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ABSTRACT

The publication presents outlines of some of the difficult experiments suggested in the chemistry syllabus for the Certificate of Sixth Year Studies in Scotland. The experiments included in the publication form a small part of the total experiments suggested in the syllabus. Simple experiments, the details of which are available in textbooks, are not included. The outlines of experiments presented are the results of pilot work conducted in selected schools. A total of 34 experiments are described. (PS)

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

Memorandum for the guidance of
teachers planning this
new course

Scottish Education Department

CERTIFICATE OF SIXTH YEAR STUDIES

Notes on Practical Work in Chemistry

The syllabus for the Certificate of Sixth Year Studies in Chemistry which has been issued by the Scottish Certificate of Education Examination Board contains a list of suggested practical work.

Some of the recommended experiments are new, and details of them are difficult to obtain from textbooks which are generally available. Schools which took part in the pilot test of the course have tried out and developed these experiments and it is felt that the results of their work should be made available to schools presenting candidates.

This document gives only bare outlines of the experiments but sufficient material is provided for their successful performance by pupils. It should, perhaps, be pointed out that this booklet does not cover the whole of the practical work for the course. The more familiar experiments for which instructions are readily available have not been included.

Thanks are due to the principal teachers of chemistry in the pilot schools and to members of the staffs of the Chemistry Departments of Edinburgh, Strathclyde and Glasgow Universities who provided the material for this booklet

CERTIFICATE OF SIXTH YEAR STUDIES

Notes on Practical Work in Chemistry

Experiment 1. Hess's Law

A suitable experiment to verify Hess's Law is to determine the heat changes in the following reactions:

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$; $\Delta H = x$ kcal mole^{-1} of Mg

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$; $\Delta H = y$ kcal mole^{-1} of Zn

$Mg + ZnSO_4 \longrightarrow Zn + MgSO_4$; $\Delta H = z$ kcal mole^{-1} of Mg

If Hess's Law is true $y + z$ should be equal to x.

1. Add 1 g of magnesium to 100 ml of 0.5 M sulphuric acid in a thermos flask and note the rise of temperature.
2. Repeat using 1 g of zinc in place of 1 g of magnesium.
3. Add 1 g of magnesium to a solution of about 15 g of $ZnSO_4.7H_2O$ in 100 ml of water and note the temperature rise. This mass of zinc sulphate provides sufficient Zn to be replaced completely by 1 g of Mg.

Some typical results were:

1. 100 ml 0.5 M H_2SO_4 + 1 g Mg. Temperature rise 47C°
   Heat absorbed = 4700 cal/g = 112.8 kcal mole^{-1} of Mg = x
2. 100 ml 0.5 M H_2SO_4 + 1 g Zn Temperature rise 1.5C°
   Heat absorbed = 1500 cal/g = 9.7 kcal mole^{-1} of Zn = y
3. 15 g $ZnSO_4$ $7H_2O$ + 100 ml H_2O + 1 g Mg. Temperature rise 43C°
   Heat absorbed = 4300 cal/g = 103.2 kcal mole^{-1} of Mg = z

   $y + z = 112.9$ kcal mole^{-1}

   $x = 112.8$ kcal mole^{-1}

The heat absorbed by the thermos flask and the thermometer have not been taken into account in the calculation. It is worth discussing whether this introduces an error.

Experiment 2. Hess's Law

Another experiment for verifying Hess's law uses the following reactions:

$NaOH(s) \longrightarrow NaOH(aq)$ $\Delta H = x$

$NaOH(s) + HCl(aq) \longrightarrow NaCl(aq) + H_2O$ $\Delta H = y$

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O$ $\Delta H = z$

If Hess's Law is true $y - x$ should be equal to z.

1. Dissolve 4 g NaOH in 100 ml H_2O in a thermos flask. Find the temperature rise.
2. Dissolve 4 g NaOH in 100 ml M/10 HCl. Find the temperature rise.
3. Dissolve 4 g NaOH in 50 ml H_2O; add 50 ml M/5 HCl. This gives a M/10 solution of NaCl (approximately). Find the temperature rise.

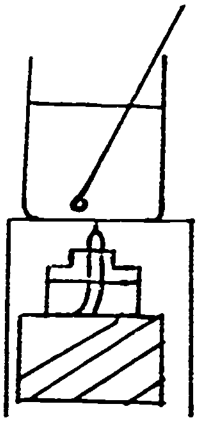
Discuss:

Is it necessary to work out the values of x, y and z in kcal mole^{-1}? Will the temperature changes do instead? Is it necessary to take into account the water formed in reactions 2 and 3?

Experiment 3. "Heats of combustion" in an homologous series.

The heat evolved when given masses of alcohol are burned is determined. The apparatus is very simple and cannot give accurate results, but the values obtained are good enough to show that there must be some connection between the "heat of combustion" and the structure of a series of compounds.

The alcohol is burned in a small spirit lamp, which can be made from a bottle, carrying a cork with a piece of glass tubing through which a wick is passed. The bottle and alcohol are weighed at the start and again after a certain amount of the alcohol has been burned. A new wick is required for each alcohol. The burner must be surrounded by a draught excluder, such as a tin can.



1. Weigh the burner and alcohol.
2. Place 100 ml of water in the beaker.
3. Take the temperature of the water.
4. Light the burner and allow the temperature to rise by about 15°C.
5. Extinguish the flame and reweigh the burner.
6. Calculate the heat given by the burning of 1 mole of the alcohol
7. Repeat for the series of alcohols - methanol, ethanol, n-propanol, n-butanol.

It is found that there is a fairly constant energy difference between each pair of alcohols.

Discuss:

1. Possible sources of error. How could the apparatus be improved?

Experiment 4. A spontaneous endothermic reaction

When a hydrated transition metal chloride reacts with thionyl chloride there is a considerable drop in temperature, although the reaction proceeds spontaneously.

To about 1 g of a transition metal chloride, e.g. hydrated cobalt (II) chloride add 3-5 g of thionyl chloride. Note the temperature and the colour change. The general reaction is:

$$MCl_2\,6H_2O + 6SOCl_2 = MCl_2 + 12HCl + 6SO_2$$

The evolution of HCl can be shown by placing a drop of silver nitrate solution on the end of a glass rod in the tube, and the SO_2 can be detected with potassium dichromate.

N.B. Thionyl chloride is dangerous to handle, rubber gloves should be worn, the experiment should be carried out in a fume chamber.

Discuss:

1. Why does this reaction proceed spontaneously?
2. How would it be possible to determine ΔH with reasonable accuracy?

Experiment 5. Determination of $\triangle S$ for the Cu/Ag reaction

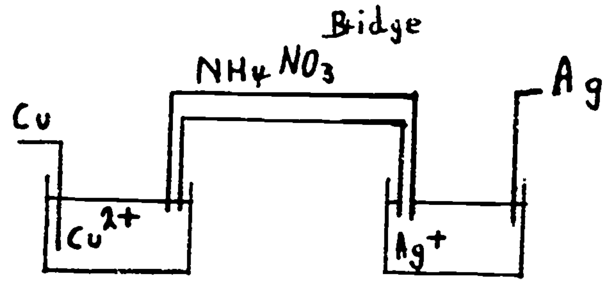
$\triangle H$ for the reaction $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$ is determined calorimetrically

$\triangle G$ is found from the e.m.f. of the cell $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

$\triangle S$ is found from the equation

$$\triangle G = \triangle H - T\triangle S$$

1. Take 100 ml. M/10 $AgNO_3$ in a thermos flask or a plastic cup. Add about 5 g copper powder. Find the temperature rise. Calculate the heat evolved per mole of Cu dissolved.
2. Set up the cell



Find the e.m.f. of the cell with a high resistance voltmeter, or a potentiometer. Take temperature.

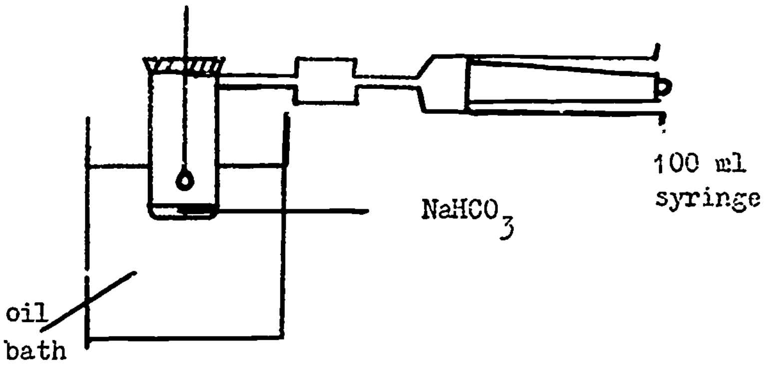
3. In an experiment $\triangle H$ was found to be - 32 kcal [literature value - 35.2 kcal] The e.m.f. of the cell was 0.47 v. $\triangle G$ calculated from $\triangle G = -nFEo$ is – 21.7 kcal [literature value is – 23.47 kcal]. From the equation $\triangle G = \triangle H - T\triangle S$, calculate $\triangle S$.

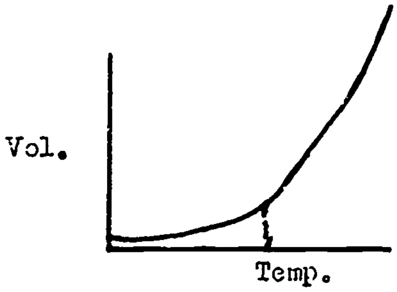
Discuss:

1. In the determination of $\triangle H$ the temperature changes. Does this make any difference to the value of T to be used in the equation $\triangle G = \triangle H - T\triangle S$?
2. Why should the $\triangle S$ term for this reaction be so much greater than for the reaction $Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$, for which $\triangle G$ and $\triangle H$ are very nearly the same?

Experiment 6. Thermodynamic predictions tested

1. By calculation the *decomposition temperature of sodium bicarbonate* is about 110°C. Set up the apparatus shown.





Plot the syringe reading against temperature.

Discuss:

How could the decomposition temperature of $MgCO_3$ be found? The value is above the range of a mercury in glass thermometer.

Devise a suitable apparatus, try the experiment and compare results with calculation.

2. The transition temperature of the change

$$Na_2SO_4\ 10\ H_2O \longrightarrow Na_2SO_4 + 10\ H_2O$$

is, by calculation, about 40°C.

Warm some sodium sulphate decahydrate until the decomposition takes place. Allow the "melt" to cool, and plot a cooling curve.

At 32° the temperature remains constant while the heat of hydration just balances the heat loss due to cooling.

There are more accurate methods of determining this transition temperature using a pyknometer, or a tensimeter. This apparatus is not difficult to construct, and could form the basis of a useful project.

Short experiments for introduction to energy and equilibrium

(a) Paper Chromatography. Experiment 7.

(i) Screened methyl orange separation is best done by ascending strip using 50:50 ethanol-water. T.L.C. separation is good on Kodak prespread strip K301 R2 (silica-gel) sold directly by Kodak Ltd. Research Chemical Sales Division, Kirkby, Liverpool.

(ii) Parker's Quink makes an interesting mixture to separate by the same method or even better by disc method.

(b) Ion Exchange. Experiment 8.

A fairly concentrated solution of copper (II) dichromate is required. This is best made by dissolving copper (II) chromate in warm dilute sulphuric acid.

A suitable cation exchanger is Zeo-Karb 225 (H or Na form).

A suitable anion exchanger is De-Acidite FF (chloride form).

Both are available from The Permutit Co. Ltd., Gunnersbury Avenue, Chiswick, London, W.4.

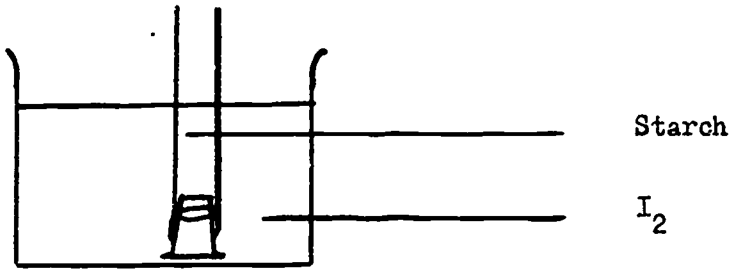
(c) Diffusion. Experiment 9.

Any from first year of circular 512, e.g. crystal in water, gas released into laboratory, etc.

(d) Osmosis, Dialysis. Experiment 10.

Dialysis tubing 6" long and stoppered at one end is filled with starch solution and then immersed in a beaker of water containing a little iodine in potassium iodide solution. Within 10 minutes the blue starch/iodine complex is seen within the tube, but no blue is seen in the beaker.

The film is permeable to iodine but impermeable to starch.



(e) Distribution of a solute between two solvents. Experiment 11.

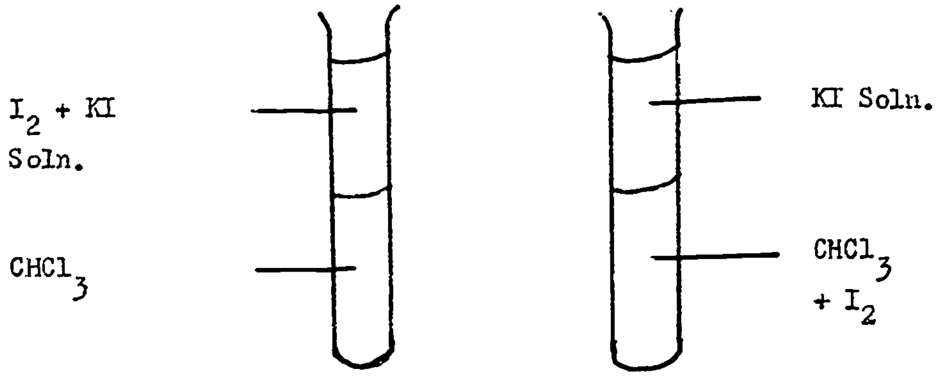
Prepare the following three solutions:-

(i) KI in water; 8.0 g/100 ml
(ii) I_2 in $CHCl_3$; 0.04 g/100 ml
(iii) I_2 + KI in water; 8.0 g KI and 0.04 g I_2/100 ml.

Take two test tubes.

In one of them place 10 ml $CHCl_3$ and in the other 10 ml of solution (ii). Now carefully add 10 ml of solution (iii) to the first test tube, and 10 ml of solution (i) to the second test tube.

In a few hours the colours of the layers in both tubes match showing that the iodine has distributed itself between the two solvents in the same way regardless of the layer in which it first appeared.



(f) Concentration Cell. Experiment 12.

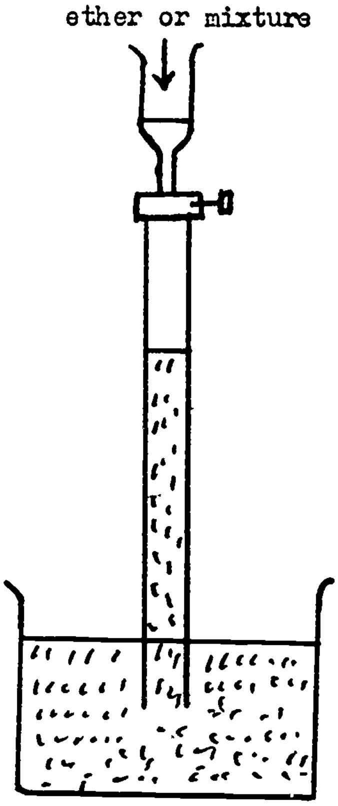
Set up a test tube with a plug of glass wool in the bend. Simultaneously pour a dilute solution of a coloured salt (e.g. $CuSO_4$) into one limb and a concentrated solution of the same salt into the other limb.

Dip a piece of metal, corresponding to the salt used (e.g. Cu) into each limb and connect these electrodes to a sensitive meter. The direction of the current is such as to tend to make the concentration of the solution in both limbs equal, i.e. electrons flow to the more concentrated solution.

(g) Lowering of Vapour Pressure. Experiment 13.

Fill two 50 ml burettes with water and invert in water (see sketch). Attach a funnel to each burette. Admit 15 ml of air into each via the stopcock. In one funnel place 5 ml of ether and in the other place 4 ml of ether and 1 ml of toluene. Slowly admit 2 ml of liquid into each burette. Compare the levels of water in each burette now. The vapour pressure of the toluene can be ignored.

Alternatively the ether or ether/toluene mixture can be introduced from a syringe at the foot of the burette.



Experiment 14. Factors affecting position of Equilibrium (Common ion effect)

Provide two 250 ml. glass cylinders, two portions of $CaCO_3$ (dry and precipitated) of 5 gms each, and 2 gms of sodium acetate crystals. Also prepare two 25 ml portions of 1 M acetic acid, and two 5 ml portions of detergent.

Place one 5 gm portion of dry $CaCO_3$ in each cylinder and add the detergent to each. Dissolve the sodium acetate in one of the 25 ml portions of 1 M acetic acid. Add the two portions of acetic acid to the two cylinders at the same time and note first, the rate at which the foam rises in the two cylinders and, second, the amount of foam formed in each cylinder.

Experiment 15. Fe^{3+}-CNS^- equilibrium

Materials:	Dilute aqueous solution of iron (III) chloride. Dilute aqueous solution of ammonium thiocyanate or potassium thiocyanate. Iron (III) chloride. Ammonium chloride.
Procedure:	Mix small quantities of Fe^{3+} and CNS^- with about 1500 ml. water to give an orange-yellow (not red) solution. Distribute equally among three beakers. Shift equilibrium by adding Fe^{3+} to one, CNS^- to another. Keep the third for comparison of colour. Solids may be added instead of solutions.

N.B. The colour changes are due to formation of various complex ions e.g. $FeSCN^{2+}$, $Fe(SCN)_2^+$, and $Fe(SCN)_4^-$

Experiment 16. Ester formation

Ethanol + acetic acid $\rightleftharpoons$ ethyl acetate + water

Prepare 5 conical flasks containing:

1. 1 mole ethanol (46 g = 58.4 ml) + 1 mole glacial acetic acid (60 g = 57.2 ml)
2. 1.5 mole ethanol + 1 mole glacial acetic acid
3. .5 mole ethanol + 1 mole glacial acetic acid
4. 1 mole ethanol + 0.5 mole glacial acetic acid
5. .75 mole ethanol + 1 mole glacial acetic acid.

Stopper the flasks securely. Keep at 50°C in a thermostatically controlled water bath for several hours. Cool the flasks rapidly, dilute to 1 litre and titrate with M/10 NaOH. Calculate the number of moles of acid left in each case, and hence the number of moles of ethanol and acid used. Calculate the equilibrium constant in each case.

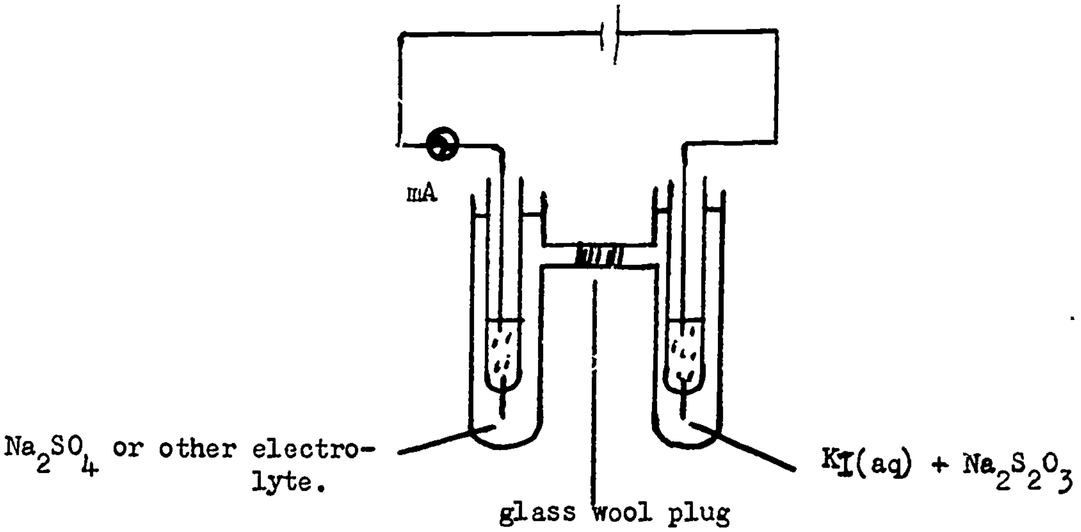
Experiment 17. Redox reactions related to electrons

Consider the reaction

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

The electrons can be used to oxidise $2I^-$ to I_2.

Set up the apparatus shown



In the anode compartment place excess potassium iodide solution + 2 ml of M/10 thiosulphate + 2 ml of starch solution. In the cathode compartment place another electrolyte such as sodium sulphate solution.

Start a stop-clock and pass a current of about 20 mA into the cell. [It is desirable to set up a trial experiment beforehand to see that the current is of this order]. Continue this until the starch just turns blue. Constant stirring is required throughout. Find the time for which the current must be passed in order to convert all the $S_2O_3^{--}$ into $S_4O_6^{--}$. Calculate the number of electrons equivalent to 1 mole of thiosulphate. This is found also to be 1 mole.

1 mole of thiosulphate ≡ 1 mole of electrons.

By adding 2 ml of M/10 $KMnO_4$ to excess KI acidified with dilute H_2SO_4 and titrating the liberated iodine with M/10 thiosulphate, it is now possible to calculate the number of electrons equivalent to 1 mole of MnO_4^-

The experiment can be repeated with other oxidising agents, e.g. $Cr_2O_7^{2-}$.

Experiment 18. Homolytic reaction between chlorine and methane initiated by U.V. light

An ordinary test-tube (Pyrex 2 × 14 mm) was filled with equal volumes of methane and chlorine and stoppered with a well vaselined cork. The methane was prepared by heating a mixture of sodium acetate and soda lime and the chlorine by the reaction between potassium permanganate and concentrated hydrochloric acid.

The filled tube was then clamped vertically with the cork uppermost behind a protective glass or plastic screen and then illuminated directly with U.V. light from a U.V. lamp. In 50 per cent of the attempts there was a reaction sufficiently strong to blow off the stopper. However, the violence was nothing like that obtained with the U.V. initiated reaction between hydrogen and chlorine (See Chemistry Takes Shape, Book 4, pp. 10 and 11). Initiation with U.V. light from a PF5 flash bulb was not successful with methane and chlorine.

Experiment 19. Hydrolysis of 2 bromo-2-methyl-propane

Solutions are made up as follows:-

A 5 ml water and 5 ml M NaOH made up to 50 ml with ethanol
B 10 ml M NaOH " " " " " " "
C 5 ml water and 5 ml M NaOH " " " " " " "

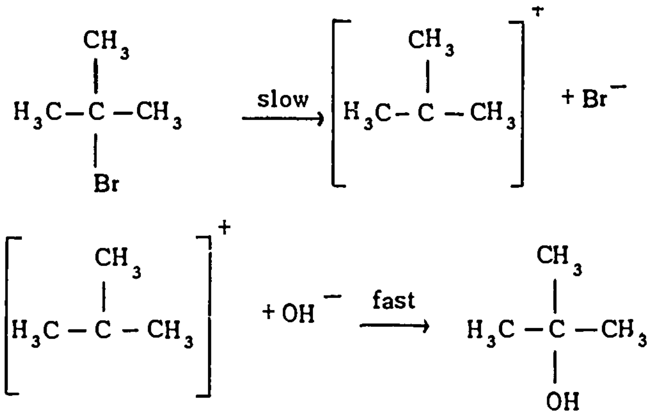
These are placed in a water bath at 25°C for a few minutes and the bromobutane added swiftly (by pipette) as follows:-

A 1 ml, B 1ml, C 2ml.

The solutions are mixed and left for 15 minutes at 25°C.

A 5 ml sample is withdrawn by pipette from each solution and placed separately in conical flasks containing 50 ml ice-cold acetone. Each solution is then titrated with M HCl using bromothymol blue.

Results indicate that the reaction rate is dependent only on the concentration of the alkyl halide. This does not prove the mechanism to be SN1, but the results can be explained by SN1 considerations.



$$H_3C-\overset{CH_3}{\underset{Br}{C}}-CH_3 \xrightarrow{slow} \left[H_3C-\overset{CH_3}{C}-CH_3\right]^+ + Br^-$$

$$\left[H_3C-\overset{CH_3}{C}-CH_3\right]^+ + OH^- \xrightarrow{fast} H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

Experiment 20. Hydrolysis of 1 - bromobutane

Solutions are made up as follows:-

A 5 ml water and 5 ml M NaOH made up to 50 ml in ethanol
B 10 ml M NaOH " " " " " " "
C 5 ml water and 5 ml M NaOH " " " " " " "

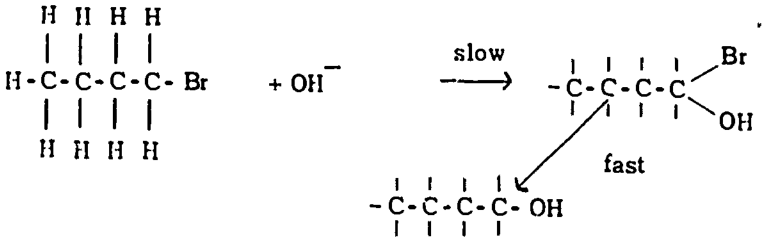
Carry out the experiment as above using a water bath at 70°C. Add the halide as follows:
-A - 5 ml; B - 10 ml; C - 5 ml.

After 15 minutes, the reaction is stopped by adding excess M HCl.

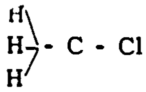
The excess acid is titrated with M NaOH.

Results show that the reaction rate is dependent both on the bromobutane concentration and the alkali concentration.

This does not *prove* that an SN_2 mechanism has been involved, but the results can be explained by SN_2 considerations.



Experiment 21. To test the ease of exchange of the nucleophilic group (i.e. the halogen) in an alkyl halide

An alkyl halide e.g.  can be attacked by any other electron rich group.

e.g. $CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$

Here the chlorine is replaced by an OH group.

The following experiment is to test how the ease of substitution depends upon the halogen involved.

(i) $R - I + OH^- \longrightarrow R - OH + I^-$

(ii) $R - Br + OH^- \longrightarrow R - OH + Br^-$

(iii) $R - Cl + OH^- \longrightarrow R - OH + Cl^-$

A series of halides ((i) 1 iodo-butane, (ii) 1 bromobutane and (iii) 1 chloro-butane) were shaken up with a solution of $AgNO_3$ in alcohol. This solution was made up in the ratio of 1000 mls ethanol to 1 mole of $AgNO_3$ crystals. Variable amounts of 1 M KOH in alcohol were added to the three mixtures until a precipitate of the halide was obtained in each case. When $AgNO_3$ in alcohol and the halide solutions were mixed with KOH an OH group is substituted for the halide group and the halogen is ppted as an insoluble silver salt.

(i) Ag I ------- yellow ppt.

(ii) Ag Br ------- creamy ppt.

(iii) Ag Cl ------- white ppt.

The more KOH which must be added to the halide for a ppt. to form the more difficult is that substitution.

Results:

(i) When 1 iodobutane was used the yellow Ag ppt. formed without the addition of any KOH *i.e.* the substitution of an OH group for an iodine group is rapid.

(ii) When 1 - bromobutane was used the creamy AgBr ppt. formed after the addition of six drops KOH *i.e.* the substitution of OH for halogen is again fairly rapid but not so rapid as (i).

(iii) When 1 - chlorobutane was used the white AgCl ppt. formed after the addition of 16 drops KOH *i.e.* the substitution of OH for C. is the most difficult reaction of the three.

Substitution of OH for halide will be in the order I, Br, Cl, iodine being the easiest to substitute and chlorine the most difficult.

Experiment 22. Halogenation of Alkenes - (Ethene)

A Simple Demonstration of the mechanism

Early in his organic chemistry course, a student learns that the double bond in alkenes is susceptible to attack by halogens and hydrogen halides - the reagent adding 'across the double bond' with the formation of a 'saturated' addition product:

$$CH_2 = CH_2 \quad + \quad Br_2 \longrightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$$

$$CH_2 = CH_2 \quad + \quad HBr \longrightarrow H\text{-}CH_2\text{-}CH_2\text{-}Br$$

In the case of the addition of a halogen such as bromine in a polar solvent, the student may be told that the reaction proceeds by an ionic mechanism in a stepwise fashion, the first step involving the formation of an intermediate carbonium ion in which only *one* of the two bromine atoms of the original Br_2 has become attached to the alkene:

step (i)

$$Br - Br \rightleftharpoons Br^- \quad + Br^+$$

$$Br^+ + CH_2 = CH_2 \longrightarrow Br - CH_2 . \overset{+}{C}H_2$$

The intermediate carbonium ion is then considered to be attacked by the second bromine atom (as Br^-) to give the final addition product:

step (ii)

$$Br^- + \overset{+}{C}H_2 . CH_2 - Br \qquad Br - CH_2 . CH_2 - Br$$

Normally the student will accept this mechanism without question and few textbooks make any effort to describe the evidence which has been accumulated in its favour. Certainly no practical manuals have simple experiments which illustrate the mechanism.

That a stepwise mechanism is involved can be quite readily and clearly demonstrated by carrying out the addition of bromine to ethylene in the presence of an additional anion such as Cl^- (from NcCl) or NO_3^- (from $NaNO_3$)[1]. Under these conditions, the carbonium ion formed in step (i) can react in step (ii) not only with Br^- to give the dibromide but also with the added anion (Cl^- or NO_3^-) to give in addition a bromochloride or a bromo-nitrate. Thus in the presence of added NaClwe have:

step (i)

$$Br^+ + CH_2 = CH_2 \longrightarrow Br - CH_2 - \overset{+}{C}H_2$$

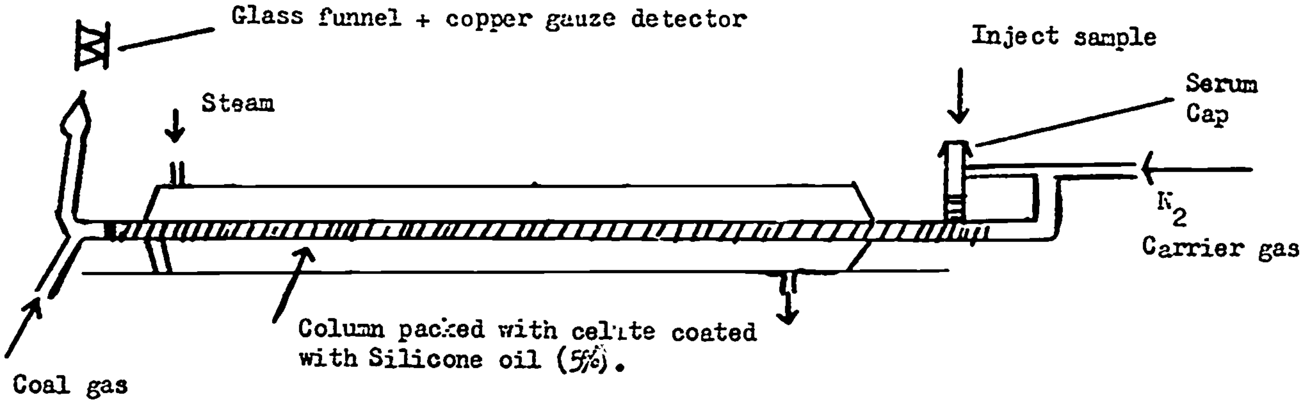
step (ii)

$$Br - CH_2 - \overset{+}{C}H_2 + Br^- \longrightarrow Br - CH_2 - CH_2 - Br \quad (A)$$

and

$$Br - CH_2 - \overset{+}{C}H_2 + Cl^- \longrightarrow Br - CH_2 - CH_2 - Cl \quad (B)$$

We have found that the reaction is in fact most readily performed using ethylene and bromine water saturated with sodium chloride. Under these conditions, almost equal quantities of the dibromide (A) and the bromo-chloride (B) are formed. The question now arises - how do we demonstrate that the product is a mixture of these two components? This is quite clearly shown by gas-liquid chromatography (g.l.c.) of the mixture in a very simple apparatus:



The product, an oily liquid, is isolated from the aqueous reaction mixture by solvent extraction and a drop of the liquid (or more usually, a drop of a solution of the product in a low boiling non-polar solvent such as pentane) is injected into the column of the g.l.c. apparatus. The two components have different physical properties and are therefore carried through the column at different rates. In this case, the lower boiling bromo-chloride (B) is eluted first followed a few minutes later by the dibromide (A). The arrival of the organic halides in the eluted vapour is readily detected by passing the vapour through a small coal-gas flame which impinges on copper gauze. The normally pale blue flame then becomes green for several seconds as each component is eluted. The retention times (t_R) of the two components are noted and are quite reproducible. These are then compared with the retention times of authentic specimens of the two liquids (available from B.D.H.) run individually on the same column under the same conditions.

Experimental Details

Ethylene gas from a cylinder is passed slowly for about 30 minutes into an aqueous solution saturated with both bromine and sodium chloride. The solution is best prepared by making a saturated sodium chloride solution and adding an excess of bromine to it. The mixture is shaken vigorously at intervals for several hours and the saturated solution is decanted from any undissolved reagents. During the passage of the ethylene, which is carried out in the fume cupboard, the product collects as oily droplets in the reaction mixture and the solution becomes paler. If it should become colourless at any time more bromine and sodium chloride may be added. When sufficient product has been formed, the oil is extracted from the aqueous suspension by means of ether or methylene chloride. The extract is washed with sodium thiosulphate solution (to remove any excess of bromine), then with water before being dried over anhydrous sodium sulphate. The volatile extracting solvent (ether or methylene chloride) is then removed by distillation on the steam bath and the residual liquid is examined by gas-liquid chromatography. This should indicate that the product consists of a mixture of 1-bromo-2-chloroethane (B) and 1,2-dibromoethane (ethylene bromide, A) in the approximate proportions of 45:55.

The G.L.C. Column [2]

The column consists essentially of a pyrex glass tube 2-5 ft. in length and ¼" internal diameter. At one end a T-piece is fitted to allow for the passage of the nitrogen carrier gas and the introduction of the liquid sample by injection with a syringe through the serum cap. The other end has a B10 joint to allow the fitting of another glass T-piece which forms the burner. The column is surrounded by a jacket by means of which it can be maintained at constant temperature by the passage of steam or the circulation of water from a thermostat. An alternative jacket made from electrothermal heating tape can also be used. The jacket is not, however, essential if the liquids being tested are fairly volatile.

The column packing in the present case was prepared from celite (80-100 mesh) coated with silicone oil S.E.30 (5 per cent by weight).

References.

1. A.W. Francis, *J. Amer. Chem. Soc.*, 1925, 47, 2340.
2. J. McLean and P.L. Pauson, *J. Chem. Ed.*, 1963, 40, 539.

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Experiment 23. Mechanism of Bromination in an alkene

Isobutene is generated by refluxing a mixture of approximately equal volumes of tert-butanol and conc. sulphuric acid. The alkene escapes through the condenser.

The isobutene is passed into a saturated solution of NaCl and bromine in water until the bromine colour is almost discharged. The dibromo and bromo-chloro compounds separate as oily droplets.

Any excess bromine is removed by shaking the mixture with sodium thiosulphate solution.

Extract the dihalogen compounds with ether and wash the ether extract several times with water.

Dry extract over anhyd. sodium sulphate and evaporate off the ether on a steam bath. A yellow product remains.

Analysis of the product:-

Perform a sodium fusion with 2-3 drops of the product, drop into water and filter. The filtrate now contains bromide and chloride ions.

Chromatographic separation of Br- and Cl^-. Eluent is 90 per cent pyridine 10 per cent water V/V. Run paper with standards for a distance of 4-6 inches by descending method.

Developer:- equal volumes of 1 per cent fluorescein solution and M/10 $AgNO_3$ soln.

Expose to u/v or daylight. Halides develop as dark spots.

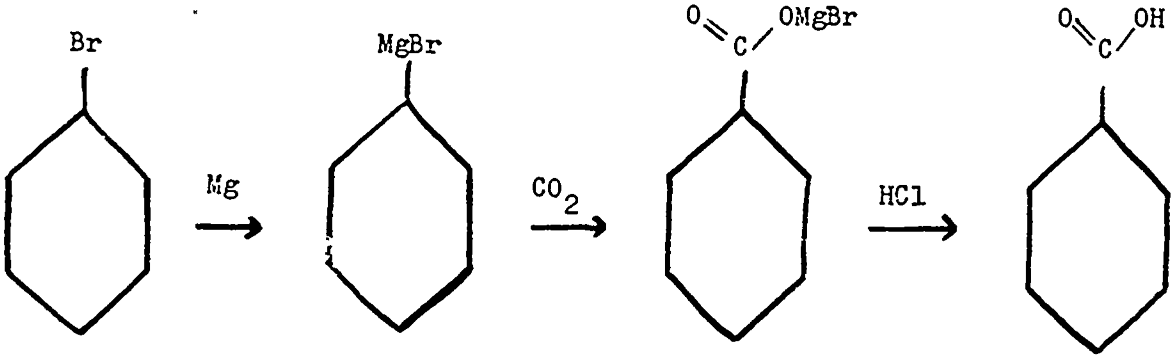
The area of bromide spot is approximately three times the area of chloride spot.

Therefore in the original mixed product there must have been roughly equal amounts of the dibromo and the bromo-chloro compound.

This indicates that. since chlorine was present only as Cl^-. the first bromine atom seems to have gone on to the bond as Br^+ leaving the other end of the bond to be attacked by either Cl^- or Br^-.

Note: As set out the method does not prove that the products are dibromo and bromo-chloro compounds. The ideal method would be to analyse the mixture by gas chromatography.

Experiment 24. Grignard Reagents - Preparation of Benzoic Acid



Materials required

Bromobenzene

Magnesium turnings (for Grignard reactions; ex B.D.H.)

Ether

Solid carbon dioxide

The bromobenzene and ether must be dried over Molecular Sieve Type 4A (1/16" pellets; ex B.D.H.).

Procedure

Remove traces of surface moisture from a Pyrex test-tube by lightly flaming it with a Bunsen burner. Allow the tube to cool and add magnesium (0.1 g.) and dry ether (7 ml.) followed by dry bromobenzene (0.4 ml.) and a minute crystal of iodine. Exclude moist air from the tube by means of a loose plug of dry cotton wool. Warm the tube gently and intermittently by means of a beaker of hot water until the reaction starts. (The brown colour of iodine will disappear and the ether will continue to boil gently in the absence of external heating). Set the tube aside until the reaction appears to be complete (10-20 mins.) and then add an excess of crushed solid carbon dioxide.* When frothing ceases, warm the tube to room temperature, add 2M hydrochloric acid (5 ml.), and shake until two clear layers are produced. With the aid of a teat-operated dropping tube, transfer the ether layer to a clean test-tube and shake it with M aqueous sodium carbonate (5 ml.) to extract the benzoic acid. Withdraw the aqueous layer (dropping tube inserted to bottom of test-tube) and acidify it with hydrochloric acid. Filter off the precipitate of benzoic acid with the aid of a filter pump; it may be recrystallised from water.

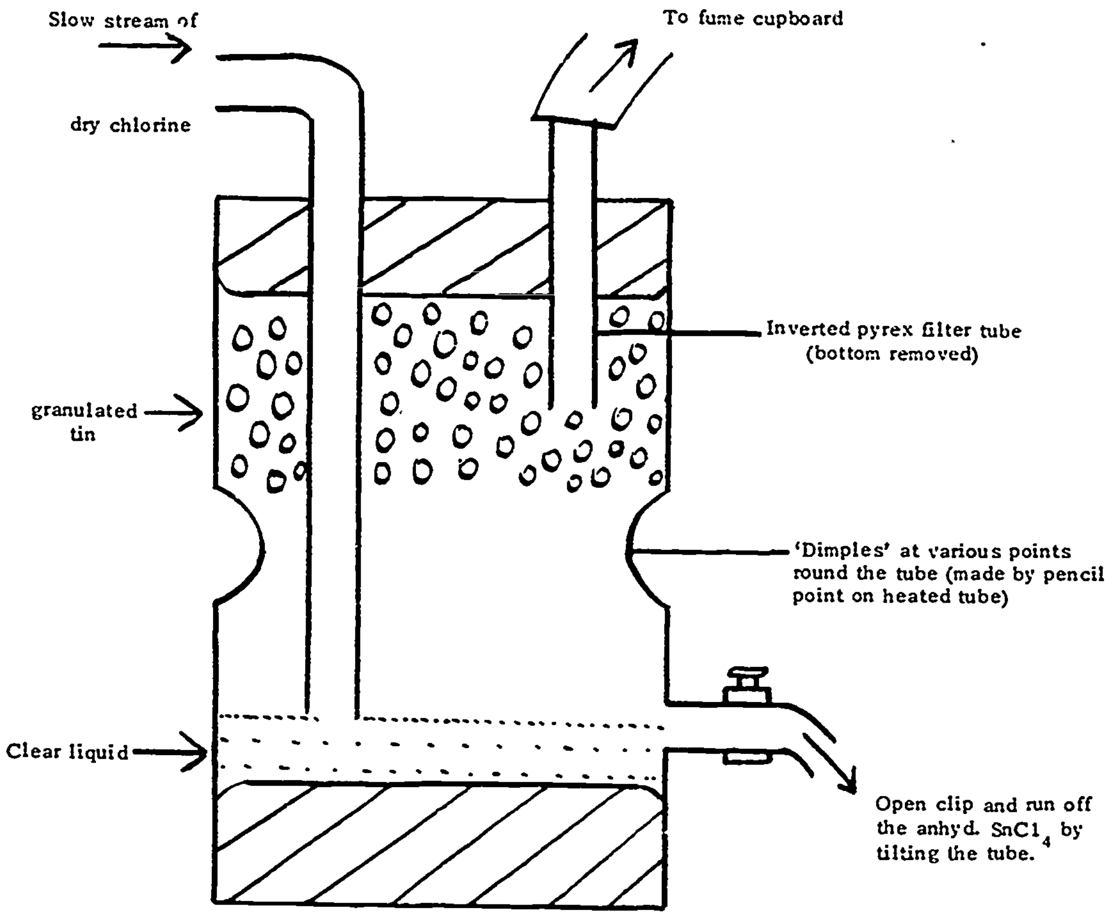
(The ethereal solution, which contains traces of biphenyl and unreacted bromo-benzene, may be discarded.)

*or bubble in *dry* CO_2 gas

Experiment 25. Preparation of Tin (IV) Iodide

Resublimed iodine was added to some benzene in a test tube. To this was added a little powdered tin metal. The test tube was heated gently in a water bath till most of the benzene evaporated. The remainder of the liquid was decanted off and the evaporation of the benzene was completed by leaving the liquid in a watch glass. The resulting tin (IV) iodide was crystalline in structure and orange in colour.

Experiment 26. Preparation of Tin (IV) Chloride, $SnCl_4$



NOTE. (1) The chlorine and the apparatus must be *dry* or white crystals of the pentahydrate, $SnCl_4.5H_2O$, are formed.

(2) No heat was required. If the chlorine is passed too quickly then the heat produced may melt the tin (m.p. 232°C), crack the tube, increase the danger of escaping fumes and give a poor yield by preventing condensation of the product (b.p. 114°C).

TESTS (1) Add a drop of hydrochloric acid (dil) and pass H_2S. A ppt. of the sulphide (yellow) is formed.

(2) Add ammonium hydroxide to give a white ppt. of stannic hydroxide.

Experiment 27. Dilution to arrive at K_w

Take 10 ml M/10 HCl and find pH. Dilute to 100 ml with glass distilled water - mix; find pH. Take 10 ml of this, dilute to 100 ml - mix and find pH.

Repeat.

Eventually further dilution gives no change in pH beyond about 6.5

Working with M/10 NaOH gives a similar set of results (not quite as good as for acids). Once again further dilution does not reduce pH below about 6.5.

pH = 7 is not easily achieved with distilled water but it is better than deionised water which sometimes has a pH = 5.

Experiment 28. Percentage dissociation of weak acids

Pupils prepare M/10 solutions of weak monobasic acids - e.g. acetic, propionic, monochloracetic, dichloracetic, trichloracetic.

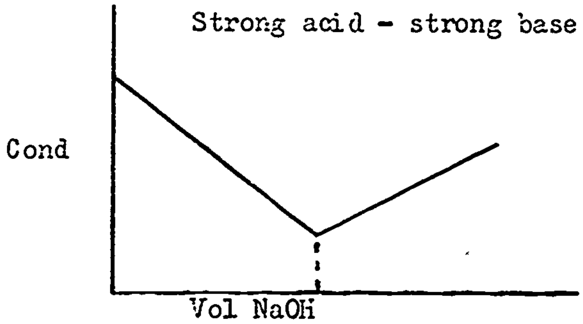
Measure the pH of these solutions with hydrion paper or pH meter.

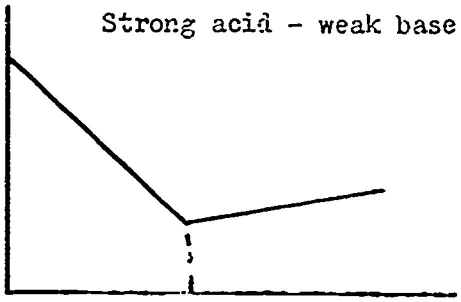
From the equation $pH = \frac{1}{2} pKa - \frac{1}{2} \log [acid]$, calculate pKa, Ka and hence percentage dissociation.

Discuss the effect of substitution of chlorine for hydrogen in acetic acid on percentage dissociation.

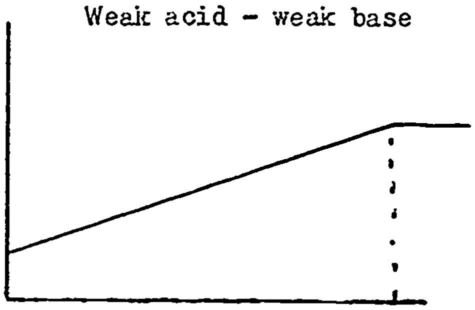
Experiment 29. Conductivity Titration Curves (about 1 hour)

Using pupil conductivity apparatus.

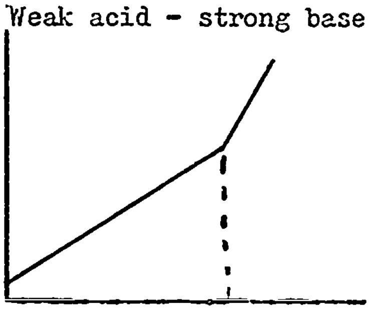




Add 10 drops bench acid, then add alkali drop by drop in presence of indicator. Change of curve corresponds to indicator change.



Indicator nc use



Therefore, conductivity shows end points where indicators fail.

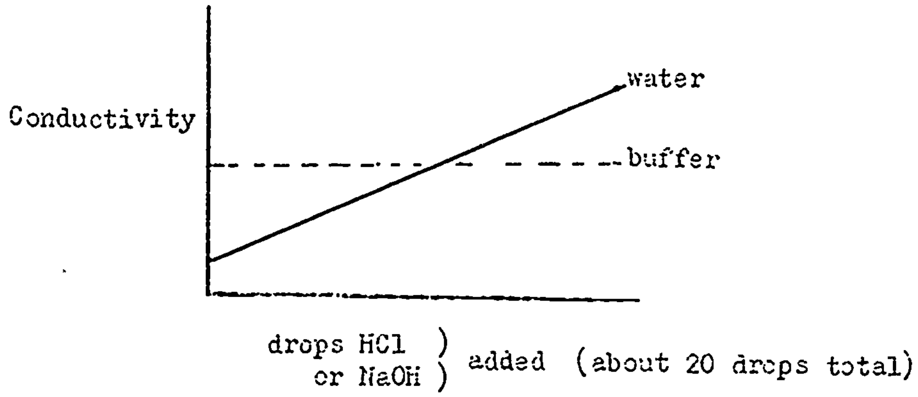
These are not meant to be conductimetric titrations as such, but the trends show how this method could be valuable.

Experiment 30. Experiment on buffers

1. A buffer solution is prepared by mixing equal volumes of M NaOH and 2M acetic acid.
2. The conductivity of this solution is measured while bench dilute HCl is added drop by drop.
3. Compare the results with the conductivity of an equal volume of distilled water to which bench dilute HCl is added drop by drop.
4. Determine the conductivity of the buffer solution when bench NaOH is added drop by drop.

5. Compare with distilled water as in (3).

Typical results



Experiment 31. Preparation of $Ni(NH_3)_4(BF_4)_2$ and NiF_2

Dissolve 6g. of hydrated nickel chloride in 10 ml. of warm water and add 10-12 ml. 0.880 ammonia until a deep blue liquid is obtained.

Dissolve the precipitate of $Ni(NH_3)_6Cl_2$ by slow addition of 15-16ml. of cold water with stirring. Filter.

Add a solution of 5 g. $NH_4.BF_4$ (B.D.H.) [20/6d for 250 g.], in dilute aqueous ammonia.

The precipitate of $Ni(NH_3)_6(BF_4)_2$ is practically invisible but can be filtered off immediately.

Wash with dilute aqueous ammonia and finally with acetone. Allow to dry in air.

On long exposure to air 2 molecules of ammonia are lost and the green tetrammine is formed.

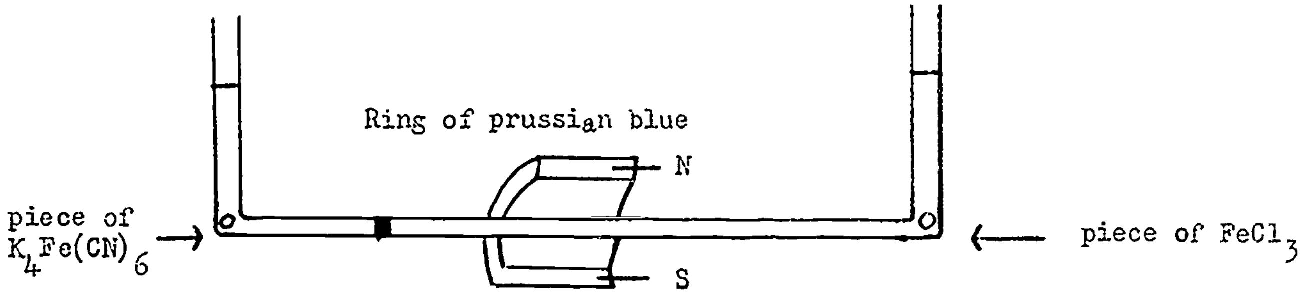
Heat 1-2g. of hexammine in a large dry test tube to give yellow NiF_2. The sublimate on the walls of the tube is $NH_3.BF_3$.

Analyse the hexammine by dissolving weighed sample (about 0.2 g.) in 50 ml. 0.1M HCl, back titrating with NaOH using methyl red as indicator.

Reference: W.G. Palmer, Experimental Inorganic Chemistry, Cambridge University Press. Price 50s.

Experiment 32. Experiments on Paramagnetism

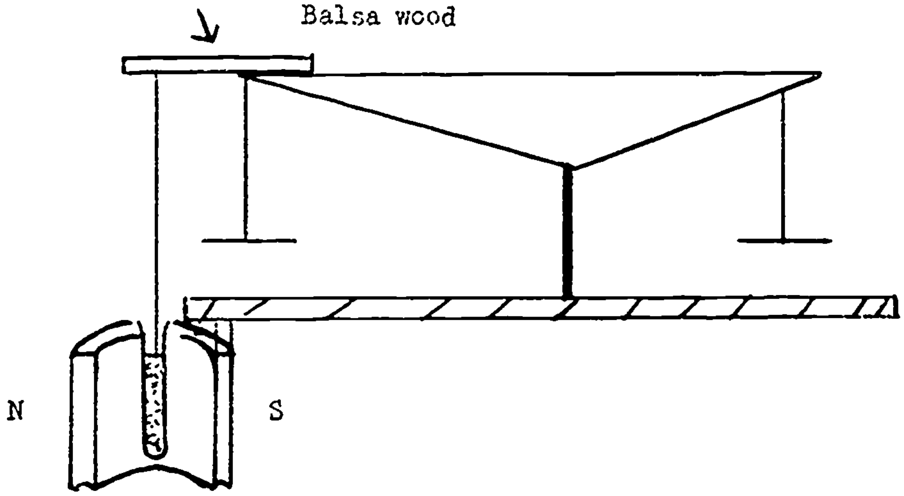
(a)



Fill the tube with water and introduce the reactants as shown. When the Fe^{3+} and $Fe(CN)_6^{4-}$ ions meet, the customary blue band of ferric ferrocyanide forms. If an Alnico magnet is placed near the blue band, the band migrates into the magnetic field.

Other combinations can be tried, e.g. Pb CrO_4, $Fe(OH)_3$

(b)



Wire a balsa rod on to an ordinary beam balance. Suspend from it a test tube containing crystals of the substance to be examined. Counter poise this to get the pointer near the middle of the scale.

When an Alnico magnet is brought in below the sample, the tube is drawn into the field if the substance is paramagnetic.

e.g.	$MnSO_4$ is drawn in very rapidly		(Mn(II) - 5 unpaired)
	MnO_2	more slowly	(Mn(IV) - 3 unpaired)
	$KMnO_4$	not at all	(Mn(VII) no unpaired)

Experiment 33. Experiments Involving coloured Vanadium Ions

Valency of V	5	4	3	2
Name	VANADATE	VANADYL	VANADIC	VANADOUS
Ion	VO_3^-	VO^{2+}	V^{3+}	V^{++}
Colour	Yellow	Blue	Green	Violet

A. Dissolve 1.5 g of ammonium metavanadate in 20 ml of 2M NaOH followed by 40 ml of M H_2SO_4. Make up to 250 ml with distilled water. (Solution A).

B. To 25 ml of solution A add approximately 3 g Na_2SO_3 and about 20 ml of bench sulphuric acid. Now boil off the SO_2 and titrate the hot solution with potassium permanganate (0.75 g/250 ml). The titre should be about 20 ml of K MnO_4.

C. To another 25 ml of solution A, add 20 ml of bench sulphuric acid and shake with zinc amalgam in a stoppered hard glass test-tube. The reduction is complete after 15 minutes shaking by the production of a pale lilac colouration. Filter this solution quickly into 50 ml of solution A. Wash the amalgam with dil.H_2SO_4 and washings to the filtrate. Heat this blue solution and titrate with K MnO_4 solution. The titre should be about 60 ml of K MnO_4 solution.

Conclusion·

The volumes of permanganate solution required in each case are in the ratio 1 : 3 corresponding to the reduction of V(5) to V(4) by SO_2 and further reduction of V(5) to V(2) by zinc amalgam.

Preparation of zinc amalgam

Shake 15 g of zinc dust with a 6% solution of mercuric chloride and add 30 ml of M HCl. Filter the amalgam and wash with distilled water.

D. Another simpler experiment can be done by taking say 30 ml of solution A and reduce using a mixture of granulated zinc and dil. H_2SO_4. With constant stirring the colour changes from yellow to blue to green to violet. However, it may be necessary to add a further quantity of zinc dust to obtain clear evidence of the purple V^{2+} ion. This process can be easily reversed by slow addition of dil. potassium permanganate or dilute nitric acid.

Experiment 34. Preparation of Tutton Salts

The aim is to show an isomorphous series and show that external similarity is related to similar internal structures (x-ray photographs will be commercially available).

Preparation

Mix equimolar amounts of K_2SO_4 and the sulphates of a series of transition elements in the (II) state. Dissolve the mixture in warm water, and leave to crystallise. A series of isomorphous crystals, having the general formula $K_2SO_4\ MSO_4\ 6H_2O$, come down.