### **BEHAVIOUR OF ELECTRONS: DISCHARGE TUBES**

set of six discharge tubes on stand

The passing of a high voltage through a number of discharge tubes, each containing a different pressure of gas. The intensity of light emitted from the tube varies with gas pressure.

- EQUIPMENT
- induction coil with leads
- PROCEDURE
  - Dim the lights.
  - Apply voltage to each tube in turn (keep voltage constant in each case).

#### CAUTION Switch off power before shifting the lever!

**RESULTS**At the highest gas pressure only a faint glow is observed in the discharge<br/>tube. As the gas pressure is decreased to 10 mmHg pink coloured<br/>"streamers" are observed between the plates. At 6 and 3 mmHg the<br/>streamers have merged and broadened. A pink glow fills the space<br/>between anode and cathode. At 0.14 mmHg one observes vertical<br/>striations surrounding the anode. Around the cathode there is a blue glow<br/>and between this blue glow and the cathode is a dark space called the<br/>*Crookes dark space*. The cathode itself begins to glow with a faint pinkish<br/>coloration. At the

lowest pressure, the tube is filled entirely with the Crookes dark space. Where the Crookes dark space meets the glass tube, the glass is seen to fluoresce.

As the gas pressure is reduced, the Crookes dark space increases, because there are fewer gas



molecules for the electrons to collide with.1

<sup>1</sup>Abbot and Wood, Elementary Physical Science, p 394.

#### **BEHAVIOUR OF ELECTRONS: THE "MALTESE CROSS"**

A high voltage is applied across a cathode ray tube containing a piece of metal in the shape of a Maltese Cross. The cross stops some electrons from striking the end of the tube, thus creating a shadow of the cross.

#### EQUIPMENT

- cathode-ray tube with Maltese Cross
  - bar magnet
  - induction coil with leads

#### **PROCEDURE** • Shake the cathode-ray tube gently to make the cross sit upright.

- Connect it to the induction coil as shown.
  - Apply voltage across the tube.
  - Reverse the polarity to the tube and select the best shadow.

**RESULTS** The electron beam will cause the glass of the tube to luminesce. The cross, blocking some of the beam, will cast a shadow.



If the magnet is brought close to the tube the electron beam will be deflected so that the shadow becomes distorted.

### **BEHAVIOUR OF ELECTRONS: THE "PADDLE WHEEL"**

A high voltage is applied across a cathode ray tube containing a paddle wheel on rails. The wheel moves along the rails.

#### EQUIPMENT

- cathode-ray tube with paddle wheel
- induction coil with leads



#### **PROCEDURE** • Connect the induction coil.

- Gradually increase the voltage across the tube.
- **RESULTS** As the voltage increases the wheel begins to rotate and move along its track. This indicates that cathode rays consist of a stream of fast moving electrons which possess momentum and therefore mass. As the voltage increases the cathode ray's average momentum increases and the paddle wheel turns faster.

Reversing the polarity will cause the wheel to turn and move in the opposite direction.

Chapter 1: The Properties of Matter

## **DEMONSTRATION 1.4**

### THE SOLVATION OF ELECTRONS

This demonstration shows the colour of electrons when they are solvated in ammonia and demonstrates Le Chatelier's principle.



When sodium ions are added, Le Chatelier's principle applies, e.g.

Na⁺ + e⁻<sub>ℕH</sub> ® Na(s)

When Na forms, the solvated electron and colour disappear.

### CONDUCTIVITY OF SOLIDS

A voltage is applied across a number of different metals and non-metals to test their electrical conduction.

#### **EQUIPMENT** • 6 V lamp wired to two probes

- variable power supply
- variable power supply

• a selection of metals, e.g. copper, zinc, magnesium etc., and some solid non-metals, e.g. sulfur, graphite

- **PROCEDURE** Set the power supply to 6 volts and connect it to the lamp/probes arrangement.
  - Touch the probes across each sample.



graphite

**RESULTS** Metals will conduct. The non-metals will not conduct electricity except graphite which only conducts parallel to its cleavage planes.

### **CONDUCTIVITY AT LOW TEMPERATURES**

A perspex rod, to which a light bulb is attached, is lowered into liquid nitrogen to illustrate that the conductivity of metals increases at lower temperatures.

#### EQUIPMENT

- perspex rod with a coil of thin copper wire
  - 6 volt lamp with terminals (refer to diagram).
  - variable power supply and leads
  - Dewar flask on a plastic tray
- liquid nitrogen
- **PROCEDURE** Dim the lights.
  - Connect the lamp & wire coil arrangement to the power supply and set the voltage so that the lamp just glows red.
  - Lower the perspex rod into the liquid nitrogen until the wire coil is fully immersed.
  - Do not leave the probe in the liquid nitrogen longer than is necessary to observe the effect of the lower temperature.
- **RESULTS** The light bulb, which was glowing dimly, begins to shine brightly.
- CAUTION Liquid nitrogen boils at -196°C and can cause frostbite.



### CONDUCTIVITY OF MOLTEN IONIC SOLIDS

To illustrate that molten salts conduct electricity, a crucible containing a solid is heated until the solid melts and the conductivity of the salt is tested.

#### **EQUIPMENT** • 6 volt lamp wired in series with one long probe

- alligator clip attached to the free wire of the circuit
- nickel crucible
- 6 volt power supply
- insulating mat with hole for crucible
- bunsen burner
- digital thermometer & high/low temperature probe (optional)
- **REAGENTS** a salt of low melting point



e.g. copper nitrate-3-water, Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, T<sub>m</sub> = 115°C silver nitrate, AgNO<sub>3</sub>, T<sub>m</sub> = 209°C potassium nitrate, KNO<sub>3</sub>, T<sub>m</sub> = 338°C sodium hydroxide, NaOH, T<sub>m</sub> = 322°C

#### PREPARATION Assemble

- Assemble the apparatus as in the diagram below. Using cork or rubber tubing, insulate the probe against the clamp.
- Osing cork of rubber tubing, insulate the probe against the clamp
   Place the digital thermometer in the view of the video camera.

PROCEDURE

- Set voltage selector to 6 volt.
  - Place some salt into the crucible and heat till molten.
  - Dim the lights.
    - Place the temperature probe into the melt without touching the bottom and observe the temperature, then dip the probe (connected to the lamp) into the melt.
- **RESULTS** Once molten the salt will become a conductor and the lamp will glow.



Chapter 1: The Properties of Matter

## **DEMONSTRATION 1.8**

### SURFACE TENSION OF WATER

Detergents reduce the surface tension of water.

- EQUIPMENT large beaker
  - light box
- **REAGENTS** powdered sulfur (2 g)
  - detergent concentrate
- **PROCEDURE** Fill the beaker with water and sprinkle enough sulfur to lightly cover the surface.
  - Touch the surface of the water with a clean, dry finger.
  - Touch the surface of the water with a detergent coated finger.
- **RESULTS** When touched with a clean finger the sulfur will remain afloat. When touched with a detergent coated finger the sulfur powder will sink to the bottom of the beaker.

### PROPERTIES OF CO<sub>2</sub>

This demonstration has two aims: firstly, to show that carbon dioxide gas is denser than air; secondly, to show that carbon dioxide will not support combustion.

- **EQUIPMENT** a large glass tank
  - 3 candles of varying heights
  - Erlenmeyer flask with side-arm
  - rubber tubing
  - glass tubing with an elbow near the end of the tube
  - dry ice, solid  $CO_2$  (40 g)
  - matches

#### **PROCEDURE** • Assemble apparatus as shown in the diagram.

- Dim the lecture theatre lights.
- **RESULTS** Carbon dioxide, being denser than air, first sinks to cover the bottom of the tank. All of the candles continue to burn. As the carbon dioxide level rises, the shortest candle is extinguished, followed by the middle then the tallest candle.

CAUTION

Solid CO, sublimes at -78°C and can cause frostbite.



### ILLUSTRATING BOYLE'S LAW

The relationship between the pressure and volume of a fixed amount of air at constant temperature is investigated by measuring its volume while varying the pressure.

#### **EQUIPMENT** • large cylinder with plunger (apparatus illustrated in diagram)

- 4 or more kilogram weights
- glycerine
- metre rule

**PROCEDURE** • Lubricate the plunger with glycerine and fill the cylinder with a set volume of air.

- Seal the outlet.
- Record the volume of air below the plunger.
- Balance one weight on the plunger and gently press down, and let the plunger spring back up.
- Record the height of the plunger and the weight.
- Calculate the volume of gas by using V = pr<sup>2</sup>h.
- Add a second, third, etc. weight and calculate the volume of gas and the weight.
- Remove the weights one at a time, again
- calculating the volume.
   Average the volumes obtained as the weights



- were removed with those obtained as the weights were added.
  Plot a graph of 1/(average volume) against weight.
- **RESULTS** The graph of 1/volume against weight should be a straight line (within experimental error). It shows that the volume of gas is inversely proportional to the weight and hence to pressure, since the pressure equals mass per unit area.

**Note**: With zero weight added, the pressure on the plunger is atmospheric pressure.

### ILLUSTRATING CHARLES' LAW

This demonstration illustrates the effects of temperature on a volume of gas at a fixed pressure.

- **EQUIPMENT** liquid nitrogen
  - boiling water
  - 3 round balloons (red, purple and blue if possible)
  - 2 x 2 L beakers
- **PROCEDURE** Inflate the balloons to an equal size.
  - Immerse the blue balloon in a beaker of liquid nitrogen. Notice that it shrinks as the air inside cools.
  - Remove the balloon from the liquid nitrogen and the balloon expands to its original size as the air inside warms up again.
  - Compare the diameter of the shrunken balloon with the purple balloon at room temperature.
  - Immerse the red balloon into the beaker of boiling water and notice that the balloon expands as the air inside it heats up.
  - Remove the balloon from the boiling water and the balloon contracts down to its original size.
  - Compare the size of the expanded balloon with the balloon at room temperature.
  - Immerse a single balloon in liquid nitrogen (-196°C) and quickly measure its diameter.
  - Allow the balloon to warm up to ambient temperature and measure its diameter.
  - Finally repeat the measurement using hot water.
  - Calculate the volume of the balloon assuming it to be spherical. Volume is 1/6**p**d<sup>3</sup> where d is the diameter of the balloon.
  - Plot a graph of volume against temperature.
- **RESULTS** A plot of volume against temperature should be linear.

CAUTION Liquid nitrogen has a boiling point of –196°C and can cause frostbite.

### THE "HYDROGEN FOUNTAIN": EFFUSION

Hydrogen gas effuses more rapidly than air through a porous cup forcing the water in an attached conical flask out through a thin glass tube. The demonstration is repeated with other gases, for example helium, methane and carbon dioxide. The relative rates of gas flow cause liquid to be forced from the flask, or air to be drawn into the flask.

#### **EQUIPMENT** • hydrogen, helium and natural gas cylinders with regulators

- dry ice, solid  $CO_2$  (5 g)
- rubber hose
- 800 mL beaker
- tall porous pot with rubber stopper
- 1 L conical flask with rubber stopper
- glass tubing
- retort stand with 2 boss heads and clamps
- water, coloured with fluorescein

#### **PROCEDURE** • Construct the apparatus as shown in the diagram.

- Hold the beaker upside down over the end of the hose and allow it to fill with hydrogen gas.
- Keeping the beaker inverted, place it over the pot.
- Repeat the demonstration using helium, natural gas and carbon dioxide instead of hydrogen gas.

CAUTION

RESULTS

# Water may be ejected from the nozzle for a considerable distance. Protect surroundings from water damage.

The low molecular weight gases flow more rapidly through the porous cup than heavier gases. Hydrogen, effusing into the porous pot faster than air, will cause excess pressure inside the pot. This will transmit to the flask and cause water to be forced out of the jet tube. The lighter the gas, the greater the force on the liquid. Removal of the beaker or filling it with  $CO_2$ , will cause the reverse phenomenon: air will be "sucked" into the flask and appear as bubbles in the water.



### GRAHAM'S LAW OF DIFFUSION AMMONIA AND HYDROGEN CHLORIDE

Graham's Law of diffusion is illustrated using the vapours from concentrated hydrochloric acid and ammonia.

#### EQUIPMENT • 2 syringes

- 2 cotton balls
- glass tube
- ruler
- REAGENTS
  - hydrochloric acid, HCl (10 M, 20 mL)
    ammonia, NH<sub>3</sub> (6 M, 20 mL)

PROCEDURE

- Place a ball of cotton wool into each end of a glass tube.
  - Seal the ends with glad wrap.
  - At one end inject 20 mL of concentrated hydrochloric acid.
  - At the other inject 20 mL of ammonia solution.
  - After several seconds, note the position of the white ring of NH<sub>4</sub>Cl formed where the NH<sub>3</sub> and the HCl gases meet.
  - Measure the distance from each cotton ball to the centre of the white ring.

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RESULTS
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where d represents distance from the cotton ball, r represents the rate of diffusion and M represents the molecular mass of the gas.

This suggests that ammonia molecules should travel 1.46 times as far as hydrogen chloride molecules in a given amount of time. Thus, the ring of ammonium chloride should form 1.46 times as far from the ammonia end of the tube as from the hydrogen chloride end. The usual result is 1.27. This result represents the ratio of diffusion coefficients rather than the ratio of diffusion rates. The deviation from Graham's Law is because the process occurring is not a simple diffusion process; there are 3 gases involved: ammonia, hydrogen chloride, and air.

## **DEMONSTRATION 2.6 (older version)**

### PARAMAGNETISM OF OXYGEN

An empty test tube is lowered into a Dewar filled with liquid nitrogen. However, when it is removed it contains a small amount of liquid oxygen. The oxygen can then be tested in a magnetic field.

- **EQUIPMENT** large horse-shoe magnet on sliding base
  - large test tube
  - Dewar flask
  - cotton thread
  - retort stand
  - boss head and rod or clamp
  - rubber tubing and pasteur pipette (optional)
  - oxygen cylinder (optional)

#### **REAGENTS** liquid nitrogen, N<sub>2</sub>

**PREPARATION** Prepare liquid oxygen as follows:

- Suspend the test tube by a length of thread from the retort stand.
- Fill the Dewar flask with liquid nitrogen.
- Immerse the empty test tube in the liquid. Ensure that the nitrogen does not enter the tube.
- After approximately one hour sufficient liquid oxygen should have collected in the tube for the demonstration to take place. Optional: In order to speed up the process, and to increase the yield, oxygen gas may be fed into the tube.
- Attach the rubber hose to the cylinder.
- Insert the pipette into the free end of the hose and feed a *gentle*, steady stream of oxygen into the test tube. (This process will shorten collection time to approximately 20 minutes).
- Set up the retort stand with the test tube still suspended from it.
- Place the horse-shoe magnet so that the test tube will later be able to hang freely between the pole pieces of the magnet.
- Return the test tube to the Dewar flask until the demonstration is about to take place.

**PROCEDURE** • Take the test tube from the Dewar flask and allow it to hang still.

- Slowly slide the magnet towards the test tube until the pole pieces are on either side of it.
- **RESULTS** The test tube will undergo a deflection in the magnetic field.
- CAUTION Liquid oxygen in the presence of organic material is explosive. Extreme care should be taken when handling it.

Liquid nitrogen boils at -196°C and can cause frostbite.

## **DEMONSTRATION 2.6 (New Version)**

### PARAMAGNETISM OF OXYGEN

A test tube with an oxygen filled balloon attached is lowered into a Dewar filled with liquid nitrogen. When the test tube is removed it contains a small amount of liquid oxygen. The liquid oxygen can then be tested in a magnetic field.

#### **EQUIPMENT** • large balloons

- long test tube
- Dewar flask
- Oxygen cylinder
- Apparatus as shown in diagram (please ask for assistance from the first year technical staff)
- **REAGENTS** liquid nitrogen, N<sub>2</sub>

PREPARATION

#### Prepare liquid oxygen as follows:

- Fill the Dewar flask with liquid nitrogen
- Fill up two Balloons with oxygen gas from the cylinder.
- Attach each balloon to the rim of a large testtube.
- Immerse the test tube in the liquid nitrogen flask.
- Leave the test tubes in the liquid nitrogen to allow the pale blue liquid to be collected at the bottom.
- The pale blue liquid is liquid oxygen.
- **PROCEDURE** Place the magnet assembly in a white tray provided and place the tray onto the overhead projector. Take the test tube from the Dewar flask and remove the balloon. Pour the liquid oxygen over the aperture between the magnet arms. Observe the aperture carefully. Repeat the procedure using liquid nitrogen.
- **RESULTS** Liquid oxygen results in a white line between the magnet arms. There are no visible lines observed when using liquid nitrogen.
- CAUTION Liquid oxygen in the presence of organic material is explosive. Extreme care should be taken when handling it.

Liquid nitrogen boils at -196°C and can cause frostbite.

### THE SOLUBILITY OF AMMONIA IN WATER "THE AMMONIA FOUNTAIN"

The partial vacuum created in a flask by ammonia gas dissolving in water creates a fountain when water is sucked into the flask.

#### EQUIPMENT

- Ammonia gas Cylinder
- Hose
- 1 L round bottom flask
- Glass tubing with a stop cock at one end and a rubber bung at the other
- Boss head and retort ring
- Wash Bottle
- Retort Stand

**REAGENTS** • ammonia gas

- phenolphthalein
- deionised water

CAUTION

## Examine the flask to ensure there are no cracks so the flask will withstand the partial vacuum.

PREPARATION •

- Fill the beaker with water and place it on the foot of the retort stand.
- Add some phenolphthalein to the water.
- Attach a hose to the outlet of the ammonia gas cylinder.
- Working in the fume hood invert the round bottom flask and insert the hose. Turn the gas cylinder on and pass a stream of ammonia gas into the round bottom flask. Gently swirl the hose around the flask for a minute to allow sufficient ammonia gas to fill the flask.
- Close the ammonia cylinder. Stopper the round bottom flask using the glass tubing assembly.
- Clamp the inverted flask such that the stop cock end of the glass tubing is immersed in the beaker of water.
- Wearing a **protective glove** hold the flask upside down and clamp it on to the retort stand as shown in the figure. Keep the flask inverted, seal it with the glass-tube assembly.
  - Raise the flask such that the glass tubing is no longer in the water. Open the stop cock and squeeze sufficient water from the wash bottle into the tubing such that a stream of



#### Chapter 3: Solutions & Suspensions

water jets from the other end. Close the stop cock and lower the flask to the original position.

- Open tap.
- **RESULTS** As ammonia dissolves in the water a partial vacuum is created. This causes the water level in the long glass tube to rise until it overflows into the inverted flask. As more water flows from the beaker into the flask, more ammonia will dissolve, and the rate at which the water rises in the tube increases dramatically. This produces a fountain effect in the inverted flask.

 $NH_3(g) + H_2O \Phi NH_3(aq)$ 

 $NH_3(aq) + H_2O(I) \Phi NH_4^+(aq) + OH^-(aq)$ 

As ammonia dissolves in the water, it forms a basic solution that causes the phenolphthalein indicator to turn a pink/magenta colour.

solubility - 22g/100 mL

solubility - 36g/100 mL

solubility - 200g/100 mL

## **DEMONSTRATION 3.2**

### CONDUCTIVITY OF SOLUTIONS

Different solutions are tested for their conductivity.

EQUIPMENT	•	6 volt lam	wired to tw	o strips of copr	per (or graphite	e electrodes)
	•			o ounpo on oopp	on (or graphic	, 0.000.0000

- variable power supply and leads
- several 250 mL beakers
- wash bottle with distilled water

REAGENTS



- copper(II) sulfate-5-water,  $CuSO_4 \cdot 5H_2O$ sodium chloride, NaCl
- sucrose,  $C_{12}H_{22}O_{11}$ 
  - hydrochloric acid, HCI (1 M, 250 mL)
- acetic acid, CH<sub>3</sub>COOH (17 M, 250 mL)
- ammonia, NH<sub>3</sub> (3 M, 250 mL)

**PREPARATION** • Prepare saturated aqueous solutions of the salts and sucrose.

- Provide the solutions, acids and bases in labelled reagent bottles as well as the distilled water.
- Provide one beaker for each liquid.

**PROCEDURE** • Pour the liquids into separate beakers.

- Immerse the electrodes and note the brightness of the lamp for each solution.
- Rinse probes between each test.

RESULTS The intensity of the bulb is proportional to the conductivity of the solution. The non-electrolytes, (water and sucrose) do not conduct - the bulb will not glow. The strong electrolytes, (salts and HCI) conduct very well - the bulb glows brightly. The weak electrolytes, (acetic acid and the ammonia solution) conduct

poorly - the bulb glows weakly.

Chapter 3: Solutions & Suspensions

## **DEMONSTRATION 3.3**

### **IMMISCIBLE LIQUIDS AND SOLUBILITY**

Illustrating that polar solids are soluble in polar solvents and non-polar solids in non-polar solvents.

EQUIPMENT • Petri dishes

- REAGENTS
- tetrachloroethene,  $C_2Cl_4$



or carbon tetrachloride, CCI,



- or trichlorotrifluoroethane,  $CCl_{3}CF_{3}$  (can also use Toluene as an alternat ive to the chlorinated solvents)
- lodine,  $I_2$  (a few crystals)
- Potassium Permanganate (few crystals)
- water

#### CAUTION The organochlorine solvents are carcinogenic.

- **PROCEDURE** Place some water in a small Petri dish.
  - Add cleaning fluid, such as tetrachloroethene, C<sub>2</sub>Cl<sub>4</sub>, carbon tetrachloride, CCl<sub>4</sub> or trichlorotrifluoroethane CCl<sub>3</sub>CF<sub>3</sub>, to form a small pool.
  - Add a few crystals of potassium permanganate, KMnO<sub>4</sub>.
  - Note whether the colour develops in the water or cleaning fluid.
  - Repeat the demonstration but add a few crystals of iodine, I<sub>2</sub>, instead of potassium permanganate.
- **RESULTS** When the cleaning fluid is added to the water it is immiscible. When crystals of potassium permanganate are added to the system, a deep colour appears in the water showing its high solubility in water. This is an example of a polar substance dissolving in a polar solvent. However, the iodine preferentially dissolves in the cleaning fluid to give a violet solution. Iodine is a non–polar substance which dissolves in a non–polar solvent.

### THE SEMI-PERMEABLE MEMBRANE

A porous pot with a semi-permeable membrane is filled with sucrose solution and sealed with a rubber bung with a glass tube attached to it so that some of the sucrose solution rises up the tube. The pot is then immersed in water and the sucrose level in the tube rises due to osmosis.

#### EQUIPMENT

- porous pot with rubber bung
- 1.5 to 2 L beaker, depending on the size of the pot
- glass tubing, 5 mm diameter
- REAGENTS
- sucrose,  $C_{12}H_{22}O_{11}$  (saturated, 500 mL)
- copper(II) sulfate-5-water, CuSO<sub>4</sub>·5H<sub>2</sub>O (125 g)
- potassium hexacyanoferrate(II)-3-water, K<sub>4</sub>[Fe(CN)<sub>6</sub>]·3H<sub>2</sub>O (211g)
- blue food dye
- vaseline
- deionised water
- PREPARATION P
- Prepare 500 mL of 1 M copper(II) sulfate solution by dissolving 125 g CuSO<sub>4</sub>·5H<sub>2</sub>O in water.
  - Prepare 500 mL of 1 M potassium hexacyanoferrate(II) solution by dissolving 211 g K<sub>4</sub>[Fe(CN)<sub>6</sub>]3H<sub>2</sub>O (or 184 g of the anhydrous compound) in water.
  - Prepare 500 mL of saturated sugar solution by dissolving 1 kg C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> in boiling water.
  - Colour it with blue food dye.
  - The preparation should be completed between 24 and 6 hours before the lecture.

Prepare a semi-permeable membrane inside the wall of the pot as follows:

- Fill the pot with 1 M aqueous copper sulfate solution. Take care that it does not spill over and contaminate the outside of the pot.
- Place some 1 M potassium hexacyanoferrate(II) solution into the beaker.
- Carefully lower the pot into the solution and add further potassium



#### Chapter 3: Solutions & Suspensions

hexacyanoferrate(II) solution to the beaker until it reaches almost to the rim of the pot.

- Ensure that the solutions do not mix through splashing or spilling. It is recommended to prepare several pots at the same time, in case of failure.
- After two or three hours a semi-permeable membrane should have formed inside the wall of the pot.
- Discard the solutions and rinse the pot(s) well with water. Cut a piece of glass tubing, about 1.5 m long.
- Bore a hole in the rubber bung to fit the tubing.
- After cooling fill one of the prepared pots with the saturated sucrose solution.
- Seal the pot with the bung.
- Insert the tube. Ensure that there is no air trapped beneath the bung: on pushing it home, some sucrose solution should appear in the tube.
- Rinse off any spilled solution and allow to dry.
- Make an air-tight seal with vaseline around the rim of the pot and the base of the tubing.
- **PROCEDURE** Tag the initial level of solution in the tubing.
  - Write date and time on it.
  - Fill a large beaker with water and carefully lower the pot and tube assembly into the water.
  - Set up this assembly and provide blank tags.
  - Note and tag the liquid-level at the end of the lecture.
  - Present the same pot the next lecture and note the new level.
- **RESULTS** The liquid level in the tube inside the pot will increase due to osmotic pressure across the semi-permeable membrane.

**Note:** The associated rise of the level in the tube is dependent, not only on the osmotic pressure, but also on temperature variations and the effectiveness of membrane and seal.

### THE "CHEMICAL GARDEN"

The chemical garden illustrates the dynamic formation of solid phases controlled by osmosis and diffusion in a system far from equilibrium.

- EQUIPMENT 1 L beaker
  - nickel spoon
- REAGENTS
- 500 mL of sodium silicate ("Waterglass") solution (27 % solution)
- copper(II) sulfate-5-water, CuSO<sub>4</sub>·5H<sub>2</sub>O (a few crystals)
   ashalt(II) shlarida 6 water, CaCl, 6H O (a few crystals)
  - cobalt(II) chloride-6-water, CoCl<sub>2</sub>·6H<sub>2</sub>O (a few crystals)
     riakal(II) culfate 6 water, NiCO club (a few crystals)
    - nickel(II) sulfate-6-water, NiSO<sub>4</sub>·6H<sub>2</sub>O (a few crystals)
  - deionised water (500 mL)
- $\label{eq:preparation} \textbf{PREPARATION} \quad \textbf{Using the beaker, dilute 500 mL of Waterglass with 500 mL water.}$ 
  - Set up the beaker with the solution.
  - Provide the nickel spoon and the salts in their original storage containers.
- **PROCEDURE** At the beginning of the lecture, sprinkle the dry crystals of the chosen transition metal salts into the silicate solution in such way that a random mixture of them covers the bottom of the vessel.
- **RESULTS** During the next hour a multi-coloured crop of slender, crystalline strands will grow upwards generating a "coral reef" of silicates. The metal ions from the salts combine with silicate ions and form membranes of insoluble silicates around the crystals. The inside of the membrane contains a more concentrated salt solution than the outside, some water passes inward by osmosis, ultimately causing breaks in the membrane and formation of more membrane surface as the salt solutions contact fresh sodium silicate.



### **OSMOSIS AND EGG MEMBRANES**

Two raw eggs, with shells removed, are placed in separate solutions of water, sucrose and dye to illustrate that osmosis can occur in either direction through a semi-permeable membrane.

- **EQUIPMENT** 4 x 1 L beakers
  - stirring rod
  - paper towels

#### REAGENTS



- 4 raw eggs
  - sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> (85 g)
  - deionised water (1.6 L)
  - hydrochloric acid, HCI (10 M, 400 mL)
  - blue or green food dye

## **PREPARATION** • Peel off the outer shells of the eggs by rolling them in a half-full Petri dish of hydrochloric acid (400 mL) for a short time.

- Blot dry with the paper towels. The eggs should now be encased only in their membranes.
- It is most important to **not cook the eggs** in the hydrochloric acid at this point!
- Prepare a 20% sugar solution by dissolving 85 g of sugar in 400 mL of water.
- Pour 400 mL deionised water into three of the 1 L beakers and pour 400 mL sugar solution into the remaining beaker.
- **PROCEDURE** Place one of the eggs in the beaker of sugar solution and another in one of the beakers of water.
  - Add the food dye to one of the remaining beakers and stir.
  - Place two eggs in this beaker.
  - Leave the eggs for one day. The eggs in water may burst if left longer.
  - Remove the eggs from the coloured solution, keep one for reference and place one in a beaker of distilled water.

**RESULTS** The egg in the sugar solution will shrink. The eggs in the water beakers will expand, and the interior of the eggs in the coloured solution will become coloured. The coloured egg loses its colour to the deionised water.

An egg has an outer shell made mainly out of calcium carbonate and this shell is lined with a membrane that is permeable to water. When the eggs are soaked in hydrochloric acid, the acid dissolves the shell.

 $CaCO_3(s) + 2H^{+}(aq) \zeta Ca^{2+}(aq) + H_2O(I) + CO_2(g)$ 

The eggs will undergo changes in their weight due to osmosis. Water will flow through the egg's membrane from a region of low solute concentration to a region of high solute concentration. When the decalcified egg is placed in water, water flows into the egg. The sugar solution is more concentrated than the contents of the egg, and the sugar molecules are too large to pass through the membrane, so that when the decalcified egg is placed in sugar solution, water will flow out of the egg. The same principle applies to the solution containing dye. The dye will flow from the solution to the egg. When the coloured egg is placed in clean water, the dye will flow from the egg (more concentrated) to the water. Chapter 3: Solutions & Suspensions

## **DEMONSTRATION 3.7**

### THE COAGULATION OF IRON(III) OXIDE

EQUIPMENT	<ul><li>1 beaker</li><li>1 stirring rod</li></ul>
REAGENTS	<ul> <li>aqueous solution of iron(III) chloride, FeCl<sub>3</sub></li> <li>aqueous solution of aluminium sulfate, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (a few drops)</li> </ul>
PROCEDURE	<ul> <li>Add iron(III) chloride to boiling water to obtain a red, hydrous colloidal solution of iron(III) oxide.</li> <li>Add a few drops of aluminium sulfate</li> </ul>
RESULTS	The suspended particles rapidly coagulate into a dark red-brown gelatinous precipitate of iron(III) hydroxide.

 $Fe^{3+}(aq) + 3OH^{-}(aq) \zeta Fe(OH)_{3}(s)$ 

## **DEMONSTRATION 3.8**

### THE TYNDALL EFFECT

Light transmitted by a colloidal suspension imitates the colours of a sunset.

EQUIPMENT	<ul> <li>piece of cardboard, 30 cm x 30 cm</li> <li>500 mL beaker</li> <li>stoppered 10 mL measuring cylinder</li> <li>stirring rod</li> <li>torch</li> </ul>
REAGENTS	<ul> <li>sodium thiosulfate-5-water, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (10 g)</li> <li>hydrochloric acid, HCI (1 M, 10 mL)</li> <li>deionised water</li> </ul>
PREPARATION	<ul> <li>Cut a hole in the centre of the cardboard the same diameter as the bottom of the beaker.</li> <li>Place the cardboard on the overhead projector.</li> <li>Place 10 mL of hydrochloric acid into a stoppered measuring cylinder.</li> <li>Dissolve 10 g of sodium thiosulfate in 500 mL of water.</li> <li>Place it in the beaker and set it over the hole in the cardboard.</li> </ul>
PROCEDURE	<ul> <li>Switch on the overhead projector.</li> <li>Darken the lecture theatre.</li> <li>Add hydrochloric acid to the sodium thiosulfate solution and stir.</li> </ul>
RESULTS	During the next minute or so the light transmitted by the liquid will change very gradually from pale blue to orange-yellow, then to reddish-gold as the colloid particles form.

### THE "COLD LIGHT" REACTION

This chemiluminescence demonstration shows that energy produced by a chemical reaction can be released as light.

#### EQUIPMENT •

- 1 L conical flask
  2 x 500 mL conical flasks
- glass tube coiled into a helix with funnel to fit
- retort stand
- boss head
- clamp

REAGENTS

- anhydrous sodium carbonate, Na<sub>2</sub>CO<sub>3</sub> (2 g)
- luminol (1 g)
- ammonium hydrogencarbonate-1-water, NH<sub>4</sub>HCO<sub>3</sub>H<sub>2</sub>O (0.25 g)
- copper(II) sulfate solution, CuSO<sub>4</sub>·5H<sub>2</sub>O (1 mL, 1 M)
- sodium hydrogencarbonate, NaHCO<sub>3</sub> (12.5 g)
- hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (3%, 25 mL)(fresh)
- distilled water

#### **PREPARATION SOLUTION A**

- Dissolve the sodium carbonate in 250 mL of distilled water.
- Add the luminol and stir until dissolved.
- Add ammonium hydrogencarbonate-1-water, sodium hydrogencarbonate, and the copper sulfate.
  - When everything has dissolved, dilute to 500 mL.

#### SOLUTION B

- Dilute the hydrogen peroxide solution to 500 mL.
- **PROCEDURE** Dim the lights.
  - Pour solutions A and B simultaneously into funnel attached to the glass helix.
- **RESULTS** When solutions A and B are poured simultaneously into the funnel, an eerie pale blue luminescence is emitted.

The luminescence is due to the luminol being converted to an excited-state product due to oxidation by the peroxide. This product then decays back to the ground state by emitting light. For equations, see Demonstration 4.2.

#### **ENERGY CHANGE: CHEMILUMINESCENCE**

This chemiluminescence demonstration shows that energy produced by a chemical reaction can be released as light.

**EQUIPMENT** A glass jar with a screw cap.

- REAGENTS
- potassium hydroxide, KOH (70 g)
- REAGENTO
- dimethyl sulfoxide, DMSO (60 mL)
- Si
- oxygen gas (from cylinder)
- luminol (0.1 g)
- **PROCEDURE** Place potassium hydroxide (70 g) in the jar and add dimethyl sulfoxide (60 mL).
  - Pass a stream of oxygen gas into the jar for a few seconds then cap the jar.
  - To start the demonstration add luminol (0.1 g) and shake the jar gently for a few minutes.
  - Pass the jar around the class.

**RESULTS**A brilliant blue luminescence which lasts half an hour is produced.<br/>Note: Vigorous shaking will result in brighter luminescence for a shorter<br/>duration of time.<br/>In this reaction DMSO acts as a solvent and the chemiluminescence results<br/>from the reaction of luminol with molecular oxygen. This is achieved by

bubbling oxygen gas through the solution and enhanced aeration is obtained by shaking. The overall reaction is an oxidation reaction and is given by:

$$\begin{array}{c} O \\ I \\ I \\ NH_2 O \end{array}^{N-H} + 2 OH + O_2 \end{array} \longrightarrow \left[ \begin{array}{c} O \\ I \\ I \\ NH_2 O \end{array} \right]^{*} + 2 H_2 O + N_2$$



### **DENSITY AND COMBUSTIBILITY: "STAR WARS"**

This demonstration illustrates that hydrogen is less dense than air and that it will burn in air.

#### EQUIPMENT

- hydrogen gas cylinder (with appropriate regulator)
- rubber hose with glass funnel in one end
  2 m long pole
- E y
- taper
   adhaaiya tar
- adhesive tape
- matches
- crystallising dish (about 15 cm diameter)
- retort stand
- boss head and clamp
- liquid soap or detergent.

#### **PREPARATION** • Fill the crystallising dish with warm water.

- Add soap.
- Set up the hydrogen cylinder and attach hose and funnel.
- Using the retort stand and clamp secure the funnel so that it dips below the surface of the soap solution.
- Attach the taper to the tip of the pole with adhesive tape.
- Provide matches.

#### **PROCEDURE** • Pass a steady stream of hydrogen gas into the soap solution.

- When a sufficiently large number of soap bubbles has formed, aggregates of them will break away from the surface and float upwards.
- Light the taper.
- Dim the lights and ignite the bubble aggregates before they reach the ceiling.

CAUTION

The explosions should take place at a distance of about 3 m from the basin, the hydrogen cylinder and the nearest member of the audience. At least two consecutive bubble aggregates should be allowed to drift away without ignition.

Experience has shown that the first bubble aggregates, if ignited, will explode with alarming violence as they contain a mixture of hydrogen and air.

It is essential to keep the lighted taper well clear of the basin at all times. This was not done on one occasion. "Premature ignition" took place in the basin and, for one moment, it seemed as if the entire lecture theatre was going to be launched skyward.

**RESULTS** The hydrogen gas contained in the bubbles will ignite and burn with a bright orange-yellow light. The equation for the reaction is:

 $2H_2(g) + O_2(g) \zeta 2H_2O(g)$ 

Chapter 4: Thermochemistry & Thermodynamics

## **DEMONSTRATION 4.4**

### THE METHANOL CANNON

The explosive combustion of methanol is demonstrated.

EQUIPMENT

#### plastic bottle

- 2 long nails
- retort stand with clamp
- tight fitting cork
- induction coil with leads

methanol, CH<sub>2</sub>OH (10 mL)

REAGENTS

**PREPARATION** • Prepare the "cannon" by inserting two large nails into the sides of a heavy plastic bottle.

- and the second s
- The points of the nails should be separated by about 1 cm.
   Add math and (about 40 ml) to the battle.
  - Add methanol (about 10 mL) to the bottle.
  - Shake the bottle to vaporise and distribute the methanol.
  - Discard excess.

Dim the lights.

- Place a tight-fitting cork in the mouth of the bottle.
- Securely fasten the bottle to the retort stand by clamping the neck of the bottle with the clamp attached to the retort stand.

Attach the leads from the induction coil to the ends of the nails. Direct the mouth of the bottle up and away from the audience.

PROCEDURE



Turn on the induction coil. **Note:** For a second firing, squeeze the bottle repeatedly to ensure oxygen is present before using the cannon again.

**RESULTS** A LOUD explosion will result, and the cork will be propelled across the room. The blue flame of the reaction is seen clearly in a darkened room.

The equation for the reaction is:

 $2CH_{3}OH(g) + 3O_{2}(g) \zeta 2CO_{2}(g) + 4H_{2}O(g)$ 



### COMPARISON OF THE COMBUSTION PROPERTIES OF VARIOUS GASES

The difference in explosive properties of hydrogen, hydrogen/oxygen mixture and helium is demonstrated by igniting a balloon of each gas.

#### **EQUIPMENT** • 3 spherical balloons, about 30 cm diameter

- long pole
- taper and matches
- cotton thread and adhesive tape
- 3 gas cylinders with regulators: hydrogen, helium and oxygen
- retort stand and retort ring
- wooden stool
- safety glasses
- ear plugs
- felt tip pen

**PREPARATION** Immediately before the demonstration, fill the balloons as follows:



- all helium.all hydrogen.
- about 1 part hydrogen and 2 parts oxygen. The gases are not to be mixed in the stoichiometric ratio as this produces too violent an explosion. The balloon must not float after filling and must fit inside a 5 L beaker to ensure that not too much gas is ignited.
- Using felt pens mark the balloons with: "He", "H<sub>2</sub>", "O<sub>2</sub>/H<sub>2</sub>".
- Secure the balloons to the lecture bench as follows:
- Ensure the greatest possible distances between each balloon, but at least 2 metres.
- Using cotton thread, tie the helium and the hydrogen balloons to a fixture so that they float at least 2 metres above the bench top.
- Attach the retort ring to the top of the retort stand.
- Rest the balloon filled with hydrogen and oxygen on the ring and secure it with thread.
- Place a stool on the bench top and put the retort stand on top of the stool.

## Ensure that the balloons are well removed from glass fixtures such as lights and windows.

Supply the pole, matches, safety glasses and ear plugs.

**PROCEDURE** Observe the following guidelines carefully:

CAUTION The light emitted is sufficiently bright to be potentially dangerous to the eyes. Therefore, the explosions must not be set off in total darkness. The audience must be warned not to look directly at the balloons. Be aware that hot rubber might fly in all directions. Ensure that members of the audience are at a safe distance. Chapter 4: Thermochemistry & Thermodynamics

- Put on safety glasses and ear plugs.
- Dim room lights and light the taper.
- Touch the flame to each balloon in the following order:

helium hydrogen hydrogen/oxygen

**RESULTS** Helium: does not burn; noise-output is merely that of an inflated balloon bursting

Hydrogen: explodes with a yellow-orange light and loud noise.

**Hydrogen/oxygen mixture:** explodes with a blinding flash and a terrifying noise.

## **DEMONSTRATION 4.6**

#### ENTHALPY OF SOLUTION OF AMMONIUM NITRATE: CHEMICAL COLD PACK

Water is added to a flask containing ammonium nitrate and a small amount of blue food dye. The temperature of the resultant solution is seen to drop rapidly.

EQUIPMENT	<ul> <li>500ml conical flask with stopper</li> <li>digital thermometer &amp; probe (optional)</li> <li>light box</li> <li>stirring rod</li> <li>towel</li> </ul>
REAGENTS	<ul> <li>ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub> (500 g)</li> <li>blue food dye</li> </ul>
PREPARATION	<ul> <li>Add ammonium nitrate (500 g) and a few crystals of blue food dye to 500ml conical flask.</li> <li>Stopper the flask.</li> <li>Place the digital thermometer display in view of the camera.</li> </ul>
PROCEDURE	<ul> <li>Place conical flask on the light box.</li> <li>Add water to the flask and stir to mix.</li> <li>Put the thermometer probe into the flask.</li> <li>Pass it around the class wrapped in a towel.</li> </ul>
RESULTS	When water is added the ammonium nitrate dissolves. Heat is absorbed from the surroundings during the solution process thereby lowering the temperature.

### ENTHALPY OF SOLUTION OF CALCIUM CHLORIDE: CHEMICAL HOT PACK

Water is added to a conical flask containing calcium chloride and a small amount of a red dye. The temperature of the resultant solution is seen to increase rapidly.

EQUIPMENT	<ul> <li>500ml conical flask with stopper</li> <li>Digital thermometer &amp; probe (optional)</li> <li>light box</li> <li>stirring rod</li> <li>towel</li> </ul>
REAGENTS	<ul> <li>calcium chloride, CaCl<sub>2</sub> (500g)</li> <li>Rhodamine WT</li> </ul>
PREPARATION	<ul> <li>Add calcium chloride (500 g) and a few drops of Rhodamine WT to conical flask.</li> <li>Stopper the flask.</li> </ul>
PROCEDURE	Place conical flask on the light box.

- Add water to the flask and stir to mix.
- Put the thermometer probe into the flask.
- Pass it around the class wrapped in a towel.
- **RESULTS** When the contents in the flask are mixed a considerable temperature increase is observed.
- CAUTION The reaction produces sufficient heat to cause burns.

### ENTHALPY OF PHASE CHANGE: CRYSTALLISATION OF SUPERSATURATED SODIUM ACETATE

A supersaturated solution is made to crystallise by adding a "seed" crystal. The crystallisation process evolves heat.

EQUIPMENT	•	3 L conical flask
/	•	digital thermometer and probe (optional)
	•	hot plate
	•	aluminium foil
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- tweezers
- watchglass
- **REAGENTS** sodium acetate-3-water, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O (1000 g)
  - water (400 mL)

#### **PREPARATION** • Place the sodium acetate in the flask.

- Add the water and slowly warm the flask to boiling.
- Swirl the flask until the solid dissolves, washing any solid remaining on the neck or sides down with a small amount of water.
- Ensure that the solution is completely clear at ambient temperature.

If re-crystallisation should occur:

- Add a small amount of water and re-heat the solution slowly until the crystals have just disappeared.
- Wrap the flask in foil and allow to cool.
- If necessary, repeat this procedure until the solution remains clear on having cooled.
- Do not disturb.
- Seal well.

**Note**: This solution may be re-used indefinitely, provided it remains sealed and is never allowed to heat up much beyond the point at which the solid dissolves.

If a previously prepared solution is to be re-used, immerse the flask containing the crystallised solution in hot water. As soon as the solution turns clear, remove the flask from the bath. Allow to cool without disturbance.

- Carefully place the flask on the light box.
- Provide tweezers and some crystals of sodium acetate.
- **PROCEDURE** Remove the foil from the flask.
  - "Seed" the supersaturated solution by adding a small crystal of sodium acetate to the beaker.
  - Place the thermometer probe near the flask.

### **RESULTS** After a few seconds, large white crystals will grow in the beaker and the flask will get hot.

### ENTHALPY OF NEUTRALISATION: SODIUM HYDROXIDE AND HYDROCHLORIC ACID

The addition of water to acid, water to base and acid to base yields a range of temperatures, illustrating the difference in the enthalpies of dilution and neutralisation.

EQUI	PM	ENT
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- Digital thermometer & probe
  - 3 x 300 mL beakers (tall-form preferable)

hydrochloric acid, HCl (6 M, 200 mL) sodium hydroxide, NaOH (6 M, 200 mL)

• 3 x 100 mL graduated cylinders

distilled water (300 mL)

• 3 x stirring rods

REAGENTS



PROCEDURE

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- Place the temperature probe in a 300 mL beaker.
- Add 100 mL of distilled water and record the initial temperature.
- Add HCI (6 M, 100 mL), stir, and record the temperature change.
- Remove the probe and rinse it with distilled water.
- Place the probe in an empty 300 mL beaker.
- Add 100 mL of distilled water.
- Add NaOH (6 M, 100 mL) while stirring.
- Briefly rinse the probe again and place it in a third beaker.
- Add NaOH (6 M, 100 mL) and HCI (6 M, 100 mL).

**RESULTS** The temperature rise for  $HCI/H_2O$  is  $\approx 3^{\circ}C$ . The temperature rise for NaOH/H<sub>2</sub>O is  $\approx 1^{\circ}C$ .

The temperature rise for HCI/NaOH is  $\approx 45^{\circ}$ C.

#### AN ENDOTHERMIC REACTION: AMMONIUM THIOCYANATE AND BARIUM HYDROXIDE

Solid ammonium thiocyanate and solid barium hydroxide-8-water react endothermically and absorb heat from their surroundings. EQUIPMENT a flat piece of wood about 20 x 20 x 1 cm thick 500 mL conical flask 2 x 100 mL beakers REAGENTS ammonium thiocyanate, NH<sub>4</sub>SCN (38 g) barium hydroxide-8-water, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (79 g) **PREPARATION** . Using the beakers weigh out ammonium thiocyanate (38 g) and barium hydroxide-8-water (79 g). Set up the empty, dry conical flask, the reagents and the piece of wood. PROCEDURE Hold the piece of wood under a tap and allow a puddle of water to form in the middle of the slab. Combine the dry reagents in the flask and shake the mixture for about • 15 seconds. Set the flask down over the puddle. RESULTS After about one minute, the endothermic reaction taking place in the flask will have drawn so much heat from its environment that the water freezes. Raise the flask to show that the piece of wood is now frozen to the bottom of the flask. Note: It is important to show that tap water is used for wetting the wood in order to allay suspicions of trickery.

 $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \zeta Ba(SCN)_2(s) + 2NH_3(g) + 10H_2O(I)$ 

Chapter 4: Thermochemistry & Thermodynamics

## **DEMONSTRATION 4.11**

### AN EXOTHERMIC REACTION: ALUMINIUM AND IRON(III) OXIDE

Aluminium powder and iron(III) oxide are mixed together and then ignited. Light and enough heat to melt iron are produced.

**EQUIPMENT** • thick-walled ceramic or carbon crucible with hole in the

- bottom (about 9 cm high)
- large insulating mat
- bucket containing dry sand
- tongs
- 2 safety screens

#### **REAGENTS** • aluminium powder, AI (5 g)

- iron(III) oxide,  $Fe_2O_3$  (20 g)
- thermite mixture,  $Fe_{3}O_{4}/Fe/AI$  (150 g), (commercial mix)
- glycerine,  $C_3H_5(OH)_3$  (5 mL)
- potassium permanganate,  $KMnO_4$  (10 g)

**PREPARATION** .

• Place a piece of filter paper over the opening in the bottom of the crucible.

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- Mix Al and  $Fe_2O_3$  in a crucible with a nickel spoon. Do not grind.
- Pour 150 g of thermite mixture on the top of the paper.
  - Pour Al/Fe<sub>2</sub>O<sub>3</sub> mixture into the top of the thermite.
  - Make a depression in the Al/Fe<sub>2</sub>O<sub>3</sub> mixture and pour 5 mL of glycerine into the depression.
  - Place the crucible in the crucible holder positioned above the bucket containing dry sand.
  - Place one safety screen between the class and the demonstration and the other between the lecturer and the demonstration.
- **PROCEDURE** Ensure that there is no flammable substance within a 2 metre radius of the reaction vessel.
  - Dim the lights.
  - Pour 10 g of finely ground potassium permanganate on the top of the glycerine and quickly stand back.
  - If the mixture fails to ignite, wait one minute then add 5 mL of glycerine and 10 g of ground KMnO<sub>4</sub>.

CAUTIONDo not use a wet crucible. Seek instruction from lecture theatre staff.<br/>A  $CO_2$  fire extinguisher must be handy. Do not use a water<br/>extinguisher as the addition of water to molten iron produces<br/>hydrogen which can lead to an explosion.

**RESULTS** The reaction will last for several seconds and is accompanied by the emission of strong orange-yellow light, flying sparks and a hissing sound.

 $3Fe_3O_4(s) + 8AI(s) \zeta 9Fe(s) + 4AI_2O_3(s)$
### A SPONTANEOUS REACTION: WHITE PHOSPHORUS AND CARBON DISULFIDE

White phosphorus burns spontaneously in air and carbon disulfide burns explosively in air.

EQUIPMENT • 1 L open mouth measuring cylinder

- 5 mL measuring cylinder
- 2 crystallising dishes, about 10 cm diameter
- piece of filter paper, 10 cm diameter
- pasteur pipette with teat
- 100 mL reagent bottle with large mouth
- knife or spatula
- tongs or tweezers
- stop cock grease or vaseline

REAGENTS

#### • white phosphorus, P (1 g)

#### CAUTION



White phosphorus must be kept under water at all times! It is spontaneously flammable in air. Combustion in air produces phosphorus pentoxide. Both white phosphorus and phosphorus pentoxide are very poisonous and can cause severe burns. Chronic effects can result from continued absorption of small amounts.

• carbon disulfide, CS<sub>2</sub> (5 mL)

CAUTION

Carbon disulfide is extremely flammable as well as toxic. The explosive range is 1-50% (V/V) in air.



**PREPARATION** Weigh out white phosphorus (1 g) following the procedure below.



Exposure of phosphorus to air should be very brief.

- Ensure that the fume-cupboard is free of flames and other sources of heat. Turn on ventilation.
- Place the container with phosphorus, the bottle with carbon disulfide, the small measuring cylinder and the empty reagent bottle into the fume-cupboard.
- Apply some stop cock grease to the lid of the reagent bottle and leave it beside the bottle.
- Pour some water into **both** crystallising dishes.
- Place one dish on the balance and tare it.
- Take the other to the fume-cupboard.

Ensure that during the following procedure all phosphorus is kept under water.

- Using tongs or tweezers, take a lump of phosphorus and transfer it quickly to the dish.
- Leaving the lump under water in the dish, cut off several small pieces.

- Now take the dish to the balance and using tweezers quickly transfer 1 gram's worth of the small pieces to the tared vessel.
- Take both dishes back to the fume-cupboard and return the unused phosphorus to the storage container immediately.
- Using the small measuring cylinder, transfer carbon disulfide (5 mL) to the reagent bottle.
- Using tweezers, add the weighed-out amount of phosphorus to the bottle. Swirl gently to ensure dissolution.
- Seal the bottle securely with the greased lid.
- Provide the 1 L measuring cylinder, filter paper and pasteur pipette.

#### **PROCEDURE** • Turn on ventilation of the fume cupboard.

- Rest a piece of filter paper over the mouth of the measuring cylinder.
- Using the pasteur pipette, transfer about 1 mL of solution from the reagent bottle to the centre of the filter paper.
- Dim the lights.
- **RESULTS** The carbon disulfide will evaporate within one or two minutes of being placed on the filter paper. The vapour, being quite dense, will move downwards into the measuring cylinder where an explosive mixture with air will form.

 $P_4(s) + 5 = O_2(g) \zeta P_4O_{10}(s)$ 

Once the phosphorus is dry, it will ignite spontaneously and cause the filter paper to burst into flames. Blue and yellow flames will appear in the top portion of the cylinder. The carbon disulfide further down will explode with a hooting sound. The burning filter paper will become airborne. A large amount of phosphorus pentoxide will evolve which must not be allowed to escape from the fumehood.

**Note**: The time taken for complete evaporation varies with room temperature and the amount of solution delivered to the paper.

**DISPOSAL** The cooled, charred filter paper should be discarded in a waste container. The cylinders can be cleaned by scrubbing with soap and water. Any remaining white phosphorus in carbon disulfide should be placed in a flat pan in a ventilated fume cupboard away from other combustible materials and allowed to evaporate and burn.

### A SPONTANEOUS REACTION: **COMBUSTION OF ACETYLENE IN BLEACH**

Chlorine gas is generated when hydrochloric acid and bleach are mixed. When a small amount of calcium carbide is added to the gas, a spontaneous reaction occurs in which a flame is produced.

EQUIPMENT

- 250 mL beaker
- watch glass

REAGENTS	,
se,	

- household chlorine bleach containing hypochlorite, CIO- (5 mL)
- hydrochloric acid, HCI (5 M)
- calcium carbide, CaC<sub>2</sub>

PROCEDURE

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- Generate chlorine gas by placing the bleach (5 mL) in the beaker and adding hydrochloric acid (2 mL).
- Cover the beaker and leave for approximately thirty seconds. •
- Remove the watch glass and add a lump of calcium carbide to the • beaker to generate the acetylene .
- Perform this demonstration in a fumehood.



The liberated acetylene reacts spontaneously with the chlorine gas to give a flame.

 $CIO^{-}(aq) + CI^{-}(aq) + 2H^{+}(aq) \zeta CI_{2}(g) + H_{2}O(I)$ 

 $CaC_{2}(s) + 2H_{2}O(I) \zeta C_{2}H_{2}(g) + Ca(OH)_{2}(s)$ 

 $C_{2}H_{2}(g) + CI_{2}(g) \zeta CICH=CHCI (g)$ 

### **BOILING LIQUIDS AT REDUCED PRESSURE**

Water boils at significantly less than 100°C when the pressure above it is reduced.

- **EQUIPMENT** thermometer (-10°C to +110°C)
  - 1 L round bottomed flask (thick walled)
  - 2-holed rubber stopper to fit round bottomed flask
  - 3-way stop cock
  - boiling chips
  - tripod
  - bunsen burner
  - retort stand
  - clamp and boss head
  - water pump, with trap and vacuum tubing
- **REAGENTS** tap water (500 mL)

### **PREPARATION** • Insert the thermometer through one hole of the 2-holed rubber stopper and insert one arm of the 3-way stop cock through the other hole.

- Half fill the flask with tap water and add several boiling chips.
- Firmly place the stopper in the mouth of the flask and adjust the thermometer so that the bulb is below the surface of the water.
- Place the flask on the tripod, open the stop cock and heat the flask with the bunsen burner until the temperature is 50–60°C.
- Remove the flask from the tripod and clamp it to the stand.
- **PROCEDURE** Attach the vacuum tubing from the trap to one of the open arms of the stop cock.
  - Connect the trap to the pump, turn the pump to maximum water flow and adjust the stop cock so that air is drawn from the flask.
  - Focus the camera on the thermometer and read the temperature that the water boils at.
- **RESULTS** When the pressure inside the flask is lowered the water will boil at less than 100°C. As the water boils the temperature decreases and the boiling will stop.

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### PHASE CHANGE UNDER PRESSURE

The passing of a weighted wire through a block of ice with the block of ice remaining intact shows how, under the influence of pressure, localised melting can occur without a change in temperature.

#### **EQUIPMENT** • tripod, 40 cm tall

- 2 rulers, 30 cm long, wood or plastic
- Nichrome wire, 29 BNS, half a metre
- 2 kg weight
- ice-cream container, plastic, 17 x 17 x 9 cm deep
- **REAGENTS** water (200 mL)
  - dry ice, solid CO<sub>2</sub> (a big piece)

## **PREPARATION** • Make a hemi-cylindrical block of ice by placing 100 to 200 mL of water into the ice-cream container.

- Put the container into a freezer resting on one *edge*.
- **PROCEDURE** Remove the ice by twisting the container.
  - Pass the wire-loop up through the centre of the tripod and slip it over the block of ice.
  - Rest the ice across the rulers, rounded surface uppermost.
  - Allow the 2 kg weight to hang down freely so that it is fully supported by the ice block.
  - Repeat the above procedure using a suitably shaped block of solid carbon dioxide.
- **RESULTS** During the following six to eight minutes the weighted wire will melt a path through the ice until it has completely passed through. Weight and wire will crash to the bench below. However, the path forced through the ice will have immediately refrozen behind the wire: the ice block is once again intact. This results from the melting point of water decreasing with increasing pressure.

The weighted wire will not pass through the "dry ice" as the melting point of carbon dioxide increases with increasing pressure.

CAUTION Solid CO<sub>2</sub> sublimes at -78°C and can cause frostbite.

### LE CHATELIER'S PRINCIPLE: EFFECT OF TEMPERATURE ON EQUILIBRIUM

Three glass bulbs containing similar concentrations of  $N_2O_4$  and  $NO_2$  are subjected to temperature changes. The intensity of the brown colour alters accordingly.

#### EQUIPMENT

- 3 sealed glass bulbs containing  $N_2O_4/NO_2$
- 4 x 1 L beakers (large enough to allow the glass bulbs to rest comfortably on the rim)
- crystallising dish, large enough to allow glass bulb to fit inside
- hot-plate
- light box
- crushed ice
- salt
- hot water

## **PREPARATION** • In one of the beakers, bring 500 mL of water to the boil and maintain its temperature on the hot-plate.

- Place crushed ice and some salt into the crystallising dish.
- Set up the light box.
- Rest each glass bulb on the rim of an empty beaker and place it beside the light box.

**PROCEDURE** • Place the beakers with the three bulbs on the light box and note the uniformity of the colour of their contents.

- Place one of the bulbs over the beaker with boiling water, set another into the crushed ice/salt mixture and maintain the third at room temperature.
- After some time, compare the contents of the three bulbs once more.
- **RESULTS** The colour of the heated gas will darken and that of the cooled gas will become pale.

# LE CHATELIER'S PRINCIPLE: EFFECT OF CONCENTRATION

Shifts in equilibrium caused by changes in concentration can be observed by means of a reaction which has a pronounced colour change.

EQUIPMENT 4 conical flasks: 1 x 3 L, 2 x 1 L 2 x 100 mL measuring cylinders light box REAGENTS iron(III) chloride, FeCl<sub>3</sub> (1.2 M, 100 mL) ammonium thiocyanate, NH<sub>2</sub>SCN (1 M, 100 mL) distilled water **PREPARATION** • Dissolve iron(III) chloride (19.46 g) in water (100 mL) in a measuring cylinder. Dissolve ammonium thiocyanate (7.61 g) in water (100 mL) in a measuring cylinder. Place the iron(III) solution (1.5 mL) and the thiocyanate solution (1.5 mL) into the 3 L flask. Make up to 2 L with distilled water. Using the 1 L flasks divide this solution into two. Set up the light box and place the flasks and cylinders on it. PROCEDURE Add 50 mL of iron solution to one of the flasks and 50 mL of thiocyanate solution to the other. RESULTS Addition of iron(III) will cause the system to turn dark red.  $[Fe(OH_2)_{a}]^{3+}(aq) + SCN^{-}(aq) \zeta [Fe(OH_2)_{a}(SCN)]^{2+}(aq) + H_2O(I)$ 

Addition of thiocyanate will also intensify the colour.

### **CARBONATE REACTIONS**

	Dry ice (solid carbon dioxide) is added to a flask of calcium hydroxide. A precipitate of calcium carbonate forms, redissolves, and re–forms when the flask is heated.			
EQUIPMENT	<ul> <li>3 measuring cylinders: 2 x 250 mL, 1 x 500 mL</li> <li>1 x 500 mL flask</li> <li>hot-plate</li> </ul>			
REAGENTS	<ul> <li>300 mL clear limewater (calcium hydroxide solution, Ca(OH)<sub>2</sub>).</li> <li>Prepare by adding a few teaspoonfuls of calcium hydroxide or calcium oxide to 1 L water.</li> <li>Prepare the demonstration one day before to allow any solid present to settle.</li> <li>dry ice, solid CO<sub>2</sub>.</li> </ul>			
PROCEDURE	<ul> <li>Place 300 mL of clear limewater in a 500 mL flask.</li> <li>Drop in a chunk of dry ice.</li> <li>Observe the formation of a precipitate and the redissolving to form a clear solution again.</li> <li>Heat over a low flame or on a hot plate.</li> </ul>			
CAUTION	Solid CO <sub>2</sub> sublimes at -78°C and can cause frostbite.			
RESULTS	<b>1)</b> Carbon dioxide reacts with water to form $CO_3^{2-}$ ions through a series of equilibria.			
	$CO_2(g) + H_2O(I) \Phi H_2CO_3(aq)$			
	$H_2CO_3(aq) \Phi H^+(aq) + HCO_3^-(aq)$			
	$HCO_{3}^{-}(aq) \Phi H^{+}(aq) + CO_{3}^{2-}(aq)$			
	<b>2)</b> If calcium ions are in excess, the carbonate ions react with the calcium ions to form insoluble calcium carbonate.			

 $\mathrm{Ca^{_2+}(aq)} + \mathrm{CO_3^{_2-}(aq)} \ \Phi \ \mathrm{CaCO_3(s)}$ 

**3)** The additional dissolving of carbon dioxide and formation of acid means that acid is now in excess causing the calcium carbonate to dissolve.

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \Phi Ca^{2+}(aq) + 2HCO_3^{-}(aq)$$

**4)** Upon heating, carbon dioxide is driven from the solution, acidity is decreased, and calcium carbonate precipitates again.

### DISTRIBUTION OF IODINE: COMPETING EQUILIBRIA

The distribution of iodine between an organic and an aqueous layer is independent of the direction in which equilibrium is approached.

- 2 large test tubes with rubber stoppers
  - test tube rack
  - 2 x 50 mL measuring cylinders
  - spatula
  - light box



EQUIPMENT

- potassium iodide, KI (1 M, 50 mL) 50 mL organic solvent (toluene)
- iodine (0.02 q)
- **PREPARATION** . Dissolve potassium iodide (8.3 g) in water (50 mL).
  - Place two very small crystals of iodine (about the size of a pinhead) of similar size, one in each test tube.
  - To one test tube add potassium iodide solution (25 mL); to the other organic solvent (25 mL).
  - Stopper both tubes and shake until the iodine dissolves completely. (This may take some time.)
- PROCEDURE Display both test tubes on the light box and draw attention to the contrast in colour.
  - Then add organic solvent (25 mL) to the test tube containing potassium iodide solution, and potassium iodide solution (25 mL) to the test tube containing organic solvent.
  - Stopper both tubes and shake.
  - Place both tubes on the light box and compare the colour intensities in both layers.
- RESULTS The colour intensities of both layers in each test tube should be identical. In the aqueous layer, the iodine forms the tri-iodide ion,

$$I_{2}(s) + I^{-}(aq) \Phi I_{3}^{-}(aq)$$

$$I_2(\text{org}) \Phi I_2(\text{aq})$$

The iodine is slightly soluble in water andmore soluble in the organic solvent. The overall equilibrium position will be the result of the two competing equilibria above.



### METATHESIS REACTION BETWEEN TWO SOLIDS

Two dry white solids are mixed together in a beaker without heating. A yellow solid forms.

- EQUIPMENT 1 L beaker stirring rod REAGENTS lead nitrate,  $Pb(NO_3)_2$  (50 g)
  - potassium iodide, KI (50 g)

PROCEDURE

- Mix 50 g of each of the two compounds in a beaker with a glass stirring rod. No heat is required.
- RESULTS

When the two compounds are mixed, lead iodide is formed. •

 $Pb(NO_3)_2(s) + 2KI(s) \zeta PbI_2(s) + 2KNO_3(s)$ 

white white vellow white

DISPOSAL Add 10% sodium sulfide solution slowly to the contents until precipitation is complete. Filter, and pour the filtrate down the sink. The black precipitate of PbS should be disposed of in a solid waste container.

## **DEMONSTRATION 5.8**

### "NATURAL" pH INDICATORS

EQUIPMENT 3 x 300 mL beakers for each pigment to be tested

REAGENTS

hydrochloric acid, HCI (1 M)



- sodium hydroxide, NaOH (1 M)
- ethanol (600 mL) red cabbage
- red roses or any bright coloured flower

PROCEDURE

Extract the pigment from the flowers by soaking them in ethanol.

sodium hydrogencarbonate, NaHCO<sub>3</sub> (solid) as a pH 7 buffer

- Boil red cabbage in 600 mL of water to extract the purple colour.
- Pour about 200 mL of each solution into each of three beakers.
- Add HCl to one, NaOH to the other and pH 7 buffer to the third.
- RESULTS Each of the pigments has a distinct alkaline and acid colour and can therefore be used as a pH indicator.

### Relative rates of reaction of strong and weak acids

This demonstration illustrates the relative rates of reaction of two different acids of the same concentration with magnesium metal .

EQUIPMENT	<ul> <li>2 x 250 mL conical flasks</li> <li>2 balloons (one purple and one red)</li> <li>lightbox</li> </ul>	
REAGENTS	<ul> <li>hydrochloric acid, HCl (1 M, 150 mL)</li> <li>acetic acid, CH<sub>3</sub>COOH (1 M, 150 mL)</li> <li>magnesium metal, Mg (2 x 2 g)</li> </ul>	
PREPARATION	<ul> <li>Place 2 g of the magnesium metal in each balloon.</li> <li>Pour the hydrochloric acid (150 mL) into one flask and the acetic acid (150 mL) into the other flask.</li> <li>Attach the neck of each balloon to the mouth of the respective conical flask (the purple balloon for the weak acid and the red balloon for the strong acid), making sure that none of the magnesium in the balloons spills into the flasks.</li> <li>Place the two flasks on the lightbox.</li> </ul>	
PROCEDURE	<ul> <li>Simultaneously dump the magnesium from the balloons into the flasks.</li> </ul>	
RESULTS	In each case the magnesium metal and the acid react to form hydrogen gas. However the red balloon is filled up faster then the purple one by the evolving hydrogen gas.	
The equation for the reaction of magnesium with acid is:		

Mg(s)+ 2H<sup>+</sup>(aq)  $\zeta$  H<sub>2</sub>(g) + Mg<sup>2+</sup>(aq)

Thus the rate of evolution of  $H_2(g)$  depends on the concentration of  $H^+(aq)$ in the acid solution. The rate of reaction with magnesium metal is much faster for the strong acid than the weak acid, since the strong acid has a greater concentration of  $H^+(aq)$ .

### ACIDIFICATION OF SODIUM HYDROXIDE WITH "DRY ICE"

The change in pH that occurs when  $CO_2$  dissolves in water can be demonstrated with universal indicator by the addition of dry ice to sodium hydroxide solution.

EQUIPMENT	<ul> <li>2 L beaker (tall thin type)</li> <li>tongs</li> <li>large universal indicator/pH chart</li> </ul>		
REAGENTS	<ul> <li>distilled or deionised water (1000 mL)</li> <li>sodium hydroxide (1 M)</li> <li>universal indicator</li> <li>dry ice, solid CO<sub>2</sub> (enough to fill a 500 mL beaker)</li> </ul>		
PREPARATION	<ul> <li>Place 1 L of distilled water into the beaker and add universal indicator.</li> <li>Add 1 M sodium hydroxide solution until the pH reaches 12 (purple).</li> </ul>		
PROCEDURE	<ul> <li>Add solid CO<sub>2</sub>.</li> <li>Observe colour changes.</li> </ul>		
RESULTS	Over the next few minutes, the pH will drop steadily to below pH 4.		
	$CO_2(s) \Phi CO_2(g) \Phi CO_2(aq) \Phi H_2CO_3 \Phi H^+ + HCO_3^-$		
	H⁺(aq) + OH⁻ ζ H₂O		

#### **BUFFERED AND NON-BUFFERED SOLUTIONS**

The difference between buffered and non-buffered solutions is shown by taking one of each solution, at the same pH, adding universal indicator to both then adding acid or base and noting the colour change or lack thereof.

- **EQUIPMENT** 1 x 2 L beaker
  - 6 x 1 L beakers
  - 2 x 50 mL measuring cylinders
  - 4 glass stirring rods
  - light box

#### **REAGENTS** • potassium dihydrogenphosphate, KH<sub>2</sub>PO<sub>4</sub> (150 g)

- sodium hydrogenphosphate (anhydrous), Na<sub>2</sub>HPO<sub>4</sub> (150 g)
- universal indicator
- sodium hydroxide, NaOH (0.1 M, 100 mL)
- hydrochloric acid, HCI (0.1 M, 100 mL)
- deionised water
- large universal indicator/pH chart

**PREPARATION** For the buffer prepare the following solutions:

- Using one of the 1 L beakers, dissolve 150 g of potassium dihydrogenphosphate in water and make up to 800 mL.
- In another 1 L beaker dissolve 150 g of sodium hydrogenphosphate (anhydrous) and make up to 800 mL.
- Add universal indicator to both solutions.
- In the 2 L beaker, combine 700 mL of the (basic) sodium hydrogenphosphate solution with 600 mL of the (acidic) potassium dihydrogenphosphate solution.
- Divide this buffer solution into two equal parts and place these in two of the 1 L beakers.
- Place similar volumes of plain water into two further 1 L beakers.
- Add universal indicator to both and, if necessary, adjust to pH 7 with small amounts of acid or hydroxide solution.
- Label all beakers clearly and line these up on the lightbox.
- Supply acid and hydroxide solutions in flasks and place one (labelled) measuring cylinder with each .
- Add 25 to 50 mL of acid solution to one of the non-buffered solutions and the same amount to one of the buffered solutions.
  - Add between 25 and 50 mL of alkaline solution to the other nonbuffered solution and to the second buffered solution.
- **RESULTS** Dramatic colour changes occur in the non-buffered liquids. The buffered systems remain green:

 $H_2PO_4^{-}(aq) + OH^{-}(aq) \Phi HPO_4^{2-}(aq) + H_2O(I)$ 

 $HPO_4^{2-}(aq) + H^+(aq) \Phi H_2PO_4^{-}(aq)$ 

### **ACID-BASE INDICATORS:** A CARBON-DIOXIDE-ACTIVATED CHEMICAL REACTION

The addition of carbon dioxide to a solution changes the colour of the indicator, showing that the solution has become acidic.

EQUIPMENT 2 x 500 mL conical flasks

REAGENTS

- ethanol, CH<sub>2</sub>CH<sub>2</sub>OH (95%, 250 mL)
- sodium hydroxide, NaOH (1 M, 3 mL)
- thymolphthalein indicator
  - phenol red indicator

**PREPARATION** .

- Place ethanol (about 250 mL) in a 500 mL conical flask.
- Add 5-6 drops of thymolphthalein indicator and just enough dilute sodium hydroxide to produce a very pale blue colour (approx' 3 mL).
- Stopper the flask until it is used.
- Prepare the second solution as directed above, except use 1-2 drops of phenol red in 250 mL of water.
- Add half a drop of sodium hydroxide to produce a red solution.
- Be sure to protect the solution from CO<sub>2</sub> in the air prior to the demonstration.
- PROCEDURE The two flasks containing the coloured solutions are passed around the class, the red solution up one side of the room and the blue solution up the other side of the room.
  - Each student is invited to remove the stopper, speak into the flask, and politely request the colour to change.
- RESULTS After approximately 30 students have talked to the solution, the red solution will suddenly turn clear with a yellow tinge!

 $H_{2}O(I) + CO_{2}(g) \Phi H_{2}CO_{3}(aq) \Phi H^{+}(aq) + HCO_{3}^{-}(aq)$ 

The blue solution will take **much** longer to change colour, but it will eventually go clear. Swirling speeds up the reaction.

### SALTS OF ACIDS AND BASES

The pH of solutions of various salts are determined.

#### EQUIPMENT • pH meter

- large universal indicator/pH chart
- light box
- 10 x 500 mL beakers
- 10 stirring rods
- pH electrode

REAGENTS

- universal indicator
  freshly deionised water (or freshly boiled out water) \*\*
- sodium hydroxide, NaOH (1 M, 30 mL)
- sodium carbonate, Na<sub>2</sub>CO<sub>3</sub> (10 g)
- sodium hydrogencarbonate, NaHCO<sub>3</sub> (10 g)
- sodium chloride, NaCl (10 g)
- ammonium chloride, NH<sub>4</sub>Cl (10 g)
- ammonium acetate,  $CH_3COONH_4$  (10 g)
- aluminium sulfate,  $Al_2(SO_4)_3$  (10 g)
- potassium hydrogensulfate, KHSO₄ (10 g)
- hydrochloric acid, HCI (1 M, 30 mL)
- **PREPARATION** Place the water (270 mL) in the beakers and add universal indicator.
  - Put the beakers on the light box, with the stirring rods.
  - Place the solids and solutions in sample tubes, in order of decreasing pH.
- **PROCEDURE** Add the substances to the beakers, one by one, with stirring.
  - Observe the colour changes and measure the pH.
- **RESULTS** The salts are arranged in order of increasing pH so that their colours with universal indicator form a rainbow.

### SOLUBILITY AND COMPLEX ION EQUILIBRIA OF SILVER: THE "ONE-POT DEMONSTRATION"

The sequential addition of clear, colourless solutions alternately precipitates and redissolves.

#### EQUIPMENT

- 1 L conical flask
- 6 x 10 mL & 2 x 25 mL measuring cylinders (stoppered)
- 1 x 50 mL & 1 x 100 mL measuring cylinders (stoppered)
- safety glasses
- light box •
- cyanide antidotes A & B (freshly prepared)

#### REAGENTS



Prepare the solutions as set out below. Note that the iodide and thiosulfate solutions must be made up freshly. The remainder may be made up in advance provided that the silver nitrate solution is kept in a dark bottle. 1 14 2 ml

sodium hydroxide

1.		1 101	
2.	sodium hydrogenphosphate	1 M	5 mL
3.	nitric acid	5 M	45 mL
4.	sodium chloride	1 M	3 mL
5.	ammonia	concentrated	50 mL
6.	potassium bromide	1 M	3 mL
7.*	sodium thiosulfate	1 M	30 mL
8.*	potassium iodide	1 M	4 mL
9.	potassium cyanide	1 M	100 mL
10.	sodium sulfide	1 M	5 mL

\* to be made fresh.

**PREPARATION** • Place the solutions into the appropriate measuring cylinders which must be clearly numbered as indicated.

PROCEDURE Line up the measuring cylinders in their numeric sequence.

- Place the flask of silver nitrate solution (start with 400ml of 0.1M ) on • the light box.
  - Add the solutions to the flask one by one swirling gently after each addition. It is essential that the numeric sequence is strictly adhered to!

#### Chapter 5: Equilibrium

RESULTS The following change should occur after each additio
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	OBSERVATION	$K_{sp}$ or $K_{stab}$
Ag+ + NO <sub>3</sub> -	colourless solution	
χ NaOH (1)	χ	
AgOH	Brown precipitate	10-7.70
$\chi Na_2HPO_4(2)$	χ	
Ag <sub>3</sub> PO <sub>4</sub>	Yellow precipitate	<b>10</b> -16
χ HNO <sub>3</sub> (3)	χ	
3Ag <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> + HPO <sub>4</sub> <sup>2-</sup>	Precipitate dissolves	
χ NaCl (4)	χ	
AgCl	White precipitate	10-9.74
χ NH <sub>3</sub> (aq) (5)	χ	
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]⁺ + Cl⁻	Precipitate dissolves	10+7
χ KBr (6)	χ	
AgBr	Pale yellow precipitate	10-12.3
$\chi Na_{2}S_{2}O_{3}$ (7)	χ	
3Na⁺ + [Ag(S₂O₃)₂]³-	Precipitate dissolves	<b>10</b> <sup>+13</sup>
χ KI (8)	χ	
Agl	Dark yellow precipitate	<b>10</b> -16.1
χ KCN (9)	χ	
K+ + [Ag(CN) <sub>2</sub> ]-	Precipitate dissolves	10+20
χ Na <sub>2</sub> S (10)	χ	
Ag₂S	Black precipitate	<b>10</b> -50

#### CAUTION

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A comparatively large quantity of cyanide is produced. Do not leave it unattended at any stage. Once the demonstration is complete, add sodium hypochlorite solution and allow to stand for 24 hours, then discard.

### **ELECTRICITY BY A CHEMICAL REACTION**

A strip of copper and a strip of magnesium are placed in sulfuric acid. The voltage produced by the electrochemical cell is sufficient to fire a flash bulb.

EQUIPMENT	<ul> <li>250 mL beaker</li> <li>low voltage light</li> <li>electrical socket</li> <li>test tube</li> <li>battery alligator clip</li> </ul>	
REAGENTS	<ul> <li>Hydrochloric acid, HCl (1 M, 200 mL)</li> <li>30 cm length of copper wire</li> <li>30 cm strip of magnesium ribbon</li> </ul>	
PREPARATION	<ul> <li>Attach the clips to the small light.</li> <li>Wind the magnesium ribbon into a spiral and connect to an alligator clip.</li> <li>Wind the copper wire into a spiral and attach it to the other alligator clip.</li> </ul>	Bulb
PROCEDURE	Lower the magnesium ribbon and the copper wire simultaneously into the Cu wire beaker containing the hydrochloric acid.	Mg ribban
RESULTS	An electrochemical cell is formed when the magnesium ribbon and the copper wire are lowered into the beaker. The voltage produced by the chemical reaction is sufficient to light the bulb.	1 M HCI
	Mg(s) ζ Mg²⁺(aq) + 2e⁻	E° = +2.36 V
	2H⁺(aq) + 2e⁻ ζ H₂(g)	E° = 0.00V
	$Mg(s) + 2H^{*}(aq) \zeta Mg^{2*}(aq) + H_{2}(g)$	E° <sub>cell</sub> = +2.36V

### THE LEMON BATTERY

A strip of copper and a strip of zinc are embedded in a lemon and a small voltage is generated.

#### **EQUIPMENT** • voltmeter

- 2 alligator clips
- 1 strip of copper (clean)
- 1 strip of zinc (clean)
- 1 lemon

**PROCEDURE** • Insert the zinc and copper strips into the lemon and attach alligator clips onto the strips.

- Connect wires onto voltmeter.
- Observe the voltage.
- **RESULTS** A cell voltage of over a volt is observed.

The cell reaction is:

Zn(s) ζ Zn²+(aq) + 2e−	E° = +0.76 V
_2H⁺(aq) + 2e⁻ ζ H₂(g)	E° = 0.00V
Zn(s) + 2H⁺(aq) ζ Zn²+(aq) + H₂(g)	E° <sub>cell</sub> = +0.76 V



### ZINC IN COPPER SULFATE SOLUTION

A strip of zinc is placed in a copper sulfate solution and left for a day. The solution becomes colourless and contains a sediment of copper metal.

EQUIPMENT	•	500 mL beaker		
REAGENTS	•	strip of zinc (about 20 cm long) copper(II) sulfate-5-water, CuSO₄·5H₂O (100 g)		
PREPARATION	•	Dissolve 125 g CuSO <sub>4</sub> ·5H <sub>2</sub> O in water and make up to 400 mL.		
PROCEDURE	Place the strip of zinc into the solution and allow to stand for one day.			
RESULTS	Much of the zinc strip disappears. The solution turns colourless and a sediment of metallic copper forms on the bottom of the vessel.			
	The reactions are:			
	Zn(s	) ζ Zn²+(aq) + 2e−	E° = +0.76 V	

Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> ζ Cu(s)	E° = +0.35 V
Zn(s) + Cu <sup>2+</sup> (aq) ζ Zn <sup>2+</sup> (aq) + Cu(s)	E° <sub>cell</sub> = +1.11 V

# COPPER IN SILVER NITRATE SOLUTION: "THE SILVER TREE"

A spiral of copper metal is placed in a solution of silver nitrate. Overnight, the copper dissolves, silver is precipitated and the solution turns blue.

EQUIPMENT	•	500 mL beaker		
REAGENTS	•	1 spiral of copper wire silver nitrate, AgNO <sub>3</sub> (0.1 M, 500 mL)		
PREPARATION	•	Dissolve 8.5 g AgNO $_{3}$ in 500 mL of water. Place the 500 mL of silver nitrate solution into the beaker.		
PROCEDURE	•	Place the copper strip into the silver nitrate solution. Allow to stand for one day.		
RESULTS	ESULTS Elemental silver is deposited on the surface of the copper as a spongy mass of small brilliant needles. The effect produced is that of a "silver tree." The solution becomes pale blue. The reaction that occurs is :			
	Ag⁺(	aq) + e⁻ ζ Ag(s)	E° = +0.80 V	
Cu(s) ζ Cu²+(aq) + 2e⁻ E° = +0.35 V				

2Ag+(aq) + Cu(s) ζ 2Ag(s) + Cu <sup>2+</sup> (aq)	E° <sub>cell</sub> = +1.15 V

EQUIPMENT

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### **IRON(II) SULFATE AND POTASSIUM PERMANGANATE**

100 mL measuring cylinder

2 L conical flask

Green iron(II) sulfate solution is oxidised by a purple potassium permanganate solution, to give a colourless solution of iron(III) and manganese(II).

	•	long glass rod light box	
REAGENTS	• • •	potassium permanganate, $KMnO_4$ (a few crystals) iron(II) ammonium sulfate-6-water, $(NH_4)_2Fe(SO_4)_26$ sulfuric acid, $H_2SO_4$ (2 M, 100 mL) distilled water	H <sub>2</sub> O (39.2 g)
PREPARATION	•	Dissolve 39.2 g iron(II) ammonium sulfate-6-water in sulfuric acid. Set up the light box . Fill the conical flask with water and add crystals of p permanganate, sufficient to produce a solution whic coloured without being opaque. Provide measuring cylinder and stirring rod.	n 100 mL of 2 M ootassium h is strongly
PROCEDURE	•	Add 100 mL of the iron(II) sulfate solution to the pot permanganate solution. Stir.	assium
RESULTS	Permanganate is reduced to Mn(II) and Fe(II) is oxidised to Fe(III).		to Fe(III).
	The I Fe <sup>2+</sup> MnC	reactions are: (aq)	E° = -0.77 V E° = +1.51 V

MnO <sub>4</sub> <sup>-</sup> (aq) + 8H <sup>+</sup> (aq) + 5Fe <sup>2+</sup> (aq) ζ Mn <sup>2+</sup> (aq) + 5Fe <sup>3+</sup> (aq) + 4H <sub>2</sub> O(I)	E°cell =+0.74V
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### **ELECTROCHEMICAL CELLS**

The following electrochemical cells are examined:

 $Zn(s) | Zn^{2+}(aq) || H^{+}(aq) | H_{2}(g) | Pt$  $Cu(s) | Cu^{2+}(aq) || H^{+}(aq) | H_{2}(g) | Pt$ Zn(s) | Zn<sup>2+</sup>(aq) || Cu<sup>2+</sup>(aq) | Cu(s).

#### EQUIPMENT

- hydrogen half cell
- voltmeter
- leads with alligator clips
- large digital display
- 3 x 250 mL beakers
- 2 salt bridges (see below) in storage vessel
- retort stand
- 2 boss heads and clamps
- tweezers or tongs and tissues
- small beaker for used salt bridges
- rubber tubing to fit regulator and hydrogen cell

#### REAGENTS

- hydrogen gas cylinder with appropriate regulator
- hydrochloric acid, HCI (1 M, 250 mL)
- copper(II) sulfate-5-water, CuSO<sub>4</sub>·5H<sub>2</sub>O (1M)
- zinc sulfate-6-water, ZnSO<sub>4</sub>6H<sub>2</sub>O (1M)
- 20 cm strip of copper sheet
- 20 cm strip of zinc sheet
- For the salt bridge: -
- potassium nitrate, KNO<sub>2</sub> (5 g)
- agar (1 g)

#### **PREPARATION** Constructing the salt bridge

- Prepare the salt bridges by making a mixture of: 50 mL distilled water, 5 g potassium nitrate, 1 g agar
- Place this mixture on a steam bath until dissolved (usually about 20 minutes).
- Make U-tubes by bending glass tubing of about 5 mm diameter to form a U-shape about 4 cm high.
- Using a small plastic funnel, fill these tubes with the hot agar solution.
- Leave the tubes to stand overnight. These salt-bridges can be kept indefinitely in a stoppered bottle containing 1 M potassium nitrate solution.
- Prepare 250 mL of 1 M copper sulfate by dissolving 62.5 g CuSO, 5H<sub>2</sub>O in water and making up to 250 mL.
- Similarly, prepare 250 mL of 1 M zinc sulfate by dissolving 67.5 g  $ZnSO_4 GH_2O$  in water and making up to 250 mL.
- Set up the Voltmeter.
- Set up a standard hydrogen half-cell by filling one of the 250 mL beakers with hydrochloric acid solution and immersing the glass apparatus containing the platinum electrode in it.

- Set the beaker on the foot of the retort stand and, using the clamp, secure the cell. Set up the hydrogen cylinder.
- Connect cell and cylinder with the tubing. Adjust the valves of the regulator so that a gentle, steady stream of hydrogen gas passes over the electrode.
- Turn off the gas flow at the main valve.
- Prepare a copper half-cell by filling a 250 mL beaker with the copper solution and placing the copper strip in it.
- Prepare a **zinc half-cell** by filling a 250 mL beaker with the zinc solution and placing the zinc strip in it.



Line up the three half-cells with the hydrogen cell in the middle.

• Supply the salt bridges in their storage vessel as well as the beaker for their disposal.

 $\mathbf{2H}^{^{+}}\left( aq\right) +\mathbf{2e}^{^{-}}\zeta \text{ H}_{2}\left( g\right)$ 

• After the demonstration, the contaminated agar may be removed from the used bridges by heating them in water.

#### **PROCEDURE** • Use salt bridges to connect the half-cells.

- Turn on the Voltmeter and attach the terminals across the half-cell electrodes
- Note the readings of each combination.
- **RESULTS** E<sup>•</sup><sub>cell</sub> for the three cells should be close to the calculated values shown below.

#### copper and hydrogen half cells:

H <sub>2</sub> (g) ζ 2H (aq) + 2e	E° = 0.00 V
Cu <sup>2+</sup> + 2e <sup>-</sup> ζ Cu(s)	E° = +0.35 V
$Cu^{2^{+}}(aq) + H_{2}(g) \zeta 2H^{+}(aq) + Cu(s)$	E° <sub>cell</sub> = +0.35 V

#### zinc and hydrogen half cells:

2H⁺(aq) + 2e⁻ ζ H₂(g)	E° = 0.00 V
Zn(s) ζ Zn <sup>2+</sup> (aq) + 2e <sup>-</sup>	E° = +0.76 V
$2H^{+}(aq) + Zn(s) \zeta Zn^{2+}(aq) + H_{2}(g)$	E° <sub>cell</sub> = +0.76 V

#### copper and zinc half cells:

Cu²⁺(aq) + 2e⁻ ζ Cu(s)	E° = +0.35 V
Zn(s) ζ Zn²⁺(aq) + 2e⁻	E° = +0.76 V
$Zn(s) + Cu^{2+}(aq) \zeta Cu(s) + Zn^{2+}(aq)$	E° <sub>cell</sub> = +1.11 V

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## **DEMONSTRATION 6.7**

### ACTIVITY SERIES OF METALS

The activity of five metals is compared.

EQUIPMENT	<ul> <li>1 large petri dish</li> <li>1 piece or strip of magnesium, zinc, iron, tin and copper metal, each of similar size</li> <li>overhead projector transparency</li> </ul>
REAGENTS	<ul> <li>hydrochloric acid, HCl (5 M, 100 mL)</li> <li>Mg, Zn, Fe, Sn and Cu metals</li> </ul>
PROCEDURE	<ul> <li>Trace the circumference of the petri dishes onto the overhead projector transparency and label 5 inside areas with Mg, Zn, Fe, Sn and Cu.</li> <li>Place the transparency on the projector underneath the petri dish.</li> <li>Fill the petri dish with acid and immerse the piece of each metal over its label.</li> </ul>
RESULTS	The order of activity of the metals is assessed from how vigorously they react: Mg > Zn > Fe > Sn > Cu.
	The general reaction is:

 $M(s) + 2H^{+}(aq) \zeta H_{2}(g) + M^{2+}(aq)$ 

### **CONCENTRATION CELL**

•

Two identical copper half cells are constructed. On the addition of sodium sulfide solution to one of them, a precipitate forms in the beaker and a voltage is detected.

#### EQUIPMENT

- U-tube salt bridge as in Demonstration 6.6
- 2 x 600 mL beakers
- 50 mL burette with stand
- voltmeter
- alligator leads
- plastic funnel.
  - large digital display



REAGENTS	<ul> <li>copper(II) sulfate-5-water, CuSO<sub>4</sub>·5H<sub>2</sub>O (25 g)</li> <li>sodium sulfide-9-water, Na<sub>2</sub>S·9H<sub>2</sub>O (24 g)</li> <li>copper metal (2 strips)</li> </ul>
PREPARATION	<ul> <li>Dissolve copper(II) sulfate-5-water (25 g) in water (1 L).</li> <li>Dissolve sodium sulfide-9-water (24 g) in water (100 mL).</li> <li>Pour 400 mL of copper sulfate solution into each beaker.</li> <li>Since sodium sulphide has a pungent smell, fill the burette with 50 mL sodium sulfide solution just before the demonstration. Leave a plastic funnel on the top of the burette.</li> </ul>
PROCEDURE	<ul> <li>Place the beakers of copper sulfate solution side by side with the salt bridge connecting them.</li> <li>Place one of the copper strips in each beaker.</li> <li>Connect the alligator leads to the copper and the voltmeter.</li> <li>Position the burette over the beaker containing the copper strip to which the negative lead is attached.</li> <li>Add a few drops of sodium sulfide solution to the beaker.</li> <li>Progressively run in the remaining solution.</li> </ul>
RESULTS	Initially, a voltage close to zero should be observed. On addition of sodium sulfide solution, the voltage should increase from zero to a maximum of 0.6 volts.
DISPOSAL	The copper sulfate and sodium sulfide solutions may be flushed down the

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sink with water. The copper sulfate solution to which sodium sulfide has been added should be filtered to remove the copper sulfide precipitate. The filtrate may be flushed down the sink and the residue discarded with solid wastes.

### A COMPARISON OF SALT BRIDGES

A galvanic cell is set up and three salt bridges are compared: a standard agar salt bridge; a sodium chloride bridge; and the human body acting as a salt bridge.

EQUIPMENT voltmeter 2 x 100 mL beakers salt bridge as used in Demonstration 6.6 filter paper one strip of Zn metal one strip of Cu metal. REAGENTS zinc chloride,  $ZnCl_{2}$  (6.1 g), (0.1M) copper(II) sulfate-5-water, CuSO, 5H,O (11.2 g), (0.1M) sodium chloride, NaCl (0.2 g) large dgitaldisplay **PREPARATION** . Dissolve solid ZnCl<sub>2</sub> (6.1 g) in distilled water (450 mL) Dissolve solid CuSO, 5H, O (11.2 g) in distilled water (450 mL). Dissolve solid NaCl (0.2 g) in distilled water (30 mL) Ø pH mV mete PROCEDURE Place the ZnCl<sub>2</sub> and CuSO<sub>4</sub> gar/KNO solutions into individual NaCl/fiterpaper s at brid ce beakers. , fingers ofone hand Set up the galvanic cell as shown in the figure. Note that Znstrip (arode) the Zn strip is connected Custrip — (cathode) call ons to the negative terminal of the voltmeter. Measure the voltage with the conventional (agar/KNO<sub>3</sub>) salt Cui bridge. Replace the agar/KNO, salt bridge with filter paper freshly soaked in 0.1 M CuSO<sub>4</sub> (aq) 0.1 M ZnCl<sub>2</sub> (aq) the NaCl solution and measure the voltage. Finally, replace the filter paper with two fingers of the same hand and measure the voltage again. RESULTS The voltages using the three salt bridges decrease in the order:

**ESULIS** The voltages using the three salt bridges decrease in the order: agar/KNO<sub>3</sub>> filter paper/NaCl > human body. The voltage for the KNO<sub>3</sub> bridge will be near the calculated E°<sub>cell</sub> below.  $Zn(s) \zeta Zn^{2+}(ag) + 2e^{-}$  E° = +0.76 V

Cu²⁺(aq) + 2e⁻ ζ Cu(s)	E° = +0.35 V
Zn(s) + Cu²+(aq) ζ Zn²+(aq) + Cu(s)	E° <sub>cell</sub> = +1.11 V

### **ELECTROLYSIS**

A voltage is applied to a solution of water containing universal indicator. Distinct gases are evolved at the cathode and anode and the reactions taking place are indicated by colour changes of the indicator.

KNO\_

neutral

(green)

₽≞

异 12 V D.C.

basic

solution

(violet)



H<sup>+</sup>(aq) is produced at the anode and the universal indicator turns red. OH<sup>-</sup> (aq) is produced at the cathode and the universal indicator turns violet.

#### COPPER TO "SILVER" TO "GOLD"

Copper disks are plated with zinc or tin to give "silver". Then the zinc and copper are heated to give a brass alloy, "gold". If copper and tin are heated, the alloy is bronze.

- EQUIPMENT 150 mL beaker
  - 250 mL beaker
  - bunsen burner
  - tripod
  - wire gauze
  - tongs
  - paper towel
  - 3 copper disks, 5 cm in diameter
  - steel wool

#### **REAGENTS** • granular zinc (25 g) (granular tin may also be used).

• sodium hydroxide, NaOH (3 M, 50 mL)

#### **PREPARATION** .

- Polish the copper disks using the steel wool until they are shiny. Place the sodium hydroxide solution in the 150 mL beaker on the tripod over the bunsen burner.
- Add the zinc granules and bring to the boil.

PROCEDURE

- When the sodium hydroxide solution is boiling, use the tongs to place two of the prepared copper disks on top of the zinc granules, ensuring that they are covered by solution.
- When the disks are silvered, remove them with the tongs and place them in the 250 mL beaker containing water.
- Once cool, dry them, and take one coin in the tongs and heat it in the blue part of the bunsen flame.
- Heat it briefly and evenly until it changes to a golden colour.
- Remove it from the flame, cool and dry.
- Place the three disks side by side for comparison.
- **RESULTS** If zinc is used, the "silver" coating is zinc, and the "gold" coating is brass. If tin is used, the "silver" coating is tin, and the "gold" coating bronze. In strongly alkaline solution, the zinc or tin dissolves to form the zincate or stannate ion respectively.

 $Zn(s) + 2OH^{-}(aq) \zeta ZnO_{2}^{2-}(aq) + H_{2}(g)$ 

 $Sn(s) + 2OH^{-}(aq) + 4H_{2}O(I) \zeta [Sn(OH)_{e}]^{2}(aq) + 2H_{2}(g)$ 

Bubbles of hydrogen are seen in the solution before it is heated; heating speeds the reaction. The electrochemistry of the deposition is not known, although it is thought to be a concentration cell based upon the reaction

$$ZnO_{2}^{2}(aq) + 2H_{2}O(I) + 2e^{\zeta} Zn(s) + 4OH^{-}(aq)$$
 and

 $[Sn(OH)_{e}]^{2-}(aq) + 4e^{-\zeta} Sn(s) + 6OH^{-}(aq)$  respectively.

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## **DEMONSTRATION 6.12**

### DRY CELL

A dry cell is constructed based on the same reaction as commercial alkaline batteries.

EQUIPMENT	•	1 slice of packing foam

- alligator clips
- voltmeter
- 1 large beaker
- pieces of string, disposable gloves, carbon rods

REAGENTS

- powdered manganese dioxide, MnO<sub>2</sub> (3-4 g)
- Ri
- ammonium chloride, NH<sub>4</sub>Cl (4 M, 100 mL)
- zinc foil (1 piece)

**PREPARATION** Prepare the ammonium chloride solution by dissolving ammonium chloride (21.4 g) in water (100 mL).

- **PROCEDURE** Cover the surface of the demonstration bench.
  - Pour the ammonium chloride solution into the large beaker and moisten the packing foam in the bottom of the beaker.
  - Squeeze the foam so that it is damp but not dripping; then sprinkle over the manganese dioxide.
  - Roll the sprinkled foam around the carbon rod.
  - Next wrap the foam in the zinc foil, ensuring that the zinc does not touch the carbon rod. (Tie the assembly together with string.)
  - Connect one alligator clip from the Voltmeter to the graphite rod, and the other to the zinc foil.
- **RESULTS** A voltage of about 1.3 volts should be observed.

Zn(s) ζ Zn²⁺(aq) + 2e⁻	E°= +0.76 V
2MnO <sub>2</sub> (s) + 2H <sub>2</sub> O(l) + 2e <sup>-</sup> ζ 2MnO(OH)(s) + 2OH <sup>-</sup> (aq)	E°= +0.57 V
(2) $(2)$	

 $Zn(s) + 2MnO_2(s) + 2H_2O(I) \zeta 2MnO(OH)(s) + Zn^{2+}(aq) + 2OH^{-}(aq)$  E<sup>o</sup><sub>cell</sub> = +1.33 V



bend and to be used again.

### **RUSTING AND CATHODIC PROTECTION**

An iron nail is placed in an agar solution and within an hour the areas around the head and tip of the nail have turned blue, while the area around the body of the nail has turned pink. Another nail wrapped with a magnesium strip is placed in the agar but shows no colour change to blue.

- **EQUIPMENT** 2 iron nails
  - 2 petri dishes
  - 1 strip of magnesium
- **REAGENTS** potassium hexacyanoferrate(III), K<sub>3</sub>[Fe(CN)<sub>6</sub>] (1.65 g), (0.1M)
  - phenolphthalein indicator (2 mL)
  - potassium nitrate, KNO<sub>3</sub> (5 g)
  - agar (1 g)
- **PROCEDURE** Prepare a 0.1 M potassium hexacyanoferrate(III) solution by dissolving 1.65 g in 50mL.
  - Prepare the agar gel by making a mixture of 50 mL distilled water, 5 g potassium nitrate, 1 g agar, 10 mL of 0.1 M potassium hexacyanoferrate(III) and 10 drops phenolphthalein indicator.
  - Place this mixture on a steam bath until the agar dissolves (usually about 20 minutes).
  - Place some agar gel into two petri dishes.
  - In one dish place an iron nail, into the other dish place a nail with magnesium strip wrapped around it.
- **RESULTS** The unprotected nail, acting as both anode and cathode, will show regions of blue and pink coloration. Iron is oxidised to Fe<sup>2+</sup>, which then reacts with potassium hexacyanoferrate(III) ion to give the dark blue precipitate known as *Turnbull's blue*. These blue regions appear around the head and tip of the nail. Oxidation occurs at these areas because the strained metal is more anodic (more active) than the body of the nail.

Fe(s) ζ Fe<sup>2+</sup>(aq) + 2e<sup>-</sup>

The  $Fe^{2+}$  reacts with  $K_3[Fe(CN)_6]$  to produce the blue precipitate

 $Fe^{2+}(aq) + [Fe(CN)_6]^{3-}(aq) + K^{+}(aq) + H_2O(I) \zeta KFe[Fe(CN)_6] \cdot H_2O(s).$ 

The electrons released at the two ends of the nail migrate to the body of the nail where they are used to reduce dissolved oxygen in the gel to  $OH^{-}(aq)$ . The increased concentration of  $OH^{-}(aq)$  causes the phenolphthalein to turn magenta.

 $\begin{array}{ll} O_{2}(aq) + 2H_{2}O(l) + 4e^{-\zeta} \ 4OH^{-}(aq) \\ \\ The overall redox reaction is \\ Fe(s) \ \zeta \ Fe^{2+}(aq) + 2e^{-} \\ O_{2}(aq) + 2H_{2}O(l) + 4e^{-\zeta} \ 4OH^{-}(aq) \\ \\ \hline 2Fe(s) + O_{2}(aq) + 2H_{2}O(l) \ \zeta \ 2Fe^{2+}(aq) + 4OH^{-}(aq) \\ V \end{array} \begin{array}{ll} E^{\circ}_{e^{-}} = +0.41 \ V \\ \\ E^{\circ}_{cell} = +0.81 \\ \end{array}$ 

The nail protected with magnesium, on which the magnesium functions as the cathode, shows no blue or black regions indicating that no corrosion of the iron nail has taken place. Here magnesium is oxidised in preference to the iron. The electrons released in the oxidation of the magnesium are again used to reduce oxygen to hydroxide which turns the phenolphthalein magenta.

Mg(s) ζ Mg²⁺(aq) + 2e⁻	E°= +2.36 V
<sup>-</sup> O <sub>2</sub> (aq) + 2H <sub>2</sub> O(I) + 4e <sup>-</sup> ζ 4OH <sup>-</sup> (aq)	E°= +0.40 V
2Mg(s) + O₂(aq) + 2H₂O ζ 2Mg²⁺(aq) + 4OH⁻(aq)	E° <sub>cell</sub> = +2.76 V

### TITRATION OF HALOGEN IONS WITH SILVER

As the titration of halide ions with silver ions is performed a graph is produced showing the potential changes of the solution.

#### **EQUIPMENT** • indicator electrode: silver, solid state, P4011

- reference electrode: mercury/mercurous sulfate
  - stand
  - Voltmeter with banana-plug adaptor
  - large digital display
- 50 mL burette and stand
- 3 x 500 mL volumetric flasks
- 4 x 100 mL measuring cylinders
- 250 mL beaker
- wash bottle with distilled water
- magnetic stirrer
- paper tissues
- transparency with graph grid
- 2 pens for over-head transparencies (fine point, 2 colours)

#### **REAGENTS** • potassium iodide, KI (0.1 M, 500 mL)

- sodium chloride, NaCl (0.1 M, 500 mL)
  - silver nitrate, AgNO<sub>3</sub> (0.1 M, 500 mL)
- nitric acid, HNO<sub>3</sub> (0.1 M, 500 mL)
- distilled water
- PREPARATION To separate 500 mL volumetric flasks add potassium iodide (8.3 g), sodium chloride (2 g), silver nitrate (8.5 g) to give 0.1 M solutions of these reagents.
  - Setup the voltmeter.
  - Place the transparency and pens on the over-head projector. Connect the projector to the mains.
  - Set up the solutions in their labelled flasks and place a labelled measuring cylinder with each.
  - Fill the burette with silver nitrate solution and set it up over the stirrer.
  - Position the electrodes so that they will reach into the beaker without interfering with each other, the burette or the spin bar.
  - Provide tissues and wash bottle.

#### **PROCEDURE** • Dim the lecture theatre lights.

- To the 250 mL beaker add KCI (10 mL), KI (20 mL) and  $HNO_3$  (20 mL).
- Place the beaker on the stirrer and allow to mix.
- Add silver nitrate solution from the burette in convenient units say 1 mL.
- After each addition allow sufficient time for mixing to complete and the mV reading to stabilise.
- Plot the mV against mL on the over-head transparency.

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#### RESULTS

 $Ag^{+}(aq) + I^{-}(aq) \zeta AgI(s)$ 

 $Ag^{+}(aq) + CI^{-}(aq) \zeta AgCI(s)$ 

The resultant curve should have the following shape:





### **ION-SELECTIVE TITRATION**

#### **EQUIPMENT** • indicator electrode: ion-specific electrode: Orion Cupric Selective,

- Cat.No.24-29A
- reference electrode: mercury/mercurous sulfate
- electrode stand
- voltmeter with banana-plug adaptor
- large digital display
- double adaptor
- magnetic stirrer
- spin bar
- 50 mL burette
- retort stand
- 100 mL measuring cylinder
- 250 mL beaker
- 2 x 250 mL volumetric flasks
- 2 x 250 mL reagent bottles
- wash bottle with distilled water
- paper tissues
- transparency with graph grid
- 2 pens for over-head transparencies (fine point, 2 colours)

REAGENTS

- copper(II) sulfate-5-water,  $CuSO_4 \cdot 5H_2O(0.62 \text{ g})$
- sodium ethylenediaminetetraacetic acid-2-water, Na<sub>2</sub>H<sub>2</sub>EDTA·2H<sub>2</sub>O (0.93 g)
- ammonia, NH<sub>3</sub> (15 M, 10 mL)

## **PREPARATION** • Prepare a 0.01 M aqueous solution of copper(II) sulfate by dissolving 0.62 g in a 250 mL volumetric flask.

- Dilute 50 mL of this with 200 mL of distilled water.
- Add 10 mL of concentrated ammonia solution.
- Place this solution into a stoppered reagent bottle.
- Prepare 250 mL of a 0.01 M solution of EDTA by dissolving 0.93 g of the EDTA salt in a 250 mL volumetric flask.
- Setup the voltmeter
- Place the graph transparency and pens on the over-head projector.
- Provide the solutions, measuring cylinder, wash bottle and tissues.
- Fill the burette with EDTA solution and set it up over the beaker.
- Place the electrodes so that they will reach into the beaker without interfering with each other, the burette or the spin bar.
- **PROCEDURE** Dim the room. Switch on instruments and appliances.
  - Place some copper(II) sulfate solution into the beaker and add the spin bar. Switch on the stirrer.
  - Add EDTA solution from the burette in convenient units say 1 mL.
  - After each addition, allow some time for mixing to complete and the reading to stabilise.
  - Plot mV against mL on the overhead transparency.
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#### **RESULTS** The final potential should be -700 mV.

**Note**: The presence of ammonia has a two-fold purpose: it fixes the pH of the system to about 10, and secondly it keeps  $Cu^{2+}$  in solution by forming ammine complexes. The complexes  $[Cu(NH_3)(H_2O)_3]^{2+}$ ,  $[Cu(NH_3)_2(H_2O)_2]^{2+}$ ,  $[Cu(NH_3)_3H_2O]^{2+}$ , and  $[Cu(NH_3)_4]^{2+}$  are all present in varying concentrations at pH 10. EDTA is a stronger chelating agent than ammonia and it will tend to displace the ammine ligands.

 $[Cu(NH_3)_4]^{2+}(aq) + Y^{4-}(aq) = [CuY]^{2-}(aq) + 4NH_3(aq)$ 

mV mV mV mL of EDTA

The resultant graph should have the following shape:

### COLOURFUL REDOX REACTIONS

This demonstration is popularly known as the 'Magic jug" and demonstrates the various oxidation–reduction reactions of iodide and iodate and colour changes of three indicators.

#### EQUIPMENT

- 1 L beaker
- 5 x 250 mL beakers
- light box

•

REAGENTS

- **S**i
- sulfuric acid,  $H_2SO_4$  (2 M, 11 mL)
  - sodium sulfite-7-water,  $Na_2SO_37H_2O$  (12.6 g)
  - sodium hydroxide, NaOH (4 g)
- potassium iodide, KI (2 g)
- potassium iodate, KIO<sub>3</sub> (3 g)
- phenolphthalein indicator
- o -cresolphthalein indicator
- deionised water
- Vitex (starch indicator)
- **PREPARATION** Dissolve 12.6 g sodium sulfite-7-water in 100 mL of water.
  - Make up in advance, label the beakers "1" through to "5" and place the specified amounts of the respective solutions into them:

4 mL

- 1. phenolphthalein in ethanol, 4% 1 mL
- 2. o-cresolphthalein in ethanol, 4% 1 mL
- 3. sulfuric acid, 2 M
- 4. sulfuric acid, 2 M with vitex 4 mL
- 5. sodium sulfite, 1 M (fresh) 5 mL
- Make up fresh: Dissolve 2 g of sodium hydroxide, 1 g of potassium iodide and 1.5 g of potassium iodate in about 30 mL of water.
- Place this solution in a 50mL volumetric flask and make up to the mark.
- Place 2 mL of this solution into the jug and make up to 1 L.
- Try out the demonstration and adjust the amount of Vitex (1 spatula will work)
- Line up the beakers on the light box and provide the 1 L beaker.
- **PROCEDURE** Pour about 200 mL of the contents of the jug into each beaker.
  - Note colour-changes.
  - Then return all solutions to the 1 L beaker.

**RESULTS** Seen from a distance, the 250 mL beakers will appear empty. After addition of the clear and colourless solution from the 1 L beaker, the beakers will appear to contain the following "drinks':

- 1. "claret" due to the phenolphthalein indicator turning pink in the presence of base.
- **2.** "port" due to the *o*-cresolphthalein indicator in the presence of base (the*o*-cresolphthalein turns clear at a pH of 8.4).
- **3.** "apple juice" due to the acidification of iodide and iodate resulting in the production of iodine (triiodide).
- **4.** "ink" due to the iodine reacting with starch to form a complex (this solution is rather thin).
- **5.** "water" sodium sulfite has no effect.

When all solutions are again combined in the jug, this will appear to contain once more just "water". Iodide and iodate are regenerated by the reaction with sulfite and the solution becomes acidic (both acid/base indicators are colourless in acidic conditions).

### ELECTROCHEMICAL WRITING

Electrochemical writing uses colour changes caused by the products of electrochemical reactions.

#### EQUIPMENT

- sheet of aluminium foil
- tape
- sheet of glass or wood (15 x 15 cm)
- 2 sheets of filter paper
- 1 sheet of typing paper
- copper wire (18 gauge or thicker)
- glass tubing
- 12 volt DC power source
- alligator clip

#### REAGENTS

- potassium iodide, KI (1.6 g)
- starch solution (1% wt/wt, 5 mL)
- water (20 mL)
- phenolphthalein indicator (5 mL)
- dilute sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (a few drops)

#### PROCEDURE

- Tape or cement the aluminium foil to the glass or wood sheet.
- Tape a sandwich consisting of filter paper, typing paper and another sheet of filter paper at one edge only onto the aluminium.
- Prepare a stylus from a length of copper wire looped at the end and passed through a length of glass tubing.
- Prepare a fresh solution consisting of potassium iodide (1.6 g), water (20 mL), starch solution (5 mL), and phenolphthalein indicator (5 mL). (If the solution darkens after standing for several days, it can be decolorised by adding drops of dilute sodium thiosulfate.)
- Soak the 3 layers of paper with the KI/starch/phenolphthalein solution.
- Connect the stylus and foil to a 12 V DC power supply, and write on the paper with the stylus.
- **RESULTS** When the stylus is the cathode, a pink colour appears from the reaction of OH<sup>-</sup>(aq) with phenolphthalein:

cathode :  $2H_2O(I) + 2e^{-\zeta} H_2(g) + 2OH^{-}(aq)$ 

When the polarity is reversed and the stylus is the anode, a black (or very dark blue) colour appears from the reaction of  $I_2$  with starch :

anode :  $2I^{-}(aq) \zeta I_{2}(aq) + 2e^{-}$ 

When the filter paper and typing paper are turned over, the writing appears in the opposite colour on the bottom sheet of filter paper.

### THERMODYNAMIC AND KINETIC STABILITY: LIGAND EXCHANGE KINETICS

The difference between kinetic and thermodynamic stability can be demonstrated by using  $[Ni(en)_3]^{2+}$  and  $[Co(en)_3]^{3+}$ .

#### EQUIPMENT

- 2 x 1 L beakers
- stirring rod
- light box

REAGENTS



- 1,2-ethanediamine, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (30 g) ("en" represents ethylenediamine, 1,2-diaminoethane or
- 1,2-ethanediamine)
- nickel(II) chloride-6-water, NiCl<sub>2</sub>·6H<sub>2</sub>O (59.5 g)
- activated charcoal (2 g)
- cobalt(II) sulfate-7-water,  $CoSO_4 \cdot 7H_2O$  (14 g)
- hydrochloric acid, HCI (10 M, 5 mL)
- sulfuric acid,  $H_2SO_4$  (2 M, 300 mL)

**PREPARATION** Preparation of [Ni(en),]<sup>2+</sup>.

- Prepare a 0.5 M solution of nickel(II) chloride by dissolving 59.5 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 500 mL distilled water.
- Prepare a 0.5 M 1,2-ethanediamine solution by diluting 30 g 1,2-ethanediamine to 500 mL.
- Prepare a fresh solution of [Ni(en)<sub>3</sub>]<sup>2+</sup> by mixing 500 mL of 0.5 M 1,2ethanediamine and 170 mL nickel(II) chloride solution.

Preparation of racemic  $[Co(en)_3]^{3+}$  (in solution).

This step requires air to be drawn through the solution for 4 hours.

- Mix 13 mL of 1,2-ethanediamine and 25 mL of distilled water in a 250 mL conical flask.
- Cool the solution in an ice bath, then add 5 mL of 10 M hydrochloric acid, a solution of 14 g of cobalt(II) sulfate-7-water in 25 mL water and 2 g of activated charcoal.
- Bubble air through the mixture for 4 hours.
- Carefully adjust the pH of the solution to 7.0–7.5 with either 1,2-ethanediamine or 3 M hydrochloric acid, added dropwise.
- Heat the mixture on a steam bath (in a fume cupboard) for 15 minutes, cool and filter off the charcoal under suction in a Büchner funnel.
- Wash the charcoal with 10 mL of water and retain the filtrate and washings.
- **PROCEDURE** Transfer the  $[Ni(en)_3]^{2+}$  to one beaker and the  $[Co(en)_3]^{3+}$  solution to the second beaker.
  - Whilst stirring, add 150 mL of the sulfuric acid to the [Ni(en)<sub>3</sub>]<sup>2+</sup>.
  - Add 150 mL of the acid to the  $[Co(en)_3]^{3+}$  solution.

#### **Chapter 7: Reaction Kinetics**

**RESULTS** The violet tris(1,2-ethanediamine)nickel(II) chloride solution will change to a green  $[Ni(OH_2)_6]^{2+}$  solution instantly. The orange tris(1,2-ethanediamine)cobalt(III) solution will remain unchanged. This demonstration demonstrates that  $[Ni(en)_3]^{2+}$  is a *labile* complex-there is rapid exchange of the en ligands by aqua ligands and hence the colour change.

 $[Ni(en)_3]^{2+}(aq) + 6H_2O(I) \ 1 \ [Ni(OH_2)_6]^{2+}(aq) + 3en(aq)$ 

The tris(1,2-ethanediamine)cobalt(III) is an example of an *inert* complex in that it takes part in ligand exchange reactions very slowly, if at all. Hence the lack of a noticeable colour change.

Both of these complexes are thermodynamically unstable; they both have enormously large K values for dissociation indicating that in reactions, such as the one above, the equilibrium lies overwhelmingly to the right hand side. Thus the distinction between the two reactions is a kinetic one.

Tip: as the Co complex doesn't change colour and takes a long time to produce, a 'fake' solution can be used, ie weak Potassium dichromate solution.

## **DEMONSTRATION 7.2**

### VARIATION OF REACTION RATES WITH TEMPERATURE

This demonstration uses a chemiluminescent reaction to illustrate the effect of temperature on rates of reaction.

- **EQUIPMENT** 2 Cyalume sticks
  - 2 beakers
- **PREPARATION** Place one Cyalume stick into a beaker of hot water and the other stick into a beaker of iced water.
- **RESULTS** The Cyalume stick in the hot water glows more brightly than the one in cold water. At higher temperatures the reaction rate is faster and produces more light.

#### **Chapter 7: Reaction Kinetics**

## **DEMONSTRATION 7.3**

### A SLOW IODINE REACTION

#### EQUIPMENT • 2

- 2 L beaker
- 3 x 500 mL volumetric flasks
- 500 mL measuring cylinder
- 250 mL measuring cylinder
- 50 mL measuring cylinder
- stirring rod
- nickel spoon
- light box

REAGENTS

- potassium iodide, KI (8.3 g)
- sulfuric acid,  $H_2SO_4$  (0.02 M, 175 mL)
- hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (30 w/v% fresh)
- Vitex
- deionised water

#### **PREPARATION** • Prepare the following fresh aqueous solutions.

- Make up 175 mL of 0.02 M sulfuric acid.
- Prepare 500 mL of 0.02 M hydrogen peroxide by dissolving 1.26 mL of 30 w/v% solution in 500 mL of deionised water; [ measure out 50 mL after dilution ]
- Prepare 500 mL of 0.1 M potassium iodide solution by dissolving 8.3 g of KI in 500 mL of deionised water.
- Place the 2 L beaker and the three solutions on the light box.
- Supply Vitex, nickel spoon and stirring rod.

#### **PROCEDURE** • Pour the iodide solution into the beaker.

- Add a full nickel spoon of Vitex and stir. (Vitex may also be omitted; see below.)
- Now add the acid and the peroxide solutions simultaneously.
- Stir briefly.
- **RESULTS** Depending on the ambient temperature, the deep-blue colour will develop gradually over the period of a minute or longer. Without Vitex a gradually deepening yellow appears.

The reaction below indicates that in acidic solution, iodide ions are oxidized by hydrogen peroxide to triiodide ions:

 $3I^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \zeta I_3^{-}(aq) + 2H_2O(I)$ 

### THE "IODINE CLOCK"

This "Clock" reaction illustrates that the rate of reaction is dependent on the concentration of the reactants.

- EQUIPMENT 3 x 500 mL beakers
  - 3 x 250 mL beakers
  - 2 x 250 mL volumetric flasks
  - 2 x 250 mL measuring cylinders
  - 2 x 25 mL measuring cylinder
  - 3 stirring rods
  - light box
  - stop watch(es)
  - nickel spoon

REAGENTS

- iodic acid,  $HIO_3$  (5 g)
  - sodium sulfite,  $Na_2SO_3$  (2.1 g)
  - Vitex

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- distilled water
- **PREPARATION** The success of the demonstration depends on the purity of the water and the freshness of the solutions; preparation should occur within 24 hours of the demonstration.

Using volumetric flasks, prepare the following two solutions:

- **Solution A**: dissolve 5 g of iodic acid in distilled water and make up to 100 mL.
- Solution B: dissolve 2.1 g of sodium sulfite in distilled water and make up to 100 mL.
- Arrange the beakers in three pairs of one large and one small beaker.
- Label the pairs "I", "II" and "III". Distribute the solutions as follows:

Pair I	large beaker	20 mL of Solution A 200 mL of distilled water 1 heaped nickel spoon Vitex
	small beaker	20 mL of Solution B 200 mL of water
Pair II	large beaker	15 mL of Solution A 200 mL of distilled water 1 heaped nickel spoon Vitex
	small beaker	15 mL of Solution B 200 mL of water
Pair III	large beaker	12 mL of Solution A 200 mL of distilled water 1 heaped nickel spoon Vitex
	small beaker	12 mL of Solution B 200 mL of water

- Set up the beakers on the light box in pairs.
- Provide stirring rods and stop watch(es).
- **PROCEDURE** For each of the pairs, pour the contents of the small beaker into the associated large beaker.
  - Note the time taken for reaction to occur in each case.
- **RESULTS** After mixing, the solutions will be clear but after some time they will sequentially (and suddenly) change to deep blue.

In the case of pair I, this will take about 3 seconds, pair II will take about 10 and pair III some 20 seconds.

**Note:** The reaction rate depends on ambient temperature, freshness of solution and the purity of reagents and water.

### THE OSCILLATING IODINE REACTION

Three solutions are added together quickly. The resultant solution then oscillates between golden brown, blue and colourless, finally stopping at a deep blue colour.

The phenomenon of the oscillating iodine clock reaction was reported by Briggs and Rauscher, J. Chem. Educ. 50, 496 (1973).

- **EQUIPMENT** 2 x 500 mL conical flasks + stoppers
  - 1 x 2 L conical flask
  - magnetic heater/stirrer and spin bar
  - long stirring rod
  - light box

#### REAGENTS

- potassium iodate, KIO<sub>3</sub> (29 g)
  - perchloric acid, HClO<sub>4</sub> [ or 10 ml of 6M sulfuric acid ]
- malonic acid,  $CH_2(CO_2H)_2$  (10.5 g)
- manganese sulfate,  $MnSO_4 H_2O(1.68 g)$
- hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (30 w/v%, 300 g fresh)
- Vitex (starch solution)
- distilled water

#### **PREPARATION** All the following solutions must be freshly prepared:

#### Solution A

- Label the flask 2 L as "A".
- Put 700 mL of distilled water into the flask.
- Place it on the warm hot plate.
- Add the stirring bar.
- Add potassium iodate (29 g). Stir to dissolution.
- Remove from heat.
- Add perchloric acid to the flask, with an amount dependent upon the strength of the available acid: for 100% acid, use 10.7 g, for 70% acid, use 15.2 g, or for 60% acid, use 17.8 g. [or 10ml of 6M sulfuric acid ]

## CAUTION Concentrated perchloric acid is explosive with organic materials or metals.

- This is essential to prevent the potassium iodate from coming out of solution as it will not readily re-dissolve under these acidic conditions.
- Make up to the 1 L mark.
- Stopper lightly.
- Allow to cool.



#### Solution B

- Calibrate a 500 mL conical flask by placing a mark at the 500 mL level.
- Label the flask "B" and put in 400 mL of distilled water.
- Add the following: manganese sulfate (1.68 g), malonic acid (10.5 g) and one nickel spoon full of Vitex.
- Stir well.
- Make up to the 500 mL mark and stopper lightly.
- Solution C
- Calibrate a 500 mL conical flask to the 500 mL level. Label "C".
- Add hydrogen peroxide (100 volume, 296.3 g) and make up with distilled water (500 mL).
- Place the three flasks A, B and C on the light box.
- **PROCEDURE** Transfer the contents of flask B and C as quickly as possible to flask A.
- **RESULTS** The frequency and number of oscillations of this reaction sequence cannot be accurately predicted. Among the determining parameters are ambient temperature, purity of reagents and the time elapsed between preparation and demonstration. Should the demonstration fail to work altogether, the most likely cause will be the quality of the peroxide used. If possible, use a previously unopened bottle.

Initially, the solution will be clear and colourless. After several seconds a rapid colour change to golden brown will occur. After several further seconds the solution will change to deep-blue, then colourless again. The above sequence should repeat itself up to 15 times before the solution settles to a permanent, deep blue.

The overall reaction is:

$$IO_{3}^{-} + 2H_{2}O_{2} + CH_{2}(CO_{2}H)_{2} + H^{+} \Phi ICH(CO_{2}H)_{2} + 2O_{2} + 3H_{2}O_{2}$$

### AN OSCILLATING REACTION TRAVELLING WAVES OF COLOUR

A blue dot spontaneously appears in a red solution, as the spot grows larger, red spots appear inside the blue spot, forming blue rings.

#### EQUIPMENT

- 4 conical flasks
- petri dish
- 10 mL measuring cylinder
- 50 mL beaker
- 5 mL graduated pipette
- stirring rod

REAGENTS

- potassium bromate, KBrO<sub>3</sub> (0.5 M, 6.0 mL)
   potassium bromide, KBr (0.5 M, 1.0 mL)
- sulfuric acid,  $H_2SO_4$  (6 M, 0.60 mL)
- malonic acid,  $CH_2(CO_2H)_2$  (2.5 mL)
- ferroin solution (0.025 M, 1.0 mL)

CAUTION

Bromates are strong oxidising agents. Mixtures of bromates with finely divided organic materials, metals, or other combustible materials are easily ignited or explosive. Malonic acid is a strong irritant to the skin, eyes and mucous membranes.

**PREPARATION** These solutions should be prepared 10 minutes before the demonstration.

- Potassium bromate solution: Dissolve 0.84 g of KBrO<sub>3</sub> in 10 mL of distilled water.
- Sulfuric acid solution: Pour 3.3 mL of 18 M H<sub>2</sub>SO<sub>4</sub> into 10 mL distilled water.
- Malonic acid stock solution: dissolve 0.52 g CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in 10 mL.
- Ferroin stock solution: dissolve 0.069 g iron(II) sulfate-6-water and 0.135 g 1,10-phenanthroline in 10 mL of distilled water.
- Potassium bromide stock solution: dissolve 0.59 g KBr in 10 mL of distilled water.
- **PROCEDURE** Pour 6.0 mL of potassium bromate into the 50 mL beaker.
  - To the above solution add 0.60 mL of sulfuric acid, 1.0 mL of potassium bromide solution and 2.5 mL malonic acid.
  - Stir the solution until the amber colour disappears.
  - Add 1.0 mL of ferroin solution. The solution will turn blue, then redorange.
  - Pour the solution into the petri dish and swirl the dish to coat the bottom of it uniformly.
  - Place the petri dish on the overhead projector and adjust the projector so that the solution is in focus on the screen.



RESULTS The induction time for this demonstration is five-ten minutes after which one or more blue dots will appear in the solution. These dots will grow slowly, and after a time, the centre of the blue dot will turn red-orange, forming a blue ring. The blue ring will expand, its red-orange interior will grow, and another blue dot will appear at the centre. By alternately turning blue, then red-orange, the centre will produce a series of concentric rings which gradually advance through the solution. When several sets of rings develop at different centres in the dish, they will eventually interact to form complex pattern of blue and orange bands. The dish may be swirled to mix the solution, to allow for the formation of new rings. The blue dots will reappear and generate a new pattern. After some time, bubbles of carbon dioxide will appear in the solution, making it difficult to observe the pattern. Eventually the solution will become completely blue, and no more patterns will develop. Traces of chloride ions in the solution will interfere with the mechanism of the reaction.

See - Showalter, Noyes & Turner, J. Am. Chem. Soc. 101, 7463 (1979).

Unlike the previous oscillating reactions, which are temporal in nature, this reaction involves spatial oscillations – rings of high [Fe(III)] moving through regions of high [Fe(II)].

The overall chemical change involves bromate oxidation of malonic acid which is catalysed by ferroin.

 $BrO_{3}^{-}(aq) + 2Br^{-}(aq) + 3H^{+}(aq) + 3CH_{2}(CO_{2}H)_{2}(aq) \zeta 3BrCH(CO_{2}H)_{2}(aq) + 3H_{2}O(I)$ 

### OXIDATION OF METHANOL CATALYSED BY PLATINUM

A heated piece of platinum gauze is brought near warmed methanol. The gauze then begins to glow.

- EQUIPMENT
- 250 mL beakerbunsen burner
- tripod and wire mat
- retort stand
- 2 boss heads and clamps
- watch glass and/or damp cloth
- fine copper wire

REAGENTS

- piece of platinum gauze (ideally, a platinum cathode such as those used in the teaching laboratories)
- methanol, CH<sub>2</sub>OH (25 mL fresh)
- hydrochloric acid, HCl

**PREPARATION** There are three things which frequently prevent this demonstration from working satisfactorily:

- the platinum has not been cleaned before use.
- old (partially oxidised) methanol has been used.
- the methanol and/or platinum had either not been pre–warmed sufficiently or it is being over-heated.
- Clean the gauze in the following way: Place some concentrated hydrochloric acid in a 100 mL beaker. Light a bunsen burner and heat the platinum gauze until it is red-hot. Plunge the gauze into the hydrochloric acid and hold the gauze over the flame until it is red-hot. Repeat three times. Rinse in alcohol.
- Set up retort stand and clamp, bunsen burner, tripod and wire mat.
- Suspend the gauze from the clamp by a thin piece of wire.
- Place some methanol (25 mL) in the beaker and set it on the wire mat over the tripod so that it is directly below the gauze.
- Provide matches and watch glass or damp cloth.

**PROCEDURE** • Light the bunsen and gently warm the methanol just enough to generate some vapour in the upper portion of the beaker.

- Remove the flame and use it to quickly warm the platinum gauze.
  - Without delay lower the gauze into the flask to within a centimetre of the surface of the methanol.
- **RESULTS** Within a few seconds the gauze will begin to glow: exothermic oxidation of methanol is taking place.

 $2CH_{3}OH(I) + 3O_{2}(g) \zeta 2CO_{2}(g) + 4H_{2}O(g)$ 

CAUTION If the glowing platinum is allowed to come too close to the methanol surface, the methanol itself will ignite. The flame can be easily extinguished by placing the watch glass or damp cloth over the mouth of the flask.

### CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

Manganese dioxide is used to catalyse the decomposition of hydrogen peroxide.

This demonstration may be performed on a small or large scale. In the instructions below, the amounts needed for the large-scale demonstration are given in square brackets [].

- **EQUIPMENT** 1 L measuring cylinder [specially made cylinder, 1.5 m high, 6 cm diameter]
  - 2 x 25 mL [2 x 100 mL] measuring cylinders
  - 100 mL [500 mL] measuring cylinder
  - plastic tray
  - glass stirring rod, length depending on the cylinder used [retort stand and clamp]
- **REAGENTS** manganese dioxide, MnO<sub>2</sub>, one nickel spoonful
  - sodium hydroxide, NaOH (1 M, 20 mL [60 mL])
  - hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (10 % w/w, 100 mL [300 mL] fresh)
  - Teepol (20 mL [60 mL])
- **PREPARATION** Prepare a 1 M solution of sodium hydroxide by dissolving 4.0 g of solid sodium hydroxide in 100 mL of distilled water.
  - Place 1 [3] heaped nickel spoonful of manganese dioxide into the cylinder.
  - Set the 1 L cylinder in the plastic tray [support the tall cylinder with retort stand and clamp].
  - Provide reagents in the appropriate measuring cylinders, as well as the stirring rod.
- **PROCEDURE** Make a slurry of manganese dioxide with the sodium hydroxide solution and Teepol.
  - Add the hydrogen peroxide and stir briefly.
- **RESULTS** The mixture will undergo rapid decomposition and oxygen will be given off. A thick grey foam will form which should fill the cylinder to over-flowing.

**Note:** The volume of foam depends on the strength of the peroxide and the effectiveness with which Teepol traps the oxygen.

$$2H_2O_2(aq) \overset{MnO_2(s)}{\zeta} 2H_2O(I) + O_2(g)$$

### COMPARISON OF CATALYSTS

The following catalysts are used to decompose hydrogen peroxide: manganese dioxide, liquid bromine, sodium bromide, ground and unground liver, and platinum gauze. A comparison is made of the rates of reaction with each catalyst.

- **EQUIPMENT** 6 x 100 mL measuring cylinders
  - platinum gauze
  - 6 drip trays
- **REAGENTS** manganese dioxide, MnO<sub>2</sub>/NaOH saturated solution
  - sodium bromide, NaBr
  - bromine water, Br<sub>2</sub>
  - liver (ground and unground)
  - hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (10% w/w)
  - Teepol
- **PROCEDURE** Place each measuring cylinder in a drip tray.
  - In each cylinder place 10 mL of  $H_2O_2$  and 6 mL of Teepol.
    - Add the following catalysts to each cylinder in turn:
      - 1. MnO<sub>2</sub>/NaOH
      - 2. platinum gauze
      - 3. NaBr(aq)
      - 4. Br<sub>2</sub>(aq)
      - 5. unground liver
      - 6. ground liver
    - Note the rate at which the foam reaches the top of each cylinder.

#### **RESULTS** The general reaction is:

 $2H_2O_2(aq) \xrightarrow{catalyst} 2H_2O(I) + O_2(g)$ 

For  $MnO_2$  as the catalyst, see Demonstration 7.8. The platinum gauze catalyses the reaction at a slower rate because it proceeds by way of adsorption of the peroxide on to the surface of the catalyst. The rates of reaction when using either bromine water or sodium bromide are the same. But the latter has a lead time as the concentration of Br<sub>2</sub> must build up first.

The ground liver has a larger surface area than the unground liver and hence more sites of catalysis; the rate of decomposition is faster. The catalyst in the case of liver is catalase.

After a series of reactions on the surface of the catalyst, water and oxygen are liberated.

### THE PRODUCTION OF AN ACTIVATED COMPLEX

A pink cobalt catalyst is added to a solution of sodium potassium tartrate and hydrogen peroxide. A green activated complex is formed and the reaction proceeds. When the green complex disappears, the reaction ceases.

#### EQUIPMENT • 600 mL beaker

- 2 x 250 mL beakers
- 100 mL measuring cylinder
- hot plate
- spatula
- scales
- thermometer

#### REAGENTS

- sodium potassium tartrate-4-water, NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O (12 g)
  - hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (5%, 80 mL)
  - cobalt(II) chloride-6-water, CoCl<sub>2</sub>·6H<sub>2</sub>O (9–13 g)
  - distilled water (300 mL)

**PREPARATION** .



- Prepare a solution of sodium potassium tartrate (200 mL) by dissolving 12 g of  $NaKC_4H_4O_6\cdot 4H_2O$  in distilled water (200 mL) in a 250 mL beaker.
- Prepare a solution of 5% hydrogen peroxide by adding 20 mL of 30% hydrogen peroxide to 100 mL of distilled water in the other 250 mL beaker.
- Pour 80 mL of the 5% hydrogen peroxide into the measuring cylinder.
- Heat the hot plate to 70°C.
- Pour the sodium potassium tartrate (200 mL) solution into the 600 mL beaker and place it on the hot plate. Checking with the thermometer heat the solution to 70°C.
  - Add the hydrogen peroxide and the cobalt(II) chloride-6-water.
- **RESULTS** This reaction involves the oxidation of tartaric acid  $HO_2CCH(OH)CH(OH)CO_2H$  by hydrogen peroxide in the presence of a cobalt(II) chloride catalyst. It is a complex set of reactions involving the production of carbon dioxide, carbon monoxide and oxygen. The green colour is due to the formation of a cobalt-tartrate activated complex. Note that the original catalyst, cobalt(II) chloride, is pink in aqueous solution. As the tartrate is oxidized, the activated complex is broken down to the original catalyst, and the pink colour returns. Oxygen and carbon dioxide gases are also produced. Oxalic acid,  $HO_2CCO_2H$ , is probably produced also.

This demonstration can also be used to show the relationship between temperature and the reaction rate. Typically, initial temperatures of 50, 60 or 70°C produce a reaction times of 200, 90 or 40 seconds, respectively. Thus as a general rule, increasing the temperature of reaction by  $10^{\circ}$ C will double the reaction rate.

### AUTOCATALYSIS

When a small amount of sulfuric acid is added to the blue solution of potassium chlorate, sodium sulfite and bromophenol blue indicator in a measuring cylinder, a yellow colour forms at the top of the cylinder and gradually moves downwards.

EQUIPMENT	•	2 x 500 mL beakers

- 500 ml measuring cylinder
- magnetic stirrer
- dropper

REAGENTS

- potassium chlorate, KClO<sub>3</sub> (20 g)
- **S**i
- sodium sulfite, Na<sub>2</sub>SO<sub>3</sub> (62.5 g) bromophenol blue indicator
- sulfuric acid,  $H_2SO_4$  (3 M, 20 mL)
- distilled water (500 mL)
- **PREPARATION** Dissolve 20 g potassium chlorate and 62.5 g sodium sulfite in 250 mL of water.
  - Do not mix the solids first.
  - Add some bromophenol blue indicator.
  - In another beaker, add 20 mL sulfuric acid to 250 mL of water.
  - Slowly, with stirring, add the diluted acid to the contents of the first beaker.
  - Stir until everything dissolves.
  - This solution should be blue-violet.
  - Fill the measuring cylinder with this solution.
- **PROCEDURE** Add two droppers-full of  $3 \text{ MH}_2\text{SO}_4$  to the top of the liquid in the measuring cylinder.
- **RESULTS** A yellow colour will appear at the top of the solution, and a yellow-blue interface will form. This interface will gradually move down the cylinder.

The overall reaction is:

 $ClO_{3}^{-}(aq) + 3SO_{3}^{2-}(aq) \zeta Cl^{-}(aq) + 3SO_{4}^{2-}(aq)$ 

When sulfuric acid is dropped on the surface,  $H^*$  and other acidic products form. These acidic products catalyse further reactions to produce more acidic products, thus the autocatalytic nature of the reaction. Bromophenol blue is yellow in highly acidic conditions. Thus, as autocatalysis proceeds, the indicator changes from blue to yellow.

### **REACTIVITY OF SODIUM**

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The reactivity of sodium is assessed in three different liquids: water, liquid ammonia, and cyclohexane. Its reactivity is seen to be remarkably different in each.

EQUIPMENT	
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- 2 petri dishes
- scalpel
- glass-walled evacuated Dewar

REAGENTS



- sodium metal, Na
- water (20 mL)
   cyclohexane, C<sub>6</sub>H<sub>12</sub> (20 mL)
  - universal indicator

PROCEDURE

- Half fill one petri dish with water and the other with cyclohexane.
- Add some universal indicator to the petri dish filled with water and place both petri dishes onto the overhead projector.
- Cut two small pieces of sodium and add one to the cyclohexane and the other piece to the water.
- Observe the reactions.

**RESULTS** There is no reaction between the sodium and the cyclohexane.

The sodium reacts violently with water and produces  $H_2(g)$  and hydroxide ions, as evidenced by the green to violet colour change of the universal indicator.

 $2Na(s) + 2H_2O(I) \zeta 2Na^{+}(aq) + 2OH^{-}(aq) + H_2(g)$ 

### **REACTION OF SODIUM AND CHLORINE**

under nitrogen or kerosene.

Sodium metal reacts with chlorine gas to produce sodium chloride. EQUIPMENT chlorine gas (reacting Potassium permanganate with conc. Hydrochloric acid in a side arm flask (buchner flask) attached to rubber tubing). spatula 2 L round bottomed flask tongs glass stirring rod (to fit flask, with 6 cm protruding) cork retort stand clamp and boss head wash bottle REAGENTS sodium metal (fresh), Na (0.5 cm<sup>3</sup>) ethanol (for washing) sand (100 g) **PREPARATION** . Pour dry sand into the round bottom flask, to a depth of approximately 1 cm. Smear some vaseline on to the glass stopper and the inside of the neck of the flask. Place the flask in the fume hood. Place the side arm flask into the fume hood. Add 3 to 4 spatulas of potassium permanganate. Attach a length of rubber tubing to the side arm of the flask. Place the other end of the tubing inside the round bottom flask. Pour 70mL of 10M HCL into the side arm flask and stopper immediately. Collect the yellowish chlorine gas generated in the round bottom flask and stopper the flask with the greased glass stopper. Clamp the flask as shown in the diagram. PROCEDURE Just before the lecture begins cut a piece of clean sodium. Using the tongs, drop the sodium onto the sand and add 2 -3 drops of water from the wash bottle, so that it makes contact with the sodium. Observe the reaction. When the reaction is complete, replace the glass stopper. RESULTS The water reacts with the sodium and the reaction generates enough heat to melt the sodium. The hot sodium reacts with the chlorine gas, yielding a bright yellow flame and white fumes of NaCl.  $2Na(s) + Cl_{2}(g) \zeta 2NaCl(s)$ CAUTION Sodium metal reacts explosively with moisture and should be stored

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#### Chlorine gas is a strong oxidising agent and an irritant.

**DISPOSAL** Open the flask in a fume hood to dissipate any unreacted chlorine then wash the flask with ethanol, to remove unreacted sodium; then wash with water.

### THE SOLVAY PROCESS

Aqueous sodium chloride reacts with ammonia gas and carbon dioxide to produce solid sodium hydrogencarbonate which decomposes to produce sodium carbonate.

EQUIPMENT	<ul> <li>250 mL beaker</li> <li>tongs</li> <li>bunsen burner</li> <li>tripod</li> <li>filter paper</li> <li>filter funnel</li> </ul>		
REAGENTS	<ul> <li>ammonia, NH<sub>3</sub> (15 M)</li> <li>dry ice, solid CO<sub>2</sub></li> <li>sodium chloride</li> <li>universal indicator</li> </ul>		
CAUTION	Concentrated ammonia solution can cause burns. It is irritating to eyes, skin and respiratory system.		
PROCEDURE	<ul> <li>Saturate the ammonia with sodium chloride.</li> <li>Add pieces of dry ice.</li> <li>After a period of time sodium hydrogencarbonate precipitates from the cold reaction mixture.</li> <li>Filter off the solid NaHCO<sub>3</sub> and heat to 175°C, whereupon the solid decomposes to solid sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>.</li> </ul>		
RESULTS	The first stage of the reaction is:		
	$NH_3(g) + CO_2(g) + H_2O(I) + Na^+(aq) \zeta NaHCO_3(s) + NH_4^+(aq)$		
	The universal indicator changes from purple to green-blue. This reaction can be thought of as a metathesis reaction of $NH_4HCO_3$ (from $NH_3 + H_2CO_3$ ) and NaCl, to yield the products $NaHCO_3$ and $NH_4Cl$ . When the filtered $NaHCO_3$ is heated to $175^{\circ}C$ , it decomposes to sodium carbonate.		

 $2NaHCO_3(s) \xrightarrow{heat} Na_2CO_3(s) + CO_2(g) + H_2O(g)$ 

### **BURNING MAGNESIUM IN CARBON DIOXIDE**

#### EQUIPMENT • tongs

- medium beaker
- wooden taper and matches
- bunsen burner

#### **REAGENTS** • dry ice, solid CO<sub>2</sub>

- magnesium ribbon (5 cm)
- water

**PREPARATION** • Place several small pieces of dry ice into the beaker and add water. Allow the beaker to fill with carbon dioxide gas.

- Light the bunsen burner.
- **PROCEDURE** Holding the magnesium ribbon with tongs light one end of the ribbon in the bunsen burner flame and insert it quickly into the beaker (into the gas only).
  - Avoid looking directly at the burning magnesium.
  - Continue holding the burning strip of magnesium in the beaker until the reaction ceases.
  - For comparison light the wooden taper and place it into the gas in the beaker.

**RESULTS** The heat from the burning magnesium is sufficient to sever the bonds in carbon dioxide, producing magnesium oxide and carbon.

 $2Mg(s) + CO_2(s) \xrightarrow{heat} 2MgO(s) + C(s)$ 

The burning wooden taper is extinguished by the carbon dioxide gas.



### THE REACTION OF CALCIUM HYDROXIDE AND CARBON DIOXIDE

Dry ice is added to a solution of calcium hydroxide and bromothymol blue indicator. Upon adding excess dry ice a colour change is observed.

EQUIPMENT tongs medium beaker . REAGENTS dry ice, solid CO<sub>2</sub> • calcium hydroxide solution, Ca(OH)<sub>2</sub>(aq) • bromothymol-blue indicator ( $pK_a = 7$ ) PROCEDURE Add a few drops of bromothymol-blue indicator to the calcium . hydroxide solution. Add a few pieces of dry ice to the calcium hydroxide solution. RESULTS The carbon dioxide from the dry ice reacts with calcium ions to give a white, milky precipitate of calcium carbonate  $Ca(OH)_2(aq) + CO_2(g) \zeta CaCO_3(s) + H_2O(I)$ Upon adding excess dry ice, the calcium carbonate dissolves and the bromothymol-blue changes to a yellow colour indicating the presence of HCO<sub>3</sub><sup>-</sup> and an acidic solution.

 $CaCO_{3}(s) + H_{2}O(l) + CO_{2}(g) \zeta Ca^{2+}(aq) + 2HCO_{3}^{-}(aq)$ 

 $HCO_3^{-}(aq) \Phi H^{+}(aq) + CO_3^{2-}(aq)$ 

### COLOURED FLAMES PRODUCED BY THE ALKALI AND ALKALINE EARTH METALS

The salts of Group 1 and Group 2 metals give off unique colours in a flame.

#### EQUIPMENT

- Wire (platinum or nichrome, clean)
  - spray bottle
  - bunsen burner

REAGENTS

- hydrochloric acid, HCI (10 M)
- **S**i
- salts of alkali metals
- salts of alkaline earth metals
- PROCEDURE
- The coloured flames may be observed by dipping a clean platinum or nichrome wire (wet with concentrated HCI) into salts of these metals and holding the wire in a bunsen flame.
- Persistent colours can be obtained if a concentrated salt solution is blown as a fine spray into a bunsen flame.



coloured flame

squirt bottle of salt solution

- **RESULTS** The following salts give a substantial colour to the flame:
  - K: violet (1M Potassium chloride)
    Na: intense yellow (1M Sodium chloride)
    Ba: apple green (1M Barium chloride)
    Sr: crimson (1M Strontium nitrate)
    Cu: pale green (1M Copper chloride)

## **DEMONSTRATION 8.7**

### **REACTION OF ALUMINIUM AND BROMINE**

Aluminium and bromine react spectacularly to produce aluminium bromide.

EQUIPMENT	<ul> <li>10 mL measuring cylinder</li> <li>600 mL beaker</li> <li>12 cm watch glass</li> </ul>	
	<ul> <li>liquid bromine, Br<sub>2</sub>(10 mL) (use direct from reagent bottle)</li> <li>aluminium foil, (5 cm x 5 cm)</li> </ul>	
	<ul> <li>Working in a fume hood, add the bromine to the beaker.</li> <li>Cover the beaker with a watch glass.</li> <li>Tear the aluminium foil into small pieces and place them on the watch glass.</li> </ul>	
PROCEDURE	<ul><li>Dim the lecture theatre lights and then invert the watch glass.</li><li>Set the watch glass back on top of the beaker.</li></ul>	
RESULTS	After approximately 1 minute, small flashes and flames moving on the surface of the liquid are observed.	
	$2AI(s) + 3Br_2(I) \zeta 2AIBr_3(s)$	
	Bromine is a strong oxidising agent which vaporises readily at room temperature to produce toxic fumes. The products of the reaction are also toxic and may cause burns.	
DISPOSAL	A mild reducing agent, such as sodium thiosulfate or sodium hydrogen- sulfite, should be reacted with the bromine. The aqueous mixture can then be flushed down the drain with water.	

### **REACTION OF ALUMINIUM AND IODINE**

Three drops of water are added to an evaporating dish containing a mixture of aluminium powder and iodine powder. After a short period, thick purplebrown fumes are seen and the reaction bursts into flames.

EQUIPMENT	<ul> <li>evaporating basin, approximately 8 cm diameter</li> <li>pasteur pipette with teat</li> <li>insulating mat</li> <li>small beaker</li> </ul>
REAGENTS	<ul> <li>aluminium powder, Al (dry)</li> <li>iodine, I<sub>2</sub></li> <li>water</li> </ul>
PREPARATION	<ul> <li>Grind 2 heaped nickel spoonfuls of iodine very finely.</li> <li>Place the powder into the evaporating basin.</li> <li>Add the aluminium powder (10 cm<sup>3</sup>).</li> <li>Mix the two powders very carefully.</li> </ul>
	<ul> <li>On very humid days the mixture can be ignited by the moisture in the atmosphere.</li> <li>Place the basin on an insulating mat in an otherwise empty, darkened fume hood.</li> <li>Provide the beaker with a little water and the pipette.</li> </ul>
PROCEDURE	<ul> <li>Using the pasteur pipette, place water (3 to 5 drops) on the surface of the mixture. (Water is the catalyst for the reaction).</li> <li>Step well back from the fume hood.</li> </ul>

**RESULTS** An initiation period will follow which can range from about ten seconds to five minutes. During the first few seconds thick, purple-brown smoke will grow into a dense cloud. The system will soon burst into bright flames. It is possible that the evaporating basin will crack under the heat. The fuming will abate relatively quickly, whereas the heat persists for a considerable time. A grey-white ash-like product will remain.

 $8 \mathsf{Al}(s) + 6\mathsf{I}_2(s) + 3\mathsf{O}_2(g) \zeta 2\mathsf{AI}_2\mathsf{I}_6(g) + 2\mathsf{AI}_2\mathsf{O}_3(s)$ 

## EXPLOSIVE DECOMPOSITION OF NITROGEN TRIIODIDE

	lodine powder is dissolved in aqueous ammonia and the resultant solution is then allowed to dry on three filter papers. These are touched with a feather on a long pole, giving rise to the violent explosion of nitrogen triiodide and emission of violet smoke.
	When dry, nitrogen triiodide (NI <sub>3</sub> ) is extremely unstable and can detonate unexpectedly. A slight touch or even an air movement can trigger the explosion. In contrast, wet nitrogen triiodide is relatively safe to handle.
EQUIPMENT	<ul> <li>50 mL beaker</li> <li>stirring rod and spatula</li> <li>filter paper, at least 9 cm diameter</li> <li>feather or a shred of tissue paper</li> <li>pole, about 2 metres long</li> <li>ear plugs</li> <li>adhesive tape</li> <li>optional: retort stand with 3 retort rings, perspex safety screen</li> </ul>
	<ul> <li>iodine, I<sub>2</sub> (3 g)</li> <li>ammonia, NH<sub>3</sub> (15 M, 15 mL)</li> </ul>
PREPARATION	<ul> <li>Use the beaker to make up nitrogen triiodide.</li> <li>Add iodine to the ammonia.</li> <li>Stir and let stand for 15 minutes.</li> </ul>
	<ul> <li>Concentrated ammonia solution can cause burns.</li> <li>It is irritating to the eyes, skin and respiratory system.</li> <li>Place three pieces of filter paper on the bench, at least half a metre apart or place them on the retort rings which are mounted on the retort stand, one above the other, with as much vertical distance between them as possible.</li> <li>Secure filter paper with adhesive tape to the desk or retort rings.</li> <li>Place the safety screen in position.</li> <li>Fasten the feather or the tissue securely to the top of the pole with adhesive tape.</li> </ul>
	<ul> <li>The following preparation must be completed within 5 minutes!</li> <li>Retaining the solid matter in the beaker, decant the supernatant liquor into a sink and flush with water.</li> <li>With a spatula, scrape the brown residue of nitrogen triiodide onto a stack of four pieces of filter paper. These will absorb most of the remaining liquid.</li> <li>Divide the solid into 3 equal parts while still damp.</li> <li>Transfer each part to one of the pieces of filter paper secured to bench or retort stand and pat down gently.</li> </ul>

• Allow the solid to dry undisturbed for 60 minutes. In humid conditions allow a longer drying time.



Nitrogen triiodide is extremely sensitive to the touch. It is a powerful explosive! Larger amounts than specified here should not be prepared! Great care must be taken even when handling these modest amounts.

CAUTION

The noise from the explosion can cause ringing in the ears. The demonstrator must wear earplugs. Students should be warned to cover their ears with their hands and be no closer than 5 metres.

Standing well back and using the pole, lightly touch the triiodide with the feather. If the retort ring assembly is used, only the sample on the bottom need be touched. The other two will be set of by the explosion below.

**RESULTS** Detonation with emission of violet smoke should occur immediately. A successful detonation will completely destroy all traces of the dry nitrogen triiodide.

 $8NH_3 \cdot NI_3(s) \zeta 5N_2(g) + 6NH_4 I + 9I_2$ 

**DISPOSAL** If a sample should not have exploded, rub it gently with the pole to encourage detonation or allow it more time to dry. Otherwise, carefully pour water on the lecture table so that it slowly flows into the sample. When totally wet, the sample should be flushed down the drain with water. Any nitrogen triiodide that remains in the preparation beaker or on the spatula should be decomposed by rinsing with ethanol. Let stand overnight and then flush the solution down the drain with water.

# PRODUCTION OF SULFUR DIOXIDE AND SULFUROUS ACID

Sulfur dioxide gas, produced by burning sulfur, is dissolved in water containing universal indicator. The indicator changes colour in the acid.

EQUIPMENT
3 x 1 L flasks
deflagrating spoon

REAGENTS

- universal indicator
- sulfuric acid,  $H_2SO_4$  (1 M)
- solid sulfur (a pea-sized chunk is sufficient)

**PROCEDURE** • Prepare three large flasks by adding about 100 mL of water to each.

- Add enough universal indicator solution to each to give the water a distinct colour (usually green is the neutral range).
- Set the first container aside as a standard.
- To the second container add a few drops of acid to produce a red colour which can be used as a standard.
- Carefully lower a deflagrating spoon containing a pea-sized piece of burning sulfur into the third container.
- Swirl the container and notice the colour change as the gas dissolves in the water.

**RESULTS** Note the production of a gas as the sulfur burns.

1) Burning sulfur produces sulfur dioxide gas

 $S_{8}(s) + 8O_{2}(g) \otimes 8SO_{2}(g)$ 

2) Sulfur dioxide dissolves in water to form sulfurous acid,

 $H_2SO_3(aq)$ , which oxidises to form sulfuric acid.

 $SO_2(g) + H_2O(I) \otimes H_2SO_3(aq)$ 

 $2H_2SO_3(aq) + O_2(g) \otimes 2H_2SO_4(aq)$ 

The acid solution causes the universal indicator to change from green to red.

## **DEMONSTRATION 8.11**

### **IRON AND SULFUR**

- **EQUIPMENT** metal or ceramic pad
- **REAGENTS** iron filings
  - sulfur  $(S_8)$

#### PROCEDURE

- Form a trail or pattern with a mixture of 12 g iron and 12 g sulfur powder on a metal or ceramic fibre pad.
  - One end of the trail is then ignited with a small, hot bunsen flame (see diagram).

## **RESULTS** A glowing red band moves along the trail as iron and sulfur combine to form iron sulfide.

Fe+S<sub>8</sub> dull red glow FeS

 $8Fe(s) + S_8(s) \otimes 8FeS(s)$ 

## **DEMONSTRATION 8.12**

### ZINC AND SULFUR

When a mixture of zinc and sulfur are ignited, a violent reaction occurs.

- **EQUIPMENT** large insulating mat
  - bunsen burner
  - length of strong wire

**REAGENTS** • powdered sulfur,  $S_{8}$  (1 g)

• powdered zinc, Zn (6 g)

**PREPARATION** • Place insulating mat and burner into the otherwise empty fume hood.

- Using a small evaporating basin, weigh out 6 g of zinc and 1 g of sulfur.
- With a small spatula mix the two powders until the colour of the mixture is uniform.
- Place the powder directly on and in the middle of the insulating mat.

### PROCEDURE

- Turn on ventilation and light the burner.Heat the tip of the wire to red heat.
- At arm's length, plunge the red-hot tip of the wire into the centre of the powder pile.



#### This is a violent reaction.

Step back as soon as the reaction has been initiated. Warn the audience not to look directly at the reaction site.

**RESULT** Almost immediately a violent reaction will occur with much hissing and sparking, and the emission of a flash of bright light and dense smoke. The smoke consists of ZnS, ZnO and SO<sub>2</sub>. The solid remaining on the insulating mat is yellow and grey.

The reactions that are thought to occur are:

 $8Zn(s) + S_8(s) \xrightarrow{heat} 8ZnS(s)$  $2Zn(s) + O_2(g) \zeta 2ZnO(s)$ 

 $S(s) + O_2(g) \zeta SO_2(g)$ 

## **DEMONSTRATION 8.13**

### ZINC IN HYDROCHLORIC ACID

A strip of metal is placed in a beaker containing acid. Gas is evolved on the metal's surface and the metal is eaten away.

EQUIPMENT	•	1 L beaker

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- REAGENTS
- strip of zinc (about 20 cm long)
- hydrochloric acid, HCI (5 M, 500 mL)

PROCEDURE				
	PR	OCE	DU	RE

- Fill the beaker with about 500 mL of 5 M hydrochloric acid.
- 5 M hydrochloric acid can be made by diluting 10 M acid twofold.
- Place the strip of zinc into it.

**RESULTS** Hydrogen gas will evolve at the surface of the zinc.

The reaction that occurs is:

 $Zn(s) + 2H^{+}(aq) \zeta Zn^{2+}(aq) + H_{2}(g)$ 

The gas may be collected and tested with a lighted splint.

REAGEN	13	
2		
4		

### POTASSIUM CHLORATE AND SUGAR

A mixture of potassium chlorate and sugar is prepared five times with small amounts of salts added to four of them. The mixture are reacted sequentially and violent reactions occur, in which characteristic coloured flames are produced. EQUIPMENT 5 small evaporating dishes pasteur pipette with teat nickel spoon and spatula insulating mat mortar and pestle REAGENTS potassium chlorate, KCIO<sub>2</sub> (30 g) sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> (10 g) sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (18 M, 1 mL) barium chloride-2-water, BaCl, 2H,O (3 g) strontium nitrate, Sr(NO<sub>3</sub>)<sub>2</sub> (3 g) sodium chloride, NaCl (2.5 g) copper(II) chloride-2-water, CuCl<sub>2</sub>·2H<sub>2</sub>O (2.5 g) (Hygroscopic, hence must prepare fresh or keep dry) **PREPARATION** . Into each of the 5 dishes weigh out 6 g of potassium chlorate and 2 g of granulated sugar. Grind it gently so as to mix the two substances together Exercise great care. CAUTION Potassium chlorate is a strong oxidising agent. A mixture with a flammable material becomes explosive ! Grind with non-metal implements (wood or plastic). Do not store this mixture! Handle with care! Leave one dish with only potassium chlorate/sugar mixture. To the others add the following ground salts:  $BaCl_{2} \cdot 2H_{2}O(3 g)$  to one dish,  $Sr(NO_{3})_{2}(3 g)$  to another, NaCl (2.5 g) to another and CuCl<sub>2</sub>.2H<sub>2</sub>O (2.5 g) to a fourth dish. Place all the dishes with the mixtures on an insulating mat on the demonstration bench. Keep the dishes well separated.

- Supply the concentrated sulfuric acid in a small reagent bottle.
- Provide pipette, spoon and spatula.

PROCEDURE • • • • • CAUTION

### Perform the demonstration in the fume hood.

- Dim the lecture theatre lights.
- With the spatula make a small depression in the top of each mixture.
- Using the pipette, place one drop of acid into the depression of one of the mixtures.
- Stand well back.
- After each reaction has completely ceased, add sulfuric acid (one drop) to the other dishes sequentially.

#### Ensure that none of the prepared mixtures are standing near the reaction site!

RESULTS After one or two seconds, the reaction begins with the evolution of smoke. Quickly, the mixture will burst into flames.

2ClO<sub>3</sub><sup>-</sup>(aq) + 2H<sup>+</sup>(aq) ζ 3O<sub>2</sub>(g) + 2H<sup>+</sup>(aq) + 2Cl<sup>-</sup>(aq)

 $12O_{2}(g) + C_{12}H_{22}O_{11}(s) \zeta 12CO_{2}(g) + 11H_{2}O(I)$ 

The addition of salts of the alkali and alkali-earth metals will create different coloured flames:

- K: violet
- Na: intense yellow
- Ba: apple green
- Sr: crimson
- Cu: pale green
- DISPOSAL Any residues should be flushed down the sink.



## ALTERNATIVE POTASSIUM CHLORATE AND SUGAR

	A test tube of layers is prepa producing diff	potassium chlorate and sugar with "impurities" in different ared. When ignited, the mixture reacts violently with the layers erent characteristic coloured flames.	
EQUIPMENT	<ul><li>pyrex te</li><li>600 mL</li><li>Pasteur</li></ul>	est tube (150 x 25 mm) beaker containing sand pipette	
REAGENTS	<ul> <li>potassiu</li> <li>sugar (2</li> <li>Barium,</li> <li>copper(</li> <li>strontium</li> <li>sulfuric</li> </ul>	um chlorate, KClO <sub>3</sub> (20 g) 20 g) Ba (3 g) II) chloride, CuCl <sub>2</sub> (2.5 g) m nitrate, Sr(NO <sub>3</sub> ) <sub>2</sub> (3 g) acid, H <sub>2</sub> SO <sub>4</sub> (18 M)	
PREPARATION	<ul> <li>Weigh c evapora</li> <li>In a sep</li> <li>Add the copper c</li> <li>Carefull instructi</li> <li>Exercise</li> </ul>	but the potassium chlorate in the quantities below into an atting dish and grind it gently. barate container, grind 20 g of granulated sugar. appropriate amounts of ground sugar and "impurity" (Barium, (II) chloride or strontium nitrate) to the potassium chlorate. y mix the substances together and place in test tube (see ons below). e great care.	
CAUTION	Potassium cl flammable m metal implem • Fill the Zone Top 2nd 3rd Bottom • Immerse • Dim the	hlorate is a strong oxidising agent. A mixture with a laterial can become an explosive one! Grind with non- nents (wood or plastic). test tube as below: <u>Mixture composition</u> 6 g KCIO <sub>3</sub> and 6 g sugar 2.5 g powdered Copper, 5 g sugar and5 g KCIO <sub>3</sub> 3 g strontium nitrate, 5 g sugar and 5 g KCIO <sub>3</sub> 3 g of Barium Chloride, 5 g sugar and 5 g KCIO <sub>3</sub> e the test tube in a 600 mL beaker containing sand. lights.	
PROCEDURE	<ul> <li>Dim the</li> <li>Place the concent</li> <li>Stand b</li> </ul>	the lights in the lecture theatre. ce the test tube assembly in the fume hood and add 1–2 drops of centrated $H_2SO_4$ , into the test tube nd back.	
RESULTS	Brilliant exoth chemical com	illiant exothermic reaction, sparks and flame, with the zones of differing emical composition producing a variety of colours.	
	Zone Top 2nd 3rd	Nature of the flame white sparks many yellow sparks blue/green	
Bottom red

It may be necessary to adjust the amounts of powdered iron and strontium nitrate used to get the most colourful flames.

**Chapter 8: Inorganic Reactions** 

## **DEMONSTRATION 8.16**

### THE REACTIONS OF CHLORINE WITH METALS

Chlorine gas reacts with the following metals: iron (steel wool), antimony and magnesium to form their chloride salts.

- EQUIPMENT 3 gas jars
  - tongs
  - bunsen burner
- **REAGENTS** chlorine gas, Cl<sub>2</sub>
  - steel wool
  - antimony powder, Sb
  - magnesium ribbon, Mg
- **PREPARATION** Fill three wide mouth containers with chlorine gas.
- **PROCEDURE** Ignite some steel wool in a flame and plunge into the chlorine gas.
  - Sprinkle some antimony powder into the chlorine gas.
    - Ignite some magnesium ribbon and plunge it into chlorine.
- **RESULTS** The steel wool burns in the chlorine forming dense brown fumes of iron(III) chloride, FeCl<sub>3</sub>, which condense on the container as reddish-black flaky crystals. The antimony powder gives bright scintillations and sparks as it reacts to form white antimony chloride, SbCl<sub>3</sub>. The magnesium ribbon continues to burn brightly in the chlorine forming white magnesium chloride, MgCl<sub>2</sub>.

### THE OXIDATION STATES OF VANADIUM

This demonstration illustrates the colour changes associated with the change in the oxidation state of vanadium from (V) to (II).

#### EQUIPMENT

- 1 L separating funnel and stopper four small beakers
- hot plate
- stirring rod
- 1 L conical flask and stopper
- 500 mL beaker
- light box
- 500 mL conical flask and stopper
- sealed jar

#### REAGENTS

- zinc wire or pellets (20-30 mesh, 50 g) mercury(II) chloride, HgCl<sub>2</sub> (1 g)
- nitric acid, HNO<sub>3</sub> (15 M, 1 mL)
- sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (2 M, 250 mL)
- distilled water
- sodium hydroxide, NaOH (3-4 g)
- ammonium vanadate, NH<sub>4</sub>VO<sub>3</sub> (5 g)

PREPARATION

### Prepare the zinc amalgam as follows:

- Place1 g of mercury(II) chloride in 150 mL of water.
- Add 1 mL of the concentrated nitric acid.
- Add 50 g of zinc wire.
- Stopper the flask and shake it for a few minutes.
- Pour off the liquid and wash the amalgam thoroughly with water.
- Store the amalgam under water in a sealed jar.

Prepare the vanadium solution as follows:

- Carefully dissolve the 3-4 g of NaOH in 100 mL of water.
- Add 5 g of ammonium vanadate (the beaker may be warmed to dissolve the solid completely), stir constantly.
- Add 250 mL of the 2 M sulfuric acid and dilute to 500 mL.
- Store in a well stoppered flask.

#### PROCEDURE

- Place 50 g of zinc amalgam in the 1 L separating funnel.
- Add 100 mL of vanadium solution and stopper the flask.
  - Pour a sample of the solution into a small beaker.
  - Gently swirl the flask and save a sample.
- Shake the flask and save a sample.
- Shake the flask more vigorously and save a sample.
- Note the different colours of all the samples.
- **RESULTS** The separating funnel initially contains a yellow solution. After gentle swirling the solution turns green. More shaking turns the solution blue. More vigorous shaking produces a violet colour. The following set of reactions explains the colour changes in terms of the oxidation states of vanadium:



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 $\begin{array}{ll} Zn(s) + 2VO_{3}^{-}(aq) + 8H^{*}(aq) \ \zeta \ 2VO^{2*}(aq) + Zn^{2*}(aq) + 4H_{2}O(I) \\ & \mbox{yellow} & \mbox{green} \\ & \mbox{(oxidation state of V)} & \mbox{(oxidation state of IV)} \\ & \mbox{Zn}(s) + 2VO^{2*}(aq) + 4H^{*} \ \zeta \ 2V^{3*}(aq) + Zn^{2*}(aq) + 2H_{2}O(I) \\ & \mbox{green} & \mbox{blue} \\ & \mbox{(oxidation state of IV)} & \mbox{(oxidation state of III)} \end{array}$ 

Zn(s) + 2V<sup>3+</sup>(aq) ζ 2V<sup>2+</sup>(aq) + Zn<sup>2+</sup>(aq) blue violet

(oxidation state of III) (oxidation state of II)

### CHROMATE/DICHROMATE EQUILIBRIUM

This demonstration illustrates the effect of acid and base on the equilibrium between chromate and dichromate ions.

### **EQUIPMENT** • 4 x 1 L flasks with corks (labelled 1 to 4)

REAGENTS

- potassium chromate, K<sub>2</sub>CrO<sub>4</sub> (4 g)
- potassium dichromate,  $K_2 Cr_2 O_7$  (6 g)
- hydrochloric acid, HCI (3 M, 500 mL)
   acidium bydrovida, NaOH (3 M, 500 mL)
  - sodium hydroxide, NaOH (3 M, 500 mL)

**PREPARATION** •

- Dissolve 4 g of  $K_2CrO_4$  in 1 L of water.
- Dissolve 6 g of  $K_2 Cr_2 O_7$  in 1 L of water.
- In the flasks labelled 1 and 2 place half of the  $K_2CrO_4$  solution, and in flasks 3 and 4 place half of the  $K_2Cr_2O_7$  solution.
- To flasks 1 and 3 add 250 mL of HCI (3 M) and to flasks 2 and 4 add 250 mL of NaOH (3 M) solution.
- **RESULTS** The equilibrium between chromate and dichromate ions is:

 $2CrO_{4}^{2-}(aq) + 2H^{+}(aq) \Gamma Cr_{2}O_{7}^{2-}(aq) + H_{2}O(I)$ 

Addition of acid shifts the equilibrium to the right causing the orange dimeric dichromate ion to dominate. The addition of hydroxide removes protons from the equilibrium causing a shift to the left and the yellow chromate ion dominates.

CAUTION

Chromium(VI) is carcinogenic.



### THE OXIDATION STATES OF MANGANESE

A solution of potassium permanganate is sequentially reduced from oxidation state VII through to VI, then from VI to IV, and finally from IV to oxidation state II.

EQUIPMENT	<ul> <li>1 L conical flask with stopper</li> <li>3 x 10 mL measuring cylinders</li> <li>1 x 50 mL measuring cylinder</li> <li>4 reagent bottles</li> <li>light box</li> </ul>
REAGENTS	<ul> <li>potassium permanganate, KMnO<sub>4</sub> (a few crystals)</li> <li>sodium hydroxide, NaOH (1 M, 10 mL)</li> <li>sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (5 M, 10 mL) + (2 M, 50 mL)</li> <li>iron(II) sulfate-7-water, FeSO<sub>4</sub> 7H<sub>2</sub>O (13.9 g)</li> <li>cyclohexene, C<sub>6</sub>H<sub>10</sub> (10 mL)</li> <li>deionised water</li> </ul>
PREPARATION	<ul> <li>Prepare 50 mL aqueous 1 M iron(II) sulfate in 2 M sulfuric acid by dissolving 13.9 g FeSO<sub>4</sub>7H<sub>2</sub>O in 50 mL 2 M sulfuric acid.</li> <li>Provide the reagents in stoppered, labelled reagent bottles and place them alongside the appropriate measuring cylinders.</li> <li>Fill the flask with 400 mL of water and place it on the light box.</li> <li>Switch on the light and add sufficient crystals of permanganate to produce a solution that is strongly coloured.</li> </ul>
PROCEDURE	<ul> <li>Add the reagents to the flask in the following sequence:</li> <li>10 mL of sodium hydroxide solution.</li> <li>10 mL of cyclohexene. This will form a layer over the surface of the permanganate solution. Swirl the flask for 1 minute.</li> </ul>
	<ul> <li>Cyclohexene is a recognised carcinogen. Provide adequate ventilation during demonstration and disposal. The flask should be stoppered as soon as the demonstration is completed until safe disposal can be effected.</li> <li>Add 5 to 10 mL of the sulfuric-acid solution.</li> <li>Add 25 to 30 mL of the iron(II) sulfate solution. Swirl the flask.</li> </ul>

#### **Chapter 9: Transition Metals**

**RESULTS** The reactions are, sequentially:

**Reduction** of permanganate (Mn(VII)) to manganate (Mn(VI))  $2MnO_4^{-}(aq) + C_6H_{10}(I) + 2OH^{-}(aq) \zeta 2MnO_4^{2-}(aq) + C_6H_{10}(OH)_2(aq)$ purple green **Disproportionation** (Mn(VI) to Mn(VII) and Mn(IV)).  $3MnO_4^{2-}(aq) + 4H^{+}(aq) \zeta 2MnO_4^{-}(aq) + MnO_2(s) + 2H_2O(I)$ purple brown

The starting material is now in acidic conditions.

Reduction of permanganate to manganese dioxide (Mn(VII) to Mn(IV)) is now possible.

 $2MnO_{4}^{-}(aq) + 2H^{+}(aq) + 3C_{6}^{}H_{10}(I) + 2H_{2}O(I) \zeta 2MnO_{2}(s) + 3C_{6}^{}H_{10}(OH)_{2}(aq)$ brown

Reduction of manganese dioxide to manganese ions (Mn(IV) to Mn(II)).

 ${\rm MnO}_{_{2}}(s) + 4{\rm H}^{\scriptscriptstyle +}(aq) + 2{\rm F}e^{_{2^{\scriptscriptstyle +}}}(aq)\,\zeta\,\,{\rm Mn}^{_{2^{\scriptscriptstyle +}}}(aq) + 2{\rm F}e^{_{3^{\scriptscriptstyle +}}}(aq) + 2{\rm H}_{_{2}}{\rm O}({\rm I})$ 

colourless/pale pink

**Chapter 9: Transition Metals** 

## **DEMONSTRATION 9.4**

### **IRON COMPLEXES**

This demonstration illustrates the relative stabilities of iron(III) complexes with water, chloride, thiocyanate and fluoride ligands. EQUIPMENT 1 L conical flask 2 x 50 mL measuring cylinders, stoppered 2 x 500 mL measuring cylinders, stoppered light box iron(III) nitrate-9-water, Fe(NO<sub>3</sub>)<sub>3</sub>9H<sub>2</sub>O (12.12 g) REAGENTS hydrochloric acid, HCI (10 M, 30 mL) potassium thiocyanate, KSCN (1.46 g) saturated sodium fluoride, NaF (12.3 g) distilled water **PREPARATION** . Prepare 300 mL saturated sodium fluoride solution by dissolving 12.3 g NaF in 300 mL water. Prepare 300 mL of 0.01 M iron(III) nitrate by dissolving 12.12 g Fe(NO<sub>3</sub>)<sub>3</sub>9H<sub>2</sub>O in 300 mL water. Prepare 30 mL of 0.05 M potassium thiocyanate by dissolving 1.46 g KSCN in 30 mL water. Place 300 mL of the iron(III) nitrate solution into one of the measuring cylinders. Place 30 mL of the potassium thiocyanate solution into a small cylinder. Measure out 300 mL of saturated sodium fluoride solution and 30 mL of 10 M hydrochloric acid. Label the cylinders clearly. Set up the light box. Place the empty flask on it and line up the solutions. PROCEDURE Transfer 300 mL of the pale-yellow iron(III) nitrate solution to the flask. Add 30 mL hydrochloric acid. Add 30 mL thiocyanate solution. Add 500 mL fluoride solution. RESULTS The reactions that occur are:  $[Fe(H_2O)_{a}]^{3+}(aq) + 6HCI(aq) \Phi [FeCI_{a}]^{3-}(aq) + 6H_3O^{+}(aq)$ pale yellow intense yellow  $[FeCl_{a}]^{3-}(aq) + 6SCN^{-}(aq) \Phi [Fe(SCN)_{a}]^{3-}(aq) + 6Cl^{-}(aq)$ deep red  $[Fe(SCN)_{a}]^{3-}(aq) + 6F^{-}(aq) \Phi [FeF_{a}]^{3-}(aq) + 6SCN^{-}(aq)$ 

colourless

### THE COLOUR OF TRANSITION METAL COMPLEXES

The colour of iron complexes depends on the oxidation state of the iron and the ligands in the complex.

#### EQUIPMENT

- spray bottleabsorbent paper
- paint brush

REAGENTS

- iron(III) chloride,  $FeCl_3$  (10 g)
- hydrochloric acid, HCl (3 M, 200 mL)
- potassium thiocyanate, KSCN (saturated)
- potassium hexacyanoferrate(II), K<sub>4</sub>Fe(CN)<sub>6</sub> (10%)

PROCEDURE

•

- Paint a message such as "transition metal complexes are coloured" on blotting paper using potassium thiocyanate.
- Paint a separate message using 10% potassium hexacyanoferrate(II).
- Allow to dry (or use a hair-drier).
- Show the colours by spraying with FeCl<sub>3</sub> (10 g) in dilute HCl (3 M, 200 mL).

**RESULTS** The saturated potassium thiocyanate produces a red colour.

The 10% potassium hexacyanoferrate(II) produces a blue colour.

The addition of iron(III) ions to thiocyanate ions results in the formation of a red coloured iron(III) thiocyanate complex:

 $[Fe(OH_2)_6]^{3+}(aq) + SCN^{-}(aq) \Phi [Fe(OH_2)_5SCN]^{2+}(aq) + H_2O(I)$ 

The addition of iron(III) ions to potassium hexacyanoferrate(II) results in the formation of an intensely blue coloured precipitate commonly known as Prussian blue:

 $4[Fe(OH_2)_6]^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \Phi Fe_4[Fe(CN)_6]_3(s) + 24H_2O(I)$ 

### **TEMPERATURE CHANGES AND COBALT COMPLEXES**

The effect of temperature on equilibrium can be demonstrated using cobalt complexes.

EQUIPMENT	<ul> <li>250 mL beaker</li> <li>3 x 50 mL beakers</li> <li>large beaker filled with ice</li> <li>hot plate</li> <li>scales</li> <li>spatula</li> </ul>
REAGENTS	<ul> <li>cobalt(II) chloride-6-water, CoCl<sub>2</sub>·6H<sub>2</sub>O (0.4 M)</li> <li>hydrochloric acid, HCl (10 M)</li> </ul>
CAUTION	Cobalt(II) chloride is toxic.
PREPARATION	<ul> <li>Dissolve 5.2 g of cobalt(II) chloride-6-water in 100 mL of distilled water.</li> <li>Place the solution in the 250 mL beaker.</li> </ul>
PROCEDURE	<ul> <li>Add hydrochloric acid to the CoCl<sub>2</sub> solution until the solution changes from pink to blue-purple. Excess hydrochloric acid (10 M) is required to get the formation of the blue complex.</li> <li>Divide the solution evenly amongst the three smaller beakers and treat them as follows:</li> <li>Place one beaker on a hot plate.</li> <li>Place one beaker in an ice bath.</li> <li>Leave one beaker at room temperature as a standard.</li> <li>After a few minutes, show that the heated sample has turned a darke blue and the cooled sample has turned a light pink.</li> </ul>
RESULTS	This reaction involves the following equilibrium:
	$[C_0(H O)]C_1(a_0) \xrightarrow{cooling} [C_0C_1(H O)](a_0) + 4H O(1)$

 $[CoCl_{2}(H_{2}O)_{2}](aq) + 4H_{2}O(l)$ pink blue

Addition of heat causes shift of equilibrium toward the products, a blue solution. Cooling causes a shift to the left, a pink solution.

For an interesting variation, heat 150 mL of CoCl<sub>2</sub> solution until it turns blue. Fill a large test tube with this solution and immerse it halfway into a beaker that contains crushed ice and salt. The bottom half of the test tube will turn pink.

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## NICKEL COMPLEXES

Solutions of nickel(II) chloride and 1,2-ethanediamine are prepared and added to one another in three different ratios. These additions result in three solutions with different colours.

#### EQUIPMENT

- 6 x 500 mL measuring cylinders of identical make
- 3 x 1 L conical flasks
- 3 stirring rods
- light box
- REAGENTS
- 1,2-ethanediamine,  $(NH_2CH_2CH_2NH_2 = en)$
- nickel(II) chloride-6-water, NiCl<sub>2</sub>·6H<sub>2</sub>O (120 g)

- Prepare a solution of 1,2-ethanediamine (30.05 g in 1 L)
- Prepare a solution of nickel(II) chloride solution by dissolving NiCl<sub>2</sub>·6H<sub>2</sub>O (120 g) in distilled water (1 L).
- Arrange the measuring cylinders in pairs and add the solutions as outlined below :

	diamine	nickel	ratio	
1.	170 mL	500 mL	1:3	
2.	330 mL	330 mL	1:1	
3.	500 mL	170 mL	3:1	

- With identical cylinders, the ratio of the volumes will become obvious.
- Place them in pairs on the light box and put one empty flask and one stirring rod with each pair.
- Variations in the purity of the 1,2-ethanediamine as well as in temperature may require some adjustments to the concentrations.
- **PROCEDURE** Combine the contents of each pair in the associated conical flask and Stir.

RESULTS	colour	composition	ratio		
	Flask 1	blue-green	[Ni(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup> & [Ni(en)(OH <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup>	1:3	
	Flask 2	light blue	mainly [Ni(en) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	1:1	
	Flask 3	purple	mainly $[Ni(en)_3]^{2+}$	3:1	
	-		ě		-

The general equation for these reactions is:

 $[Ni(OH_2)_6]^{2+}(aq) + x(en)(aq) \Phi [Ni(OH_2)_{6-2x}(en)_x]^{2+}(aq)$ 

### **COPPER COMPLEXES**

A variety of coloured solids and solutions can be generated by reactions of the copper(II) aqueous ion.

- **EQUIPMENT** 8 large test tubes
  - perspex test-tube rack
  - 500 mL beaker
  - 3 pasteur pipettes

REAGENTS

- **S**i
- copper(II) chloride-2-water,  $CuCl_2 \cdot 2H_2O$  (20 g)
- hydrochloric acid, HCI (3 M, 20 mL)
- ammonia,  $NH_3$  (15 M, 20 mL)
- acetic acid, CH<sub>3</sub>COOH (17 M, 10 mL)
- potassium hexacyanoferrate(II) solution, K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1 mL)
- sodium dithionite, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (2 g)
- **PREPARATION** Prepare a copper(II) stock solution by adding 20 g of copper chloride-2-water to 80 mL of 3 M hydrochloric acid in the 500 mL beaker.

PROCEDURE



- Pour some of the copper(II) stock solution into two test tubes and keep one for comparison.
- To the other test tube, add a few drops of potassium hexacyanoferrate(II) solution.
- Dilute the remaining stock solution to 200 mL with distilled water.
- Put a test tube of this solution aside for comparison.
- Pour some of the diluted stock solution into another test tube.
- Add ammonia, a few mL at a time, until a light blue precipitate is formed.
- Put a test tube of this solution aside for comparison.
- Continue to add ammonia to the remaining test tube until a deep blue solution forms.
- Put a test tube of this solution aside for comparison.
- Slowly add acetic acid to the remaining test tube of tetraammine complex until a change occurs.
- Put a test tube of this solution aside for comparison.
- To the solution remaining from the acetic acid step, add the sodium dithionite, and stir. This solution may be heated to speed up the reaction.

**RESULTS** The copper(II) chloride complex is yellow and the copper(II) water complex is blue. When both the water and chloride are complexed, as in the first step, the solution will appear green.

The hexacyanoferrate(II) ion then reacts with the copper ion to produce the deep rose copper(II) hexacyanoferrate(II) precipitate.

 $2Cu^{2+}(aq) + [Fe(CN)_{e}]^{4-}(aq) \zeta Cu_{2}[Fe(CN)_{e}](s)$ 

deep rose

When ammonia is added, the copper(II) aqueous ions react to produce a blue precipitate of copper(II) hydroxide.

 $Cu^{2+}(aq) + 2NH_{3}(aq) + 2H_{2}O(I) \zeta Cu(OH)_{2}(s) + 2NH_{4}^{+}(aq)$ 

light blue

When excess ammonia is added, the copper hydroxide reacts to form the deep blue tetraammine copper(II) complex.

 $Cu(OH)_{2}(s) + 4NH_{3}(aq) \zeta [Cu(NH_{3})_{4}]^{2+}(aq) + 2OH^{-}(aq)$ 

dark blue

Acetic acid added to the tetraammine complex will cause it to revert to the hydrated form.

 $[Cu(NH_{3})_{4}]^{2+}(aq) + 4H^{+}(aq) \zeta Cu^{2+}(aq) + 4NH_{4}^{+}(aq)$ 

green

Finally, addition of dithionite to the hydrated copper(II) ion reduces it to metallic copper.

 $S_2O_4^{2-}(aq) + 2H_2O(I) \zeta 2SO_3^{2-}(aq) + 4H^+(aq) + 2e^-$ 

Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> ζ Cu(s)

 $Cu^{2+}(aq) + S_2O_4^{2-}(aq) + 2H_2O(I) \zeta Cu(s) + 2SO_3^{2-}(aq) + 4H^{+}(aq)$ 

### PARAMAGNETISM OF TRANSITION METAL COMPLEXES

The relationship between paramagnetism of a salt and its number of unpaired electrons is demonstrated using a Guoy balance.

#### EQUIPMENT

Guoy balance (available from Inorganic Chemistry Room 440)Guoy tube



- **REAGENTS** potassium chromium(III) sulfate-12-water, KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (3 unpaired electrons)
  - manganese(II) sulfate-4-water, MnSO<sub>4</sub>·4H<sub>2</sub>O (5 unpaired electrons)
  - ammonium iron(III) sulfate=6=water,  $NH_4Fe(SO_4)_2 \cdot 6H_2O$ (5 unpaired electrons)
  - mercury(II) tetra-N-thiocyanatocobaltate(II), HgCo(NCS)<sub>4</sub>
     (3 unpaired electrons)
  - ammonium nickel(II) sulfate–6–water, (NH<sub>4</sub>)<sub>2</sub>Ni(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O
     (2 unpaired electrons)
  - copper(II) sulfate=5-water, CuSO<sub>4</sub>·5H<sub>2</sub>O
  - (1 unpaired electron)
     sodium chloride, NaCl
    - (diamagnetic)

### **PROCEDURE** • Place a sample of the salt in the Guoy tube (two-thirds full).

- Place the tube into the apparatus (between the poles of the magnet).
- **RESULTS** The transition metal compounds are attracted to the magnet. Sodium chloride (diamagnetic) is repelled.

### COMPLEXES THAT CHANGE COLOUR WHEN HEATED

Transition metal complexes that have different colours at high and low temperatures.

- **EQUIPMENT** beakers
  - bunsen burner
  - ice bath

#### **REAGENTS** • copper(II) sulfate solution, CuSO<sub>4</sub> (0.1 M, 100 mL)

- sodium chloride, NaCl.
  - cobalt(II) chloride solution, CoCl<sub>2</sub> (0.5 M, 20 mL)
  - sodium chloride solution, NaCl (saturated 16 mL)
  - chromium(III) nitrate, Cr(NO<sub>3</sub>)<sub>3</sub>
  - dilute nitric acid, HNO<sub>3</sub>

#### PROCEDURE Part A (Cu<sup>2+</sup>)

- Add excess NaCl to copper(II) sulfate solution.
- Heat the solution to 95°C.
- Let the solution cool to room temperature.
- Observe any colour changes.

#### Part B (Co<sup>2+</sup>)

- Mix 20 mL of the 0.5 M CoCl<sub>2</sub> solution with 16 mL of saturated NaCl solution.
- Chill the mixture.
- Heat the mixture to 95°C.
- Alternate heating and cooling is possible.
- Observe any colour changes.

#### Part C (Cr<sup>3+</sup>)

- Prepare a solution of  $[Cr(OH_2)_6]^{3+}(aq)$  by dissolving  $Cr(NO_3)_3$  in dilute  $HNO_3$  until a purple colour is obtained.
- Add excess NaCl.
- Heat to boiling and then allow to cool to room temperature.
- Observe any colour changes.

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**RESULTS** In part A the blue solution turned green when heated and returned to its original colour when cooled. In the solution there is an equilibrium between the six coordinate aqua copper(II) complex and a variety of four coordinate chloro copper (II) complexes.

$$[Cu(OH_2)_6]^{2+}(aq) \Phi [CuCl_4]^{2-}(aq)$$

blue green

In part B the chilled solution is pink and the heated solution is blue. The heating and cooling processes are reversible. In the solution there is an equilibrium between the six coordinate aqua cobalt(II) complex and a variety of four coordinate chloro cobalt (II) complexes.

$$[Co(OH_2)_6]^{2+}(aq) \Phi [CoCl_4]^{2-}(aq)$$

pink blue

In part C the addition of the excess NaCl produces no observable colour change. Boiling the solution gives a green colour due to  $[CrCl_2(OH_2)_4]^+(aq)$ . The green remains as the solution is cooled to room temperature indicating that it is stable.

 $[Cr(OH_2)_6]^{3+}(aq) \Phi [CrCl_2(OH_2)_4]^{+}(aq)$ 

purple green

### AMPHOTERIC PROPERTIES OF HYDROXIDES

Chromium, lead and zinc hydroxides dissolve in both acid and base.

- EQUIPMENT 6 petri dishes
- REAGENTS chromium
  - chromium(III) sulfate, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (0.16 g) or chromium potassium sulfate, CrK(SO<sub>4</sub>)<sub>2</sub> (0.28 g)
  - zinc nitrate,  $Zn(NO_3)_2$  (0.95 g)
    - lead(II) nitrate,  $Pb(NO_3)_2$  (1.66 g)
    - sodium hydroxide, NaOH (1 M)
    - nitric acid, HNO<sub>3</sub> (1 M, 15 mL)

**PREPARATION** • Dissolve chromium(III) sulfate (0.16 g) or chromium potassium sulfate (0.28 g) in water (50 mL).

- Dissolve zinc nitrate (0.95 g) in water (50 mL).
- Dissolve lead nitrate (1.66 g) in water (50 mL).
- Place the petri dishes on top of the overhead projector. Into two pour chromium(III) solution (25 mL); into another two zinc solution (25 mL), and into the last two lead(II) solution (25 mL).
- **PROCEDURE** To the chromium(III) samples, add sodium hydroxide (1 mL) and swirl.
  - To the zinc and lead(II) samples, add sodium hydroxide (5 mL) and swirl.
  - To one of the chromium(III) samples, add additional sodium hydroxide (2 mL) and to the other, nitric acid (2 mL) and swirl.
  - To one of each of the zinc and lead(II) samples, add additional sodium hydroxide (5 mL) and to the other, nitric acid (8 mL) and mix.
- **RESULTS** Initially a green precipitate forms:

 $Cr^{3+}(aq) + 3OH^{-}(aq) \zeta Cr(OH)_{3}(s)$ 

Upon the addition of excess sodium hydroxide or acid the precipitate dissolves:

 $Cr(OH)_{3}(s) + 3OH^{-}(aq) \zeta [Cr(OH)_{6}]^{3-}(aq)$ 

 $Cr(OH)_{3}(s) + 3H^{+}(aq) + 6H_{2}O(I) \zeta [Cr(OH_{2})_{a}]^{3+}(aq) + 3H_{2}O(I)$ 

A white precipitate forms:

 $Zn^{2+}(aq) + 2OH^{-}(aq) \zeta Zn(OH)_{2}(s)$ 

Upon the addition of excess sodium hydroxide or acid the precipitate dissolved:

 $Zn(OH)_{2}(s) + 2OH^{-}(aq) \zeta [Zn(OH)_{4}]^{2-}(aq)$ 

 $Zn(OH)_{2}(s) + 2H^{+}(aq) + 2H_{2}O(I) \zeta [Zn(H_{2}O)_{4}]^{2+}(aq)$ 

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A white precipitate forms:

 $Pb^{2+}(aq) + 2OH^{-}(aq) \zeta Pb(OH)_{2}(s)$ 

Upon the addition of excess sodium hydroxide or acid the precipitate dissolves:

 $Pb(OH)_2(s) + 2OH^{-}(aq) \zeta [Pb(OH)_4]^{2-}(aq)$ 

 $Pb(OH)_{2}(s) + 2H^{+}(aq) + 4H_{2}O(I) \zeta [Pb(OH_{2})_{6}]^{2+}(aq)$ 

# **DEMONSTRATION 9.12**

## **MERCURY (II) COMPLEXES**

	Bright orange mercury(II) iodide is precipitated upon the mixing of mercury(II) chloride and potassium iodide. Addition of further potassium iodide removes the colour.
EQUIPMENT	<ul> <li>3 measuring cylinders: 2 x 250 mL, 1 x 1000 mL</li> <li>1 x 2 L beaker</li> <li>stirring rod</li> <li>light box</li> </ul>
REAGENTS	<ul> <li>mercury(II) chloride, HgCl<sub>2</sub> (0.1 M, 250 mL)</li> <li>potassium iodide, KI (0.1 M, 1000 mL)</li> <li>distilled water</li> </ul>
CAUTION	Mercury (II) chloride is highly toxic and corrosive. Handle with care!
PREPARATION	<ul> <li>Dissolve mercury(II) chloride (6.79 g) in water (250 mL).</li> <li>Dissolve potassium iodide (16.6 g) in water (1000 mL).</li> <li>Place beaker, measuring cylinder, stirring rod and the two solutions in labelled reagent bottles on the light box.</li> </ul>
PROCEDURE	<ul> <li>Place 250 mL of each solution in the beaker and stir.</li> <li>Add additional potassium iodide solution (750 mL).</li> </ul>
RESULTS	A bright orange precipitate will result from the mixing of equal amounts of the two solutions.
	$Hg^{2+}(aq) + 2I^{-}(aq) \Phi HgI_{2}(s)$
	With further addition of iodide, the solution will become clear again.
	$Hgl_2(s) + I^-(aq) \Phi [Hgl_3]^-(aq)$
	$[Hgl_3]^-(aq) + I^-(aq) \Phi [Hgl_4]^{2-}(aq)$

### AN ADDITION REACTION

This demonstration illustrates the addition of bromine to the double bond in cyclohexene, but not to cyclohexane or benzene.

#### EQUIPMENT

- perspex test tube rack
  3 x 25 cm test tubes
- 10 mL measuring cylinder
- light box

REAGENTS



- cyclohexene (25 mL)
  - cyclohexane (25 mL)
- benzene (25 mL)
  - bromine in DCM (2%, 30 mL)
- **PREPARATION** Pour 25 mL of each of the first three of the above reagents into separate labelled test tubes.
  - Provide the bromine solution in a stoppered reagent bottle.
  - Set up light box with the test tubes in their rack.
  - Provide measuring cylinder.

**PROCEDURE** Add bromine solution (10 mL) to each test tube.

**RESULTS** An addition reaction occurs when bromine is added to cyclohexene, as indicated by the loss of colour of the bromine solution. There is no colour loss with benzene or cyclohexane.



### **OXIDATION OF ALCOHOLS**

Four alcohols, when mixed with potassium dichromate are oxidised to different extents.

EQUIPMENT	•	perspex test tube rack
		3 test tubes 25 cm lon

- 3 test tubes, 25 cm long
- measuring cylinder, (10 mL)
- 250 mL conical flask
- light box
- thermometer, (0-100°C)
- water bath
- bunsen burner

REAGENTS

- ethanol,  $CH_{3}CH_{2}OH$  (25 mL)
- n-butanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (25 mL)
- 2-butanol, CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub> (25 mL)
- tert-butanol,  $(CH_3)_3COH$  (25 mL)
- potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.2 M, 100 mL)
- sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (18 M, 10 mL)

PREPARATION

- Provide 100mL of 0.2M potassium dichromate solution in a 250mL conical flask.
- Provide 10mL of 18M sulphuric acid in a stoppered 10mL measuring cylinder
- Place 25 mL of each alcohol into a separate, labelled test tube.
- Set up the light box with test tubes and rack .
- **PROCEDURE** Using the conical flask, acidify 100 mL of the potassium dichromate solution with 10 mL of the concentrated acid.
  - This process will heat up the solution..
  - Add 10 mL of the potassium dichromate solution to each test tube.
- **RESULTS** Ethanol is oxidised: The colour changes to olive green.

3CH<sub>3</sub>CH<sub>2</sub>OH + 2Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 16H<sup>+</sup> ζ 3CH<sub>3</sub>COOH + 4Cr<sup>3+</sup> + 11H<sub>2</sub>O

n-butanol is oxidised: After some 20 seconds the colour changes to greenish brown.

 $3CH_3CH_2CH_2CH_2OH + 2Cr_2O_7^{-2} + 16H^+ \zeta 3CH_3CH_2CH_2COOH + 4Cr^{3+} + 11H_2O$ 

2-butanol is oxidised: After 30 seconds the colour changes to blue-green.

3CH<sub>2</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub> + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 8H<sup>+</sup> ζ 3CH<sub>2</sub>CH<sub>2</sub>C(O)CH<sub>3</sub> + 2Cr<sup>3+</sup> + 7H<sub>2</sub>O

tert-butanol (CH<sub>3</sub>)<sub>3</sub>COH is not oxidised: No colour change takes place.



### AN ALDOL CONDENSATION REACTION

To observe the formation of dibenzalacetone or dicinnamalacetone.

- EQUIPMENT
- 400 mL beaker
- stirring rod
- light box

REAGENTS

- **S**i
- cinnamaldehyde [or benzaldehyde], C<sub>6</sub>H<sub>5</sub>CHCHCHO [or C<sub>6</sub>H<sub>5</sub>CHO] (20 mL)
- ethanol, CH<sub>3</sub>CH<sub>2</sub>OH (125 mL)
- potassium hydroxide, KOH (2 M [4 M], 75 mL)
- acetone, CH<sub>3</sub>COCH<sub>3</sub> (10 mL)
- **PROCEDURE** Dissolve the cinnamaldehyde (or benzaldehyde) in the ethanol in the beaker on the light box.
  - Stir in the potassium hydroxide to achieve a homogeneous solution.
  - Add the acetone.
- **RESULTS** The solution will remain clear for thirty seconds, after which time bright yellow crystals will appear throughout the solution.











benzaldehyde

acetone

dibenzalacetone

Chapter 10: Organic Reactions

## **DEMONSTRATION 10.4**

### THE "PROOF TEST"

The ignition of gun powder with ethanol.

EQUIPMENT	• • •	3 x evaporating basins, 8 cm diameter 3 x 50 mL conical flasks, with stoppers 3 x sample tubes with lids insulating mat taper and matches
REAGENTS	•	gun powder (15 g) absolute ethanol, CH <sub>3</sub> CH <sub>2</sub> OH (300 mL)
PREPARATION	• • •	Using the sample tube, weigh out 5 g of gun powder. Stopper the tube. Set up the basin on the insulating mat. Provide gun powder, taper, matches and safety glasses. Place ethanol in the flask and seal with the stopper.
PROCEDURE	• • •	Put the gun powder into the basin. Use sufficient ethanol to cover the powder completely. Repeat using a mixture of 75% ethanol:water. Repeat using a mixture of 50% ethanol:water.
	Rem Warr	ove any flammable substance within a 3 metre radius. I the audience to avoid looking directly at the basin.
	•	Light the taper and standing well back ignite the alcohol at arm's length.

**RESULTS** In tests 1 and 2, the ethanol will burn off quietly. Then, suddenly, with a blinding flash and a puff of greenish white smoke, the combustion of the gun powder will take place. In the third test with 50% ethanol:water the gun powder will not ignite.

### POLYMERISATION: THE NYLON ROPE

The synthesis of nylon can be successfully and conveniently performed with reagents contained in a 250 mL beaker.

#### EQUIPMENT

- 2 x 250 mL beakers
- tongs
- rotating rod on stand

REAGENTS



- sebacoyl chloride (1 mL) Hexane (50 mL)
- 1,6-diaminohexane (1.2 g)
- anhydrous sodium carbonate (2 g)
- distilled water

**PREPARATION** .

Perform this demonstration in a fume hood.

- Using one of the beakers, dissolve 1 mL of sebacoyl chloride in 50mL of hexane
- Fill the other beaker with 50mL mL distilled water.
- Add 1.2 g of 1,6-diaminohexane and 2 g of sodium carbonate.
- Mix well.
- Set up the solutions and the special apparatus.
- Provide tongs.
- PROCEDURE Pour the aqueous solution carefully on top of the carbon tetrachloride solution.
  - A nylon membrane will form at the interface of the two solutions. •
  - Using the tongs, take hold of it and pull it up.
- RESULTS The lifting of the membrane will cause it to collapse into a rope. If you draw the rope over the roller and wind it up, new material will continuously form as long as both solutions are present.
- CAUTION Both 1,6-diaminohexane and sebacoyl chloride are irritants to the respiratory system.

### DEHYDRATION OF SUCROSE

Sulfuric acid is added to a beaker containing sugar. After a short period, a reaction occurs in which a black foam is produced.

This demonstration should be performed in a fume hood.

EQUIPMENT	• 200 mL beaker	
REAGENTS	<ul> <li>sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub></li> <li>sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (18 M, 5-10 mL)</li> </ul>	
PROCEDURE	<ul> <li>Fill about one-third of the beaker with sugar (sucrose).</li> <li>Add the sulfuric acid carefully and do NOT stir.</li> <li>Stand at a safe distance.</li> </ul>	
RESULTS	After a short time a violent reaction will occur, in which a "carbon snake" i produced. Care must be taken as sulfur dioxide is in the fumes. Also, handle the snake with gloves as it still contains sulfuric acid.	

 $C_{12}H_{22}O_{11}(s) \zeta 12C(s) + 11H_2O$ 

The sulfuric acid is acting as a dehydrating agent.

### **OPTICAL ACTIVITY: ROTATION OF LIGHT**

Two solutions are observed to rotate plane polarised light in opposite directions, thus indicating that they are optically active.

- **EQUIPMENT** glass cylinders on an extended, flat base, about 50 mL
  - 2 sheets of polarising material: -
    - sandwiched between perspex about 10 x 10 cm
       sandwiched between perspex about 50 x 50 cm
    - small watch glasses to cover the cylinders
  - small labels for the watch glasses
  - tissues

#### **REAGENTS** • R(+)-limonene

- S(-)-limonene
- deionised water
  - and if desired also: L-menthol, D-menthol sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

### **PREPARATION** • Place each of the concentrated limonenes into a separate cylinder.

- Place water into a third one.
- Do not fill the cylinders to more than three-quarters.
- If desired, make up also the following solutions:
   100 g of a menthol in 200 mL of ethanol
  - 100 g of sucrose in 200 mL deionised water
- Place each solution into a separate cylinder.
- Label the watch glasses and cover the solutions with these.
- Place the larger of the perspex/polaroid sandwiches on the over-head projector.
- Set the vessels containing the solutions on a tray alongside the projector.
- Provide the smaller of the perspex/polaroid sandwiches and the tissues.

## CAUTION Avoid spillage onto the overhead projector - There is a risk of a short circuit and corrosion of the perspex surface and polarising material.

- **PROCEDURE** Dim the lecture theatre lights.
  - Place the solutions and the water over the polarising material on the projector.
  - Hold the other polarising material horizontally above the cylinders.
  - Rotate the sheet until the extinction of the light transmitted by the water is at a maximum.
  - From here, slowly continue to rotate the sheet clockwise and anticlockwise.
- **RESULTS** All solutions will prove to be optically active. They will differ from each other by the degree and the direction in which they rotate light. Water is inactive.

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# **DEMONSTRATION 10.8**

## CANNED HEAT: ALCOHOL GELS

Two clear liquids, when mixed together, produce a solid gel which may then be ignited.

EQUIPMENT	<ul> <li>metal can, with a capacity of 500 mL, or 500 mL beaker</li> <li>matches (optional)</li> </ul>
	<ul> <li>ethanol, CH<sub>3</sub>CH<sub>2</sub>OH (95%, 300 mL)</li> <li>calcium acetate-1-water, Ca(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>H<sub>2</sub>O (40 g)</li> </ul>
PREPARATION	<ul> <li>Prepare 100 mL saturated calcium acetate solution by placing 40 g calcium acetate-1-water in a stoppered flask with 100 mL of water.</li> <li>Shake occasionally over a period of a few days.</li> <li>Add more solid if it all dissolves.</li> <li>Decant the saturated solution from the solid that settles in the bottom.</li> </ul>
PROCEDURE	<ul> <li>Pour 300 mL ethanol and 60 mL of the saturated calcium acetate solution simultaneously into the clean, dry beaker or metal can.</li> <li>Do not stir.</li> <li>Wait 10 seconds and invert the beaker.</li> </ul>
RESULTS	A gel will form and remain in place when the container is inverted. It may be ignited if the demonstration is done in the metal can (glass may shatter due to the heat). The flame may be seen in a darkened room.

The gel forms due to the reduction of solubility of calcium acetate when ethanol is added. The calcium acetate precipitates rapidly, forming a network of solid throughout the liquid, which entraps the liquid within it, forming a gel.

## AN UNSATURATION TEST

Bromine water is discoloured in the presence of a common unsaturated (non-aromatic) compound.

#### EQUIPMENT •

- 1 L flask bunsen burner
- tongs
- stopper
- bacon

REAGENTS

• 300 mL of bromine water



- Quickly open a large (e.g. 1 L) flask containing the bromine water and drop in strips of well-done (crispy) bacon.
- Shake the flask.

RESULTS

The colour of bromine disappears.

Bromine adds to the unsaturated aldehyde  $CH_2 = CH - CHO$  (the bacon odour).

 $\mathsf{CH}_{_2} \texttt{=} \mathsf{CH} - \mathsf{CHO} \texttt{+} \mathsf{Br}_{_2}\, \boldsymbol{\zeta}\, \mathsf{CH}_2\mathsf{Br} - \mathsf{CHBr} - \mathsf{CHO}$ 



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## **DEMONSTRATION 10.10**

### PREPARATION OF ACETYLENE

Acetylene is generated, then used to discolour bromine water.

EQUIPMENT	
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Set up the apparatus as in the diagram below

#### REAGENTS

- calcium carbide,  $CaC_2$
- sand
- water

PROCEDURE



- Prepare some acetylene by adding water to calcium carbide in the apparatus shown below.
- Collect several test tubes of gas (after displacing the air from the system).
- Test as follows :
- Burn the gas in the test tube.
- Shake an aqueous solution of bromine.

RESULTS

The gas produced burns with a smoky flame.

Bromine adds to the triple bond of acetylene, decolourising the bromine water.

Note the distinctive odour of acetylene.

 $C_2H_2$  + 2  $Br_2 \zeta C_2H_2Br_4$ 



### THE DEHYDRATION OF FORMIC ACID BY SULFURIC ACID

Concentrated sulfuric acid is added to formic acid to produce carbon monoxide which burns in air with a blue flame.

#### EQUIPMENT •

- 1 x 250 mL Erlenmeyer flask
- 1-holed rubber stopper to fit flask
- glass tubing
- matches
- taper
- **REAGENTS** sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (18 M, 50 mL)
  - formic acid, HCO<sub>2</sub>H (50 mL)

#### Carbon monoxide is a colourless, odourless gas that is very toxic. Carry out this demonstration in a fume hood.

PREPARATION .

CAUTION

- Form a nozzle out of one end of the glass tubing.
- Make a 90° bend about half way along the length of the tubing.
- Insert the glass tubing into the stopper.

PROCEDURE

- Add 50 mL of sulfuric acid to 50 mL of formic acid and insert rubber stopper/glass tubing assembly into the neck of the flask.
- When sufficient gas has been generated, ignite the gas with a lighted taper.

RESULTS

The gas liberated burns in air with a blue flame.

$$HCO_{2}H(I) \longrightarrow CO(g) + H_{2}O(I)$$

The carbon monoxide is produced by the dehydration of formic acid.



## THE "CARBON SNAKE"

Sulfuric acid is added to 4-nitroacetanilide, then stirred and heated. A violent reaction occurs, in which a black foam is produced.

EQUIPMENT	<ul> <li>10 mL measuring cylinder</li> <li>tall 250mL beaker</li> <li>small insulating mat with 5 cm diameter hole</li> <li>large insulating mat</li> <li>retort stand with ring</li> <li>Meker burner and matches</li> <li>20 cm stirring rod</li> <li>portable fume hood</li> </ul>
REAGENTS	<ul> <li>4-nitroacetanilide, O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NH-CO-CH<sub>3</sub> (10 g)</li> <li>sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (18 M, 6 mL)</li> </ul>
PREPARATION	<ul> <li>Set up the portable fume hood so that the flexible duct leads into the fume cupboard.</li> <li>Place the retort stand on the large insulating mat in the fume hood.</li> <li>Place the burner on the foot of the stand.</li> <li>Use the retort ring to support the small mat over the burner.</li> <li>Weigh out fresh 4-nitroacetanilide (10 g).</li> <li>Place it in the tall beaker and set over the hole in the mat.</li> <li>Using the measuring cylinder, provide sulfuric acid (6 mL).</li> <li>Lay out stirring rod and matches.</li> </ul>
PROCEDURE	<ul> <li>Turn on the ventilation of the fume hood and fume cupboard.</li> <li>Light the burner.</li> <li>Add the acid to the acetanilide and stir.</li> <li>It is essential that this mixing be thorough and that all of the 4-nitroacetanilide is wetted by the acid.</li> <li>With agitation and heating the mixture turns dark and syrupy.</li> <li>Within one or two minutes, the mixture will boil and smoke.</li> <li>The stirring rod should be taken well away from the reaction mixture, otherwise the formation of a well-shaped product is jeopardised by the collision of the evolving foam with the rod.</li> </ul>
CAUTION	SULFUR TRIOXIDE! Agitation should cease when smoke evolution becomes distinct.
RESULTS	Amid effervescent hissing and smoke evolution a long, black body of stiff, spongy foam will shoot up from the vessel, reaching a length of about 1 metre. This is the "Carbon Snake"! When the smoke abates, the "snake" will probably stand quietly towering over the vessel. On rare occasions, however, the "snake" will form with such speed and energy that it leaps completely out of the vessel. It is therefore advisable to be "on the ready" to catch it in mid-air if necessary.

This reaction is complex, involving sulfonation, cyclisation and finally dehydration. The mechanism for it is not known.

### PHENOL-FORMALDEHYDE POLYMERISATION

Concentrated hydrochloric acid is added to a mixture of aqueous formaldehyde, glacial acetic acid, and phenol. After approximately one minute the solution turns pink and solidifies into a cake-like material.

EQUIPMENT
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- 250 mL beaker
- 100 mL graduated cylinder

phenol, C<sub>e</sub>H<sub>e</sub>OH (20 g)

- stirring rod
- gloves, plastic or rubber

REAGENTS

- i l
- **PROCEDURE** In a 250 mL beaker, mix 25 mL of aqueous formaldehyde, 55 mL of glacial acetic acid, and 20 g of phenol.

formaldehyde, HCHO (formalin, 37 %) (12 M, 25 mL)

glacial acetic acid, CH<sub>2</sub>COOH (17 M, 55 mL)

hydrochloric acid, HCI (10 M, 55 mL)

- Quickly add 55 mL of concentrated hydrochloric acid while stirring.
- After about a minute, the solution will turn pink and solidify.
- If not stirred, the resulting polymer is friable, but continuous stirring during polymerisation results in a solid mass more resistant to crumbling.

## CAUTION All compounds used in this demonstration should be handled in a fume cupboard. Plastic or rubber gloves should be worn.

Formaldehyde vapours are extremely irritating to mucous membranes. Skin contact can cause dermatitis. Extended exposure to high concentrations of vapour can cause chronic effects such as laryngitis, bronchitis, conjunctivitis, or skin problems. Moreover, mixing of formaldehyde with hydrogen chloride can result in the generation of a potent human carcinogen.

Phenol is toxic and causes burns. It can be absorbed rapidly through the skin. Prolonded inhalation can have chronic effects.

#### Glacial acetic acid and concentrated hydrochloric acid can produce skin burns, eye irritation, and irritation of the respiratory tract.

**DISPOSAL** The product contains acid and probably unreacted formaldehyde or phenol; before handling it should be washed thoroughly with dilute aqueous sodium hydroxide solution and then water. The washed polymer should be discarded in a waste container.

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**DISCUSSION** In general, phenol-formaldehyde resins are condensation polymers consisting of aromatic rings linked by methylene groups. The product linkages occur primarily in the ortho or para position to the phenolic hydroxyls. In addition, ether linkages are found under conditions of excess formaldehyde and neutral pH.



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In this demonstration, prepared with a molar excess of formaldehyde and under acidic conditions, the product resin is formed by reactions that lead mostly to methylene bridges. The reaction sequence can be illustrated as follows:





All possible bridges do not form, because all phenolic rings do not lie in the same plane. These gaps in the resin weaken the polymer. The presence of occluded reaction materials and by-products, such as water, causes further weakening.

## POLYSTYRENE

Clear, liquid styrene is mixed with an initiator, benzoyl peroxide, and the mixture is then heated in a boiling water bath. The styrene slowly polymerises to form a transparent solid.

- **EQUIPMENT** 2 x 800 mL beakers
  - stirring rod
  - 11 cm filter funnel
  - test tube, 16 mm x 150 mm, with stopper
  - hot plate
  - gloves, plastic or rubber



- styrene,  $C_6H_5CH=CH_2$  (20 mL)
- alumina,  $Al_2O_3(3 g)$
- benzoyl peroxide,  $(C_6H_5CO)_2O_2(0.5 \text{ g})$
- **PROCEDURE** To remove the inhibitor from the styrene, place 20 mL of styrene in a small beaker and add 2-3 g of alumina.
  - Stir the mixture well to form a slurry.
  - Filter the mixture through filter paper supported in a small funnel.
  - Place the styrene in a test tube.
  - Add 0.5 g of benzoyl peroxide; stopper and shake the tube well to dissolve the initiator.
  - Remove the stopper and heat the tube in a boiling water bath for 10-20 minutes.
  - The styrene will become viscous with heating.
- CAUTION The demonstation should be performed in a fume cupboard. Plastic or rubber gloves should be worn. Styrene is flammable, and it is irritating to the eyes and mucous membranes. In high concentrations, it can be narcotic.

Benzoyl peroxide (dibenzoyl peroxide) is highly flammable and shock sensitive. It should not be stored in screw-capped bottles, because the friction produced by opening the bottle could cause an explosion.

**DISPOSAL** Although the polymer will ignite in a direct flame, it is otherwise inert and should be discarded in a waste container.

DISCUSSION Free radical polymerisation of styrene can be carried out by bulk, solution, suspension, or emulsion techniques. The reaction equation can be represented as:



The arrangement of styrene in the polymer is considered to be "head-totail". The initiator, benzoyl peroxide, is cleaved by heat into two benzoyl radicals:



Polystyrene is one of the major commercial plastics widely used in appliances, toys, food containers, packaging, etc. It is a good electrical insulator. Many copolymers of styrene with other monomers have been investigated, and some, such as styrene-acrylonitrile copolymers, are commercially important.

## "Slime": Gelation of Poly(vinyl alcohol) with Borax

Two clear, colourless liquids are mixed and almost immediately form a gel. The gel can be formed into a ball, but if left unhandled, it will flatten and run.

EQUIPMENT	<ul> <li>250 mL beaker</li> <li>stirring hot-plate, with stir bar</li> <li>thermometer, -10 °C to +110 °C</li> <li>100 mL disposable plastic cup, or beaker</li> <li>flat-bladed wooden stirrer</li> </ul>
REAGENTS	<ul> <li>distilled water (50 mL)</li> <li>poly(vinyl alcohol), [-CH<sub>2</sub>CH(OH)-]<sub>n</sub> (2.5 g). The polymer should be &gt;99% hydrolysed (average molar mass at least 105 gmol<sup>-1</sup>)</li> <li>aqueous solution of sodium tetraborate, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (4% by weight, 5 mL). (To prepare 100 mL of solution, dissolve 7.6 g of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O [borax] in 100 mL of distilled water.)</li> </ul>
PREPARATION	<ul> <li>Pour 50 mL of distilled water into the 250 mL beaker.</li> <li>Place a stir bar in the beaker, and set the beaker on the stirring hot plate.</li> <li>Warm the water to a temperature not to exceed 90 °C.</li> </ul>
PROCEDURE	<ul> <li>While stirring the warm water, slowly sprinkle 2 g of poly(vinyl alcohol) on the surface of the water. This procedure prevents the formation of a sticky mass of polymer that is difficult to dissolve.</li> <li>Pour the poly(vinyl alcohol) solution and 5 mL of sodium borate solution together into a plastic cup and stir the mixture vigorously with the wooden stirrer.</li> <li>Gel formation begins almost immediately, and a material, "slime".</li> <li>Knead the gel into an elastic ball. Hold the ball in the palm of your hand and tip your hand. The ball will stretch out into a long column. Attempt to stretch the column abruptly; it will break.</li> </ul>
DISPOSAL	The plastic cup and wooden spoon used to prepare the gel should be discarded in a solid-waste container. The gel can be discarded in a solid- waste container, or by mixing with plenty of water and flushing the mixture down the drain with more water.
**DISCUSSION** Poly(vinyl alcohol) is a polymer with a structure composed of repeating vinyl alcohol units:



The average value of n for the poly(vinyl alcohol) used in this demonstration is at least 2300.

Sodium borate hydrolyses in water to form a boric acid-borate ion buffer with a pH around 9.

$$B_4O_7^{2}(aq) + H_2O(I) + H_8O_7^{-}(aq) + OH^{-}(aq)$$

In this demonstration, the borate ions react with the hydroxyl groups of the polymer to form cross links possibly with the elimination of water. These cross links probably involve hydrogen bonds that break and reform under flow. Such relatively weak cross-linking is necessary to produce the viscoelastic gel and the interesting physical properties of "slime". The capability of poly(vinyl alcohol) to engage in extensive hydrogen bonding is suggested by its high solubility in water.

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## **DEMONSTRATION 10.16**

## CHROMATOGRAPHY

Separation and purification are demonstrated using column chromatography.

EQUIPMENT

- glass chromatography column, 2cm diameter
- chromatography silica for gravity column (63-200 mm particle size, 22g)
- measuring cylinder, (100mL)
- 250 conical flask
- three 100mL beakers
- sample vial and pasteur pipette

REAGENTS

- hexane,  $CH_3(CH_2)_4CH_3$  (90mL)
  - dichloromethane, CH<sub>2</sub>Cl<sub>2</sub> (90mL)
  - diethyl ether, CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> (20mL)
- ferrocene, FeCp<sub>2</sub> (20mg)
  - acetylferrocene, Fe(AcCp)Cp (20mg)
- **PREPARATION** Mix the solvents
  - Place a small plug of cotton wool at the bottom of the column and half fill with solvent
  - Pour in the silica and allow to settle
  - Mix the ferrocene and acetylferrocene in a sample vial
  - Just before the lecture, run the solvent so it is ½ cm above the top of the silica
- **PROCEDURE** Dissolve the compound mix in 1mL of dichloromethane and load into the column
  - Carefully add more solvent to the column
  - Elute into beakers
- **RESULTS** The compounds quickly separate, the yellow ferrocene eluting first followed by the red acetylferrocene.

