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AN ELEMENTARY
LABORATORY COURSE
IN CHEMISTRY

BY

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PREFACE

The course of practical chemistry outlined in this book is intended for students who are beginning the subject and at the same time taking a course of lectures on general chemistry. It was arranged primarily for the first year Arts course of the University of Toronto, in which all science students—whether they are taking chemistry for two years only or whether they intend to specialise in this subject—are required to do exactly the same work in their first year. It has been necessary therefore to keep in view the twofold object of giving the former class of students, in a very limited period, as fair an idea as possible of the general nature of chemistry, and at the same time, of providing the latter class with a good working basis for their subsequent course.

Owing to the shortness of time in the laboratory (two afternoons a week) many important principles have been necessarily omitted. The principles especially emphasised, however, are those which, on account of their inherent difficulty or of some traditional error in previous instruction, generally appear to give most trouble to the student.

Particular emphasis has been laid on the importance of the quantitative side of chemistry. Where purely qualitative experiments have been introduced it has been done largely with a view to relieving the over-crowding at a too limited number of balances (one to five students).

Especial attention has also been given to the method of note-keeping in the laboratory, as it is believed that the habit of accurately and honestly recording all observations is one of the most important results of a laboratory training. The use of Arabic numerals has been avoided in numbering the experiments and sections of the book, so as to prevent confusion with the student's individual system of numbering in his note book, where Arabic figures are the more convenient.

Although much has necessarily been left to personal instruction, it is intended that the student shall follow *all* the directions given in the book. These have been purposely distributed among the theoretical discussions so that they cannot be found without careful reading. More concise explanations of some of the fundamental principles, together with a few extra experiments, are given in the appendix. With a view to encouraging resourcefulness, the apparatus used has been restricted to the simplest possible kind.

The experiments on qualitative analysis (pages 50-58) are intended only to show the principles and difficulties of such work. A short set of directions for the conventional separation of bases and acids is given

in Part II, for the benefit of those students who are so unfortunate as to have to pass an examination in this subject.

All reference to the atomic and molecular theories has been avoided, not because the authors are prejudiced against these excellent hypotheses, but in order to counteract a prejudice in the opposite direction on the part of the students. A large number of students still continue to come to the University with their minds simply stuffed with atoms and molecules, which they take to be the fundamental facts of chemistry.

The authors are indebted to Professor W. Lash Miller for his permission to use the table for separation of acids from Miller and Smale's "Qualitative Analysis" and the experiment on the reduction of permanganate from "New Requirements in Chemistry for Junior Matriculation."

<div align="right">THE AUTHORS</div>

The University of Toronto
August, 1905.

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COURSE OF PRACTICAL CHEMISTRY

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PART I

COURSE OF PRACTICAL CHEMISTRY

GENERAL INSTRUCTIONS

Before beginning any set of experiments read over the *whole section* carefully. In many cases important points that may modify the whole method of procedure are not mentioned until the end of the section. The directions, as far as they are given, must be followed implicitly, but many details and precautions are purposely omitted, and must be thought of, or found out by experience, by the student. The work should not be done hurriedly. There is only one allowable method of hurrying, namely by carrying on several experiments simultaneously so that there may be no time wasted. The habit of doing this should be acquired

On keeping notes. Page the note book before beginning work and date the account of each day's experiments. Record all operations and observations on the right hand page of the book and reserve the left side for calculations, conclusions, etc. Number all experiments, parts of experiments, summaries, etc., *consecutively* throughout the year, with *Arabic* numerals, and head each experiment and part with a short, concise *underlined* title, which will show clearly the object of the work. Always record *quantities* of materials used, even when these are only roughly known. Record " bad " results as well as " good " ones, remembering that the *correct* result is always the one you actually get and not necessarily the one you expect. All records must be made in the laboratory, *during the progress of the experiments*. There is a temptation to write results on scraps of paper with the intention of copying them out later in the note book. This should never be given way to. Full conclusions must be drawn from the experiments and written in the book, and any questions suggested in the text should be considered and answers thereto written. From time to time short summaries should be made, where possible, in tabular form. Neatness is of course desirable, but fulness, clearness and accuracy are of much greater importance.

SECTION I

SOLUTION AND CRYSTALLISATION

Exp. i. Recrystallisation of impure copper sulphate (blue stone).
Grind the substance fine in a mortar, transfer it to a beaker and add
sufficient water to dissolve most of the material. (Avoid addition of too
much water.) Filter the liquid obtained, using a long-necked funnel,
and collect the clear solution (" the filtrate ") in a flask or beaker. The
filter paper should fit closely in the funnel, and care should be taken not
to fill the funnel to within less than three millimetres of the top of the
paper. The paper should be moistened with distilled water before filter-
ing. Next evaporate the clear filtrate in a porcelain basin, using the sand
bath and Bunsen burner. (If the liquid does not remain perfectly clear
it must be re-filtered.) The liquid may be allowed to boil quietly at first,
but when the solution becomes more concentrated the heat must be
reduced to prevent the substance spurting over ("bumping"). From
time to time transfer a few drops of the liquid into a dry test tube with the
aid of a glass tube, cool them under the water tap, and shake vigorously.
If crystals of copper sulphate are seen to separate in the test tube the
evaporation has proceeded far enough, and the whole of the liquid must
be transferred to a beaker and cooled. If, on the other hand, the liquid
remains clear, the evaporation must proceed farther. If the few drops in
the test tube change, upon cooling, almost completely to a solid, the
evaporation has gone too far (Why ?) and a little water must be added
to the liquid in the dish before cooling. When the liquid is completely
cold, pour it, together with the crystals, into a fresh filter and allow the
fluid part to drain off as much as possible. Finally transfer the moist
crystals to a piece of coarse filter paper and dry them by pressure. When
dry, label the substance and keep it as a specimen.

How have the insoluble impurities been separated ? What has
become of any *soluble* impurities that may have been present ? Why
not dry the crystals by heat ?

While the above is going on the following experiments should be
made.

Exp. ii. Shake a crystal of pure copper sulphate about the size of a
pea in half a test tube of water, and note the time it takes to dissolve.
Repeat the experiment, having first ground the substance. Also compare
the rate of solution in hot and cold water. (No chemical process takes
place instantaneously, and all are accelerated by rise of temperature.
See p. 80.)

Exp. iii. Place pure powdered copper sulphate in a test tube to a depth of about two centimetres and add enough water to just cover it. Heat this to boiling, and if after a minute or so the crystals have all disappeared add more and more salt till some remains solid in spite of the boiling. Then, after allowing the liquid to settle for a few seconds, pour off the clear solution into another test tube, and add water to the latter so as to double the volume. Heat again and allow the tube to cool without shaking. When cold, shake vigorously. Heat again, cool, and try the effect of adding a few grains of solid copper sulphate Record all results and conclusions.

SECTION II

SEPARATION BY SOLUTION

Exp. iv. *To ascertain whether a material is uniformly soluble in water or is a mixture of soluble and insoluble substances.* Treat the substance in a beaker with distilled water. Stir for a few minutes and filter the liquid, being careful to pour as little as possible of the solid into the filter. Evaporate a small drop of the filtrate on a perfectly clean watch glass, held in the fingers over the flame. If a dry residue remains on the glass repeat the treatment of the original substance with distilled water, in the beaker, and pour the liquid through the original filter paper. Test the filtrate again for a residue and repeat the whole operation until either no residue is obtained on evaporating the drop, or until further washing of the substance does not appear to diminish the amount of residue obtained on the watch glass from the filtrate. Evaporate a drop of distilled water and a drop of tap water.

The stirring rod used in the above experiment should be covered at the end with a small piece of rubber tubing, otherwise many beakers will be broken.

Exp. v. Investigate the second substance given in exactly the same manner as described above, and record the results and conclusions.

Exp. vi. Repeat the investigation of the latter substance, using boiling water throughout, instead of cold. What differences do you observe?

Care must be taken to distinguish a *solution* from a *suspension*. When a material is *dissolved*, the liquid, although perhaps coloured, is perfectly *clear*. When fine particles are *suspended* in the liquid a turbidity is noticeable. Of course the liquid containing the suspension may itself be a solution.

Compare the appearance of some of the reagent "potassium bichromate," diluted about fivefold with water in a test tube, with the appearance of the same solution, to which a drop of reagent "silver nitrate," diluted with a little water, has been added. The former is a solution, the latter a solution with solid particles suspended in it.

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SECTION III

EXPERIMENTS WITH AIR

Exp. vii. (Two adjacent students may work at this experiment together.) Dry out two small round flasks *completely* by warming them (well above the flame) and drawing air through them by means of a glass tube. (Would simply warming the flasks dry them?) Fit both with corks, softened by gently rolling them under the foot, and into one flask drop a minute particle of the white substance provided The particle should not be larger than a grain of sand. Into the other flask put several pieces about the size of a match head, and cork both flasks tightly. Also place aside correspondingly large and small grains on a piece of glazed paper. Examine all these after half an hour or more, and note carefully any changes. Can you account for what you observe?

In spare time make a short summary in your book of the conclusions to be drawn from experiments of Sections I and II, regarding the solubility of substances and the separation of soluble from insoluble. Refer to the experiments by the numbers in *your own* notes. Remember that the note book must be intelligible independently of these instructions.

Exp. viii. Wash out and dry completely a small flask. Provide it with two tubes exactly as shown in the diagram (Fig. 1), and prepare two caps, A, made of rubber tube and glass rod, for closing the tubes of the flask. Fill a U-tube to within two centimetres of the side tubes with the same substance as was used in *Exp. vii*, and insert wads of cotton wool to keep the material in place. Soften the corks, insert them firmly and make sure that the whole is perfectly air-tight.
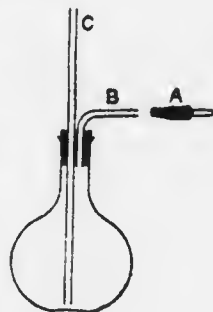
In perforating corks both the borer and cork should be given a rotary motion and very slight pressure should be employed. A cork borer

FIG. 1.

should never be used without first making sure that the previous boring has been poked out of the tube. The hole should be bored slightly smaller than the glass tube to be inserted, and if necessary enlarged with a rat-tail file.

Connect the U-tube with tube B of the flask by means of the rubber of one of the caps and suck air very slowly through C for some minutes with another piece of tubing. Then disconnect, and immediately close the tubes B and C with the plugs. Obtain a fresh sample of the white

substance and quickly drop in a minute grain of it through C, shaking it through the tube to the bottom of the flask. Replace the cap at once and leave the flask for half an hour or so, or until the next day.

A good way to put in the grain without opening the tube is as follows. Close the rubber tube near C by pinching between the finger and thumb, remove the plug, insert the grain and replace the plug before releasing the rubber. The grain may then be shaken down.

Explain the results you obtain.

Note. The U-tube, filled with the material, is to be kept for future use, with the side tubes closed by the two caps prepared above. The flask and fittings also will be required in a subsequent experiment.

Exp. ix. Fit a softened cork into a test tube, cutting off the bottom part so that not more than five millimetres project into the tube, and gum a narrow strip of paper lengthwise on the glass. Pour into the test tube about 4 cubic centimetres of the concentrated ferrous sulphate solution provided (not the solution from the reagent bottle). An ordinary test tube holds from 25 to 30 cc; 5 cc can be therefore roughly estimated by filling the tube one sixth deep with the liquid. (See graduated vessels provided for inspection.) Then add about 3 cc of solution from the bottle labelled potassium hydrate, being careful not to warm the tube with the hand. Close the test tube, shake it continually for five minutes, stand it in an upright position till the liquid has settled to a definite surface, and make a mark on the paper at the top of the liquid. Next invert the tube in a mortar full of water and carefully loosen the cork *slightly*, but not enough to allow the substance to escape into the mortar. Replace the cork firmly, under the water, set the tube upright, etc., and again mark the height of the liquid. Repeat the shaking and other operations till no more liquid enters the tube on inverting it in the mortar.

Test the gas remaining in the tube with a glowing *pointed* match, and compare the result with that obtained with an ordinary test tube of air. What is the ratio between the original volume of air and the volume which has disappeared ? Why did the liquid cease rising in the tube in spite of continued shaking ? Was a constituent of the air entirely used up, *r* was the absorbing power of the liquid exhausted ? Devise an experiment to decide this point.

SECTION IV

COMBUSTION OF MAGNESIUM

Exp. x. To determine the change in weight when magnesium is burnt in air. (Do not begin this experiment until instructed in the use of the balance.) Clean a porcelain crucible and lid and heat them for a few minutes over the Bunsen burner. When thoroughly cold weigh them accurately on a watch glass. Clean about 25 cm magnesium ribbon with emery paper, fold it loosely together and weigh it in the crucible. Then heat the crucible and magnesium over the Bunsen, adjusting the flame to about the height shown in Fig. 2. The crucible must be heated in the perforated iron square, and must be covered almost completely with the *inverted* lid, as shown, leaving an opening between the edge of the lid and the crucible not more that one millimetre in width. It may take from 20 to 30 minutes to complete the combustion. When cold weigh the crucible and contents as before and repeat the ignition till no further change in weight occurs. (*This is the only sure sign of complete combustion.*)   Keep the resulting substance for use in Section V, which may be proceeded with in spare time.
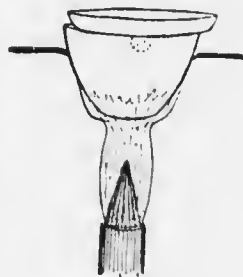
FIG. 2.

Exp. xi. Repeat the whole experiment, using about 15 cm ribbon.

Record all results concisely, giving particulars as to time of heating, cooling, etc., and note, and give reasons for any precautions which you find it necessary to observe. Spare time may be used also in fitting up the apparatus described under *Exp. xiii*, p. 10.

Notes. The change which takes place in this experiment is a combination of the oxygen of the air with the magnesium to form a new substance called magnesium oxide. The crucible is heated before weighing, in order to free it from dust and to have its surface in the same *state of moisture* as when it is weighed subsequently. Glass and porcelain objects exposed to the air become covered with a film of moisture which affects their weight considerably. As this film begins to form again after the crucible cools, it is necessary, when great accuracy is required, to make all weighings at the same interval of time after heating, a good method being to leave the object in the room where the weighing is done for at least five minutes after it is thoroughly cold. The difference

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between the weight of a crucible *just* cooled, and the weight five minutes later may be as much as 0.003 g. This might be tried in spare time.

If the crucible is not sufficiently covered white fumes will be seen escaping. These are caused by the metal evaporating and the vapour oxidising outside the crucible. If the crucible is covered too closely the access of the air is hindered and the combustion takes place very slowly. After the first few minutes there is not so much fear of the metal vaporising and the flame may be slightly raised.

The object in using the square of metal and in inverting the lid is to prevent the fumes from the gas flame from entering the crucible, where they would react with the magnesium and deposit *carbon*. If, after cooling, the crucible should be found to be jammed in the iron square it may be loosened by placing it carefully on the table, steadying it with the hand and pressing the square downwards.

In each experiment calculate the amount of oxygen which combines with a unit weight (1 g) of magnesium, and calculate the *per cent.* effect on these values produced by an error of 0.001 g in the weights of the oxide found (see Appendix, p. 84). All calculations should be made on the left page of the note book, as it is of great advantage to have the actual work of a calculation accessible in case of possible search for an error. The habit of using logarithms should be acquired.

Would your results justify you in thinking that the same amount of oxygen always combines with a definite amount of magnesium ?

What possible sources of error are there in this experiment ?

Make a summary of the results of the two experiments as follows :

No. .... *From Exp.* .....

Wt. of Mag'm.... Wt. of Mag., Cruc., Lid, and Watch Glass

after ...... minutes heating ..... -.---- g.

" ..... " " ..... - ----

" ..... " " ..... -.----

" ..... " " ..... -.-- -

Wt. of Cruc., Lid, and W. G. .... -.----

Hence Wt. of Magnesium Oxide .... -.----

Wt. of Magnesium................... -.----

Hence Wt. of Oxygen absorbed .... -.----

Therefore 1 g *Magnesium combined with* ..... - - g *Oxygen.*

From Exp. ......

Wt. of Mag'm ......

(Record results as above.)

No. .... *Effect of experimental error :*

In *Exp.*...an error of 0.001 g in wt. of oxide causes an error

in the above result of ....-.-- %

In *Exp.*...the same error causes an error of......... .....-.-- %

SECTION V

PROPERTIES OF MAGNESIUM OXIDE

Exp. xii. Remove the whole of the white magnesium oxide from the crucible (*Exp. x* or *xi*), place it in a test tube and add a little water. Shake, and note if any apparent change occurs. Allow the solid to settle and taste a drop of the liquid. Then add about a quarter of a test tube of dilute hydrochloric acid and warm. There is generally a small quantity of black insoluble substance (carbon from the flame); if so, this should be filtered out. Pour the *whole* of the liquid into an evaporating dish, previously weighed to 0.01 g, and heat gently till the substance has boiled dry, but not longer. (How can you separate the whole of the liquid from the filter paper? See *Exp. iv*, p. 4.)

Is this substance still magnesium oxide? Weigh it roughly (*i.e.*, to 0.01 g). Put some of it in a test tube and add a *little* water. Does it behave like magnesium oxide? Taste the liquid. Weigh the rest of the solid in the dish roughly and leave it exposed to the air over night, or breathe on it for a few minutes, and note any change that occurs. Is there any change in weight?

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CHEMICAL SUBSTANCES.   THE COMPOSITION OF WATER

One important conclusion from the last experiments is that the composition of magnesium oxide is always the same, in spite of the fact that no special precautions were taken to perform all experiments at the same temperature and to allow always the same amount of oxygen to enter the crucible.   Indeed, it might be shown that the composition of the thin layer of oxide on the ribbon formed by long exposure to the air at ordinary temperature is also exactly the same, namely, 1 g magnesium to 0.65 g oxygen.

Substances such as this whose composition does not vary gradually with the conditions under which they are produced are called *chemical substances*, or better, chemical *individuals*.   It is important to remember this definition.

The substance formed by addition of hydrochloric acid to the magnesium oxide is also a chemical individual, although this cannot be shown very well by your experiments, as it tends to decompose on heating.   It is known as magnesium chloride, and is one of a large class of materials (salts) obtained by the action of an acid on the oxide of a metal.   Magnesium chloride has the property of absorbing water vapour very readily and may be used for removing moisture from air and other gases.   The white substance used in *Exp.viii* was a similar material, calcium chloride.

Exp. xiii.   The composition of water.   When a current of electricity is passed through water the water gradually disappears, and two gases called oxygen and hydrogen are formed in its place.   Hydrogen may be made to recombine with oxygen (*i.e.*, may be burnt) and water is re-formed.   The object of the following experiment is to determine the ratio by weight in which hydrogen and oxygen combine to form water.
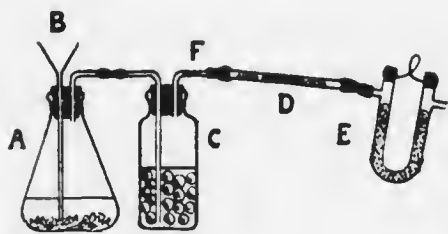
FIG. 3.

Set up an apparatus as in Fig. 3.   Hydrogen may be generated in the flask A by bringing together granulated zinc and dilute sulphuric acid. The hydrogen gas which is given off will, however, be " moist," *i.e.*, it will be mixed with some water vapour, which must be removed by bubbling the gas through the bottle C containing concentrated sulphuric acid, a substance like magnesium chloride having the power of absorbing

water vapour. This bottle should contain glass marbles, to prevent the bubbles rising too rapidly through the liquid. A small plug of cotton wool must be inserted in the tube at F to catch liquid *spray*, formed by the bursting of bubbles at the surface of the acid in A. These two vessels, then, constitute a generator of "dry" hydrogen. In order to burn this hydrogen to water in such a way that both the weight of oxygen used up and the weight of the water formed may be determined, it is passed over some copper oxide, heated in the hard glass tube D. This substance is somewhat analogous to the magnesium oxide of *Exp. vii*, and was prepared by burning copper wire in air. It contains oxygen, which it gives off readily, when hot, to hydrogen, thus burning it to water. The water vapour which is formed passes along the tube, mixed with any hydrogen which may remain unburnt, and is collected in the U-tube E, which is loosely filled with calcium chloride.

The amount of water obtained is determined from the increase in the weight of the U-tube. The quantity of oxygen used to burn the hydrogen is found by determining the loss in weight of the tube containing the copper oxide. The amount of hydrogen which has been burnt will be the excess of the weight of the water over that of the oxygen.

Before proceeding to the experiment it is necessary to see that the apparatus is completely air-tight. This can be ascertained by testing A and C separately by blowing the liquid up into the vertical tube, closing the opening into which the air has been blown and noting whether the liquid maintains its level in the tube.

The tube B must next be disconnected and about half filled with oxide of copper, 3 or 4 cm being left free at each end, and small plugs of glass wool being inserted to keep the oxide in position. As copper oxide generally contains a little moisture it must be thoroughly dried by heating over the Bunsen and drawing air through the tube. Then weigh both the oxide tube and the calcium chloride tube. The latter should be weighed with the caps on the openings, the rubber of one of the caps being used to connect D and E, so that any moisture collecting in it during the experiment will be included in the subsequent weighing of the tube.

The next step is to generate the hydrogen by pouring dilute sulphuric acid down the funnel B, and expel completely the air from the apparatus. The reason for this is that a mixture of hydrogen and air is extremely explosive, and most dangerous accidents may occur if the copper oxide is heated before all the air has been expelled from the apparatus. For this reason DO NOT BRING A FLAME NEAR THE APPARATUS until assured by the instructor that it is safe to do so.

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Care must be taken in heating the copper oxide that water condensed in the forward part of the tube does not run back and crack the glass. To avoid this, slope the tube downwards as shown in Fig. 3. When the oxide appears to be completely covered with metallic copper, any water remaining condensed in the tube should be carefully driven over by gentle heat into the U-tube.

Before disconnecting the tubes in order to reweigh them, let the apparatus cool with the current of hydrogen passing through it. Then suck dried air through the two tubes so as to replace the hydrogen by air Why is this necessary ?

From the results calculate how much oxygen has combined with one gram of hydrogen.

Make a list of all sources of error in this experiment that you can think of, stating what effect each would have on the result.

DETERMINATION OF WEIGHT OF HYDROGEN GIVEN OFF WHEN MAGNESIUM DISSOLVES IN AN ACID

Exp. xiv. You have already made use of the fact that zinc and an acid react together to give off hydrogen. Most metals react with acids in this way. The object of the following experiment is to determine the weight of hydrogen produced when a certain quantity of magnesium dissolves in an acid.

Since it is very difficult to weigh directly the hydrogen evolved, it will be more convenient to determine the *loss* in weight of the acid and magnesium caused by the removal of the hydrogen. If precautions are taken at nothing escapes except the hydrogen, such as water vapour or acid fumes, then this loss in weight will be exactly the weight of the hydrogen produced. This is by no means an easy experiment, and unless great care is taken it may have to be repeated many times before an accuracy of even 5 per cent. can be attained.

Attach a wire loop to the upper end of a clean, dry test tube, so that it may be hung on the hook above the pan of the balance. Prepare a plug of cotton wool with a loop of wire round it so that it may be easily inserted and withdrawn from the mouth of the test tube. In another test tube make a mixture of about 4 cc of water and an equal volume of concentrated sulphuric acid. When cold, pour this mixture, by means of a funnel, carefully into the prepared test tube without wetting the sides of the glass. Then insert the cotton plug, rinse off the outside of the tube with water, dry it completely with the handkerchief, leave it for five minutes in the balance room (Why ? See p. 7.), and then weigh the tube very accurately on the hook of the balance. Next drop into the acid a weighed quantity of cleaned magnesium ribbon (about 35 cm) tightly folded together, replace the plug at once and

FIG. 4.

immediately hold the tube in a gentle stream of water from the tap, being careful not to splash water on the wool. The tube should be shaken from time to time, but not sufficiently to splash the acid up to the plug. When the evolution of gas has ceased, remove the plug for a minute or so to allow any hydrogen remaining in the tube to escape, and then *dry* and *weigh exactly as before*.

Notes. Sulphuric acid evaporates extremely slowly at ordinary temperatures, so that there is no fear of vapour of this acid escaping with

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the hydrogen. It has, moreover, the property of decreasing the tendency of water to evaporate and consequently very little water vapour escapes. With rise of temperature, however, all liquids become more volatile, and it is therefore necessary to keep the contents of the test tube *cool*, as otherwise the heat given out by the reaction would produce appreciable quantities of steam. After the first few minutes the reaction will go much more slowly and the cooling by water will not be necessary. The object of the wool is to catch the fine spray of liquid thrown up by the hydrogen bubbles breaking at the surface of the solution. (See *Exp. xiii.*) Would the cotton wool prevent the escape of water vapour?

From the result of the experiment calculate how much hydrogen would be evolved by *one* gram of magnesium. Compare this value with the weight of oxygen which combined with *one* gram of magnesium. (*Exps. x* and *xi.*) What is the ratio of these weights of oxygen and hydrogen? Compare this ratio with the ratio of the weights of oxygen and hydrogen which united to form water (*Exp. xiii*).

Re-calculate these ratios to the basis of 16 grams of oxygen, *i.e.*, find how much hydrogen would react with 16 grams of oxygen, how much magnesium would react with 16 g oxygen, how much hydrogen would be evolved by that amount of magnesium which unites with 16 g oxygen. Also calculate from your results how much water would be formed in a reaction in which 16 g oxygen take part, and how much magnesium oxide would be produced when 16 g oxygen are involved.

Roughly, what per cent. error is caused in the result of the above experiment by an error in weighing of 0.001 g? Compare this with the per cent. error in *Exps. x* and *xi* caused by the same absolute error in weighing. (See Appendix, p. 84.)

SECTION VIII

The results of the last experiment, taken in conjunction with those of *Exps. x* and *xiii*, afford an example of a very important principle which has been found to underlie all *chemical reactions*.[1]

Your experiments showed, namely, that (allowing for experimental error):

(a) With one gram magnesium, 0.657 g oxygen unite to form oxide (*Exp. x*).

(b) From one gram magnesium + acid 0.082 g hydrogen are given off (*Exp. xii*).

(c) With one gram hydrogen, 7.98 g oxygen unite to form water (*Exp xiii*).

or, since 0.082 : 0.657 :: 1 : 7.98,

with 0.082 gram hydrogen, 0.657 g oxygen unite to form water. That is, the proportions of oxygen and hydrogen which are involved in reaction with the same weight of magnesium, are also the proportions in which they react together to form water.

The relations will appear more clearly if you reduce a, b and c to some common standard, for instance, 16 g oxygen :

24.36 g magnesium combine with . . . . . 16 g oxygen

24.36 g magnesium + acid give off. . . . 2.02 g hydrogen

2.02 g hydrogen combine with . . . . . . 16 g oxygen

In other words, in the *three* reactions investigated, the three substances involved always take part in the proportion of 2.02 g hydrogen, 16 g oxgyen, and 24.36 g magnesium.

These numbers are called Reacting Weights, that of oxygen being arbitrarily taken as 16.

16 is the reacting weight of oxygen by agreement. 24.36 is the reacting weight of magnesium because 24.36 g magnesium react with 16 g oxygen and *also* because 24.36 g magnesium take part in a reaction with 2.02 g hydrogen, which is the weight of hydrogen that reacts with 16 g oxygen.

2.02 is the reacting weight of hydrogen because 2.02 g hydrogen react with 16 g oxygen and *also* because 2.02 g hydrogen are given off from an acid by that amount of magnesium (24.36 g), which reacts with 16 g oxygen.

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[1] The term *chemical reaction* is used here and in the rest of the book to indicate reactions in which only *chemical individuals* (see p. 10) are involved or considered.

In a similar way chemists have determined the reacting weights of all chemical substances, *e.g.*, sulphur 32.06, copper 63.6, chlorine 35.45, copper oxide 79.6, etc., etc.

The important general principle referred to above, which is the result of a great many careful experiments, consists in the discovery that *the reacting weights, determined as above described for every chemical substance, not only give the proportions by weight in which these substances take part in the particular experiments used for their determination, but these weights, or simple multiples of them,* ALWAYS *represent the proportions in which they react among themselves to form other chemical substances.* This principle may be called the *Law of Reacting Weights.* It includes the laws of multiple and reciprocal proportions.

You have also determined by your experiments the reacting weight of *magnesium oxide* and of *water.* You found that :

7.98 g oxygen + 1 g hydrogen gave 8.98 g water (*Exp. xiii.*)

or, 16.00 g oxygen + 2.02 g hydrogen gave 18.02 g water.

Here, 18.02 g water have reacted in a process in which 16 g oxygen took part. Hence, 18.02 is the reacting weight of water.

Similarly, 0.657 g oxygen + 1 g magnesium gave 1.1657 g magnesium oxide,

or, 16.00 g oxygen + 24.36 g magnesium gave 40.36 g magnesium oxide.

Hence, 40.36 is the reacting weight of magnesium oxide.

Thus, taking for granted the law of reacting weights, it might be predicted that *if* magnesium oxide does combine chemically with water it will do so in the proportion of some simple multiple of 40.36 g magnesium oxide to some simple multiple of 18.02 g water. Chemists have found that this is the case, and that the proportions are actually 40.36 to 18.02, the simple multiples in this reaction being 1 and 1.

In some cases two substances will react together in more than one proportion. When this happens it has been found that the one proportion is always some simple multiple of the other—a special case, of course, of the general law of reacting weights.

For instance,

not only does 2.02 g hydrogen react with 16 g oxygen to form water, but also, 1.01 g hydrogen reacts with 16 g oxygen to form an entirely different substance, namely, hydrogen peroxide.

It is evident, therefore, that the reacting weight of hydrogen will depend on what particular reaction is chosen for its determination, but the various values obtained for it will all bear a *simple* relation to each

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other. The same ambiguity might arise in the case of other substances, and consequently, owing to the importance of having fixed numbers so as to avoid confusion, the particular multiples have been decided upon for each chemical substance by convention. (For example, it has been found more convenient to use 1.01 as the reacting weight of hydrogen than the 2.02 suggested by the above experiments.) In the case of the elements (see App., p. 75), the particular reacting weights fixed upon are called " International Atomic Weights," the term being based partly on historical grounds. In the case of compounds the least ambiguous unit to employ for reacting weight is the " Formula Weight," *i.e.*, that represented by the ordinarily accepted chemical formula. (See App. on atomic and molecular weights, p. 75-6.)

These particular weights of substances[1] are so important that definite symbols have been assigned to them. They are as follows for a few substances :

	REACTING WEIGHT	SYMBOL
Oxygen, taken arbitrarily as 16.00		O
Hydrogen	1.01 (2.02/2)	H
Magnesium	24.36	Mg
Magnesium Oxide	40.36 (24.36 + 16)	MgO
Water	18.02 ($2 \times 1.01 + 16$)	H_2O
Sodium	23.05	Na
Sulphur	32.06	S
Copper	63.8	Cu
Chlorine	35.45	Cl

(For complete list of elements see App., p. 88.)

By means of these symbols the *compositions* and *reacting weights* of compounds may be represented very concisely and chemical changes may be quantitatively recorded. (Chemical " equations"). *e.g.*,

$$H + Cl = HCl$$

means that 1.01 g hydrogen reacts with 35.45 g chlorine, giving 36.46 g hydrochloric acid.

Write in your note books by means of such symbols, the reactions of *Exps. x, xii, xiii*, and *xiv*, as far as the actual experiments justify you to do so (not further), and give the calculations on which you base the equations.

These *reacting weights* are used by chemists as extremely convenient *units* in which to measure different substances. Just as we measure milk

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[1] In the following pages the term reacting weight (RW) will be frequently used both for atomic and formula weight.

by the quart (2.5 lbs.), wheat by the bushel (60 lbs.), and potatoes by the bag (90 lbs.), so, for instance, oxygen is measured in lots of 16 grams, magnesium in lots of 24.36 grams, and hydrogen in lots of 1.01 grams. It is much more convenient, for example, to remember that 2 RWs (reacting weights) hydrogen and 1 RW oxygen react to give 1 RW water than that 2.02 grams hydrogen and 16 grams oxygen give 18.02 grams water.

Explain in your note books concisely why the reacting weight of a compound will always be the sum of the reacting weights (atomic weights) of the elements represented in the symbol.

SECTION IX

THE PROPERTIES AND COMPOSITION OF ACIDS

Exp. xv. Make the following experiments with dilute hydrochloric acid, dilute sulphuric acid, and acetic acid, taking for each test a fresh quantity of the material in a test tube. (a) To each add a small piece of magnesium and apply a match to the mouth of the test tube. (b) To each add a small piece of zinc. (c) Taste each after diluting considerably with water and test the diluted solution with litmus paper. (d) To each add a drop of silver nitrate solution, and (e) to each a drop of barium chloride solution.

Tabulate the results. In what respects do the three acids behave similarly and in what respects differently ? What constituent do they appear to have in common ?

Exp. xvi. Take *not more than 2 cc* dilute sulphuric acid in a test tube and add magnesium piece by piece until no further effervescence occurs. Gentle warming will hasten the process. (See p. 80.) Dilute a small quantity of the liquid obtained, with water, and test the solution as before by taste, blue litmus and barium chloride. What properties have disappeared with the ability to give off hydrogen, and what properties are retained ?

Evaporate the rest of the undiluted liquid in an evaporating dish. When the liquid becomes thick and shows signs of "bumping" (see 5, p.80) cover it with a small watch glass with the convex side uppermost. When the substance is completely dry remove it to a clean watch glass.

Exp. xvii. Next burn about 25 em of magnesium ribbon as in *Exp. x.* It need not be weighed and the crucible lid may be left partly open to hasten the combustion. Warm the oxide with not more than 25 drops of dilute sulphuric acid, filter, and evaporate the solution as described above. Compare this material with the one obtained in *Exp. xvi.* Dissolve both in a little water and test both by taste, barium chloride and a small piece of magnesium. Do they appear to be the same substance ?

When the solution obtained by dissolving the magnesium in sulphuric acid was evaporated, the only substance given off was water. (This fact could have been proved by condensing the vapour and investigating its properties.) It is therefore evident that the white substance formed contains all the magnesium. Hydrogen was given off when the metal dissolved and the solution lost all properties common to acids. It is therefore probable that all the acid was used up in the process, and that all

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the constituents of the acid except hydrogen, and perhaps water, remained with the magnesium in the form of the white solid. When the oxide dissolved no hydrogen was given off (except possibly a few bubbles from a little unburnt magnesium). What do you suppose became of the hydrogen in this case?

SECTION X

ACIDS, BASES AND SALTS

The behaviour of the substances investigated in Section IX would lead to the view that acids contain hydrogen, and that the properties which they have in common are probably due to this common constituent. They all gave off hydrogen with metals, turned litmus red and tasted sour.

Another common property of acids is illustrated by *Exps. xvi* and *xvii*. The magnesium reacted with sulphuric acid solution, whose composition is represented by the formula $H_2SO_4 + xH_2O$, replacing the hydrogen (which was evolved as a gas) and producing magnesium sulphate solution, $MgSO_4 + yH_2O$. When this was heated the water was driven off and dry magnesium sulphate was left. If all the materials had been accurately weighed, the reaction would have been found to be represented by the following equation (neglecting the water used as solvent. See foot-note[2], page 35.):

$$Mg + H_2SO_4 = MgSO_4 + H_2$$

Similarly, the magnesium oxide would have been found to react with the acid according to the equation :

$$MgO + H_2SO_4 = MgSO_4 + H_2O$$

In this case the hydrogen is not given off as gas, but unites with the oxygen of the oxide to form water, which was evaporated off with the rest of the water originally present in the acid solution. The oxide which was present in excess of the amount necessary to react with the 25 drops of sulphuric acid was left unchanged and was separated from the solution by filtration.

Most *acids* behave in this way. They react with *metals* to give *salts* and hydrogen gas, and with *oxides* of *metals* to give *salts* and water, and in so doing lose all their common properties. The oxides of metals which react with acid solutions to form salts are called *basic oxides*. They often unite with water to form *hydroxides* (often less suitably called *hydrates*). These hydroxides turn litmus *blue*. Calcium oxide, or lime, for instance, combines with water to form calcium hydroxide or slaked lime. (Test the reagent with litmus.) The reagent bottle labelled " potassium hydrate" contains a solution of the hydroxide of the metal potassium. (Test it with litmus.) The general term *base* is used for the hydroxides of the metals. What are some of the common properties of solutions of bases ?

SECTION XI

Exp. xviii. *Solubility of sodium chloride.* The object of this experiment is to find how much of this substance dissolves in a unit weight of water at ordinary temperature. Powder some of the salt fine, and add some of it to one third of a test tube of water. Shake, and note whether it all dissolves. Add more and more until finally a considerable quantity remains at the bottom undissolved. After this shake for at least five minutes and then filter some of the liquid into a weighed crucible (15 or 20 drops are enough). Weigh quickly and then evaporate very carefully to dryness on the iron drying table. (*Avoid spurting.*) Finally cover the crucible, heat over the Bunsen burner and weigh. Calculate the result to the unit weight of water. Compare this result with your neighbour's, who probably did not take the same amount of salt and water as you did. (What conclusions ?)

Use any spare time, now and subsequently, in performing the experiments described on page 23, Section XII.

Exp. xix. Make a solution of sodium chloride by boiling an excess of the salt with water for a couple of minutes in a test tube and filtering while still hot. Cool and shake the liquid. (What conclusions ? Compare also *Exp. iii*). Wherein do *solutions* differ from *chemical substances* which you have investigated ? Determine the amount of salt per gram of water in this cooled solution. (See " Equilibrium," p. 79.)

The reacting weight of sodium chloride is $23.05 + 35.45 = 58.50$. When the proportions of salt and water just found are expressed in chemical units, *i.e.*, in reacting weights, instead of grams, do you find any simple relation between them? Do not jump at conclusions, but actually work this question out.

The composition of a *solution*, as well as that of a chemical substance, can thus be represented by means of symbols, *e.g.*, x NaCl.yH$_2$O, but in this case we need not expect to find any *simple* relation between the numbers, x and y, of reacting weights of the constituents. The law of reacting weights applies only to reactions between chemical individuals, *i.e.*, to *chemical reactions*. (See, however, foot-note [2], p. 35.)

SECTION XII

PROPERTIES OF AQUEOUS SALT SOLUTIONS

Exp. xx. (*To be done in spare time*). Add a few drops of (a) *Silver nitrate sol., (b) Barium nitrate sol., (c) *Dil. Sulphuric acid, (d) Ammonium sulphide sol., to small quantities (about 3 cc) of solutions of the following substances, using a fresh quantity of the solution for eacn experiment :

*Dil. Nitric acid (Hydrogen nitrate).　　Copper nitrate.
*Dil. Sulphuric acid (Hydrogen sulphate).　Copper sulphate.
*Dil. Hydrochloric acid (Hydrogen chloride). Copper chloride.
*Acetic acid (Hydrogen acetate).　　Lead nitrate.
Potassium sulphate.　　　　　*Lead acetate.
Potassium chloride.　　　　　Barium nitrate.
*Potassium bichromate.　　　　*Barium chloride.
*Potassium hydroxide.　　　　Barium hydroxide.
Ammonium sulphate.　　　　*Calcium sulphate.
*Ammonium chloride.　　　　Calcium chloride.
Ammonium bichromate.　　　*Calcium hydroxide.
*Ammonium hydroxide.

Solutions marked * will be found in the ordinary set of reagents.

The results are to be briefly recorded as the experiments are carried out, especial note being made of the quantities of solutions used and the appearance of any precipitates that may be produced. The results are also to be entered in tabular form on pages reserved for the purpose at the end of the note book, and references there given, by number, to the experiments in which details may be found. The following example shows how the tables should be arranged.

Effect of Silver Nitrate Sol. on :

	Hydrogen	Potassium	Ammonium	Copper	Lead	Barium	Calcium
Nitrate......							
Sulphate.....							
Chloride.....	Wht. ppt. Ex. No.—						
Acetate......	No. ppt. Ex. No.—						
Bichromate...							
Hydroxide....							

Similar tables should be made out for the other three reagents, and also one for the colour of the various *solutions*.

In some cases where the solution itself is highly coloured it may be necessary, in order to be sure of the colour of the precipitate, to filter out the latter and wash it once or twice with water. If this is done mention of it should be made, of course, in the note book. Occasionally a very slight precipitate may be produced owing to a trace of impurity in the solutions. In such cases the result should be recorded but not entered in the table.

Note. The student should have in his rack a number of the solutions in labelled test tubes so that the tests may be made rapidly in spare moments; for instance, while waiting for the balance, etc.

SECTION XIII

QUANTITATIVE SEPARATION BY SOLUTION

Exp. xxi. In Section XI you carried out a "chemical analysis" in that you estimated the amounts of salt and water in a solution containing these two substances. The method was based on the fact that one constituent was volatile, *i.e.*, could be driven off by heat, while the other was not. In another important method of separation advantage is taken of the difference in solubility of the substances in liquids. You have already made use of this *qualitatively* in *Exp. iv*, p. 4.

Make up a mixture of *about* half a gram each (accurately weighed) of common salt and powdered quartz, which is practically insoluble in water. The object of the experiment is to analyse this mixture and see how nearly the result of the analysis agrees with the weights originally taken. The soluble substance is to be separated from the insoluble as in *Exp. iv*. The quartz powder must then be collected on the filter and dried completely by spreading out the paper flat on the glass plate and heating it on the drying table. In order to wash the solid completely into the funnel from the beaker, the latter should be held in a partly inverted position over the funnel while water is squirted up into the beaker from the wash bottle. For this purpose a short piece of rubber tubing should be inserted between the wash bottle and the jet, so as to form a flexible joint.

While the substance is drying make the following experiment. Weigh a sheet of filter paper, then heat it for a minute or two on the drying table and weigh it again. What conclusion ? Was there any difficulty in getting the second weight accurately ?

When the quartz is dry its weight must be determined. To do this, stand a weighed crucible on a perfectly clean piece of glazed paper, and scrape as much as possible of the quartz into it from the filter with a penknife. Then fold the filter paper twice across in the old creases and once again, roll it up tightly from the point to the outside, and twist the platinum wire[1] spirally round it. (Fig. 5.) Then light this roll and let it burn completely to ash, holding it over the crucible during the operation. When burnt, shake it into the crucible, and sweep in, by means of a
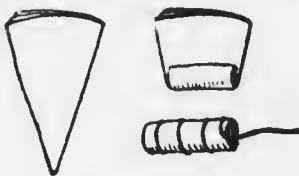
FIG. 5.

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[1] *Caution.* Articles of platinum should never be touched when hot by any metal (except iron) as fusible amalgams are very easily formed. It should also be remembered that platinum is injured by a *smoky* flame.

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camel's hair brush, any quartz and ash that have fallen on the paper The crucible must then be heated until no further change in weight occurs.

To find the weight of the filter ash, burn five papers as above (one by one), collect them in a crucible and weigh them together. (Do not mistake black, charred paper for ash.)

What objection would there be to weighing the filter paper before filtering off the quartz, and then subtracting this weight from the combined weight of quartz and paper ?

Note. In many cases the substance to be weighed is partially altered by heat or by the action of the paper, and consequently this method cannot be employed in such cases unless the changed material can be restored to its original form before weighing.

What is the per cent. difference between the weights of quartz and of salt found and those originally taken ?

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SECTION XIV

"PRECIPITATION OF COPPER"

It is often necessary to determine the quantity of one soluble substance in the presence of another. In this case it is necessary to convert one of them into an insoluble material, the relation between the weight of which, and that of the substance to be determined, can be found.

Exp. xxii. Dissolve a little copper sulphate (*Exp. i*) in water, in a test tube. Test it with litmus. Then add, drop by drop, potassium hydrate solution, testing after every few drops with litmus. Continue adding the alkali till apparently no further change is produced. Heat the liquid to boiling, filter the solution, test it with litmus, and add a drop more potassium hydrate to the filtrate. Add some ammonia. Do not forget to record quantities in all cases.

Exp. xxiii. Dissolve a minute piece of copper sulphate in a test tube of water and add some ammonia to it. Does the presence of potassium hydroxide interfere with the colour?

Was there any copper sulphate in the filtrate from *Exp. xxii*? Why was the litmus not turned blue after the first few drops of potassium hydroxide had been added to the copper sulphate? Why did the filtrate turn litmus blue? Find out if the black substance is at all soluble in water. (See *Exp. iv*, p.4.)

SECTION XV

Exp. xxiv. The experiments with copper sulphate (*xxii* and *xxiii*) lead to the conclusion that the whole of the copper can be removed from the heated solution by potassium hydrate and converted into a black substance insoluble in water. The fact that there was no copper left in the filtrate shows, moreover, that it is not soluble in potassium hydrate solution. This substance is copper oxide. (The blue, flocky material formed on adding the alkali to the cold solution was copper hydroxide, which on being warmed was converted into the oxide by loss of water.) This oxide then will be a convenient substance into which to convert copper salts in order to separate them from other soluble materials. It remains to be found exactly how much copper is represented by a certain amount of copper oxide.

Weigh out accurately about 0.2 g of cleaned copper wire, add just enough conc. nitric acid to dissolve the metal, dilute to about 100 cc with water, heat nearly to boiling, and then add potassium hydroxide solution in slight excess of the amount necessary to convert the copper completely into copper oxide, *i.e.*, till the liquid turns litmus blue. It is to be noted that nitric acid does not behave like other acids in its action on metals. The reason for this is that besides being an *acid* it is an *oxidising agent*, that is, it gives off oxygen readily to substances which are easily oxidised (see p. 81). Thus, the hydrogen which would otherwise be given off as a gas is oxidised to water and the nitric acid is changed to a brown gas (oxides of nitrogen) which is evolved.

The copper oxide must next be separated completely from the solution which contains the excess of potassium hydroxide and the nitric acid which was originally added, and must then be dried on the paper. (How can the separation be made complete? See *Exp. iv*, p. 4.) In burning the filter paper some of the copper oxide will become reduced to copper by the carbon of the paper. (Cf. Action of hydrogen on copper oxide, *Exp. xiii*, p. 11), and consequently the following procedure must be adopted. Remove as much as possible of the oxide to a clean, smooth sheet of paper, then burn the filter and drop the ash into the crucible. To this add one drop of conc. nitric acid and warm gently till dry. Finally add the rest of the precipitate to the crucible and heat strongly till the weight is constant. (The nitric acid dissolves the copper, forming copper nitrate which decomposes, on heating, into copper oxide and gaseous oxides of nitrogen.)

This whole determination, and all others of a quantitative nature, must be carried out *in duplicate*, as little reliability can be placed on a single determination, however experienced the worker may be. The per cent. difference, moreover, in the two results, gives an idea of the probable accuracy of the method. (See p. 84.) To save time, the two experiments should be performed as far as possible simultaneously.

Calculate from each experiment the amount of copper which corresponds to one gram of copper oxide. Find also the *reacting weight* of copper from the results. (The particular multiple of the amount that reacts with 16 g oxygen is taken as *one* in this case. See Atomic weights, p. 75.)

CHEMICAL REACTION IN SOLUTION. MEASUREMENT OF LIQUIDS

Exp. xxv. In *Exp. xvi*, p. 19, it was found that a certain quantity of sulphuric acid would react with a definite quantity of magnesium and no more.   Similarly, in *Exp. xvii*, only a limited quantity of magnesium oxide would react with a certain amount of acid.   When this point was reached the power of turning litmus red and other acid properties disappeared and a solution was produced which was found to contain a *salt* (see p. 21).   If these reactions had been carried out under varying conditions of temperature, pressure, etc., the *composition* of the product would have been found to have been the same in each case (although perhaps the rate of formation and quantity produced might have been different).   They are, therefore, *chemical reactions*, as distinguished from *solution*, in which the composition of the product varies with the conditions.   (Cf. *Exps. xviii* and *xix*, and Appendix, p. 75).   It was explained further in Section X, p. 21, that the potassium hydrate bottle contained a solution of a substance somewhat analogous to magnesium oxide, namely the hydroxide of potassium.   Find how many drops of this solution are necessary to exactly remove the acid properties of 20 drops of dilute hydrochloric acid.   Try the same experiment with 40 drops. See if raising the temperature affects the ratio.

In order to determine these and similar relations more accurately, it will be necessary to have some more accurate and convenient method of measuring liquids than by counting drops.   For this purpose make a *pipette*, a *burette* and a *measuring flask*.

The *pipette* should be made from a piece of glass tubing about 1 cm in diameter and 15 cm long.   One end must be drawn out to a fine point in the flame of the Bunsen, and a slight constriction must be made about 5 cm from the other end.   At the narrowest part this constriction must not be less than 5 mm in diameter.   The upper end must be cut off straight and rounded slightly in the flame.   (See Glass Blowing, p. 85) Round the constricted part, stick a narrow band of gummed paper, and cover it with melted paraffin.   Fill the tube to the top edge of the band with water, by suction, and then run the liquid into a test tube previously weighed with a cork.   (The last drop may be blown out.)   The weight of the water gives the number of cubic centimetres which the pipette will deliver.   The weighings need be made only to a centigram. (Why?)   With the help of this pipette a definite volume of liquid can be quickly and accurately measured out.

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A *burette* is an instrument for measuring out varying quantities of liquid. It can be made as follows. Take a tube about 45 cm in length and 1 cm in diameter. Draw out one end to a diameter of about 5 mm. Attach to this end, by means of about 4 cm of rubber tubing, a short piece of glass tube drawn to a fine point, as in Fig. 6, having previously inserted in the rubber an oblong bead of glass, made by rounding in the flame about 5 mm of glass rod. When the burette is filled with liquid this bead completely closes the lower end of the tube, but by slightly pinching the rubber at the side the liquid may be allowed to flow past the bead and to drop from the burette in any desired quantity.

To *graduate* the burette proceed as follows. First stick a narrow strip of paper along the whole length of the tube, nearly fill the tube with water and make a fine pencil mark exactly at the meniscus of the liquid. Always read from the same part of the meniscus and keep the eye at the same level as the reading to avoid parallax. The most convenient part to read from is the lower edge of the dark band seen on holding a piece of white paper behind the burette. (See Fig. 6). Next fill the pipette with water, allow it to run out again, blowing out the last drop exactly as before, and then, closing the point firmly with the finger, run in water from the burette till the pipette is filled exactly to the mark.
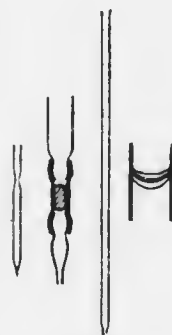
FIG. 6.

(For this purpose it will be convenient to hang the burette by a string to the shelf). After the liquid has had time to run down the walls of the burette, make a mark on the paper at the meniscus. Repeat the operation till the burette is empty, and measure with millimetre paper the distance between the various marks on the tube. These will probably not all be exactly equal owing to the tube not being quite cylindrical. For short distances, however, the tube may be assumed to be uniform in bore. Calculate the number of millimetres to a cubic centimetre in each section of the tube and mark off the latter accurately on the paper, numbering them from the top of the burette.[1] The strip of paper may be made water-proof by warming the whole burette by passing it quickly backwards and forwards through the Bunsen flame and then rubbing the paper with a lump of paraffin wax.

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[1] The position of each mark should be measured from the top of the burette and not from the preceding mark. By the latter method a large error would have accumulated by the time the bottom of the burette was reached.

The *measuring flask* is made from a small r   flask by gumming a strip of paper evenly round the neck about h   down, and weighing the vessel first dry, and then filled to the mark with water.

In using the burette the following precautions must be observed. Always wait a minute or so before making the readings in order to give the liquid time to run down the sides of the glass. The burette should always be washed out with the solution to be subsequently used in it. Since the readings cannot be judged to a greater accuracy than about 0.1 cc, at least 15 or 20 cc of liquid must be used in each measurement to insure an accuracy of 0.5%. (See Appendix, p. 84).

SECTION XVII

VOLUMETRIC ANALYSIS

Exp. xxvi. In the preceding section you found that a definite quantity of potash solution was required to remove completely the acid properties of a definite quantity of hydrochloric acid, or to "neutralise" it. Quantities of acids and bases which exactly neutralise each other are called "equivalent quantities." Make up the following solutions as they are required. "Diluted hydrochloric acid": 1 pipetteful of dil. hydrochloric acid made up to the volume of the measuring flask with distilled water; "Diluted sulphuric acid": 1 pipetteful of dil. sulphuric acid diluted to volume of measuring flask; "Diluted potassium hydrate": 3 pipettefuls of potassium hydrate diluted to volume of measuring flask.

With these solutions make the following comparisons, using a few drops of a dilute alcoholic solution of phenol phthalein instead of litmus paper for determining the point of neutralisation. (1) Find the number of cubic centimetres, A, of diluted hydrochloric acid which neutralise 1 cc of diluted potassium hydrate. (2) the number of cc, B, of the barium hydroxide solution provided which neutralise the A cc of diluted hydrochloric acid, (3) the number of cc, C, of diluted sulphuric acid which neutralise the B cc of barium hydroxide solution, (4) the number of cc, D, of diluted potassium hydroxide which neutralise the C cc of diluted sulphuric acid.

In making these experiments the pipette should be used for measuring out one of the solutions into a beaker, while the other solution is added from the burette. If much more of one solution is required than of the other, naturally the pipette should be employed for measuring the smaller volume. It must be remembered that so many pipettefuls must be taken that the burette reading may be sufficiently large to ensure accuracy. Each comparison must be made in duplicate, or until good agreement is obtained. Tabulate the results as follows:

1 cc diluted potass. hydrox...reacts with...A cc diluted hydrochl. acid.
D cc   "   "   ⟶

  ⬆   react with   react with   ⬇

C cc diluted sulphuric acid...react with...B cc barium hydroxide sol.

Can you account for the peculiarity of the result?

Exp. xxvii. Weigh out accurately on a watch glass about 1 g oxalic acid, dissolve it in water and make up the volume to that of the

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measuring flask. Find how many cc of this solution react with one cc of the barium hydroxide solution. The formula of oxalic acid has been found by analysis to be $H_2C_2O_4.2H_2O$. What is its reacting weight (formula weight)? How many reacting weights per litre are there in the solution you have just prepared? Now, experiments have shown that oxalic acid combines with barium hydroxide (to form barium oxalate) in the proportion of *one* reacting weight of the former to *one* of the latter. Assuming this, calculate the number of reacting weights of barium hydroxide per litre in the solution provided.

It has been found further that the particular multiples of the reacting weights involved in the other reactions you have investigated are as follows: Barium hydroxide reacts with sulphuric acid in the proportion of 1 RW to 1 RW. Potassium hydroxide with hydrochloric acid, 1 to 1, hydrochloric acid with barium hydroxide, 2 to 1, and potassium hydroxide with sulphuric acid, 2 to 1. Taking these facts for granted (which themselves, of course, are the result of careful analysis) calculate the number of RWs per litre of the various chemical substances in the reagent solutions.

Note. It may be found that phenol phthalein does not show the "end point" sharply, and that the pink colour keeps fading as the alkali is added. This is due to a little potassium carbonate in the potassium hydroxide solution, formed by the absorption of carbon dioxide from the air. Add to a beaker containing water and phenol phthalein just enough potash solution to impart a slight pink colour to the liquid. Then breathe into the beaker.

LAW OF REACTING WEIGHTS IN SOLUTION

The peculiar result obtained in *Exp. xxvi*, of the preceding section, may be explained as follows[1]. When the acid was neutralised by the alkaline solution a *complete* reaction took place between chemical individuals, *i.e.*, the whole of the acid reacted with the whole of the base, forming a salt[2]. That this was the case was proved by the fact that at a certain point both acid and alkaline properties entirely disappeared. In all *chemical reactions* the quantities taking part are proportional to simple multiples of the reacting weights (p. 16). Consequently, when the potash reacted with the hydrochloric acid it must have done so in the ratio of 1 RW of potash to 1 (or some simple multiple) RW of hydrochloric acid. If, then, x represents the number of RWs of potash (KOH) in 1 cc of solution, that is, if x is the fraction of 56.16 g potash in 1 cc, there must have been the same number, x (or some simple multiple of x) RWs of hydrochloric acid in the A cc required to react with the potash. Similarly, there must have been x RWs (or simple multiple) of barium hydroxide in the B cc of barium hydroxide solution, and x RWs (or simple multiple) of sulphuric acid in the C cc of sulphuric acid solution. It is natural, therefore, that these C cc of sulphuric acid solution should exactly react with the 1 cc (or simple multiple) of potash solution. These experiments afford another illustration of the law of reacting weights. They are also an example of a very important practical method of analysis, known as the "volumetric" method.

From the results of the determination of the number of RWs of barium hydroxide per litre in the solution provided (*Exp. xxvii*) calculate the number of *grams* of the substance per 100 cc of solution. The formula of barium hydroxide is $Ba(OH)_2.8H_2O$. Try to make up a solution from solid barium hydroxide of the same concentration as the given solution, and see how nearly it corresponds with the latter by "volumetric analysis." Two causes will prevent the result turning out quite

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[1] This experiment is given here as an *illustration* of the law of reacting weights. As a matter of history, however, this was one of the first experiments that led to the discovery of the law.

[2] This statement is not literally correct. An acid solution reacted with an alkali solution to give a salt solution, so that *none* of these substances are really chemical individuals. In such cases, however, it is often convenient to think of the reaction as taking place independently of the solvent. The justification for this is that the pure acid and pure hydroxide *might* have been taken, water added, the salt formed, and finally the water removed again by evaporation, leaving pure salt.

accurately: firstly, the barium hydrate will contain a little carbonate, and secondly, some will have become changed to another compound, $Ba(OH)_2 H_2O$, by evaporation of water into the atmosphere. It is therefore not a good substance to take as a starting point for volumetric analysis, *i.e.*, from which to make up a solution containi g a known number of RWs per litre. Oxalic acid is rather better.

VOLUME RELATIONS OF GASES

The importance of reacting weights, in connection with the proportions by weight in which chemical substances react among themselves, has already been discussed (Sections VIII and XVIII). The following two experiments will illustrate their importance in reference to an entirely different law.

Exp. xxviii. To find the volume occupied by one reacting weight of hydrogen. Set up an apparatus according to the diagram (Fig. 7). The bottle *B* and the tube *D* must be filled completely with water. *C* is a beaker weighed to 0.1 g on the rough balance. Fill the flask *A* about three quarters full of water and drop in about 25 cm of magnesium ribbon, cleaned and weighed, and folded together tightly. When the apparatus is ready (air-tight) open *A*, pour in quickly about half a test tube of dilute hydrochloric acid and replace the cork immediately. The volume of water forced into the beaker is equal to the volume of hydrogen evolved and can be determined by weighing on the rough balance.
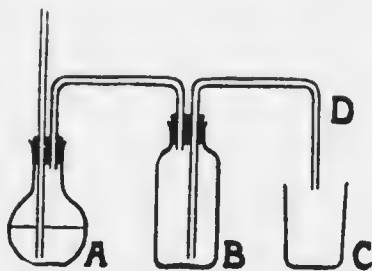
FIG. 7.

Calculate from the result the volume of hydrogen at 0° and 760 mm pressure that would be given off by one reacting weight of magnesium. By the law of reacting weights this amount of hydrogen must weigh some simple multiple of its reacting weight, 1.01. What multiple it is can be seen from your equation calculated from *Exp. xiv*, p. 13.

Exp. xxix. To find the volume occupied by one reacting weight of oxygen. Weigh accurately a test tube containing about half a gram of potassium chlorate. This substance gives off oxygen on heating and leaves potassium chloride. Fit the test tube with a well-bored cork and delivery tube, and connect the latter by a piece of rubber tube to the gas-measuring apparatus used in the last experiment. Next heat the test tube carefully until finally the moulten substance has become completely solid. Some gas will have been driven over into the pickle bottle by the expansion of the oxygen in the test tube by heat. In order that this may not introduce an error in the result the beaker must be

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[1] This section may be omitted or postponed without affecting the continuity of the course.

raised so that the end of the tube D dips below the surface of the water, and must be held in that position until the apparatus is quite cold and no more water is sucked back into the bottle.

From the weight of the water and the decrease in the weight of the test tube, calculate the volume occupied by one reacting weight of oxygen at standard temperature and pressure.

For both experiments the temperature of the room and the barometric pressure must be known.

What relation do you find between the reacting weights and volumes of the two gases ? The results illustrate a very important general law.

SECTION XX

SOME EXPERIMENTS TO ILLUSTRATE THE INFLUENCE OF CONDITIONS
ON REACTIONS

Exp. xxx. The quantities mentioned in the following directions may be measured with sufficient accuracy in a test tube which has been graduated into cubic centimetres on a strip of paper by means of the burette. Make the following experiments.

(a) Dilute 2 cc lead acetate solution to 10 cc and add 10 drops of dilute hydrochloric acid.

(b) Repeat (a) heating the solution to boiling before adding the acid.

(c) To 5 cc barium chloride solution add concentrated hydrochloric acid drop by drop till about 5 cc have been added.

(d) Dilute 1 cc barium chloride to 5 cc and add the same amount of concentrated hydrochloric acid as in (c).

(e) Dilute two drops of potassium bichromate solution to 20 cc, divide this into two parts and add to one part 2 cc of dilute sulphuric acid. Then to both solutions add 5 drops of silver nitrate solution.

(f) To about 3 cc of the following solutions: ammonium chloride, calcium chloride and sodium chloride (made by dissolving a little common salt in water), add 3 drops of silver nitrate solution.

(g) Repeat (f), but before adding the silver nitrate, add to each solution about 3 cc of 5% sodium thiosulphate solution.

(h) To about 3 cc of 5% alum solution add, drop by drop, potassium hydroxide solution till about 2 cc have been used.

SECTION XXI

A REVERSIBLE REACTION

The experiments described in the last section and others performed during the course show that changes often occur in the nature of substances and that these changes depend, to a very large extent, on various conditions such as temperature, amount and concentration of materials and the presence or absence of certain substances. It is evident, therefore, that in order to produce any desired result, the necessary conditions must first be discovered; and further, in order to be sure of reproducing the effect in question, these conditions must be rigidly adhered to. A study of the general principles which govern chemical reaction will simplify the problem of finding out these conditions in the innumerable special cases to be met with in the chemical laboratory. The following experiments will serve to illustrate one of the most important of these principles.

Exp. xxxi. Make up a test tubeful of a solution of potassium permanganate, so dilute that on looking through the tube from end to end at a piece of white paper a distinct light purple colour is seen. Pour this solution into two test tubes to exactly the same depth of about 5 cm, and compare the appearance on viewing a piece of white paper lengthwise through the tubes. Add water to one so as to double the depth of the liquid. Does any appreciable change occur in the shade of colour? Pour out the dilute solution till it stands at the same height as t. ~ "quid in the other tube. What is the appearance? It is clear that the colour of the solution may be used as a measure of the amount of potassium permanganate in the test tube. If the concentration of the solution is halved and the length of the column looked through is doubled the depth of colour remains unchanged. This is preliminary to the next experiment.

Exp. xxxii. Dilute one drop of ammonium sulphocyanate solution to 10 cc, and one drop of ferric chloride solution to the same volume. Mix these solutions together and divide the mixture in four test tubes so that the depth of liquid in each is the same. (On looking down at the paper through the four tubes the shade should appear the same in each if the solutions have been properly mixed.) To one test tube add a drop of ammonium sulphocyanate from the reagent bottle, to another add a drop of ferric chloride from the reagent bottle, and to a third add five drops of ammonium chloride solution. Use the fourth test tube for comparison. Can you explain why the addition *both* of ferric chloride and of ammonium sulphocyanate should increase the depth of colour?

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SECTION XXII

THE MASS LAW

The following is extremely important and should be read carefully. The last experiments showed that a red substance was produced by mixing ferric chloride solution with ammonium sulphocyanate solution, and further, that the amount of a coloured substance could be judged by the depth of colour of the liquid. It must be concluded, therefore, that the addition both of ferric chloride and of ammonium sulphocyanate to the solution produced *more* of the red substance. Now the fact that more ferric chloride produced more red substance shows that in the solution there must have been *some* ammonium sulphocyanate still unchanged, and similarly the formation of more red substance by addition of sulphocyanate shows that *some* unused ferric chloride was also present in the same solution. In other words, although ferric chloride and ammonium sulphocyanate react together to form a certain substance, this reaction is only *partial*, and *an increase in the concentration of either of the two substances increases the extent of the reaction.* Now from this solution a red substance may be obtained with the composition $Fe(SCN)_3$, called ferric sulphocyanate, and also ammonium chloride, NH_4Cl. It is, therefore, natural and convenient to suppose that the reaction in question takes place according to the equation:

$$FeCl_3 \ + \ 3NH_4SCN \ \rightleftharpoons \ Fe(SCN)_3 \ + \ 3NH_4Cl$$
(ferric chloride) (amm. sulphocyan.) (ferric sulphocyan.) (amm. chloride)
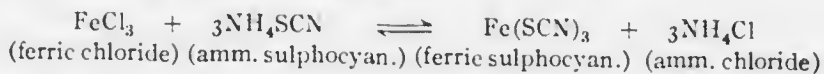
and that, as the reaction is not complete, *there will be some of all four substances together* in a solution made by mixing ferric chloride and ammonium sulphocyanate solutions. (See foot-note [2], p. 35).

In this reaction an increase in the concentration of the substances on the left side of the equation increased the amount of the ferric sulphocyanate (the red substance), and, of course, of the ammonium chloride also, *i.e.*, caused the reaction to proceed further "from left to right." It is not surprising, therefore, that an increase in the concentration of the *ammonium chloride*, on the right hand side, should drive the reaction " to the left," decreasing the amount of ferric sulphocyanate, as was shown by the experiment.

Such processes as this, which go either one way or the other depending on circumstances, are called *reversible reactions*, and the equations representing them are often written with the sign $\rightleftharpoons$ instead of the sign of equality.
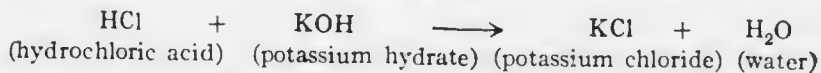
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Almost all reactions *in solution* are similar to the one just studied, but the degree of incompleteness is extremely varied. In every case, if the concentration of one of the substances is *increased* in any way (for instance, by adding more of it to the liquid), the reaction will proceed further in that direction which tends to *use up* that substance. Conversely, if the concentration of any substance is *decreased* (for instance, by the material falling out of the solution as a solid precipitate, or by its escaping as a gas), the reaction will take place in such a way as to *form more* of that substance. In every case the reaction proceeds until a definite relation between the concentrations of the various reacting substances has been reached.

For example, in the reaction between ferric chloride and potassium sulphocyanate, careful investigation of the colour of the solutions by Gladstone (1855) has shown that when equivalent quantities of the two salts are dissolved in water (1 formula weight of ferric chloride, $FeCl_3$, to 3 formula weights of potassium sulphocyanate, KSCN), about 17 per cent. of them become changed to ferric sulphocyanate and potassium chloride. Or, to take a special case, if 5.408 g ferric chloride and 9.725 g potassium sulphocyanate be dissolved in a litre of water these substances will go on reacting until 1.304 g ferric sulphocyanate and 1.268 g potassium chloride have been formed.[1] (How much of each would be formed if the reaction were complete ?) Addition of excess of *either* one of the original substances will, of course, make the reaction more nearly complete.

Gladstone also arrived at the important result that the same quantities of the four substances were produced whether he mixed equivalent amounts of ferric chloride and potassium sulphocyanate, or corresponding quantities of ferric sulphocyanate and potassium chloride. This is the criterion of true equilibrium. (See Appendix, p. 79, and compare results of *Exps. xviii* and *xix*.)

In the case of the neutralisation of acids by bases the reaction is very nearly complete, *e.g.*, in the process represented by the equation:

$$HCl \quad + \quad KOH \quad \longrightarrow \quad KCl \quad + \quad H_2O$$
(hydrochloric acid)   (potassium hydrate)   (potassium chloride)   (water)

the reaction goes almost completely in the direction indicated by the arrow, so that practically no acid or base is left free.

When, however, sulphuric acid is mixed with sodium chloride solu-

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[1] In this process equilibrium is reached almost instantaneously. Compare this with the reaction between solid salt and water, in which equilibrium was obtained only after several minutes shaking. (*Exp. xviii*). See Appendix, p. 79 and p. 80.

tion (or any salt) a *partial* formation of hydrochloric acid and sodium sulphate takes place, according to the equation :

$$H_2SO_4 + 2NaCl \rightleftharpoons 2HCl + Na_2SO_4$$

although, as all four substances are colourless, no change is visible to the eye. In the following experiment of a similar nature, however, the fact that reaction takes place is quite obvious.

Exp. xxxiii. Dissolve a little copper oxide in conc. hydrochloric acid. What is the colour of the solution ? Make up a saturated solution of copper sulphate, dilute about threefold, divide into two parts in test tubes, having a depth of about 4 cm in each tube, and add to one, drop by drop, conc. hydrochloric acid, until about one cc has been added. Explain the result.

One very important application of this effect of *concentration* on the final state (state of equilibrium) is the following. If for any cause a product of the reaction should be continually removed from the solution, then the reaction will proceed continually in the direction which tends to produce this substance until either the cause is removed or until the concentration of one or more of the reacting materials becomes reduced to a certain limit. Such a cause may result either from the " *insolubility*" (slight solubility) of one of the products of the reaction, in which case it separates out from the solution as fast as it is formed, or from the volatility of one of the products in which case the substance passes out of the solution as a gas. In both these cases the reaction becomes practically complete. But it must be remembered that the term " complete " is only relative, as no substance is strictly insoluble, and that the completeness will depend on the degree of insolubility of the product of the reaction and upon the concentrations of the reacting substances.

The law relating to the effect of concentration on reaction is called the *Mass Law*.

SECTION XXIII

APPLICATIONS OF THE MASS LAW

Make the following experiments, considering the results carefully from the point of view of the discussion in the preceding section. If you know, from any source, the equations of the reactions involved, write them in the note book. Considering the results of recent experiments it will hardly be necessary to remind you of the necessity of stating *quantities* in every case.

Where substances are not otherwise designated the laboratory reagent solutions are to be understood.

Exp. xxxiv. Dilute 2 cc lead acetate solution to 20 cc. Dilute 2 cc of this solution to 20 cc, thus obtaining a solution of the original acetate diluted in the ratio of 1 : 100. In this way make up a set of four solutions of the acetate diluted in the ratios of 1 : 10, 1 : 100, 1 : 1000, and 1 : 10000, labelling the test tubes accordingly. Using a fresh quantity of these each time add to about 4 cc of each 10 drops of the following : dilute hydrochloric acid, dilute sulphuric acid, potassium iodide, ammonium sulphide. The reagents should be added drop by drop, and the solutions should be vigorously shaken after each addition, as the latter often hastens precipitation. (Cf. *Exp. iii*, and see Appendix, p. 80.) Tabulate the results. What conclusions can be drawn as to the relative solubility of the chloride, sulphate, etc., of lead?

Exp. xxxv. Dissolve about half a gram of sodium chloride in 3 cc of water in an evaporating dish, and add to the solution about 5 cc conc. sulphuric acid, keeping the dish in the fume cupboard. Dilute a few drops of the liquid with water and add a drop of silver nitrate solution. (The white ppt. is silver chloride and is a delicate test for the presence of *chlorides*, including hydrochloric acid). Next heat the dish to boiling for at least five minutes, allow the liquid to cool completely, and, after diluting, again test a few drops with silver nitrate. Write a full explanation of the result.

DISSOCIATION OF SALTS IN WATER

On comparing the results of the experiments of Section XII, p. 23, as recorded in your tables, it will be seen that in each horizontal and vertical column there are sets of properties which are identical throughout.

For instance, all the solutions in the vertical column headed "Copper" are of the same shade of blue, and all give black precipitates with ammonium sulphide.

Again, all the solutions under " Hydrogen," *i.e.*, all acids, are sour, turn litmus red and evolve hydrogen with magnesium.

Similarly, in the horizontal rows, the solutions opposite "Bichromate" are orange in colour, give red precipitates with silver nitrate and a yellowish green precipitate with ammonium sulphide.

All the solutions opposite "Chloride" give a white, curdy precipitate with silver nitrate; and so on throughout the table.

In fact, careful inspection of the tables shows that all the properties investigated *may be divided into two groups in each case, as if each solution contained two independent component substances, each with constant characteristic properties.* (In these cases the properties are said to be "additive.")

Nomenclature of salts dissolved in water. The substance that causes the transparent blue colour, and the black precipitate with ammonium sulphide is called *copperion* (or cupricion), to distinguish it from copper which is opaque and red. The colourless substance which causes the white precipitate with silver nitrate is called *chloridion*, to distinguish it from chlorine, which is a yellow gas. Similarly the names of the other substances common to the vertical columns are: hydrogenion, potassiumion, ammoniumion, calciumion and bariumion, and to the horizontal rows : sulphation, nitration, chloridion, acetation, and hydroxidion.

It is also convenient to use special symbols for the chemical units of weight, or reacting weights, of these so-called *ions*. They may be formed by appending dots·, in the case of metals and similar substances (cations), and dashes′ in the other cases (anions), to the ordinary symbols of the substances.[1]

H·, for instance, means 1.01 gram of hydrogenion, just as H means 1.01 g hydrogen. Cl′ means 35.45 g chloridion, just as Cl means 35.45 g chlorine, etc.

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[1] It is customary to indicate the *valency* of the substances (p. 77) by the number of dots or dashes appended.

According to this nomenclature, for example, aqueous solutions of hydrochloric acid contain, besides the water, *hydrogenion* and *chloridion;* aqueous copper sulphate solutions, *copperion* and *sulphation*, and so on.

From the results of the experiments (from Section XII) write down the properties, as far as you have ascertained them, of hydrogenion, bariumion, sulphation, and leadion (plumbicion). Any further properties of leadion that you may discover in spare time may be recorded. They will be useful later.

The principle of additive properties and the conception of ions, make it very easy to remember the properties of a great many salts. For when the properties of a comparatively small number of ions are known, the properties of the solutions of all the various possible pairs can be obtained by simply adding together the two sets of properties for the individual ions. It will be seen later that this generalisation is very important in chemical analysis. It is embodied in the theory of electrolytic dissociation, or the ion theory.

What properties would you expect to find in dilute solutions of chromic acid and of copper chromate ? What common properties of alkaline solutions have you observed ? To what constituent would you attribute them ?

It must be carefully noticed that the law just discussed, namely, that the properties of salts (the term salt here includes acids and bases) dissolved in water are the sum of the properties of two components, each with constant characteristic properties, applies *only to dilute AQUEOUS* solutions. What are the colours of the *solid* copper salts and the *alcoholic solutions* of copper chloride, nitrate and acetate, provided for inspection ?

SECTION XXV

SOME EXPERIMENTS ON DISSOCIATION

The following experiments will lead to another generalisation of great importance.

Exp. xxxvi. Prepare some of the red solution of ferric sulphocyanate described in *Exp. xxxii*, p. 40. Take equal depths of about 5 cm each in two test tubes, dilute one with an equal volume of water and look down through both tubes at a piece of paper.

Exp. xxxvii. Take a little copper chloride (about 2 grams) and, roughly, twice the quantity of copper sulphate. Dissolve them separately in as little water as possible with the aid of heat. (The chloride will require only two or three cc.) Note the colours of the solutions. Then dilute both to about 20 cc and note the colours again.

Exp. xxxviii. Make up a little solution of copper chloride and note the change in colour produced by adding concentrated hydrochloric acid.

Are the results of these experiments what you expected? Can you think of any explanation of them ?

SECTION XXVI

APPLICATION OF MASS LAW TO DISSOCIATION

The results of the experiments of Section XXV might seem at first sight to stand in contradiction to the generalisation arrived at in Section XXIV, namely, that dilute aqueous solutions of salts appear to contain two independent component substances. (Read pages 45 and 46 again carefully.) According to this law, copper chloride and sulphate solutions should be both *blue*. (Why?) whereas *Exp. xxxvii* shows that the strong solutions of these salts are *green* and *blue* respectively. A careful consideration of the facts, however, leads, not to a contradiction, but to an amplification and extension of the principle. If it be assumed, namely, that when a salt (or acid or base) is dissolved in water it is only *partially* broken up, or " dissociated," into two independent substances —ions—then these facts, and innumerable others besides, appear at once clear and connected.

Let us consider some of the facts from this point of view.

(a) Acids have certain common properties, but possess these properties in varying degrees of intensity. (Sections IX and X.)

Explanation. Every acid is partially dissociated into two substances. For instance, hydrochloric acid dissolved in water is partially broken up into hydrogenion and chloridion according to the equation :

$$HCl^\circ \rightleftharpoons H^\cdot + Cl'$$

so that the solution contains three things, namely, undissociated hydrochloric acid,[1] hydrogenion and chloridion. Similarly in the case of sulphuric acid and acetic acid :

$$H_2SO_4^\circ \rightleftharpoons 2H^\cdot + SO_4'' \text{ and } HCH_3CO_2^\circ \rightleftharpoons H^\cdot + CH_3CO_2'$$

in which, again, only *partial* dissociation is assumed.

The common properties of acid solutions are thus accounted for by the presence of the common substance, hydrogenion. The varying *intensity* of these common properties, or the difference in " *strengths* " of

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[1] It is unfortunate that although special words have been coined to designate the ions into which substances are supposed to dissociate no simple nomenclature has been introduced for the part of the substance remaining *undissociated*. When it is necessary to represent this part by a chemical symbol it is suggested that the sign ° be appended to the ordinary chemical formula of the compound. The sign HCl°, for instance, may be employed for one reacting weight of the undissociated part of hydrochloric acid when it is desired to consider this part separately. When the acid is considered as a whole, without reference to its dissociation, the ordinary formula HCl should be used

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the acids, is explained by the varying extent of the dissociation. Acetic acid, which tasted less sour than the others and reacted less vigorously with magnesium (*Exp. xv*, p. 19), is assumed to be only slightly dissociated, *i.e.*, to consist *chiefly* of undissociated hydrogen acetate and *a little* hydrogenion and acetation, while hydrochloric acid, and strong acids generally, consist *almost entirely* of hydrogenion and the other ion, and contain very little undissociated substance. (See list, p. 83.)

(b) Strong solutions of copper sulphate and chloride are *different* in colour, while dilute solutions are the *same*.

Explanation : Copper chloride is partially dissociated as follows :

$$CuCl_2{}^{\circ} \rightleftharpoons Cu{}^{\cdot\cdot} + 2Cl{}'$$
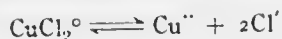
Now according to the mass law a decrease in the concentration of the undissociated copper chloride will cause some of the copperion and chloridion to unite to form more copper chloride, and a decrease in the concentration of *either* the copperion or the chloridion will cause some of the copper chloride to dissociate into the two ions. When the *whole solution* is diluted the concentrations of all three substances are momentarily reduced to the same extent, *i.e.*, for *one* substance whose concentration is reduced on the left of the equation *two* are reduced in concentration on the right. The effect of these two will overbalance that of the one, and as a final result of the dilution, more of the copper chloride will dissociate to form chloridion and copperion. Now undissociated copper chloride is *yellow*, while copperion is *blue*. Hence, the greater the dilution the more blue substance in solution and the less yellow.

Explain in the same way the change in colour that occurs on diluting a solution of ferrie sulphocyanate. (*Exp. xxxvi*, p. 47.)

Note. Ferricion is almost colourless and sulphocyanation quite colourless.

Try to explain also the result of *Exp. xxxviii* and the precipitation of barium chloride solution by concentrated hydrochloric acid, (*Exp. xxx*, (c), p. 39.)

Exp. xxxix. Make a *saturated* solution of sodium chloride in a test tube. (See *Exp. xviii*, p. 22) In another test tube, fitted with a cork and bent delivery tube, generate hydrogen chloride gas by adding conc. sulphuric acid to dry sodium chloride and warming, and bubble the gas into the sodium chloride solution. There are two good applications of the mass law in this experiment. Explain them.

For further illustrations see p. 82.

SEPARATION AND IDENTIFICATION OF SUBSTANCES

The formation of *insoluble precipitates* (the word " insoluble " is often used for " slightly soluble ") affords a means of separating and identifying the different constituents of a solution of several substances. This problem of separating and identifying is much simplified by the principle discussed in Section XXIV, by virtue of which many substances (most acids, bases and salts),behave as if they were partly dissociated in aqueous solution. For instance, nearly all the salts of *lead* may be considered partly dissociated into leadion and the corresponding acid-ion, so that any reagent which forms a precipitate with *leadion* will give this precipitate with nearly all lead salts. Similarly, nearly all *sulphates*, including sulphuric acid, will give the same precipitate with a reagent for *sulphation*. (Compare effect of barium chloride on sulphuric acid and magnesium sulphate, *Exp. xv*). It is, therefore, possible, for instance, to speak of " tests for lead " (leadion) and " tests for sulphuric acid " (sulphation) without reference to the acid or base with which they may be respectively connected.

In order to be able to make such separations and identifications, a very comprehensive and detailed knowledge of the compounds of the various bases and acids is necessary, especially in regard to the *conditions* under which these will form *precipitates* with certain reagents.

With this end in view, make a detailed investigation of the reactions of lead acetate solution with the following reagents : Sodium carbonate, dil. hydrochloric acid, potassium bichromate, potassium hydroxide, potassium iodide, dil. sulphuric acid, and dil. nitric acid. Some of the experiments have already been performed and need only be referred to here by number. In each case investigate the effect on the reaction of : (a) *excess* of the reagent, (b) presence of nitric acid, (c) *excess* of potassium hydroxide, and in the case of the hydrochloric acid, the effect of temperature and concentration. The term " excess " is necessarily somewhat vague, but the table of concentrations of laboratory solutions, p. 88 will help you to decide in each case what volume of one solution will exactly react with a certain volume of another. The concentrations are expressed in "formula weights per litre,"[1] and, therefore, represent the numbers of

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[1] The number of formula weights is the number of grams divided by the reacting weight represented by the formula For instance. a solution of sodium chloride with 5.85 g sodium chloride (NaCl) per litre would contain:

$$\frac{5.85}{23.05 + 35.45} = 0.10 \text{ form. wts., per litre.}$$

reacting weights of the various substances per litre. (If you are not yet quite clear as to why this is so make a point of having it explained to you.) It must be remembered that these reacting weights will not always express the proportions in which the substances in question combine; but some *simple multiple* of these weights will in every case give the proportions. In many cases you will be able to make a fairly safe guess at the chemical equation (see " Valency," p. 77), and therefore at the multiples of these reacting weights which express the proper proportions.

The following illustration will make this clearer. Find how many cc dil. hydrochloric acid sol. exactly react with 1 cc lead acetate sol. The concentration of the laboratory lead acetate is given in the table as 0.24 formula wts. per litre; that of hydrochloric acid as 4. Now the valency of lead is 2 and chlorine 1 (see p. 78); the formula of lead chloride is therefore *probably* $PbCl_2$ and the equation is therefore *probably*

$$Pb(C_2H_3O_2)_2 + 2HCl = PbCl_2 + 2HC_2H_3O_2$$
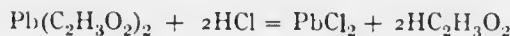
or *one* formula wt. of lead acetate requires *two* formula wts. of hydrochloric acid. (Experiment has shown that this is the case.)

1 litre lead acetate sol. contains 0.24 form. wts. (by table)

∴ 1 cc lead acetate sol. contains 0.00024 form. wts.

∴ 1 cc lead acetate sol. requires 2×0.00024 form. wts. of HCl,

but 4 form. wts. HCl are contained in 1 litre or 1000 cc of lab. sol.

∴ 2×0.00024 form. wts. cont'd in $\dfrac{2 \times 0.00024 \times 1000}{4}$ = 0.12 cc lab. sol,

∴ 1 cc lab. lead acetate sol. requires 0.12 cc lab. hydrochl. acid.

Having ascertained the equations (from a text-book or otherwise) make a rough calculation of this kind for each of the seven reagents, and collate the results, together with all the observations, in the form of a table as on p. 52.

Only small quantities of the solutions should be used, but they must, of course, be mentioned in the note book.

Note. The addition of excess of the reagent in many cases causes an entirely different reaction to take place, in which a larger multiple of the reacting weight of the reagent combines with the other substance. (See law of reacting wts., multiple proportions, p. 16). Example : Lead acetate and potassium hydroxide react together to form insoluble lead hydroxide in the proportion of one RW lead acetate to two RWs potassium hydroxide, whereas if " excess" of potash be used, one RW lead acetate reacts with *four* RWs potassium hydroxide to from a soluble substance called potassium plumbite, K_2PbO_2.

SECTION XXVIII

The following tables, which embody the results of experiments similar to those described in Section XXVII, give the solubilities of the commoner compounds of *lead*, *mercury*, *silver*, *copper*, *bismuth*, and *cadmium*. The column headed "in water" will apply also to dilute solutions of salts, such as those produced when the ordinary reagents are added to solutions of salts of the metals in question.

cc Reagent to 1cc lead acetate		LEAD								MERCUROUS							
		Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reag.	In Dil. Acids	In Potash	In Sod. Thiosul.	Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reag.	In Dil. Acids	In Potash	In Amm. Chloride
.12	Acetate	Wt	S	S		S	S	S		Wt	s(^{a})		d		s		
	Bromide	Wt	s			S	s	S		Wt	i		d	i	i		
	Carbonate	s								GvBk	i		d				
	Chloride									W't	i	Bk	d	i	i	d	
	Chromate	(^{1})								Yw	i	Bk	d	i	i	d	
	Cyanide	Wt	i			s		S			KCN ppts metal. Hg						
	Ferrocyanide	Wt	i			i	i	S		Wtgl	i	Bk	d			d	
	Ferricyanide	Bn	s					s		RdBn	i	Bk	d				
	Hydroxide										potash ppts Hg₂O						
	Iodide								S	GnYw	i	Bk	d	s			
	Nitrate									Wt	S(^{a})	"	d		S		
	Oxalate	Wt	i			i	S	S		Wt	i	"	d	i	s	d	
	Oxide	Yw	i							Bk	i	i		i	S	i	
	Phosphate	Wt	i			i	S	S		WtYw	i	Bk	d	i	S	d	
	Sulphate								S	Wt	s(^{a})	"			s		
	Sulphide	Bk	i	i	i	i	i(^{4})	i			H₂S ppts HgS & Hg						
	Sulphocyanate	Yw	s					S		Wt ?	i						
	Thiosulphate	Wt	s			S		S		Wt	s			S			

		SILVER								MERCURIC							
		Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reag.	In Dil. Acids	In Potash	In Sod. Thiosul.	Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reag.	In Dil. Acids	In Potash	In Amm. Chloride
	Acetate	Wt	S	S	S	S	d	S		Wt	S(^{a})						
	Bromide	LYw	i	s	S	s	i	i	S	Wt	s		S				
	Carbonate	LYw	i	S	S	S	S	i	S	Bn	i	s	S				s
	Chloride	Wt	i	S	S	i	i	i	S	Wt	S(^{a})						
	Chromate	RdBn	i	S	S	i	s		S	Rd	s						
	Cyanide	Wt	i	S	S	S	d		S	Wt	S		S				
	Ferrocyanide	YwWt	i	i	S	i	i(^{3})		S	Wt	i		S	i			s
	Ferricyanide	RdBn	i	S	S	i			S	Yw	i		S				
	Hydroxide		potash ppts oxide								potash ppts oxide						
	Iodide	LYw	i	i	S	S	i	i	i	Rd(^{a})	i		S	S	s		S
	Nitrate	Wt	S	S	S	S	S		S	Wt	S(^{a})		S		S		
	Oxalate	Wt	i	S	S	s	S		S	Wt	i not ptd from HgCl₂						
	Oxide	BnGy	i	S	S		S		S	RdYw	s		S				S
	Phosphate	Yw	i	S	S	i	S		S	Wt	i		S		S		S
	Sulphate	Wt	s	S	S	s	s		S	YwWt	s		S				
	Sulphide	Bk	i	i	i	i	i(^{4})	i	i	Bk	i	i	i	i(^{5})	i	i	
	Sulphocyanate	Wt	i	S	S	s			S	Wt	s(^{a})		S	S			
	Thiosulphate	Wt	i(^{a})	S	S	S	d		S								

SOLUBILITY TABLES

Notes to the Tables on opposite page and additional Information.

Abbreviations : i very insoluble, s slightly soluble, S soluble, d decomposed, Bk black, Be blue, Bn brown, Gn green, Gy gray, Rd red, Wt white, Yw yellow, L light, gl gelatinous.

The terms "excess of reagent" and "dil. acids" are necessarily vague, the results often depending on the nature of the acid or reagent.

Organic substances in solution often interfere with precipitation.

Lead

(¹) Potassium bichromate precipitates chromate.
(²) If the acid is not very dilute red basic sulphide is precipitated.

Iver

All compounds heated on charcoal with sod. carbonate give metal.
(³) Nitric acid changes ferrocyanide into ferricyanide.
(⁴) Sulphide is insoluble in dilute acids *except* nitric.
(⁵) Thiosulphate is changed by heat and by acids into sulphide.

Mercury

Ammonia reacts with most compounds to form mercury-ammonium compounds : *e.g.,* with mercurous chloride forming Hg_2NH_2Cl, black, soluble in aqua regia; with mercuric chloride forming "white precipitate," of varying composition, soluble in dil. hydrochloric acid.

Mercuric compounds are reduced to mercurous by stannous chloride (characteristic test), thiosulphates and sulphites. Mercurous compounds are oxidised to mercuric by aqua regia, chlorine, bromine, etc.

(⁶) Soluble salts of mercury, except mercuric chloride and cyanide, are partially decomposed by water, forming insoluble basic salts.

(⁷) Mercuric sulphide is insoluble in dil. acids, *including* nitric, but is dissolved by aqua regia.

(⁸) Mercuric iodide is precipitated first yellow, turning to red.

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	COPPER							BISMUTH						CADMIUM						
	Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reagent	In Dil. Acids	In Potash	Colour	In Water	In Ammonia	In Excess Reagent	In Dil. Acids	In Potash	Colour	In Water	In Ammonia	In Pot. Cyanide	In Excess Reagent	In Dil. Acids	In Potash	In Amm. Chloride
Acetate	Be	S	S	S	—	S	—	Wt	S,S	—	—	S,S,S	—	Wt	S,S,S	S,S	S	—	S	—	S
Bromide	Gn	S	S	S	S	—	—	Yw	S	—	—	—	—	Wt	—	—	S	S	—	—	—
Carbonate	Gn	—	S	S	—	—	—	Wt	—	—	—	—	—	Wt	—	S	S	—	—	—	S
Chloride	RdBn	—	S	S	—	—	—	Yw	S	—	—	S	—	Yw	S,S,S	S	S	S	S,S,S	—	S
Chromate	YwGn	—	S	S	—	S	—							Wt	S	S	S	—	S,S,S	—	S
Cyanide	RdBn	—	S	S	—	—	—	WtYw	S	—	—	—	—	Wt	—	—	S	—	—	—	S
Ferrocyanide	YwGn	—	S	S	—	—	—	BnYw	—	—	—	—	—	Yw	—	—	S	—	—	—	—
Ferricyanide	Be	—	S	S	—	—	—	Wt	—	—	—	—	—	Wt	S	S	S	—	—	—	—
Hydroxide		S	S	S	—	S	—	Bn	—	—	—	—	—	Wt	—	—	S	—	—	—	—
Iodide	Be	—	S	S	—	—	—	Wt	S	—	—	S	—	Wt	S,S	—	S	S	S,S	—	S
Nitrate	Be	S	S	S	S	S	—	Yw	—	—	—	—	—	Wt	S	S	S	S	S	—	S
Oxalate	BeWt	—	S	S	—	S,S,S	—	Wt	S	—	—	S,S	—	Wt	—	—	S	—	S	—	—
Oxide	Bk	—	S	S	—	S	—	Wt	—	—	—	S,S	—	Bn	—	—	—	—	—	—	—
Phosphate	BeWt	—	S	S	—	S	—	Wt	—	—	—	S,S	—	Wt	S,S	—	—	—	—	—	S
Sulphate	Be	S	S	S	—	S	—	Wt	S	—	—	—	—	Wt	S,S	S	S	S	S,S	—	S
Sulphide	Bk	—	—	S	—	(*)	—	Bk(12)	—	—	—	S,S	—	Yw	—	—	—	—	S(14)	—	—

(in conc. sol. KI ppts Cu'I) KCN ppts Bi(OH)₃

NOTES AND ADDITIONAL INFORMATION

Copper.

Cupric compounds are reduced to cuprous by stannous chloride, potassium iodide, cyanide and sulphocyanate

(*) Sulphide is insoluble in dilute acids except nitric.

Bismuth.

Tartaric acid prevents precipitation of most bismuth salts.

BiO, black, is precipitated from bismuth salts by potassium stannite (stannous chloride with excess of potash) The

(10) Soluble bismuth salts are decomposed by water, forming insoluble basic salts. These are soluble in acids precipitation of bismuth chloride solution by water is a delicate and characteristic test for bismuth.

(11) Bismuth hydroxide changes to Bi_2O_3 at boiling point of water.

(12) Sulphide is insoluble in ammonium sulphide (distinction from arsenic, antimony and tin.)

(13) A distinction from lead

Cadmium.

(14) Sulphide is insoluble in ammonium sulphide and in dilute acids, except hot dilute sulphuric.

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Method of Separating and Identifying Silver, Lead and Mercury (-ous ("Group I")

On examining the solubility tables it will be seen that the only chlorides *insoluble* or *slightly soluble* in dilute acids are silver, lead and mercurous chlorides. This fact affords a means of separating silver and mercury *almost completely*, and lead *partially*, from the other metals, under certain conditions.

Write in your note book any conditions that will interfere with th s eparation.

Although, of all the ordinary metals, the three mentioned are the only ones whose chlorides are insoluble in dilute acids, the addition of hydrochloric acid to a solution may cause precipitates which are *not* the chlorides of any of these metals. An example of this you have already met with, namely, barium chloride and conc. hydrochloric acid. Solutions, moreover, such as the one obtained by the action of excess of potash on alum solution will give precipitates with hydrochloric acid, owing to he neutralisation of the excess of potash. This precipitate, however is re-dissolved by the addition of more acid.

Having obtained a precipitate by the addition of hydrochloric acid to a solution, the next step is to filter it out and wash it thoroughly to free it from the adhering liquid, which might contain other substances whose chlorides are soluble in water. Cold water must be used to avoid dissolvng too much of the lead chloride. The examination of the filtrate to find out when the washing is complete is best effected by testing for *acid* by litmus paper. (Not that the acid itself does any harm, but it is fairly safe to assume that when this is washed out of the precipitate the latter will be also free from other soluble matter. Why would it be useless to test for chloridion by silver nitrate ?)

The precipitate thus obtained may contain the chlorides of lead, silver and mercury (-ous) To separate these, advantage is taken of their different behaviour with *hot water* and with *ammonia*. (See above tables and your own table for lead.) On treating the precipitate with hot water the *lead chloride* is dissolved.[1] The *solution* obtained must then be tested for lead by as many *characteristic* reactions as possible. Any residue must be washed repeatedly with hot water until the washings give no indication of lead with the most delicate test. (Which is the most delicate test for lead ? See *Exp. xxxiv*, p. 44.) The residue so obtained

[1] The most thorough way of dissolving out one precipitate from another is to perforate the bottom of the filter with a pointed match, wash the whole solid through into the test tube below and digest the material, in the test tube, with the solvent in question—in this case hot water.

may contain silver and mercurous chlorides. Treatment of this residue with *ammonia* dissolves the *silver chloride* (see table), and converts the mercury chloride into insoluble black mercuro-ammonium chloride. The ammoniacal solution, which may contain silver, must then be tested for this metal. (Look up suitable tests in the solubility table.) Any residue, in which mercury may be present, must be washed with diluted ammonia until the filtrate is shown by ammonium sulphide to contain no more silver. It must then be dissolved in a few drops of "aqua regia."[1] This will convert the black mercurous salt into mercuric salts, which must be tested for, after removing excess of acid by evaporating the liquid to dryness in a dish and re-dissolving in a little water. It must be remembered that most substances are soluble in strong acids and that, therefore, no tests can be made until the free acid has been removed from solution.

There are many difficulties in carrying out such separations.

Firstly. Precipitates are often formed which are not caused by the substances being tested for. The only way to avoid this source of error is to make numerous and careful *confirmatory tests*, and unless these accord strictly with the behaviour of the metal looked for it is not safe to draw any conclusion as to its presence. In case of doubt as to the identity of a precipitate, the same test should be made with a *known* solution for comparison.

Secondly. There are so many materials which hinder the precipitation of certain substances that the non-formation of an expected precipitate is no proof of the absence of the metal looked for, unless you are assured that no substance is present which prevents precipitation. The only way to be sure of this is to add to a portion of the liquid which has been tested a *very small* quantity of the substance *tested for*. If a precipitate is formed the absence of interfering substances is proved. Except in cases where there is absolute certainty that no interfering substance can be present, this general precaution should always be observed and recorded.

Thirdly. The addition of the *right quantity of the reagent*. If not enough reagent is added to completely precipitate all the substances intended to be separated, not only may some metals be *missed* altogether, but the non-precipitated substances will interfere with the subsequent investigation of the filtrate for other metals. Moreover, other precipitates, such as aluminium hydroxide (see p. 39) may remain undissolved if sufficient reagent be not added. Consequently, *never omit to test the filtrate from a precipitate with a little more of the same reagent that was used*

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[1] This is frequently used as a solvent and oxidising agent. It is made by mixing about one volume of conc. nitric acid with three of conc. hydrochloric.

to produce the precipitate. If a precipitate is formed it must be filtered out and added to that already obtained.

Fourthly. In case the material to be analysed is not already *in solution* there is often great difficulty in getting it dissolved, without at the same time introducing interfering substances (strong acids, etc.). See p.61.

Exp. xl. A solution containing silver, lead and mercurous salts is provided for investigation. Before beginning the analysis write out a full account of the method you intend to employ, giving all details of experiments, including confirmatory tests, in the order in which they are to be carried out. *It will be advisable to submit your method for criticism before proceeding with the experiments.*

In recording the actual work it will be found convenient to make three columns in the note book, the first for the *operations* performed, the second for the *observations*, and the third for the *conclusions* from the observations.

Exp. xli. Investigate the unknown mixtures provided.

METHOD OF SEPARATING AND IDENTIFYING COPPER, BISMUTH, MERCURY (-IC) CADMIUM, AND LEAD (GROUP II B)

It is assumed that all silver and mercury (-ous) and most of the lead have been removed by hydrochloric acid, and further, that arsenic, antimony and tin are absent.

In the following directions all details as to washing, freeing the solutions from interfering substances, etc., will be omitted; they must be supplied by the student himself. The confirmatory tests will have to be sought from the solubility tables, Section XXVIII.

To the slightly acid solution([1])(or filtrate from "Group I"),heated to nearly boiling, add excess of hydrogen sulphide gas from the Kipp. Add the gas slowly, remembering that all the gas which bubbles out of the liquid is wasted. It should be passed in until the odour of hydrogen sulphide is distinctly noticeable after vigorous shaking. (These operations must be performed in the fume-cupboard.) Filter, wash till free of acid, and proceed as directed in the table below. If the solution was too strongly acid the precipitation of the sulphides will not have been complete. Therefore, before testing the filtrate to see if sufficient hydrogen sulphide has been added dilute it about threefold with water.

The following is an outline of the method of separation of the five metals :—

Precipitate : HgS, PbS, Bi₂S₃, CdS, CuS; Boil with dilute nitric acid.				
Residue : HgS and possibly a little PbSO₄, also probably Sulphur Dissolve in a little aq. regia and confirm for Mercury.	Solution : add dilute sulphuric acid.			
	Precipitate : PbSO₄	Filtrate : add excess of ammonia([1])		
		Precipitate : Bi(OH)₃ dissolve in a very little conc. HCl and add water, ppt : BiOCl	Filtrate: add KCN([2])till any blue colour has disappeared : then H₂S	
			Precipitate : CdS, dissolve and confirm for Cd.	Solution : CuCN KCN, confirm for Cu. (How ?)

The above are typical of the methods of qualitative analysis. Similar tables have been made to cover all the common metals and acids.

Exp. xlii. Find the metals in the mixtures submitted.

([1])If nitric acid is present it must be got rid of by evaporating to dryness, as it oxidises the hydrogen sulphide.
([2])Blue solution indicates copper
([3])The fumes from potassium cyanide are dangerously poisonous. All work with this substance should be done in the fume-cupboard.

SECTION XXX

QUANTITATIVE ANALYSIS OF A SILVER COIN

Exp. xliii. Having proved the absence of everything but silver and copper by qualitative analysis, separate the silver first as chloride and then the copper as oxide, as in *Exp. xxiv*, using the two halves of a five cent piece for the duplicate analyses. In the case of the silver chloride, after burning the filter paper add to the ash a couple of drops of concentrated nitric acid, warm and then add a drop of concentrated hydrochloric acid (Why ?); finally heat to dryness, and proceed as with the copper.

What is the per cent. difference between the original weight of coin taken and the sum of the amounts of silver and copper determined from the analysis ?

PART II

QUALITATIVE ANALYSIS

PRELIMINARY INVESTIGATION

Before proceeding with the systematic analysis in solution a preliminary examination should be made with the solid substance, or with the residue from evaporation in the case of a solution, as in this way a few minutes' work will often give much information as to the composition of the material.

CLOSE INSPECTION, especially with the aid of a magnifying-glass, will often reveal the presence of some known substance, particularly in the case of coloured crystals. The student should become familiar with the appearance of the commoner substances. By *tasting*, the presence of iron salts, alum, alkaline chlorides, etc., may be detected, but it is dangerous to taste substances indiscriminately. Cyanides and some ammonium salts may be identified by their *odour*. The material should always be tested with moistened *litmus* paper.

HEATING ON IRON FOIL. Blackening usually indicates the presence of organic substances (also copper and cobalt salts). Volatilisation indicates compounds of mercury, arsenic and ammonium. Oxalic acid and ammonium nitrate decompose to gases.

HEATING IN A DRY TEST TUBE. Condensation of water on the side of the tube indicates moisture, " water of crystallisation," etc. Odour of ammonia : some salts of ammonia. Odour of sulphur dioxide . sulphites, thiosulphates and some sulphates. Red-brown fumes : nitrates and nitrites. Oxygen (detected by glowing splinter): chlorates.

WARMING WITH CONCENTRATED SULPHURIC ACID. The presence of the salts of certain acids is indicated as follows :

Coloured gas : Red-brown, bromides, bromates, nitrites, nitrates (slight evolution); *Yellow*, chlorates, hypochlorites; *Violet*, iodides, iodates.

Odour : Hydrogen cyanide, cyanides, ferro and ferri-cyanides, sulphocyanates ; *Hydrogen chloride*, chlorides; *Hydrogen sulphide*, sulphides; *Sulphur dioxide*, sulphites, thiosulphates (sulphur deposited from the latter); *"Burnt sugar odour,"* tartrates; *Acetic acid* (vinegar), acetates.

Colourless and odourless gas : *Carbon dioxide* (detected by a drop of lime water on a glass rod), carbonates, oxalates, and some other organic compounds; *Carbon monoxide* (combustible), oxalates.

No evolution of gas : Arseniates, arsenites, borates, phosphates, silicates, sulphates, some organic acids. Also many salts of the above mentioned acids.

FLAME TEST ON PLATINUM OR IRON WIRE. *Yellow*, sodium; *Violet*, potassium; *Crimson*, lithium; *Crimson-red*, strontium; *Red*, calcium; *Yellow-green*, barium; *Green*, copper and borates. The flame is usually more strongly coloured if the salt be first moistened with hydrochloric acid; a borate shows better with sulphuric acid. An indigo solution, or a layer or two of blue glass will cut off the yellow sodium light which otherwise obscures the other colours.

BORAX BEAD ON PLATINUM WIRE.

	In oxidising flame	In reducing flame
Chromium	Green (red when hot)	Green.
Cobalt	Blue	Blue.
Copper	Blue (green when hot)	Red.
Iron	Yellow (red when hot)	Green.
Manganese	Violet	Colourless.
Nickel	Red-brown	Grey.

HEATING ON CHARCOAL WITH SODIUM CARBONATE.—In the reducing flame many salts are reduced to the metals.

ANALYSIS IN SOLUTION

Solution of the material.—Before beginning the analysis the substance must be brought *completely* into solution—a process often attended with considerable difficulty.

Powder the material very finely and treat it with distilled water, heating if necessary to hasten solution. If it does not completely dissolve, filter the liquid and treat the residue with a little hydrochloric or nitric acid. If part still remains undissolved it must be filtered out and treated with aqua regia. After treatment with each solvent find out if any of the substance has dissolved by evaporating a drop of the liquid and comparing it with the residue from a drop of the solvent. Except when silver, lead or mercurous salts are present it is better to use hydrochloric acid than nitric acid, as the latter interferes with the precipitation of the second group (see p. 58). If nitric acid or much hydrochloric acid has

been used, it must be got rid of by evaporating the liquid to dryness and re-dissolving the residue in water or dilute hydrochloric acid, before beginning the analysis.

If any of the material remains, insoluble both in water and acids, fuse this part in a crucible with three or four times its bulk of a mixture of sodium and potassium carbonates, then extract the excess of carbonates and the sodium and potassium salts of the acids originally present by repeated treatment with hot water, and dissolve the residue (carbonates of the metals) with dilute nitric or hydrochloric acid.

If several solutions in different solvents have been obtained they may be mixed together, provided this does not cause precipitation. It is, however, often more convenient to analyse the different solutions separately.

SEPARATION OF THE METALS

The common metals may be divided into six groups according to their precipitation by various reagents. The student is reminded that the formation of a precipitate is caused by an alteration in conditions involving a readjustment of equilibrium, during which one substance is produced in quantity more than sufficient to saturate the solution. It may result either from the formation of a new substance (e.g., sulphuric acid added to barium chloride gives a precipitate of barium sulphate) or occasionally from an increase in the amount of a substance already present, as when hydrochloric acid is added to barium chloride giving a precipitate of barium chloride (see p. 39). The student is urged to read again Sections XXI to XXVII of Part I, and to endeavour to explain each reaction met with from the point of view of the mass law, as in this way the study of analytical methods is greatly simplified.

The chief sources of error in qualitative analysis (see Section XXVIII p. 56) must be again emphasised :

The presence of interfering substances.

Neglect to wash precipitates and test washings.

Incompleteness of precipitation.

Carelessness in making confirmatory tests.

Another source of error, not previously mentioned, arises from allowing the solution to become too greatly diluted during the course of the analysis. It must be remembered that no precipitate is quite insoluble and that therefore the delicacy of a test decreases with the dilution of the substance.

The analysis should be made according to the following scheme. Confirmatory tests and other information are added at the foot of each

table. The directions here given are mere outlines, and should be supplemented by the reading of a text-book on general chemistry as well as by instruction in the laboratory.

TABLE OF THE SEPARATION OF THE GROUPS

I Add dilute *hydrochloric acid* drop by drop as long as a precipitate is produced; warm(0), cool(2) thoroughly, and filter.

PRECIPITATE	II. To filtrate from Group I add *hydrogen sulphide* in excess, warm(1) and filter (See p. 58).		III. In the absence of phosphates(2) boil for a few minutes(3), add a few drops of *conc. nitric acid*(5), boil again and add *ammonium chloride*(6) and excess of *ammonia*(7), filter quickly(8).	IV. To the filtrate from III B(9) add *ammonium carbonate and ammonia*, warm for some minutes (10) without boiling, and filter.	V. The filtrate from IV. contains salts of :
GROUP I.	**PRECIPITATE**		**PRECIPITATE**	**PRECIPITATE**	Magnesium
Lead, $PbCl_2$, white	**GROUPS II A AND II B**		**GROUP III A**	**GROUP IV.**	Ammonium
Silver, AgCl, white	(Separation of II A and II B see p.65)				Potassium
Mercury (ous), HgCl, white			Aluminium, $Al(OH)_3$, white gelatinous.	Barium, $BaCO_3$, white	Sodium
(Analysis, p. 55)	**II A. Sulphides soluble in yellow ammonium sulphide**		Chromium, $Cr(OH)_3$, bluish green	Strontium, $SrCO_3$, white	Lithium
	Arsenic, As_2S_3, yellow		Iron, $Fe(OH)_3$, brown(7)	Calcium, $CaCO_3$, white	
	Antimony, Sb_2S_3, orange				(Analysis, p. 70)
	Tin, SnS, brown		(Analysis, p. 67)	(Analysis, p. 69)	
	SnS_2, yellow				
	(Analysis, p.66)		To filtrate from III A add *ammonium sulphide*(9) and filter :		
	II B. Sulphides insoluble in yellow ammonium sulphide.		**PRECIPITATE**		
	Lead, PbS, black		**GROUP III B**		
	Bismuth, Bi_2S_3, black				
	Copper, CuS, black		Manganese MnS, pink		
	Mercury (ic), HgS, black		Cobalt, CoS, black		
			Nickel, NiS, black		
	(Analysis, p. 58)		Zinc, ZnS, white		
			(Analysis, p. 68)		

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Notes to Table of Separation of Groups

(1)   The solution is warmed to coagulate the precipitate and thus cause it to filter more easily.

(2)   Lead chloride is soluble in hot water, therefore cool thoroughly.

(3)   If a test with ammonuim molybdate has shown the presence of phosphates or if the preliminary investigation has indicated organic matter proceed as directed on p. 68.

(4)   Boil to drive off hydrogen sulphide, as otherwise it will be oxidised by the nitric acid, depositing sulphur, and some of it may be left over which will precipitate the III B sulphides when ammonia is added.

(5)   To oxidise the ferrous salts to ferric, so that all the iron will be precipitated as ferric hydroxide which is more insoluble than the ferrous in alkaline solutions, and filters more easily.   If too much nitric acid is added manganous salts will be oxidised to manganic, and manganic hydroxide will be precipitated by the ammonia in spite of the presence of ammonium chloride.(See following note.)

(6)   Ammonium chloride is added to prevent the precipitation of magnesium, zinc and manganous hydroxides.   It should always be added *before* the ammonia, because if the precipitate of manganous hydroxide were allowed to form it would rapidly oxidise to manganic, which is insoluble in ammonium chloride. The precipitate of III A should be filtered quickly, as manganic hydroxide is formed slowly even from the solution, in contact with the air.   Aluminium hydroxide is slightly soluble in ammonia, and consequently the presence of ammonium chloride makes its precipitation more nearly complete.   (Explain this.)

(7)   If the precipitate of III A is greenish black it shows that insufficient nitric acid has been added to oxidise the ferrous salts completely.

(8)   The difference in the action of hydrogen sulphide and ammonium sulphide is due to the greater concentration of *sulphidion* in the latter solution (see list, p. 83).   The sulphides of Group II are so insoluble that the small concentration of sulphidion in hydrogen sulphide solution is sufficient to precipitate them, whereas the sulphides of Group III, being less insoluble, require a much greater concentration of sulphidion to produce them in sufficient quantity to supersaturate the solution.   The presence of hydrochloric acid in the filtrate from Group I still further reduces the concentration of the sulphidion.   (Why ?)

(9)   Here again the presence of ammonium chloride is necessary to prevent the precipitation of magnesium hydroxide.   Why could not the ammonium carbonate be relied upon to prevent the precipitation ?

(10)   The precipitation of Group IV is slow and incomplete in a cold solution. Boiling would drive off the ammonia, which is added to decrease the solubility of the carbonates.

ANALYSIS OF GROUP I

For details of the analysis see p. 55

SEPARATION OF GROUP II A FROM II B

Treat the well-washed sulphides of Group II for several minutes with *a little* warm, yellow ammonium sulphide (containing polysulphides, $(NH_4)_2S_x$); filter, and acidify a few drops of the filtrate with dilute sulphuric acid, which will precipitate any sulphides which have dissolved, together with sulphur.   If the precipitate consists of sulphur only[1] Group II A is absent, in which case proceed to analyse the Group II precipitate for II B.   If a curdy yellow or brown precipitate is formed[2] Group II A is present, and the whole of the filtrate must be analysed for II A. The residue, Group II B, must be treated with several successive small portions of ammonium sulphide and then analysed for Group II B.

Notes

[1]   Sulphur is set free from yellow ammonium sulphide by acids.   It can be distinguished from the sulphides by its fine milky appearance and by its burning without residue on a splinter of glass.

[2]   The precipitate may be brown owing to the presence of copper sulphide which is slightly soluble in yellow ammonium sulphide.   The sulphide of tin formed is the yellow SnS_2, not SnS which is brown.

ANALYSIS OF GROUP II A

Acidify the ammonium sulphide solution with dilute sulphuric acid, filter and wash the precipitates till free of hydrogen sulphide[1], and dissolve in concentrated hydrochloric acid, if necessary adding a small crystal of potassium chlorate[2]. Filter off any sulphur, expel chlorine (if chlorate was used) by gentle heating—not boiling[2]—and transfer the solution and any white residue (oxides of tin and antimony) to a Marsh's apparatus[3]. Pass the gas into a little silver nitrate solution as long as a precipitate is produced. Filter and wash the precipitate. Wash also the residue in the Marsh apparatus.

Residue from Marsh apparatus: Sn and Zn. Dissolve in dilute hydrochloric acid and test for tin by mercurous chloride: White or grey ppt. [5] denotes tin[3].	Precipitate from sil. nitrate sol. Ag and Ag_3 Sb. Treat with warm conc. hydrochloric acid, dilute [6], filter and test solution with: (a) hydrogen sulphide, orange ppt. $Sb_2 S_3$ (b) large excess of water, white ppt. SbOCl. For "spot" tests see Note [4].	Filtrate from sil. nitrate: $H_3 AsO_3$, $AgNO_3$, etc. Add just enough dil. hydrochloric acid to ppt. the silver and filter. Test the solution for As by hydrogen sulphide: yellow ppt. $As_2 S_3$ [7]. For "spot" tests see Note[4].

Notes

[1] If hydrogen sulphide is not completely washed out it may be given off from the Marsh apparatus and precipitate silver sulphide.

[2] The presence of oxidising agents interferes with Marsh's test. Consequently add very little potassium chlorate and expel all chlorine. The liquid must not be boiled as arsenic chloride is slightly volatile.

[3] Marsh's apparatus consists of a small flask provided with a cork fitted with a long-necked funnel and delivery tube. The latter is bent twice at right angles so as to lead the gas into the silver nitrate solution. A *little* zinc is placed in the flask and the hydrochloric acid solution of II A, diluted with water, is poured in through the funnel. By the action of the zinc the compounds of tin are reduced to the metallic state, while if arsenic and antimony salts are present the gases, arsine, AsH_3, and stibine, SbH_3, pass out through the delivery tube, precipitating Ag and $AgSb_3$ respectively from the silver nitrate. As the zinc is apt to contain tin, a blank experiment should be made to test its purity. Small quantities of arsenic are also commonly present in zinc.

[4] Instead of passing the gases into silver nitrate they may be treated as follows. Replace the bent delivery tube by a short up-right tube drawn out to a fine jet. After making sure that the apparatus is *completely free of air* (see *Exp. xiii*, p 11), ignite the gas. The flame will be bluish white if arsenic or antimony is present. A piece of porcelain (crucible lid) held in the flame will be spotted with deposits of metallic arsenic and antimony : *Arsenic*, shiny brownblack, soluble in alkaline hypochlorite, turned yellow by warming with ammonium sulphide, soluble in dilute nitric acid, and if silver nitrate and ammonia are added to this solution yellow Ag_3AsO_4 is formed. *Antimony*, dull black, insoluble in hypochlorite, turned orange by ammonium sulphide, turned white by dilute

nitric acid, and if to this silver nitrate and ammonia are added, black Ag_4O is formed, more quickly on warning.

5   White mercurous chloride and grey metallic mercury (usually mixed)

6   If the hydrochloric acid solution is not diluted, some silver will remain in solution, and when the hydrogen sulphide is added black silver sulphide will be precipitated.

7   A black precipitate here shows that all the silver has not been removed from the solution.

ANALYSIS OF GROUP II B

(For details of the analysis see p. 58.)

ANALYSIS OF GROUP III.A

Boil the well-washed hydroxides of III A with potassium hydroxide for several minutes, and filter hot [1].

Solution : potassium aluminite, $KAlO_2$ Barely acidify with dilute hydrochloric acid and add ammon. carbonate[2] : White gelatinous ppt. $Al(OH)_3$ Sometimes a little silicic acid is precipitated here. See p. 74	Residue : Fe $(OH)_3$ and Cr $(OH)_3$	
	Test part for iron by dissolving in dil. hydrochloric acid and adding (a) pot. ferrocyanide : blue ppt. of $Fe_4(Fe(CN)_6)_3$: (b) amm. sulphocyanate : red solution of $Fe(SCN)_3$. Test original substance for ferric and ferrous salts [3].	Test part for chromium as follows : Fuse the solid with mixture of nitre and sod. carbonate, add hot water, filter, acidify filtrate with acetic acid and test for chromate by: (a) Sil. nitrate, red-bn. ppt.; (b) Lead acetate, yellow ppt. Test original substance for chromates [4].

Notes

1   Cold potash dissolves also $Cr(OH)_3$, forming $KCrO_2$, decomposed on boiling.

2   Salts of weak acids like carbonates, sulphides, etc., precipitate aluminium hydroxide.   The aluminium salts of these acids, if they exist, are decomposed by water.

3   Any ferric salts present in the original substance will have been reduced to ferrous by the hydrogen sulphide and again oxidised by the nitric acid.   The following tests distinguish ferrous from ferric salts :

Pot. ferricyanide with ferrous salts : blue ppt. of ferrous ferricyanide.

Pot. ferricyanide with ferric salts : brown sol. of ferric ferricyanide.

Amm. sulphocyanate with ferrous salts : no apparent change.

Amm. sulphocyanate with ferric salts : red coloration.

4   Chromates in the original substance will have been reduced to chromic salts by the hydrogen sulphide and not re-oxidised by the nitric acid.   A yellow colour, common to all soluble chromates, would indicate their presence in the original solution.

ANALYSIS OF GROUP III B

Treat the well-washed precipitates of the sulphides of group III B with dilute ([1]) hydrochloric acid (less than 1 RW per litre), and filter.

Solution : $ZnCl_2$, $MnCl_2$, ([2]). Add potash in excess and digest in the cold, filter.		Residue: NiS, CoS
Solution : $K_2 ZnO$. Add ammonium sulphide : White ppt. ZnS.	Precipitate : Mn $(OH)_2$ ([1]), quickly oxidising in the air to Mn $(OH)_3$. Oxidise to manganate([3]), or to permanganate ([4]). Test also with borax bead.	Dissolve in aqua regia, evaporate to dryness and redissolve in water. To a part of the solution add a drop or two of potash to neutralise last traces of acid, precipitating as little as possible of the hydroxides of nickel and cobalt. Add acetic acid and sodium acetate and then some conc. potassium nitrite sol. If cobalt is present a yellow crystalline ppt. of $K_3 Co(NO_2)_6$ is formed, on standing. Filter, and to the filtrate add potash. A light green ppt. of Ni $(OH)_2$ indicates nickel. To another part of the solution add pot. cyanide until the ppt.([5]) redissolves. (a) Add dil. hydrochloric acid and boil; add more hydroch. acid drop by drop; Ni $(CN)_2$ precipitates and dissolves in excess of acid ([6]). (b) To another part add potash and bromine water : Ni $(OH)_3$ precipitates, black. Test also with borax bead.

Notes

([1]) The sulphides of nickel and cobalt are slightly soluble in dil. hydrochloric acid. Therefore very dilute acid should be used. If traces dissolve, the hydroxides will be precipitated along with $Mn(OH)_2$ when potash is added to the solution.

([2]) Zinc sulphide is insoluble in moderately dilute acetic acid, while manganous sulphide is soluble. Hence if excess of sod. acetate is added to the dil. hydrochloric acid solution and hydrogen sulphide passed in, zinc sulphide will be precipitated. (Separation from manganese).

([3]) Fuse with mixture of nitre and sod. carbonate. The mass becomes bright green.

([4]) Boil with nitric acid and red lead, in excess. The sol. turns purple.

([5]) $Co(CN)_2$ and $Ni(CN)_2$ are first precipitated; these dissolve in excess of the cyanide to give $Co(CN)_2 2KCN$ and $Ni(CN)_2 2KCN$.

([6]) Hydrochloric acid decomposes the double salt of nickel giving a precipitate of $Ni(CN)_2$, while the cobalt salt is converted into $H_3 Co(CN)_6$ in which there is no cobaltion to form $Co(CN)_2$.

ANALYSIS OF GROUP III IN PRESENCE OF PHOSPHATES AND ORGANIC MATTER

If phosphate is present, warming the solution with concentrated nitric acid and excess of ammonium molybdate produces slowly a yellow

precipitate of ammonium phospho-molybdate.[1] The presence of organic matter is shown by charring (preliminary investigation). Both phosphates and organic matter interfere with the precipitation of Group III A, and, if present, must be removed before proceeding with the analysis. Evaporate the filtrate from Group II and ignite gently to free it from organic material. Re-dissolve in dilute hydrochloric acid. To get rid of phosphates digest the filtrate from Group II in an evaporating dish with strong nitric acid and granulated tin, until a test with molybdate shows the absence of phosphoric acid. Care must be taken that the nitric acid is not all expelled by the heat as its presence is necessary to keep Group III A in solution. Evaporate most of the nitric acid, filter, dilute the filtrate with water, remove any lead that has been dissolved from the tin, by hydrogen sulphide, and examine as usual for Group III A.

ANALYSIS OF GROUP IV

Dissolve the well-washed precipitate of the carbonates of Group IV in dilute acetic acid. To a small portion of the solution add potassium bichromate and if a precipitate is produced [2] add more of the reagent to the whole solution as long as a precipitate is formed. Filter.

Solution : $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$, and $K Cr_2O_7$. Add ammonia and ammon. carbonate, filter, wash the precipitate and dissolve it in acetic acid.		Precipitate: $BaCrO_4$, yellow, soluble in dil. hydrochloric acid, and precipitated from this solution by sulphuric acid as barium sulphate, a fine white ppt. insoluble in acids, passing readily through filter paper.
Solution: $Sr(C_2H_3O_2)_2$ and $Ca(C_2H_3O_2)_2$.		
Test a part for strontium: Add calcium sulphate, boil and let stand for some time; white ppt. of $SrSO_4$. Test also in the flame.	Test a part for calcium: Add potassium sulphate sol. to remove all strontium present and filter. Add ammonium oxalate; white ppt. insoluble in acetic acid. Test also in the flame.	

[1] A yellow precipitate is also formed with arsenic acid.

[2] If no precipitate is formed test the solution for strontium and calcium as given in the table.

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Analysis of Group V

Test the filtrate from Group IV for lithium by the flame. If lithium is present proceed by (a), if absent, follow (b).

(a) Evaporate the filtrate from IV to dryness, ignite[1] gently, dissolve the residue in a little dil. hydrochloric acid, evaporate to dryness[2] again and dissolve in water. To this solution add ammonium oxalate, boil, and add excess of acetic acid[3].

Precipitate MgC_2O_4 white. Dissolve in dil. hydrochloric acid, add excess of ammonia and then sodium phosphate: white ppt. $MgNH_4PO_4$	Solution: salts of Li, K, Na. Add sodium phosphate: white ppt. of Li_3PO_4. Test by flame.

(b) To filtrate from IV add a little ammonia, enough amm. chloride to dissolve any ppt. that may be formed, and sodium phosphate: white ppt. $MgNH_4PO_4$.

The filtrate from Group IV cannot, of course, be examined for ammonium salts. Heat some of the original substance with conc. potash. Evolution of ammonia may be recognised by its odour and effect on litmus[4].

Potassium and sodium may be recognised by their flame reactions. It is better to use the original substance for this purpose, as many of the reagents employed often contain enough of these metals to give the characteristic colours to the flame. Flame tests with known substances should be made side by side with the tests of the substance under investigation.

Notes

[1] To expel ammonium salts, as these dissolve lithium phosphate.
[2] To drive off hydrochloric acid, as magnesium oxalate is soluble in strong acids.
[3] Magnesium oxalate is insoluble in acetic acid (See p. 82).
[4] Nessler's test for ammonium compounds is very delicate. The reagent may be made by adding potassium iodide to mercuric chloride solution until the precipitate first formed is almost re-dissolved, and then adding potassium hydroxide and allowing the liquid to settle. If a compound of ammonium is added to the clear solution a brown precipitate of NHg_2I is formed. As this precipitate is soluble in potassium iodide care must be taken not to add excess of this reagent in making up the solution.

A knowledge of the bases present often restricts the number of acids to be tested for. For example, a soluble substance found to contain barium need not be tested for sulphuric acid. Much information is also obtained from the preliminary investigation (see p. 60).

Dissolve the substance in water or potash solution, or fuse with sodium carbonate and extract the sodium salts of the acids present with water, neutralising the excess of sodium carbonate with dilute hydrochloric acid.

If any bases other than the alkalis are present they must be first removed, as their presence might affect the investigation. This may be done by precipitating with sodium carbonate and filtering, after which the filtrate must be carefully neutralised with hydrochloric acid before testing for the acids.

The acids may be grouped roughly as follows :

I. Those whose calcium salts are insoluble in water.

II. Those remaining whose silver salts are insoluble in water.

III. Other acids.

As the grouping of the acids is rather unsatisfactory, great care should be taken in making the confirmatory tests.

I. THE CALCIUM GROUP. To the neutral solution from which all the bases but the alkalis have been removed, add *calcium nitrate;* if a precipitate appears, boil, cool thoroughly and filter. To the washed precipitate add acetic acid :

Solution with evolution of gas : carbonate, sulphite.

Solution without evolution of gas : arseniate, arsenite, borate, citrate, phosphate, tartrate.*

Residue, soluble in dilute hydrochloric acid : fluoride, iodate,* oxalate.

Residue, insoluble in dilute hydrochloric acid : silicate, sulphate.*

II. THE SILVER GROUP. To the filtrate from Group I add *silver nitrate*, filter. To the washed precipitate add dilute nitric acid and boil : *Solution :* acetate, chromate,* hypophosphite, sulphide, thiosulphate.

Residue, soluble in ammonia : benzoate, bromate, bromide,* chloride, chromate, cyanide, ferricyanide, hypochlorite, iodate, salicylate, sulphocyanate

Residue, insoluble in ammonia : bromide,* iodide, ferrocyanide.*

III. OTHER ACIDS. The filtrate may contain : chlorate, nitrate nitrite, perchlorate.

N.B.—*Slightly soluble in water.

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REACTIONS OF THE ACIDS

ACETIC ACID, $C_2H_4O_2$. *Sulphuric acid*, hot, conc.: odour of vinegar; to this add alcohol : odour of ethyl acetate. *Ferric chloride :* deep red colour of ferric acetate; colour destroyed by mercuric chloride (cf. sulphocyanate). On boiling with excess of acetate, red-brown precipitate.

ARSENIC ACID, H_3AsO_4. See the table of analysis of Group II A for tests for acids of arsenic. A neutral solution of an arseniate gives a red-brown precipitate with *silver nitrate;* with *ammon. molybdate*, yellow precipitate.

ARSENIOUS ACID, H_3AsO_3. Arsenites decolorise *permanganates*. A neutral solution of an arsenite gives a yellow precipitate with *silver nitrate*.

BENZOIC ACID, $C_7H_6O_2$. *Sulphuric acid*, conc.: brown coloured solution from which benzoic acid is precipitated by water. *Ferric chloride :* from neutral solutions, a pink precipitate.

BORACIC ACID, H_3BO_3. *Flame test :* a fragment of a borate mixed in a crucible with conc. sulphuric acid and alcohol, and ignited, green flame.

BROMIC ACID, $HBrO_3$. *Sulphuric acid*, hot, conc.: liberation of bromine. *Silver nitrate :* white precipitate decomposed by hydrochloric acid with evolution of bromine (cf. bromides). *Potassium iodide* in acid solution : liberation of iodine which turns starch blue.

CARBONIC ACID, H_2CO_3. *Acids* decompose carbonates with liberation of carbon dioxide, which may be recognised by the turbidity it produces in a drop of lime water on a glass rod.

CHLORIC ACID, $HClO_3$. *Sulphuric acid*, conc.: evolution of green-yellow gas. *Aniline sulphate*, in acid solution : intense blue coloration,

CHROMIC ACID, H_2CrO_4. For confirmatory tests see table of analysis of Group III A.

CITRIC ACID, $C_6H_8O_7$. *Sulphuric acid*, conc.: decomposition with evolution of carbon dioxide and carbon monoxide (inflammable). *Chars* only on prolonged heating. *Calcium hydrate :* white precipitate on prolonged heating.

FERRICYANIC ACID, $H_3Fe(CN)^6$. *Sulphuric acid*, hot, conc.: evolution of hydrogen cyanide ; test the solution for iron. *Ferrous sulphate :* dark blue precipitate. *Ferric chloride :* brown coloration, no precipitate.

FERROCYANIC ACID, $H_4Fe(CN)_6$. *Sulphuric acid*, hot, conc. : evolution of hydrogen cyanide; test the solution for iron. *Ferrous sulphate :* light blue precipitate becoming darker on standing. *Ferric chloride :* deep blue precipitate. *Cupric sulphate :* red-brown ppt.

HYDRIODIC ACID, HI. *Sulphuric acid*, hot, conc.: liberation of iodine. *Oxidising agents :* liberation of iodine. *Silver nitrate :* light yellow precipitate, insoluble in ammonia (cf. chloride and bromide).

HYDROBROMIC ACID, HBr. *Sulphuric acid*, hot, conc.: liberation of bromine. *Oxidising agents :* liberation of bromine. *Silver nitrate :* yellow-white precipitate, sparingly soluble in ammonia (cf. chloride and iodide).

HYDROCHLORIC ACID, HCl. *Sulphuric acid*, hot, conc.: liberation of hydrogen chloride (cf. iodide and bromide), giving white fumes with ammonia. *Potassium bichromate and conc. sulphuric acid, heated:* brown vapours of chromyl chloride.

HYDROCYANIC ACID, HCN. *Sulphuric acid*, hot. conc.: evolution of hydrogen cyanide.

HYDROFLUORIC ACID, HF. *Sulphuric acid*, hot, conc.: evolution of hydrogen fluoride which etches glass.

HYPOCHLOROUS ACID, HClO. *Silver nitrate :* white precipitate, silver hypochlorite, which quickly decomposes into silver chloride and silver chlorate. *Aniline sulphate*, in dilute sulphuric acid solution: blue coloration. *Dilute acids :* liberation of chlorine.

HYPOPHOSPHOROUS ACID, H_3PO_2. *Cupric sulphate :* heated to 70°C, black precipitate of copper hydride; decomposed on heating. *Oxidising agents* are reduced. *Silver nitrate :* black precipitate of reduced silver.

IODIC ACID, HIO_3. *Sulphuric acid*, hot, conc.: no evolution of iodine. *Ferrous sulphate and concentrated sulphuric acid :* liberation of iodine.

NITRIC ACID, HNO_3. *Brown ring test :* one cubic centimetre each of a solution of a nitrate and of ferrous sulphate solution are mixed in a test tube and conc. sulphuric acid is added, allowing it to fall along the wall of the tube; at the boundary between the two liquids a brown ring or coloration will be observed, arising from the solution of nitric oxide in ferrous sulphate. *Phenyl sulphate :* brown-red coloration becoming yellow or green upon addition of ammonia.

NITROUS ACID, HNO_2. *Brown ring test :* obtained by the action of ferrous sulphate on a nitrite without the addition of sulphuric acid (cf. nitrate).

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OXALIC ACID, $C_2H_2O_4$. *Sulphuric acid*, hot, conc.: evolution of carbon dioxide and carbon monoxide (inflammable).

ORTHOPHOSPHORIC ACID, H_3PO_4. *Excess of ammonium molybdate with nitric acid on warming :* yellow precipitate (cf. arsenic acid). *Magnesia mixture* (prepared by the addition of ammonia to a solution of magnesium sulphate containing enough ammonium chloride to prevent the formation of a precipitate): white crystalline precipitate of magnesium ammonium phosphate. *Silver nitrate :* yellow precipitate of silver phosphate (cf. pyrophosphoric acid).

PYROPHOSPHORIC ACID, $H_4P_2O_7$. *Ammonium molybdate :* no precipitate. *Magnesia mixture :* no precipitate. *Silver nitrate :* white precipitate.

SALICYLIC ACID, $C_7H_6O_3$. *Ferric chloride :* intense violet coloration. *Alcohol and conc. sulphuric acid on warming :* odour of wintergreen. *Heated with lime :* odour of carbolic acid.

SILICIC ACID, H_2SiO_3(etc.). *Hydrochloric acid :* precipitation of a jelly-like mass, insoluble when once dried. *Silica skeleton :* if a small fragment of a silicate be dissolved in the microcosmic salt bead silica is liberated and floats undissolved in the bead. (Aluminum hydroxide in small quantity gives a clear bead.)

SULPHURIC ACID, H_2SO_4. *Barium chloride :* white precipitate of barium sulphate which is insoluble in all acids and passes readily through filter paper.

All acids containing sulphur : fused with sodium carbonate on charcoal form sodium sulphide, a solution of which stains a silver coin black.

SULPHURETTED HYDROGEN, H_2S. *Sulphuric acid*, hot, conc.: liberation of hydrogen sulphide recognised by its odour and by blackening lead acetate paper.

SULPHUROUS ACID, H_2SO_3. *All acids :* evolution of sulphur dioxide. *Barium chloride :* white precipitate, soluble in dilute hydrochloric acid; addition of dilute *nitric acid* and heating causes the formation of insoluble barium sulphate.

SULPHOCYANIC ACID, HCNS. *Ferric chloride :* blood-red coloration destroyed by mercuric chloride (cf. acetic acid).

TARTARIC ACID, $C_4H_6O_6$. *Sulphuric acid*, hot, conc.: charring and odour of burnt sugar. *Silver mirror :* warm the substance with ammonia and silver nitrate, metallic silver forms slowly on the walls of the test tube.

THIOSULPHURIC ACID, $H_2S_2O_3$. *All acids :* evolution of sulphur dioxide and precipitation of sulphur. *Silver nitrate :* white precipitate which blackens on heating.

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APPENDIX

CLASSIFICATION OF SUBSTANCES

All substances may be divided into two classes, *homogeneous*[1] and *heterogeneous*. The latter, when roughly uniform, are called *mixtures*. The properties of the components of a mixture are the same as those of the substances in the unmixed state. The heterogeneity of a mixture can usually be detected by the microscope. (Examples : milk, granite, gunpowder.)

Homogeneous substances are divided into *Chemical Substances* (or Chemical Individuals) and *Solutions* (or Physical Compounds). Chemical substances are those whose composition does not vary gradually with the conditions (temperature, pressure, and concentrations of surrounding media) under which they are produced. When reaction takes place between members of this class to form other chemical substances, the proportions involved follow the law of reacting weights. (Examples : magnesium oxide, water, sodium chloride, hydrogen.) All other homogeneous substances are called solutions. (The term solution includes solid solutions and so-called mixtures of gases. Examples : salt solution, the atmosphere, brass.)

Chemical substances are divided into *Elements* and *Chemical Compounds*. Elements are chemical substances which, up to the present time, have never been broken up, either directly or indirectly, into other substances. (For list see p. 88). All other chemical substances are called chemical compounds. (Examples : magnesium oxide, water, blue stone.)

ATOMIC WEIGHTS AND THE PERIODIC SYSTEM

Reference was made on page 17 to the selection of particular simple multiples of the reacting weights as standard units, called atomic weights. The choice was made with a view to arriving at the most generally useful set of numbers. One of the most important considerations in this choice is the fact that when these particular numbers are chosen a very striking relation between them and the general properties of the elements is observed.

When, namely, all the known elements are arranged in horizontal rows in ascending order of their atomic weights so that every eighth element falls in the same vertical column, it is found that a natural grouping of the elements has been arrived at, the vertical columns

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[1] Gradual changes from point to point through the mass, such as those due to inequality of temperature, concentration, etc., are not here considered as affecting the homogeneity.

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containing elements with the same valency (see p. 77), and roughly similar general properties. The elements with base-forming properties fall in the lower left hand part of the table, while in the upper right hand part are found the elements with most strongly marked acid-forming properties. (For further details consult any text-book on chemistry.)

FORMULA WEIGHTS OR MOLECULAR WEIGHTS

Just as particular multiples of the reacting weights were chosen for the elements with the idea of conveying as much information as possible by one number, so also, for the same good reason, special multiples of the reacting weights of chemical compounds have been selected and called *formula weights* or molecular weights. The information conveyed by the formula weight, in addition to that based on the law of reacting weights (for which, of course, one simple multiple would be as good as another), has reference to the *volume* relations of gases. It has been discovered, namely, that *the weights of equal volumes of gaseous chemical substances stand approximately in the ratio of simple multiples of their reacting weights*, when the pressure and temperature are the same. (See *Exps*, p. 37.) Hence, by choosing these particular multiples of the reacting weights *the numbers obtained will represent approximately the weights of equal volumes of the gaseous substances*. These are called molecular or *formula weights*, because the chemical formulæ are so chosen as to represent these weights, in addition to the composition. (The volume occupied by one formula weight of a gas at $0°$ and 760 mm pressure happens to be 22.4 litres.) For instance, if the law of reacting weights were the only thing considered, we might use HCl, H_2Cl_2, H_3Cl_3, etc., for hydrochloric acid, H_2O, H_4O_2, etc., for water, CH_2O, $C_2H_4O_2$, etc., for acetic acid, as reacting weights, but since the same volumes (22.4 litres) of these gases weigh about 36.46 g, 18.02 g, and 60.04 g respectively, the formula weights are chosen as HCl, H_2O and $C_2H_4O_2$. Of course, *all* the formula weights might be doubled or trebled, etc., and the volume taken as 44.8, or 67.2, etc., but for convenience the *smallest* possible set is chosen that will in no case cause a fraction of an atomic weight to appear in a formula.

Since many of the elements are gaseous, formula or molecular weights have been assigned to them in addition to their atomic weights. For example, 22.4 litres of hydrogen weigh about 2.02 g, the same volume of oxygen about 32 g, and the same volume of phosphorus vapour about 124 g (*i.e.*, 4×31.0); consequently the formula weights of these elements are taken as H_2, O_2, and P_4 respectively.

Definite formula weights are also assigned to substances which cannot be gasified, but this is for an entirely different reason which need not be gone into here. In a few cases there is no reason at all.
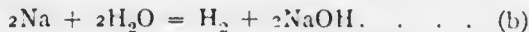
VALENCY

Although the reacting weights of substances may be known, it is still necessary to ascertain what particular multiples of these are involved in any special reaction before our knowledge of the quantitative relations of the process is complete. Although this knowledge can be gained with certainty only by direct experiment, nevertheless there are certain rough generalisations which render it possible to make fairly good guesses as to what will happen in specific cases, and which moreover help us to remember easily a large number of experimental results.

These generalisations are embodied in the principle of valency. When two elements react to form a chemical compound, or *vice versa*, or when one element reacts with a chemical compound setting free another element (" replacing" it) and forming another chemical compound, in the proportion of one reacting weight (RW) of one element to one RW of the other, the two elements are said to have the same valency. Example : Since magnesium and oxygen react according to the equation,

$$Mg + O = MgO \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (a)$$
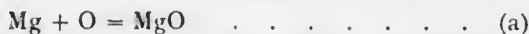
they have the same valency in this reaction. Or, since

$$2Na + 2H_2O = H_2 + 2NaOH. \qquad . \qquad . \qquad . \qquad (b)$$

sodium and hydrogen have here the same valency.

In general, when, in such reactions as the above, two elements take part in the proportion of x RW of one to y RW of the other the valencies of the two elements are said to be in the inverse ratio of x to y. For example, since

$$Mg + 2HCl = H_2 + MgCl_2 \qquad . \qquad . \qquad . \qquad . \qquad (c)$$

the valency of magnesium is said to be twice that of hydrogen in this reaction.

Now, *it has been found that, by a judicious choice, a constant valency can be assigned to each element which will be in accord with the above definition in a large number of reactions.* For instance, if the valency of hydrogen be taken as *one* as a starting point, that of magnesium must be taken as 2 on account of reaction (c) above, and consequently that of oxygen must be taken as 2 also, owing to reaction (a). Now these valencies also accord with the reaction between oxygen and hydrogen to

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form water, in which two RW hydrogen unite with one RW oxygen, and are, therefore, so far consistent. Again, since

$$3H + P = PH_3$$

the valency of phosphorus must be taken as 3, which is also in accord with the reaction

$$2P + 3O = P_2O_3$$
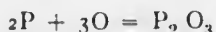
according to which the valencies of phosphorus and oxygen must stand in the ratio of 3 to 2. And so on in many other cases.

There are, however, many reactions with which this idea of constant valency cannot be made consistent, and in a number of cases it is found necessary to attribute two or more valencies to the same element in order that there may be no contradictions.

The following table of the commoner elements with their valencies covers most of the ordinary cases, and will be found a useful aid in remembering and predicting quantitative relations.

TABLE OF VALENCIES

Generally constant				Commonly variable	
Monovalent	Divalent	Trivalent	Tetravalent	Element	Valency
Hydrogen	Calcium	Boron	Carbon	Nitrogen	3, 5, etc
Lithium	Strontium	Aluminium	Silicon	Phosphorus	3, 5
Sodium	Barium			Arsenic	3, 5
Potassium	Magnesium			Antimony	3, 5
Silver	Zinc			Bismuth	3, 5, 2
Chlorine	Cadmium			Iron	2, 3
Bromine	Copper			Cobalt	2, 3
Iodine	Nickel			Mercury	1, 2
	Lead			Tin	2, 4
	Oxygen			Chromium	3, 6, etc.
				Sulphur	6, etc.
				Manganese	2, 7, etc.

Owing to the convenience of the principle of valency it has been found advantageous to extend it to a number of *imaginary compounds.* For instance, since the compositions of sulphates are represented by H_2SO_4, Na_2SO_4, $ZnSO_4$, $Al_2(SO_4)_3$, etc., the constant valency 2 can be consistently assigned to the imaginary compound SO_4, just as if sodium sulphate could be formed by the reaction

$$2Na + SO_4 = Na_2SO_4$$
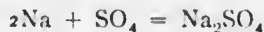
zinc sulphate by the reaction

$$Zn + SO_4 = ZnSO_4$$

aluminium sulphate by the reaction

$$2Al + 3SO_4 = Al_2(SO_4)_3, \text{ etc.}$$

The following list gives the valencies assigned in a similar way to a number of imaginary compounds (so-called "radicals"), which will lead in most cases to consistent results :

TABLE OF VALENCIES OF THE COMMONER RADICALS

Monovalent	Divalent	Trivalent
NO_3	SO_4	PO_4
C_2H_3O (Acetic acid radical)	CrO_4	PO_3
OH	CO_3	AsO_4
NH_4		AsO_3
MnO_4		

It will be readily seen that since hydrogen is monovalent the valency of an acid radical is the same as the number of reacting weights of hydrogen that can be set free from one reacting weight of the acid by a metal. This is called the *basicity* of the acid.

The student should practise guessing at chemical equations with the aid of the above valencies and should compare his results with the experimental facts recorded in books on chemistry. (See Section XXVII, p. 51.) It should be remembered, however, that the principle of valency may lead to ambiguous results in many cases, and even to erroneous ones.

REVERSIBLE REACTIONS AND EQUILIBRIUM

It has already been pointed out that almost all reactions in solution are reversible (p. 42). There are also many other reversible reactions, such as the evolution of carbon dioxide by chalk, the change of water to water vapour, the solution of one substance in another, etc. In all these reactions the process can be made to go in either one direction or the other by slight changes of conditions. When the state has been arrive at in which, under the existing conditions, there is no tendency for the process to take place one way or the other *equilibrium* is said to be established.

In some cases equilibrium is reached almost instantaneously; in others it may require many hours or even years. In the solution of common salt in water (*Exps. xviii* and *xix*, p. 22), the state of equilibrium (at ordinary temperatures 1 part of water to 0.36 of salt) was arrived at from two different sides; on the one hand, from water and

salt by combination, and on the other hand, from the "supersaturated solution" and salt by separation of salt from the liquid. Both these processes required considerable time. Compare also Gladstone's experiment, mentioned on p. 42, in which equilibrium is reached almost instantaneously. In all cases of true equilibrium the same state is eventually reached from whichever side the reaction proceeds.

RATE OF REACTION

Many of the experiments described in this book afford evidence of the fact that the rates of reaction in different cases vary between very wide limits. Compare, for instance, the slow solution of copper sulphate (*Exp.* i, p. 2), or magnesium (*Exp. xvi, p.* 19) with the almost instantaneous precipitation of lead chromate, sulphide, etc. (p. 50). It is also evident from the experiments that the rate of a particular reaction is much affected by conditions, such as temperature, state of division of solids, concentration of solutions, etc.

The laws governing rate of reaction are rather complex, but, qualitatively, they may be stated as follows :

(1) The rate increases rapidly with rise of temperature.

(2) The rate generally increases with the concentration of substances which *disappear* during the reaction, and *decreases* with the concentration of the *products* of reaction.

(3) Where changes from one state (liquid, solid or gaseous) to another are involved the rate increases with the area of the surface separating the two states. (Example : solution, evaporation, etc.)

(4) The presence of some materials, not apparently directly concerned in the process, has often an accelerating effect on the rate. These are called *catalysers*. Hydrogenion and platinum black are examples.

(5) In many cases where a change in state is involved the reaction will not begin unless a small quantity of the product of the reaction is already present. (Examples : separation of salts from some supersaturated solutions as in *Exp. iii*, p. 3 ; "bumping" of liquids, *Exp. i*, p. 2). A liquid when raised above its boiling point will always evaporate from the surface, but often will not form bubbles of vapour within the liquid unless minute bubbles are already present, or unless the temperature is raised considerably above the boiling point. Consequently, bumping may be prevented by the presence of porous materials, such as unglazed porcelain, etc. Bubbles of air, sharp points, shaking, crystals isomorphous with the product of reaction, also aid in initiating such "delayed reactions."

OXIDATION AND REDUCTION

Experiment.—The following experiment shows the effects of concentration, temperature, and the presence of a catalyser (manganese sulphate, one of the products of reaction, in this case) on the rate of reduction of potassium permanganate by oxalic acid. Three solutions are required : 0.64 g potassium permanganate, 1.3 g crystallised oxalic acid, and 20 cc conc. sulphuric acid, each made up separately to about 200 cc with water. They will be designated *Pm*, *Ox* and *Ac* respectively. Equal volumes of these solutions contain the permanganate and oxalic acid in the proportions required by the equation,

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

but sixty times as much sulphuric acid.

Compare the times required to decolorise the following solutions, mixing them in the order given, and counting the time from the moment of adding the *Pm*. The volume may be measured by means of the graduated test tube, *Exp. xxx*, p. 39.

(a) Water 2 cc, *Ox* 20 cc, *Ac* 40 cc, *Pm* 2 cc, (total volume 64 cc)
(b) " 32 cc, " 20 cc, " 10 cc, " 2 cc " " "
(c) " 0 cc, " 20 cc, " 40 cc, " 4 cc " " "
(d) As in (a), but heat solution to nearly boiling before adding *Pm*.
(e) To solution (a) after reduction of first portion of *Pm* add a second portion of 2 cc.

In drawing the conclusions as to the rates of reaction, note that in experiment (c) *twice as much* permanganate has to be reduced as in (a).

See also experiment (a) p. 83.

OXIDATION AND REDUCTION

These terms are in common use to designate certain classes of chemical reactions. In the more limited sense, when a chemical substance combines with oxygen or takes up oxygen from a compound it is said to be oxidised (*e.g.*, magnesium and oxygen changing to magnesium oxide, burning of charcoal by potassium nitrate). Conversely, when a chemical substance loses oxygen it is said to be reduced (*e.g.*, reduction of sulphate of sodium to sulphide by charcoal, reduction of copper oxide to copper by hydrogen, *Exp. xiii*, p. 10). Owing, however, to the frequency of reactions in which oxygen is removed by the action of hydrogen with the formation of water, the addition of hydrogen to a chemical substance is called reduction, and the removal of hydrogen, oxidation, although water may not be formed at all. The term oxidation is even extended to reactions involving an increase in the proportion of things which easily replace oxygen in compounds, such as chlorine, sulphur, acid radicals,

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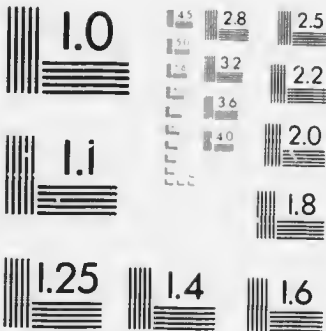
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etc. For instance, the change of mercurous chloride, HgCl, into mercuric chloride, $HgCl_2$ (see p. 56), is called oxidation. The reverse changes are called reduction. Hence the term *oxidising agent* as applied to aqua regia (see foot-note, p. 56), and *reducing agent* in the case of stannous chloride (see " Mercury," p. 53.)

Common oxidising and reducing agents used in the laboratory are :

Oxidising Agents	*Reducing Agents*
Potassium permanganate	Potassium stannite
Potassium chlorate	Hydrogen
Manganese dioxide	Stannous chloride
Nitric acid	Hydrogen sulphide
Aqua regia	Sodium sulphite
Chlorine	Ferrous sulphate
Potassium bichromate	Oxalic acid
Ferric chloride	Carbon

FURTHER APPLICATIONS OF THE MASS LAW AND DISSOCIATION

Solution of precipitates in acids. When the slightly soluble salt, lead oxalate, is shaken up with water until a saturated solution is formed, the small amount of oxalate dissolved is largely dissociated into leadion and oxalation, which are in equilibrium with the minute quantity of still undissociated lead oxalate. The latter substance is in equilibrium with the solid salt. If anything should occur to reduce the concentration of the oxalation the dissociation will increase (see p. 49), the undissociated oxalate will decrease in concentration, and consequently more of the solid salt will dissolve. This is exactly what happens when a strong acid is added to the solution. Hydrogenion is added in a large quantity, which immediately forms undissociated oxalic acid with the oxalation (see list below, p. 83), whose concentration is thereby greatly reduced. Try the experiment, using nitric acid.

With the salt of a *strong* acid, such as lead sulphate, the case is different, for the hydrogenion added will not unite, to any great extent, with the sulphation to form undissociated sulphuric acid. (See list.) Consequently, the solubility of lead sulphate is not much affected by the addition of acids.

It may be predicted, therefore, that slightly soluble precipitates, consisting of the salts of weak (slightly dissociated) acids will probably be dissolved by strong acids, whereas if the precipitate is the salt of a strong acid its solubility will be little affected by other acids. The rule, however, is not general, as it is possible that the salt may be so extremely

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insoluble that even a great reduction in the concentration of the acid-ion in solution will not cause appreciable quantities of it to dissolve. This is the case with many of the sulphides.

The solubility of salts may also be increased by removal of the metal-ion from solution. Lead salts, for instance, are mostly dissolved by the addition of potassium hydroxide which forms a "complex ion," PbO_2, with the lead. (See p. 51.) Solubility of copper salts in potassium cyanide is explained in the same way.

Experiment to illustrate precipitation caused by change in dissociation. Prepare and wash thoroughly some calcium sulphate. Make a saturated solution (cf. *Exp. xviii*) by shaking it with water for a few minutes to establish equilibrium between the solid precipitate and the solution. Filter, take two portions of the filtrate, about 5 cc each, and add to one a drop of dil. sulphuric acid and to the other a drop of calcium chloride solution, and shake vigorously. Explain the results.

Experiment to illustrate change in dissociation of an acid.

(a) First show that the rate of separation of sulphur from thiosulphate solution depends on the concentration of hydrogenion present. Arrange three test tubes containing each about 10 cc of, roughly, 5% sodium thiosulphate solution. In three other test tubes put, respectively, a drop of dil. hydrochloric acid, a drop of a solution of dil. hydrochloric acid diluted fifty-fold with water, and a drop of acetic acid. Pour into these test tubes the three measured quantities of thiosulphate and note in each case the interval of time between the moment of mixing the solutions and the first appearance of a turbidity (sulphur). Note also the apparent amounts of sulphur precipitated in the same interval of time (say three minutes).

(b) Next make two experiments in the same way, using a drop of acetic acid in one test tube and a mixture of a drop of acetic acid and a drop of a 5% sodium acetate solution in the other, and adding 10 cc of thiosulphate to each, as above. The experiment may be varied by using different quantities of sodium acetate.

What effect has the sodium acetate had on the acetic acid? How may the effect be explained by the mass law?

EXTENT OF DISSOCIATION

The following rough classification gives an idea of the relative dissociation of substances in aqueous solutions of ordinary strength.

Almost completely dissociated : All neutral salts, except mercuric salts and cadmium iodide, (salts of di- and trivalent metals are consider-

ably less dissociated than those of monovalent ones); hydrochloric, hydrobromic, hydriodic, nitric, chloric, perchloric, sulphocyanic, and sulphuric acid; hydroxides of the alkali metals and of calcium, strontium and barium; the tetra-alkyl-ammonium bases.

Moderately dissociated : Phosphoric, sulphurous, hydrofluoric and oxalic acid; magnesium hydroxide and cadmium iodide.

Slightly dissociated : Acetic and many other organic acids; carbonic, hydrosulphuric, hydrocyanic, boracic and silicic acid; mercuric salts.

EXPERIMENTAL ERROR

It is important that the influence of experimental error on numerical results should be thoroughly understood.

When the result sought is *proportional* to some experimental measurement, *i.e.*, is obtained from the latter by multiplication or division by accurately known numbers, the relative error in the result will be the same as in the original experimental value. When, however, the result is obtained by subtracting a value from an experimental number the relative error may be much greater in the result than in the measurement. For example, if the weight of the magnesium oxide produced in *Exp. x*, p. 7, be considered as the experimental value subject to error (owing to incomplete combustion, etc.), then the relative error in the ratio of oxygen to magnesium will be the same as that in the weight of magnesium oxide found, assuming, of course, no appreciable error in the other quantities involved. If, however, the actual error in *weighing* is considered, then, in order that the weight of magnesium (say 0.1 g) may be accurate to (say) 1 in 1000, the weight of the crucible plus magnesium (about 15 g) must be determined to about 1 in 15000.

Per cent. error. Per cent. error is the error per 100 in the value considered. For instance, if the result 200 is wrong by 1 the per cent. error is 0.5; if the result 20000 is wrong by 100 the error is 0.5 per cent., and if the value 0.00200 is wrong by 1 in the fifth decimal place the per cent. error is again 0.5. It is clear, therefore, that it is quite meaningless to say that two results agree to such and such a decimal place, unless the numbers expressing the results are also mentioned. The statement of the *per cent.* difference, however, gives at once all the information necessary for gauging the reliance to be placed upon the determination.

In all experimental work it is important to bear in mind the accuracy desired or possible in the result. In *Exp. xxviii*, p. 37, for example, it is probably not possible to attain a greater accuracy than about 0.5%. It would, therefore, be waste of time to weigh the water

driven over (about 100 g) to less than a decigram, which gives an accuracy of 0.1 in 100, or 0.1%.[1] The weight of the magnesium, upon which the final results also depend, must, however, be determined to the fourth decimal place in order to obtain the same relative accuracy.

GLASS BLOWING

Under this head will be given a few general directions for performing some of the simplest operations in glass blowing. Full instructions are of little use, as the difficulty is not so much in knowing what to do as in doing it, and skill in the more advanced work can be acquired only by lengthy and patient practice.

Cutting Glass. An indispensable tool of the glass blower is the glass knife. An ordinary old penknife of good steel (Rodger's blades always give satisfactory results) may be converted very easily into a most convenient form of glass cutter. The blade should be heated to a bright red heat in the blow pipe, and plunged suddenly into a beaker of water held as close as practicable to the flame. The edge should then be ground to a somewhat more obtuse angle than the original, as it thus becomes more durable than the acute edge which rapidly chips off.

To cut a tube of any size up to about 15 cm diameter a single deep scratch on one side of the tube is all that is necessary. By breaking the tube away from the notch a perfectly straight edge on both pieces of glass is usually obtained. It is a mistake to use a sawing motion with the knife. The best effect is got by pressing the tube with the thumb firmly against the knife, held under the four fingers in the palm of the hand, and giving the former a rotation through a small angle. This method cannot be employed if the glass is very thin-walled (*e.g.*, a test tube).

To cut very large tubes or bottles, or thin-walled tubes. A short scratch should be made with the glass knife in the direction of the desired cut. By holding a red-hot, iron rod (a large nail in a handle or the soft end of a file will do) about one mm in front of the scratch for a few moments a crack will start towards the iron, and may then be led in any direction desired by keeping the rod a few millimetres in its advance.

Position of hands in glass blowing. When a piece of tube is to be drawn out, or two pieces are to be joined together, the longer and heavier

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[1] It is also waste of time to work out a result to six or seven significant figures when the experimental value from which it is derived is accurate to (say) only 0.1 per cent. On the other hand, if a result, *e.g.*, a weight, is known to (say) a milligram, and the three figures after the decimal point happen to be zeros, it is a mistake not to write them down, as they show with what accuracy the determination has been made.

part should be held in the left hand with the knuckles upwards, and the lighter part in the right hand with the knuckles downwards. (See Fig. 8.) In this way, by rolling the glass back and forth over the end
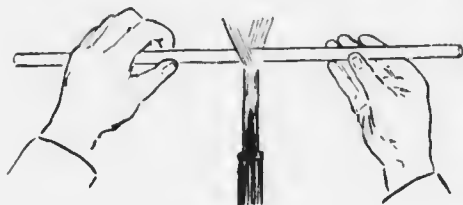
FIG. 8.

of the left thumb, and over the tips of the fingers of the right hand, a slow, rotary motion backwards and forwards may be produced. This motion must be kept up *both when the glass is in the flame and also while it is being drawn out or blown, outside the flame.*

It is worth while practising this motion with two pencils. These must be kept revolving axially and at the same rate.

Position of glass in the flame. The glass should be held about two thirds of the way up the flame, and in such a position that the flame laps round evenly on both sides of the tube. The blow pipe should be placed so that the flame points at a slight angle away from the operator.

Drawing out tubes. The main point to be remembered in addition to the above is that the tube must be removed from the flame before beginning to draw the hands apart. For very thin glass the Bunsen burner may be used with advantage instead of the blow pipe. Beginners will find great difficulty in getting the drawn out part coaxial with the original tube.

Joining tubes end to end. Seal up the longer tube by drawing out the end to a capillary and then fusing the thin glass together. This closed tube must be held in the left hand. Rotate the two tubes in a fairly large flame till the edges just begin to fuse evenly. It is easy to see if the heating is uniform by watching the sodium light imparted to the flame by different sides of the glass. Each part of the edge should give the yellow light to the flame to the same extent. Then bring the two pieces of glass *lightly* together, remove them quickly from the flame and blow at once into the end of the tube so as to swell out the glass slightly at the joint. Then immediately replace the work in the flame (reduced to a small jet), and heat the joint thoroughly till the glass begins to fall together and thicken. Then remove the tube from the flame again and blow it out to a uniform thickness. Difficulty will be experienced in not pulling the tubes apart while blowing and thus making the glass too thin at the juncture. It is better to get it too thick, as this can be easily corrected afterwards by gentle blowing and pulling asunder.

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It must be remembered that it should never be necessary to blow hard. The glass should always be soft enough to be blown out *easily*. The natural tendency at first will be to heat the glass insufficiently owing to the difficulty of turning the two halves of the tube axially when they cease to support one another.

Opening tubes. The ends of closed tubes may be opened by heating strongly and blowing the glass out into a large, thin bulb, which may be then knocked off close to the thick part of the tube. The jagged end may be rounded in the flame till the glass falls somewhat together, after which the end of a file may be inserted and the edges broached out to the original size of the tube, or further, if necessary, so as to form a flange. This method may also be used to make holes in the sides of tubes or bulbs, for instance in the manufacture of T-tubes.

Bending tubes. Tubes up to about 4 or 5 mm diameter may be bent without any difficulty by heating in the Bunsen or blow pipe flame till just soft. If the tube is larger than this, but not more than about 8 mm in diameter, and not too thin-walled, it may be heated by holding it in the plane of a fish-tail illuminating flame till viscous. The tube can then be bent without much flattening at the curve. In all other cases blowing must be resorted to to prevent flattening. After closing one end, the tube must be rotated evenly in the flame till quite soft. It must then be removed from the heat, and while blowing very gently into the end, bent quickly into the desired form. By immediately blowing *hard* into the tube after it is bent the flattening may be removed.

TABLE OF INTERNATIONAL ATOMIC WEIGHTS—1905

Element	Sym.	Wt.	Element	Sym.	Wt.	Element	Sym.	Wt.
Aluminium	Al	27.1	Hydrogen	H	1.008	Rubidium	Rb	85.5
Antimony	Sb	120.2	Indium	In	115	Ruthenium	Ru	101.7
Argon	A	39.9	Iodine	I	126.97	Samarium	Sm	150.3
Arsenic	As	75.0	Iridium	Ir	193.0	Scandium	Sc	44.1
Barium	Ba	137.4	Iron	Fe	55.9	Selenium	Se	79.2
Bismuth	Bi	208.5	Krypton	Kr	81.8	Silicon	Si	28.4
Boron	B	11	Lanthanum	La	138.9	Silver	Ag	107.93
Bromine	Br	79.96	Lead	Pb	206.9	Sodium	Na	23.05
Cadmium	Cd	112.4	Lithium	Li	7.03	Strontium	Sr	87.6
Caesium	Cs	132.9	Magnesium	Mg	24.36	Sulphur	S	32.06
Calcium	Ca	40.1	Manganese	Mn	55.0	Tantalum	Ta	183
Carbon	C	12.00	Mercury	Hg	200.0	Tellurium	Te	127.6
Cerium	Ce	140.25	Molybdenum	Mo	96.0	Terbium	Tb	160
Chlorine	Cl	35.45	Neodymium	Nd	143.6	Thallium	Tl	204.1
Chromium	Cr	52.1	Neon	Ne	20	Thorium	Th	232.5
Cobalt	Co	59.0	Nickel	Ni	58.7	Thulium	Tu	171
Columbium	Cb	94	Nitrogen	N	14.04	Tin	Sn	119.0
Copper	Cu	63.6	Osmium	Os	191	Titanium	Ti	48.1
Erbium	Er	166	Oxygen	O	16.00	Tungsten	W	184
Fluorine	F	19	Palladium	Pd	106.5	Uranium	U	238.5
Gadolinium	Gd	156	Phosphorus	P	31.0	Vanadium	V	51.2
Gallium	Ga	70	Platinum	Pt	194.8	Xenon	Xe	128
Germanium	Ge	72.5	Potassium	K	39.15	Ytterbium	Yb	173.0
Glucinum(Be)	Gl	9.1	Praseodymium	Pr	140.5	Yttrium	Yt	89.0
Gold	Au	197.2	Radium	Ra	225	Zinc	Zn	65.4
Helium	He	4	Rhodium	Rh	103.0	Zirconium	Zr	90.6

TABLE OF CONCENTRATIONS OF LABORATORY SOLUTIONS

Reagent	Formula	"Formula weights per Litre"[1]
Conc. hydrochloric acid	HCl	13
Conc. sulphuric acid	H_2SO_4	18.8
Conc. nitric acid	HNO_3	14.5
Dil. hydrochloric acid	HCl	4
Dil. sulphuric acid	H_2SO_4	3
Dil. nitric acid	HNO_3	5
Potassium bichromate	$K_2Cr_2O_7$	0.27
Ferric chloride	$FeCl_3$	0.6
Ferrous sulphate	$FeSO_4$	0.22
Potassium iodide	KI	0.09
Calcium hydrate	$Ca(OH)_2$	0.01
Calcium chloride	$CaCl_2$	0.7
Calcium sulphate	$CaSO_4$	0.01
Magnesium chloride	$MgCl_2$	0.4
Ammonium oxalate	$(NH_4)_2C_2O_4$	0.26
Sodium phosphate	Na_2HPO_4	0.22
Mercuric chloride	$HgCl_2$	0.22
Lead acetate (and a little free acetic acid)	$Pb(C_2H_3O_2)_2$	0.24
Silver nitrate	$AgNO_3$	0.15
Ammonia (Ammonium hydroxide)	NH_4OH	7
Ammonium chloride	NH_4Cl	1.9
Ammonium carbonate	$(NH_4)_2CO_3$	1.2
Ammonium sulphide	$(NH_4)_2S.S_x$	3
Potassium hydrate	KOH	1.7
Barium chloride	$BaCl_2$	0.
Acetic acid	$HC_2H_3O_2$	1.3
Sodium carbonate	Na_2CO_3	0.4
Alcohol (methylated)	C_2H_6O	
Ammonium sulphocyanate	NH_4SCN	1.2
Potassium ferricyanide	$K_3Fe(CN)_6$	This solution does not keep well, and should be made up in small quantities when required.

[1] See foot-note, p. 50.

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