$
10. $C\ell_2 + 2\ I^- \rightarrow 2\ C\ell^- + I_2$
11. $2\ Li + 2\ H_2O \rightarrow 2\ Li^+ + 2\ OH^- + H_2$
12. $Cu + 2\ NO_3^- + 4\ H^+ \rightarrow Cu^{2+} + 2\ NO_2 + 2\ H_2O$
13. $Cu + SO_4^{2-} + 4\ H^+ \rightarrow + Cu^{2+} + SO_2 + 2\ H_2O$
14. $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$
15. $Cr_2O_7^{2-} + 8\ H^+ + 3\ C_2H_5OH \rightarrow 2\ Cr^{3+} + 3\ CH_3CHO + 7\ H_2O$
16. $Mg + 2\ H_2O \rightarrow Mg^{2+} + H_2 + 2\ OH^-$
17. $Cu_2O + 2\ H^+ \rightarrow Cu + Cu^{2+} + H_2O$
18. $4\ Au + 16\ CN^- + 3\ O_2 + 12\ H^+ \rightarrow 4\ [Au(CN)_4]^- + 6\ H_2O$
19. (a) $I_2 + 2\ e^- \rightarrow 2\ I^-$ (b) $S_2O_3^{2-} + 5\ H_2O \rightarrow 2\ SO_4^{2-} + 8\ e^- + 10\ H^+$
    (c) $S_2O_3^{2-} + 5\ H_2O + 4\ I_2 \rightarrow 2\ SO_4^{2-} + 10\ H^+ + 8\ I^-$
20. (a) $CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2\ H^+ + 2\ e^-$ (b) $O_2 + 2\ H_2O + 8\ e^- \rightarrow 4\ OH^-$
    (c) $2\ CH_3CH_2OH + O_2 \rightarrow 2\ CH_3COOH$
21. (a) $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$ (b) O_2 is reduced and C in the glucose is oxidised
    (c) O_2 is the oxidising agent, $C_6H_{12}O_6$ is the reducing agent
22. (a) Ox: $Mg \rightarrow Mg^{2+} + 2\ e^-$ Red: $Ti^{4+} + 4\ e^- \rightarrow Ti$ RedOx: $2\ Mg + TiC\ell_4 \rightarrow 2\ MgC\ell_2 + Ti^{4+}$
    (b) $TiC\ell_4$ is reduced, Mg metal is oxidised
23. (a) $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$ (b) NO_2 is both (c) A disproportionation reaction

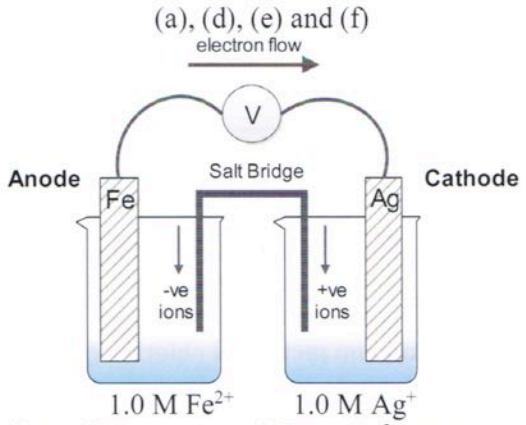
Set 21: Galvanic cells

1. (i)



(b) $Zn \rightarrow Zn^{2+} + 2e^-$ // $Sn^{2+} + 2e^- \rightarrow Sn$
(c) $Zn + Sn^{2+} \rightarrow Zn^{2+} + Sn$
(g) $E^o = +0.62$ V

(ii)



(b) $Ag^+ + e^- \rightarrow Ag$ // $Fe \rightarrow Fe^{2+} + e^-$
(c) $2Ag^+ + Fe \rightarrow 2Ag + Fe^{2+}$
(g) $E^o = +1.24$ V

2. (a) $Cr + 3\ Ag^+ \rightarrow Cr^{3+} + 3\ Ag$ $E^o = +1.54$ V
   (b) $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$ $E^o = +2.70$ V
   (c) $Mg + 2\ Ag^+ \rightarrow Mg^{2+} + 2\ Ag$ $E^o = +3.61$ V
   (d) $Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 7\ H_2O + 6\ Fe^{3+}$ $E^o = +0.59$ V
   (e) $C\ell_2 + 2\ I^- \rightarrow 2\ C\ell^- + I_2$ $E^o = +0.82$ V

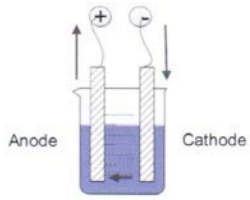
3. (a) yes $E^o = +0.97$ (b) no $E^o = -0.94$ (c) no $E^o = -1.53$ (d) no $E^o = -0.34$

4. (a) $Mg + 2\,H^+ \rightarrow Mg^{2+} + H_2$ $E^o = +2.36$ V
$Sn + 2\,H^+ \rightarrow Sn^{2+} + H_2$ $E^o = +0.14$ V
$Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$ $E^o = +0.76$ V
$Sr + 2\,H^+ \rightarrow Sr^{2+} + H_2$ $E^o = +2.90$ V
$Cu + 2\,H^+ \rightarrow Cu^{2+} + H_2$ $E^o = -0.34$ V
$2\,Ag + 2\,H^+ \rightarrow 2\,Ag^+ + H_2$ $E^o = -0.80$ V
Only those with a positive E^o will be spontaneous. Mg, Sn, Zn, Sr
(b) The total E^o must be positive for the first but negative for the second.
(i) Sn or Ni (ii) acidified H_2O_2 or MnO_4^- (iii) Pb, Sn, Ni, Co
(iv) $O_2/4H^+, Cr_2O_7^{2-}, C\ell_2$ (v) Au, $C\ell^-$

5. (a) $Fe^{2+} + Fe^{2+} \rightarrow Fe^{3+} + Fe$ $E^o = -1.21$V not spontaneous
(b) $H_2O_2 + H_2O_2 \rightarrow 2\,H_2O + O_2$ $E^o = +1.06$ V spontaneous
(c) $C\ell_2 + C\ell_2 \rightarrow 2\,HOC\ell + 2\,HC\ell$ $E^o = -0.27$ V not spontaneous

6. (a) $C\ell_2 + 2\,Br^- \rightarrow 2\,C\ell^- + Br_2$ +0.28 V (b) No reaction
(c) $2\,A\ell + 6\,H^+ \rightarrow 2\,A\ell^{3+} + 3\,H_2$ +1.68 V (d) $Fe + Sn^{2+} \rightarrow Fe^{2+} + Sn$ +0.30 V
(e) No Reaction (f) $Cr_2O_7^{2-} + 8\,H^+ + 3\,H_2S \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,S$ +1.19 V
(g) No Reaction (h) Both Br^- and Fe^{2+} are oxidized

Set 22: Electrolytic Cells



1. (a) See diagram
(b) Anode: $2\,H_2O(\ell) \rightarrow 4\,e^- + 4\,H^+ + O_2(g)$ Cathode : $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$
(c) -1.23 + 0.34 = -0.89 V The cell would require at least 0.89 V to be supplied
(d) The blue solution would fade and a colourless odourless gas would bubble off.

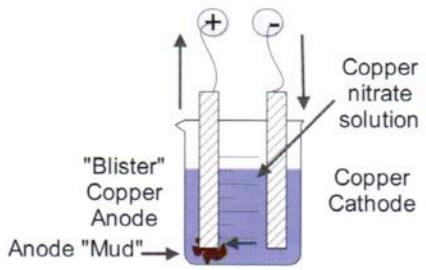
2.

	HBr (aq)	NiI_2 (aq)	$KC\ell$ (ℓ)
Products	H_2 and Br_2	Ni and I_2	$C\ell_2$ and K
Anode	$2\,Br^-(aq) \rightarrow 2\,e^- + Br_2(aq)$	$2I^-(aq) \rightarrow I_2(aq) + 2e^-$	$2\,C\ell^- \rightarrow 2\,e^- + C\ell_2$
Cathode	$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$	$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	$K^+ + e- \rightarrow K$
Overall	$2\,H^+(aq) + 2\,Br^-(aq) \rightarrow H_2(g) + Br_2(aq)$	$2\,I^-(aq) + Ni^{2+}(aq) \rightarrow Ni(s) + I_2(aq)$	$2\,K^+ + 2\,C\ell^- \rightarrow K + C\ell_2$
Min Voltage	1.08 V	0.78 V	Cannot be determined from data sheet as not standard conditions
Observe	Colourless gas and orange solution	Colourless gas and brown solution	Green pungent gas and silver solid

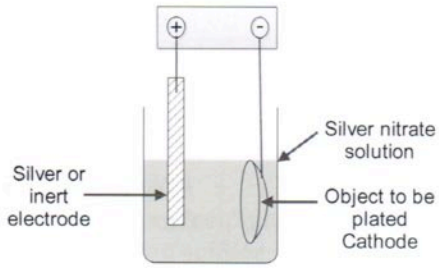
	$PbBr_2$ (ℓ)	$CoCl_2$ (ℓ)
Products	Pb and Br_2	Co and $C\ell_2$
Anode	$2\,Br^-(aq) \rightarrow 2e^- + Br_2(aq)$	$2\,Cl^- \rightarrow 2\,e^- + Cl_2$
Cathode	$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$	$Co^{2+}(aq) + 2\,e^- \rightarrow Co(s)$
Overall	$Pb^{2+} + 2\,Br^- \rightarrow Pb + Br_2$	$Co^{2+} + 2\,C\ell^- \rightarrow Co(s) + C\ell_2(g)$
Min Voltage	Cannot be determined from data sheet as not standard conditions	Cannot be determined from data sheet as not standard conditions
Observe	Red liquid and silver/grey solid	Green pungent gas and silver solid

3. (a) Aluminium metal and chlorine gas (b) Hydrogen gas and oxygen gas. E^o favours less reactive substances

4.



Electrorefining of copper



Silver plating a spoon

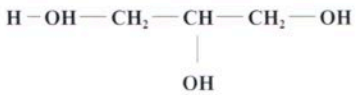
Set 23: Oxidation and Reduction: no answers provided

Organic materials

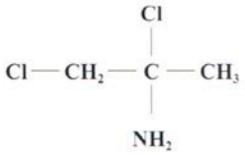
Set 24: Organic compounds

1.
(a) propan-2-ol
(b) 2-methylbutan-l-ol
(c) propan-1-amine
(d) 5-methylhexan-3-ol
(f) 2-methylbutan-2-ol
(g) 4-chloro-4-methylhexan-l-ol
(h) 3-methylcyclopentanol
(e) 5-chloro-4-ethylheptan-2-amine

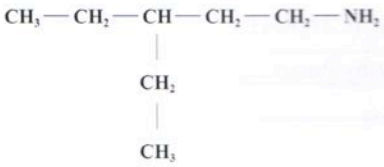
2.
(a) $CH_3CH_2CH_2CH_2CH_2OH$
(b) $CH_3CH_2CHCH_2CH_2NH_2$
(c)



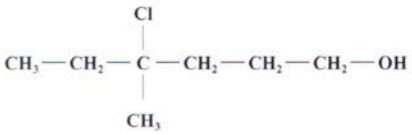
(d) $BrCH_2CH_2CH_2OH$
(e)



(f)



(g)



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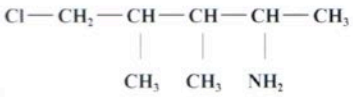
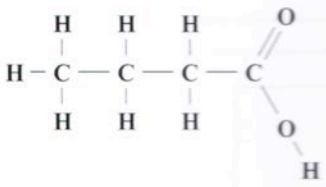
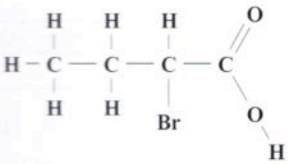
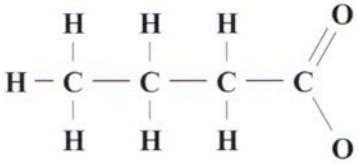
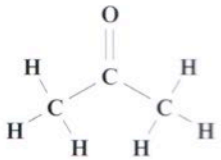
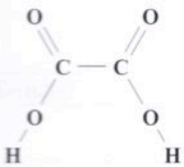
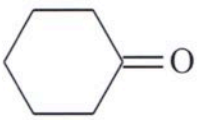
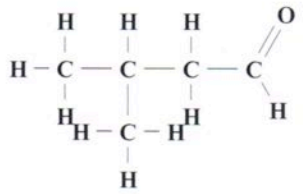
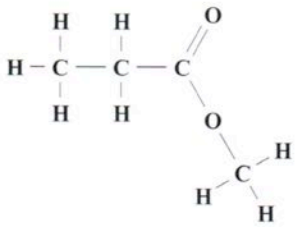
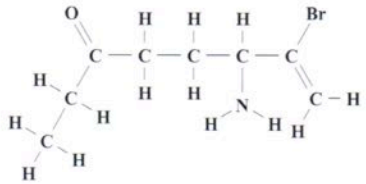
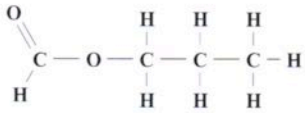


(i)

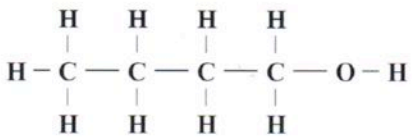
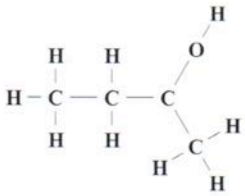
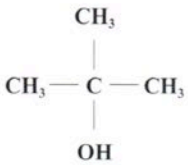
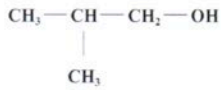
3.
(a) methanal
(b) pentan-2-one
(c) propanal
(d) 2-chloro-4-methylhexanal
(e) butanone (butan-2-one)
(f) 2,5-dimethylhexan-3-one
(g) butanoic acid
(h) 3-chloropropanoic acid
(i) sodium propanoate
(j) methyl ethanoate

4.

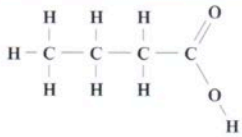
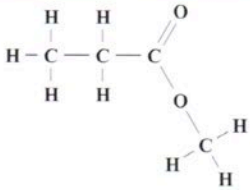
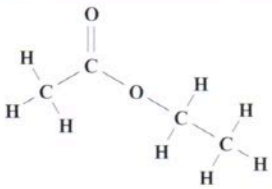
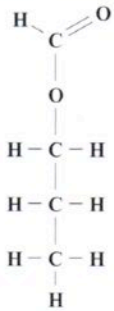
(a) 	(e) 	(i) 
(b) 	(f) 	(j) 

(c) 	(g) 
(d) 	(h) 

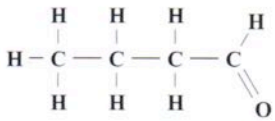
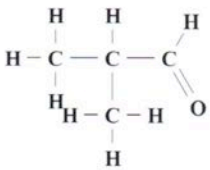
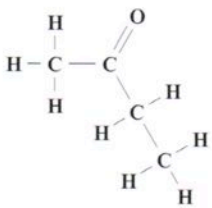
5. (a)

	 $CH_3CH_2COHCH_3$	 $CH_3C(CH_3)OHCH_3$	 $CH_3CH(CH_3)CH_2OH$
butan-l-ol	butan-2-ol	2-methylbutan-2-ol	2-methylpropan-l-oI

(b)

			
butanoic acid	methyl propanoate	ethyl ethanoate	propyl methanoate

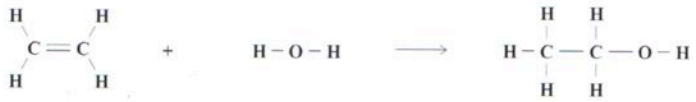
(c)

		
butanal	methyl propanal	butan-2-one

Set 25: Reactions of organic compounds

1. $CH_3CH_2CH_3 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$
2. (a) $CH_4 + C\ell_2 \rightarrow CH_3C\ell + HC\ell$ chloromethane (b) $CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$ 1,2-dibromomethane
   (c) $CH_3CHCHCH_3 + H_2O \rightarrow CH_3CH_2COHCH_3$ butan-2-ol
   (d) $CH_3CHCH_2 + H_2 \rightarrow CH_3CH_2CH_3$ propane
   (e) $C_6H_{10} + HBr \rightarrow C_6H_{11}Br$ 1,2-dibromocyclohexane

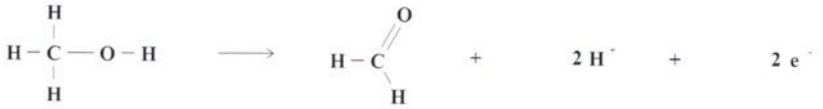
3. (a) ethene and water. Step 1: ethene and water (steam).



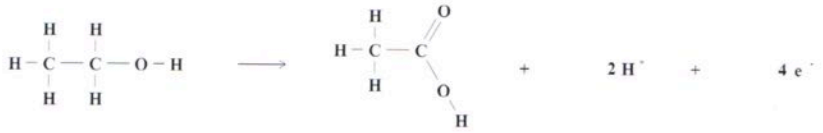
(b) chlorofluromethane Step 1: methane, limited chlorine, ultraviolet light.

Step 2: chloromethane, limited fluorine and ultraviolet light.

4. (a)



(b)



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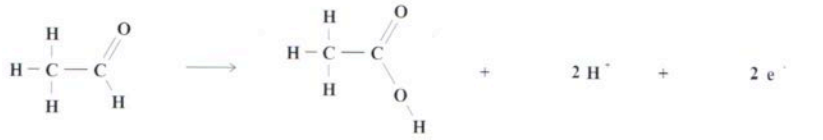
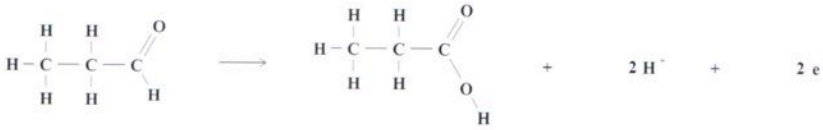
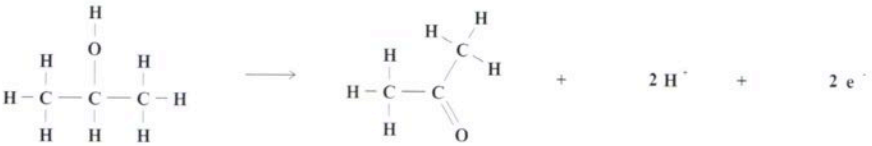


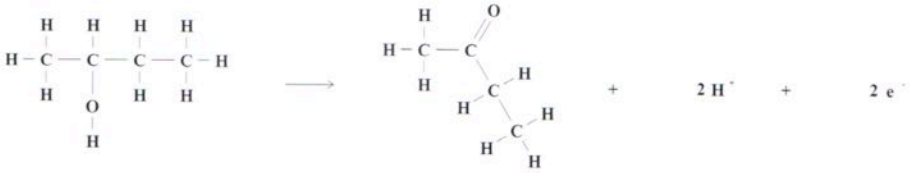
(d)



(e)



(f)



5 (a) $5\ CH_3CH_2CH_2CH_2COH + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ CH_3CH_2CH_2CH_2COOH + 2\ Mn^{2+} + 3\ H_2O$ pentanoic acid

(b) $5\ CH_3CH_2CH_2OH + 4\ MnO_4^- + 12\ H^+ \rightarrow 5\ CH_3CH_2COOH + 4\ Mn^{2+} + 11\ H_2O$ propanoic acid

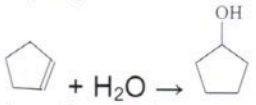
(c) $5\ CH_3CHOHCH_3 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ CH_3COCH_3 + 2\ Mn^{2+} + 8\ H_2O$ propanone

(d) $3\ CH_3CH_2CH_2CH_2OH + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3CH_2CH_2CCHO + 2\ Cr^{3+} + 7\ H_2O$ butanal

(e) $3\ CHCCHO + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3COOH + 2\ Cr^{3+} + 4\ H_2O$ ethanoic acid
(f) $3\ CH_3OH + 2\ Cr_2O_7^{2-} + 16\ H^+ \rightarrow 3\ HCOOH + 4\ Cr^{3+} + 11\ H_2O$ methanoic acid
(g) $3\ CH_3CHOHCH_2CH_3 + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3COCH_2CH_3 + 2\ Cr^{3+} + 7\ H_2O$ butan-2-one
(h) $5\ CH_3CH_2CH_2OH + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ CH_3CH_2CHO + 2\ Mn^{2+} + 8\ H_2O$ propanal

6. (a) $2\ CH_3OH + 2\ Na \rightarrow H_2 + 2\ CH_3O^- + 2\ Na^+$ methoxide ion
(b) $2\ CH_3CHOHCH_3 + 2\ Na \rightarrow H_2 + 2\ CH_3(ONa)CHCH_3$ sodium prop-2-oxide
(c) $CH_3CH_2COOH + CH_3CH_2CH_2CH_2OH + H^+ \rightarrow CH_3CH_2COOCH_2CH_2CH_2CH_3 + H_2O$ butyl propanoate
(d) $HCOOH + CH_3CHOHCH_3 \rightarrow HCOOCH(CH_3)CH_3 + H_2O$ 2-propyl methanoate
(e) $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O$ propanoate ion
(f) $CH_3COO^- + H^+ \rightarrow CH_3COOH$ ethanoic acid

7. (a) butan-2-ol, and acidified MnO_4^- or acidified $Cr_2O_7^{2-}$.
$5\ CH_3CHOHCH_2CH_3 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ CH_3COCH_2CH_3 + 2\ Mn^{2+} + 8\ H_2O$
(b) methane, CH_4, and chlorine. $CH_4 + C\ell_2 \rightarrow CH_3C\ell + HC\ell$ then
$CH_3C\ell + C\ell_2 \rightarrow CH_2C\ell_2 + HC\ell$ finally $CH_2C\ell_2 + C\ell_2 \rightarrow CHC\ell_3 + HC\ell$
(c) pentan-l-ol, $CH_3CH_2CH_2CH_2CH_2OH$, and acidified MnO_4^- or acidified $Cr_2O_7^{2-}$.
$5\ CH_3CH_2CH_2CH_2OH + 4\ MnO_4^- + 12\ H^+ \rightarrow 5\ CH_3CH_2CH_2CH_2COOH + 4\ Mn^{2+} + 11\ H_2O$
(d) propanoic acid, propan-l-ol, $CH_3CH_2CH_2OH$ and conc sulfuric acid.
$CH_3CH_2COOH + CH_3CH_2CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$
(e) Cyclopentene and water (steam).



(f) hex-2-ene, $CH_3CH{=}CHCH_2CH_2CH_3$ and bromine.
$CH_3CH{=}CHCH_2CH_2CH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_2CH_2CH_3$
(g) propene, $CH_3CH{=}CH_2$ and hydrogen chloride. $CH_3CH{=}CH_2 + HC\ell \rightarrow CH_3CHC\ell CH_3$
(h) pentan-l-ol, $CH_3CH_2CH_2CH_2CH_2OH$, and acidified $Cr_2O_7^{2-}$ in limited quantities.
$3\ CH_3CH_2CH_2CH_2CH_2OH + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3CH_2CH_2CH_2CHO + 2\ Cr^{3+} + 7\ H_2O$
(i) ethanol, CH_3CH_2OH, methanoic acid and sulfuric acid. $CH_3CH_2OH + HCOOH \rightarrow HCOOCH_2CH_3 + H_2O$
(j) but-1-ene, $CH_2{=}CHCH_2CH_3$, and water. $CH_2{=}CHCH_2CH_3 + H_2O \rightarrow CH_3CHOHCH_2CH_3$

Set 26: Calculations Involving Carbon Compounds

1. $m(CH_3CH{=}CH_2) = 0.700$ kg
2. (a) $m(CH_3ONa) = 421$ g (b) $V(H_2)stp = 88.6$ L (c) Using $PV = nRT$, $V_2 = 93.8$ L
3. (a) $V(CO_2) = 3.00$ L
4. (a) $m(CH_3(CH_2)_{11}C_6H_4SO_3Na) = 68.3$ kg (b) $m(NaOH)_{left} = 659\ g = 0.659\ kg$
5. (a) $[C_{10}H_8] = 1.56\ mol\ L^{-1}$ (b) $V(H_2O)_{to\ remove} = 111$ mL
6. 12.6%
7. (a) $[titratable\ acid] = 1.23 \times 10^{-5}\ mol\ L^{-1}$ (b) pH = 2.609
8. (a) $[CH_3CH_2OH]_{wine} = 3.12\ mol\ L^{-1}$ (b) $[CH_3CH_2OH]_{wine\ in\ g\ per\ L} = 144\ g\ L^{-1}$
9 (a) $[CH_3NH_2] = 0.632\ mol\ L^{-1}$ (b) $\%CH_3NH_2 = 1.83\%$
10. $[CH_3CHOHCH_3]$in g per L = 219 g L^{-1}

Set 27: Empirical, molecular and structural formula

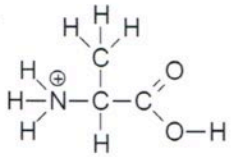
1. (a) CH_2 (b) C_4H_8
(c) $CH_3CH_2CH{=}CH_2$ $CH_3CH{=}CHCH_3$ $CH_3CCH_3{=}CH_2$
(d) Bromine adds to atoms either end of the double bond so the double bond is between atoms 2 and 3 therefore formula is $CH_3CH{=}CHCH_3$ that is but-2-ene
2. (a) C_2H_6O
(b) $M_r(C_2H_6O) = 46.068$ Relative molecular mass is the same as the relative empirical formula mass so the molecular formula is C_2H_6O
(c) Possible structures include: CH_3CH_2OH and $H_3C\text{-}O\text{-}CH_3$
(d) As the compound reacts with sodium it is most likely an alcohol that is CH_3CH_2OH

3. (a) CH_3O (b) $M_r = 61.975$, C_2H_6O
   (c) As the compound reacts with sodium it is most likely an alcohol so possible structures are.
   $HOCH_2CH_2OH$ or $CH_3CH(OH)_2$
4. (a) C_2H_5NO (b) $M_r(C_2H_5NO) = 59.007$ Molecular formula C_2H_5NO
   (c) Possible structures for a compound with this molecular formula include. NH_2CH_2CHO CH_3CONH_2
5. (a) C_6H_7N (b) C_6H_7N (c)
6. (a) $C_4H_{10}O$ (b) $M_r(C_4H_{10}O) = 74.12$, $C_4H_{10}O$
   (c) Possible structures include:
   $CH_3CH_2CH_2CH_2OH$ $CH_3CH_2CHOHCH_3$ $CH_3C(CH_3)OHCH_3$ $H_3CH(CH_3)CH_2OHCH_2OH$
   (d) Based on the observed reactivity's the structure of the compound is $CH_3C(CH_3)OHCH_3$
7 (a) C_2H_4O (b) $C_4H_8O_2$
   (c) $CH_3COOCH_2CH_3$ or $HCOOCH_2CH_2CH_3$ or $CH_3CH_2COOCH_3$

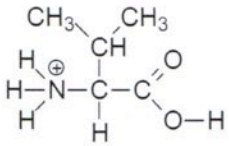
Set 28: Amino Acids

1.

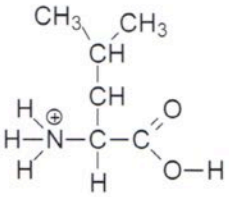
(a) Acid forms (pH3):



Alanine

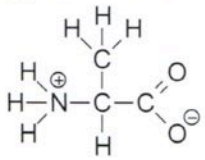


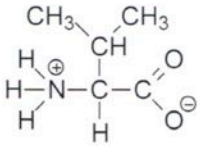
Valine

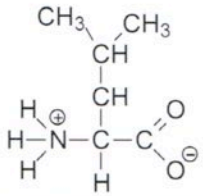


Leucine

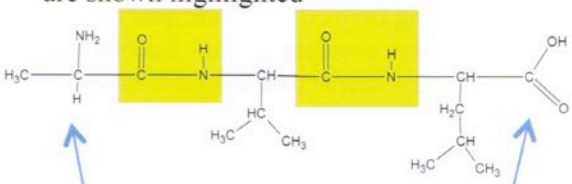
(b) Zwitterion forms





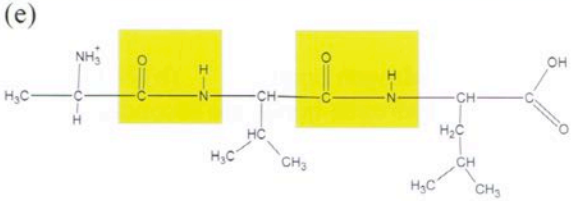


(c) The groups and the resulting peptide bonds are shown highlighted

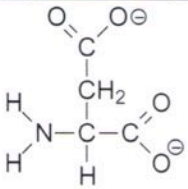
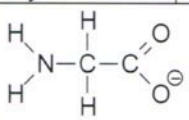
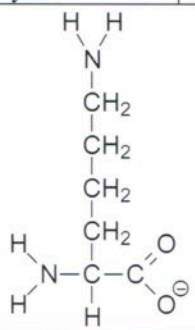


(d) amino terminus ---------- carboxy terminus
By convention, peptides are names from the amino to the carboxy terminus

(e)

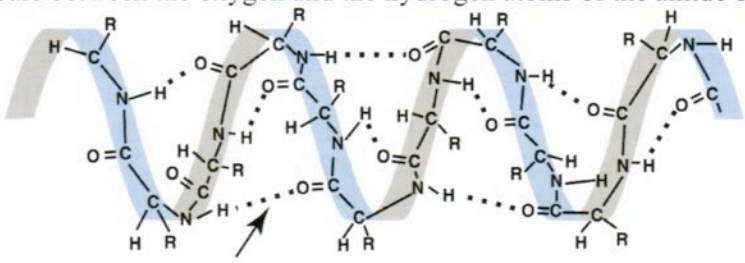


2. Enzymes are biological catalysts that speed up chemical reactions. In biological systems, other ways of speeding up reactions, such as increasing temperature, concentration or pressure are often not achievable without killing the organism. Without enzyme catalysts, many cellular reactions would not take place under cellular conditions.
3. 3 4. 99
5.

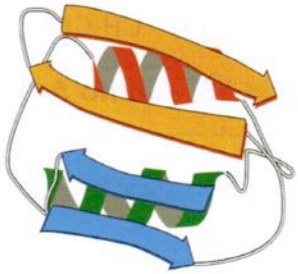
Name	Symbol	Name	Symbol	Name	Symbol
Aspartic acid	Asp	Glycine	Gly	lysine	Lys
					

Set 29: Proteins

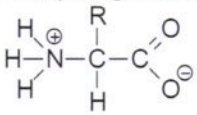
1. The primary structure is the linear sequence of amino acid residues in a protein.
   The secondary structure (figure below) is the structure that arises from the arrangement of hydrogen bonds that occurs between the oxygen and the hydrogen atoms of the amide bonds that occur in the proteins backbone.



Hydrogen bonds between amino acids at different locations in polypeptde chain



α-helix

   The tertiary structure is the overall shape that a polypeptide chain forms. This shape arises largely through the interactions of the side chains, and includes hydrogen bonding, hydrophobic interactions, ionic bonding (NH_3^+ ….. COO^-), and disulphide bonding between cysteine side chains (cys-S-S-cys). See figure on the right.
2. Primary: covalent bonds. Secondary: hydrogen bonds.
   Tertiary: dispersion forces, hydrogen bonds, ionic bonds, disulfide bonds
3. (a) The α-helix secondary structure, every N-H group donates a hydrogen bond to the C=O group of an amino acid eight residues earlier in the chain. Beta sheets consist of strands connected by at least two backbone hydrogen bonds, forming a pleated sheet.
   (b) A quaternary structure because there are multiple peptide chains (protein molecules) in each complex.
   (c) Glutamic acid is hydrophilic and would aggregate around water molecules, valine is hydrophobic. It could also disrupt any hydrogen bonding or ionic bonding (salt bridges) the glutamic acid residue was involved in.
4. The different amino acid sequences and consequently their 3d structure, makes different proteins unique.
5. A protein's shape is determined by its sequence of amino acids. The different side chains on these determine the mix of hydrogen bonds, ionic bonds, disulfide bridges or dispersion forces that give it its shape.
6. (a) 
   (b) The length and nature of the amino acids and their affinity for other species.
7. (a) hydrogen bonds (b) N-H and C=O (c) multiple hydrogen bonds (d) N-H and C=O
   (e) Hydrogen bonds are secondary bond and will rupture at high temperatures – eg: cooking meat.
8. Disulfide bridges are the strongest and most thermo stable. They are covalent bonds requiring approximately 60kJ/mole to break, compared to 20kJ/mol for hydrogen bonds.
9. The presence of concentrated sodium hydroxide will cause the amide groups to hydrolyse. This means that proteins will split into their component amino acids. At lower concentrations, hydrogen bonding and tertiary structure will be disrupted. The flesh will dissolve.

Properties, reactions and chemical synthesis

Set 30: Reaction Types

1. (a) $CH_3COOH(\ell) + H_2O(\ell) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$
   (b) $NH_3(g) + H_2O(\ell) \rightarrow NH_4^+(aq) + H_3O^+(aq)$ $NaHCO_3(s) \rightarrow Na^+(aq) + HCO^-(aq)$
   (c) $NaHCO_3(s) \rightarrow HCO_3^-(aq) + Na^+(aq)$ $HCO_3^-(aq) + H_2O(\ell) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
   (d) $NaHSO_4(s) \rightarrow Na^+(aq) + HSO_4^-(aq)$ $HSO_4^-(aq) + H_2O(\ell) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
   (e) $K_2CO_3(s) \rightarrow 2\,K^+(aq) + CO_3^{2-}(aq)$ $CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
   (f) $NH_4CH_3COO(s) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$ $NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   $CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

2. (a) i) $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$
ii) Two colourless solutions are mixed together. No visible reaction; some heat evolved.
(b) i) $Ba(OH)_2(s) + 2\,H^+(aq) \rightarrow Ba^{2+}(aq) + 2\,H_2O(\ell)$
ii) A white solid dissolves in a colourless solution.
(c) i) $MgO(s) + 2\,H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(\ell)$
ii) A white solid dissolves in a colourless solution.
(d) i) $CH_3COOH(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$
ii) Two colourless solutions mixed. No visible reactions. There is a reduction in the vinegar smell.
(e) i) $Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
ii) A silver solid dissolves in a colourless solution; colourless, odourless gas evolved
(f) i) $2\,CH_3COOH(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + 2\,CH_3COO^-(aq) + H_2(g)$
ii) A silver solid dissolves in a colourless solution; colourless, odourless gas evolved.
(g) i) $Cu(s) + 4\,H^+(aq) + 2\,NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O(\ell)$
ii) Brown solid dissolves in colourless solution to produce brown, pungent gas and a blue solution.
(h) i) $Ni(s) + 2\,H^+(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$
ii) Silver solid dissolves in colourless solution forms colourless, odourless gas and green solution.
(1) i) $Fe(s) + 2\,H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$
ii) Silver solid dissolves in colourless solution, colourless, odourless gas evolved and a pale green soln.

3. (a) i) $Br_2(\ell) + 2\,I^-(aq) \rightarrow 2\,Br^-(aq) + I_2(s)$
ii) Brown/orange liquid added to colourless solution. Brown/orange fades and dark brown solid forms
b) i) $Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$
ii) Silver solid to pale green solution. Black precipitate on silver solid; pale-green soln to colourless.
c) i) $Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$
ii) Brown solid to colourless solution. Black precipitate on brown solid; colourless solution turns blue.
d) i) $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$
ii) Silver solid to green solution. Black precipitate on silver solid; green solution fades to colourless.
e) i) $2\,Na(s) + 2\,H_2O(\ell) \rightarrow 2\,Na^+(aq) + 2\,OH^-(aq) + H_2(g)$
ii) A silver/white solid reacts vigorously with a colourless liquid to form a colourless, odourless gas.
f) i) $2\,K(s) + 2\,H_2O(\ell) \rightarrow 2\,K^+(aq) + 2\,OH^-(aq) + H_2(g)$
ii) A silver/white solid reacts vigorously with a colourless liquid to produce a colourless, odourless gas.
g) i) $C\ell_2(g) + 2\,Br^-(aq) \rightarrow 2\,C\ell^-(aq) + Br_2(aq)$
ii) A green pungent gas dissolves in a colourless solution to form a brown/orange solutions.

4. a) i) $Ag^+(aq) + C\ell^-(aq) \rightarrow AgC\ell(s)$
ii) Two colourless solutions are mixed to form a white precipitate.
b) i) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
ii) Two colourless solutions are mixed to form a cream/white solid.
c) i) $Pb^{2+}(aq) + 2\,I^-(aq) \rightarrow PbI_2(s)$
ii) Two colourless solutions are mixed to form a yellow precipitate.
d) i) $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$
ii) Two colourless solutions are mixed to form a white precipitate
e) i) $Ba^{2+}(aq) + 2\,OH^-(aq) + SO_4^{2-}(aq) + 2\,H^+(aq) \rightarrow BaSO_4(s) + 2\,H_2O(\ell)$
ii) Two colourless solutions are mixed to form a white precipitate.
f) i) $Fe^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3(s)$
ii) Pale green solution mixed with colourless solution forms pale green precipitate. Green solution fades.
g) i) $3\,Zn^{2+}(aq) + 2\,PO_4^{3-}(aq) \rightarrow Zn_3(PO_4)_2(s)$
ii) Two colourless solutions are mixed together to form a white precipitate.
h) i) $Cu^{2+}(aq) + 2\,OH^-(aq) \rightarrow Cu(OH)_2(s)$
ii) Blue solution mixed with a colourless solution to form a blue precipitate. Blue solution colour fades.
i) i) $2\,Cr^{3+}(aq) + 3\,CO_3^{2-}(aq) \rightarrow Cr_2(CO_3)_2(s)$
ii) Green solution mixed with colourless solution to form a green precipitate. Green solution colour fades.

Set 31: Percentage composition and yield

1. a) $M(Fe_2O_3) = 159.7\ g\ mol^{-1}$ %F = 69.9% b) %Hematite: 65/69.9 × 100 = 92.9%
2. $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ %Zn = 76.8%
3 a) C_6H_6 is LR $m(C_6H_5Br) = 121\ g$ b) %yield: 93.2/121 × 100 = 77.3 %
4. a) $Ca(OH)_2 \rightarrow CaO + H_2O$ b) %CaO: 4.33/5.67 × 100 = 76.4 %

5. a) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ (b) $m(BaC\ell_2) = 0.926$ g (c) %yield: 45.5 %
6. $n(Na_2S_2O_7) = ½\ n(S)$ %yield: 82.5 % 7. $\%Na_2CO_3 = 74.9$ % 8. 97.2%
9. 20.5% 10. 85.9 % 11. 96.7% 12. $m(FeO) = 0.4296$ g $m(Fe_2O_3) = 0.3214$ g

Set 32: Limiting reagents

1. (a) KI is LR (b) $m(PbI_2) = 92.2$ g
2. (a) $HC\ell$ is LR (b) $m(NaC\ell) = 7.82$ g
3. (a) $CaCO_3$ is LR (b) $m(CO_2) = 0.976$ g (c) $m(Ca(CH_3COO)_2) = 3.51$ g
4. (a) H_2SO_4 is LR (b) $m(H_2) = 0.411$ g (c) $n(MgSO_4.7H_2O) = 50.3$ g
5. (a) H_2SO_4 is LR (b) $m(Na_2SO_4) = 2.13$ g (c) $m(NaOH) = 0.400$ g
6. (a) Ag is LR (b) $m(NO) = 1.51$ g (c) m(HNCh) = 5.75 g
7. (a) KO_2> is LR $m(K_2CO_3) = 4.86$ g (b) $m(O_2) = 3.36$ g (c) $m(CO_2) = 7.43$ g
8. H_3PO_4 is LR $m(Ca(H_2PO_4)_2) = 5.37 \times 10^7$ g (53.7 tonne)
9. $\%Na_2CO_3$: 98.3% 10. $\%MnO_2$: 99.0%

Set 33: Calculations involving gases

1. (a) 0.0217 mol (b) 0.0338 mol (c) 1.462 mol
2. (a) 93.8 g (b) 11.0 g (c) 92.7 g
3. (a) 28.04 g (b) C_2H_4
4. 0.108 g sample of $CaCO_3$
5. (a) NH_3 is LR (b) m $(NH_4)_2SO_4$ produced = 4.36 g (c) 0.09397 mol H_2SO_4 in excess
6. (a) $NaHCO_3$ is the LR (b) $V(CO_2) = 0.085$ L
7. (a) Cu is the LR (b) $V(NO_2) = 1.02$ L
8. $HC\ell$ is LR $C\ell_2$ gas pressure = 238 kPa
9. (a) KNO_3 is the LR (b) $m(NH_4)_2SO_4$ left over = 7.78 g (c) $P(N_2) = 1{,}814$ kPa

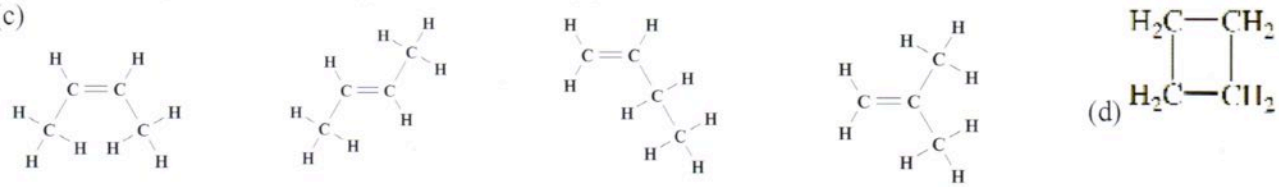
Set 34: Empirical formulas 1

1. (a) $FeC\ell_2$ (b) C_2H_5 (c) $KMnO_4$ (d) $NaSO_4$
2. (a) CaO_2H_2 ($Ca(OH)_2$) (b) PbN_2O_6,($Pb(NO_3)_2$) (c) C_3H_8O
3. SO_3 4. $C_5H_{10}O_2$ 5. TeO_2 6. C_2H_6O
7. Fe_2O_3 8. $FeC\ell_2$ $FeC\ell_3$ 9. N_2O NO NO_2
10. $TiC\ell_3$ 11. C_3H_6O 12. CH_2O 13. $C_3H_7O_3N$

Set 35: Empirical formulas 2

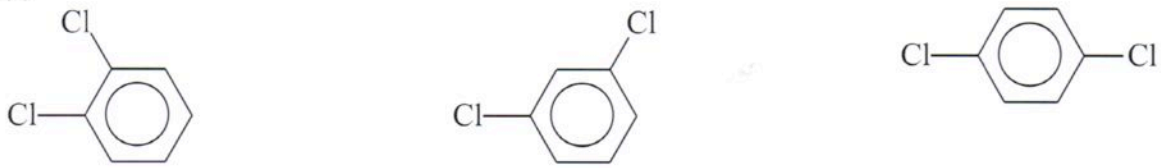
1. $Cu_3(CO_3)_2(OH)_2$ 2. (a) EF: CH_2 (b) MF = C_4H_8

(c)



3. $Pb_3C\ell_2O_2$ 4. (a) EF: C_2H_6O (b) MF: C_2H_6O (c) CH_3CH_2OH
5. (a) EF: CoC_4O_4 (b) MF = 2 x EF = $Co_2C_8O_8$
6. (a) EF: C_3H_9N (b) MF = C_3H_9N
7. (a) EF: $C_3H_2C\ell$ (b) MF = 2 x EF = $C_6H_4C\ell_2$

(c)



8. (a) EF: C_6H_7N (b) MF: C_6H_7N 9. EF: $K_2Ni(C_2O_4)_2{\cdot}2H_2O$ 10. EF: $S_4C\ell_4O_{17}$

Set 36: Chemical Synthesis: no answers provided