PRACTICAL CHEMISTRY

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PREFACE

The purpose of this work is to provide a course of practical chemistry suitable to the needs of students in the latter part of their School Certificate course and throughout their preparation for Higher School Certificate. By including experimental work in elementary biochemistry, it is hoped that the book will also satisfy the needs of medical students preparing for 1st M.B. examinations. While it is expected that students will have had three or four years' experience in experimental chemistry, it is realised that some may have had less opportunity than others to cover the preliminary work; the course has therefore been designed to facilitate the work of those who have lacked laboratory experience.

The choice of experiments, and the order in which they are arranged, are based on many years' experience in teaching practical chemistry to senior students in grammar schools; the book has also been divided into parts to correspond with the accepted divisions of the subject in the text-books. As the order chosen by the authors may not conform to the treatment of the theoretical work by other teachers, the division into parts should give a flexibility of presentation to meet individual needs. It is also realised that pressure of work may, on occasions, prevent the teacher from giving individual attention to a student, or to a group of students. The instructions given for each experiment have therefore been fully described, so that a student may work with a minimum of supervision. The amount of practical work covered will depend, very largely, on the limiting factor of the time-table; but with a reasonably generous allowance of time during the two years of preparation for Higher School Certificate, there should be opportunity to cover, if not the whole, at any rate the majority of the experiments.

Although individual views about the relation between the practical and theoretical aspects of the subject may differ, it is generally agreed that a sound knowledge of practical work, permitting individual observations and experience, is of the utmost importance. Wherever possible in this book, the theoretical considerations have been given as adjuncts to the practical work which is to be performed; but where it is desirable to have a brief introduction of theory prior to the performance of experiments, this latter method has been adopted. It is hoped that this intermingling of theoretical and practical work will prevent the unfortunate tendency to dissociate the practical work of the laboratory from the theoretical knowledge of the lecture-room. It is also hoped that the cross-references from one part of the book to another, may help the student to appreciate how closely related are the parts into which the subject is divided for teaching purposes.

Wherever possible, reactions which have been chosen to illustrate properties have been described as small scale test-tube experiments. This has been done for the dual reasons of economy in the use of material and inculcation of the practice of manipulating small quantities. At the same time practice in the use of larger scale apparatus, particularly in organic preparations, has been included in order to familiarise the student with apparatus which has been designed for specific purposes; it will also afford him the satisfaction of proceeding with the preparation of a given compound to a state of reasonable purity. A list of apparatus and material which is required has been given below the title of each experiment, but, to avoid unnecessary repetition, it is assumed that a number of pieces of apparatus and a certain range of material are usually readily accessible in the laboratory; a list of these has been given in the Appendix.

Part I, Physical Chemistry, has been planned to include those topics which may readily be illustrated by the use of simple apparatus. Some work of a revisionary character has also been included. This part is not intended to take the place of a theoretical textbook; but the student who has followed the experimental work with understanding will have become acquainted with much of the physical chemistry which he is required to study. He will also be able to apply his knowledge to reactions which occur in the course of practical work in other parts of the book.

Part II, Inorganic Chemistry, is based on the Periodic Table. The dependence of properties on atomic structure would, in itself, be sufficient justification for arranging the elements, for the purpose of study, in the groups of the Table. There is also the further advantage of maintaining a close relation between the theoretical considerations of chemical properties and the practical observations on which the theory is based. It must, however, be acknowledged that the comparatively small selection of elements which the student is required to study for examination purposes makes it difficult to show, experimentally, the gradation of properties which a more comprehensive study would make evident.

Part III, Organic Chemistry, is sub-divided in the traditional manner into an aliphatic and an aromatic section. The experimental work exceeds the requirements of many examining boards; but no apology is needed for exceeding minimum demands in favour of a reasonably comprehensive course. If the amount of time does not allow for all the work to be covered, a judicious selection may be made from the preparations which are described.

Part IV, Volumetric Analysis, has stood the test of a very wide experience as a separate publication entitled *The Essentials of Volumetric Analysis*. The text has been revised, and the range of experiments affords a sound ground-work for external examinations.

Part V, A System of Analysis, is the scheme of analysis usually followed, but the use of organic reagents in analysis has been included. While it may be found possible in the future to replace the present scheme by one based on spot-tests, using organic reagents or otherwise, the value of the present scheme as an illustration of ionic reactions is generally admitted, and the book's intention is to use the suggested organic reagents purely as confirmatory tests.

Part VI, Gravimetric Analysis, is intended to serve as an introduction to the subject. Experience shows that little is gained at this stage by a wide range of gravimetric exercises, and a comparatively few illustrations of a fairly simple character have been selected.

Part VII, Elementary Biochemistry, has been included primarily for its value to medical students and students of biology; but even those students of chemistry who are not studying biology will benefit from some practical work in this highly important branch of chemistry.

It is hoped that the book will prove useful to teachers and students, and the authors will welcome criticisms and suggestions.

Acknowledgments

We have pleasure in thanking Messrs. John Murray and Messrs. G. Bell and Sons for permission to use experiments from the *Science Master's Book* and *Lecture Experiments in Chemistry* respectively—with special gratitude to Mr. G. Fowles, the author of the latter work. We thank the various examination boards for permission to use their questions. The following is a list of these Boards, with the abbreviations used at the end of the questions set by them, to indicate the source of each particular question:—

Central Welsh Board . . .	(C.W.B.)
University of Durham . . .	(Durham)
University of London . . .	(London)
Joint Matriculation Board . .	(N.U.J.B.)
Oxford Local	(Oxford)
Oxford and Cambridge . . .	(O. & C.)

We also thank the Examination Syndicates of the Universities of Oxford and Cambridge for permission to use some of their scholarship questions (Schol.).

Our thanks are due to Messrs. J. P. Chippendale (of Ormskirk Grammar School) and Alan Dale (of King Henry VIII School, Coventry) for reading the MS. and making valuable suggestions; to Messrs. A. J. Gess, J. B. Guy and A. R. Muir for making many constructive comments on the proofs; and above all to Mr. E.

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Finally, to our publisher's Educational Manager, with whom it has been a pleasure to work, we render our sincere thanks.

J.L.
March, 1947. T.A M.

INTRODUCTION FOR THE STUDENT

The following general points will assist the student to interpret the directions and arrangement of the book.

(1) After the title of each experiment is given a list of the apparatus and materials required. Because ice is not usually readily available, it is given in heavy type thus: **ICE.**

In giving this list it is assumed that certain simple apparatus and commonly used materials are to hand.

A list of these is given on p. 370.

(2) A conveniently small quantity of material is termed a "salt-spoonful"; this represents approximately 0·25 to 0·5 gm. and is sufficient to cover the bottom of a test-tube. It will be helpful to note that a test-tube (6 in. × $\frac{3}{4}$ in.) holds approximately 30 c.c.

(3) The abbreviation "conc.", used in connection with liquids, signifies the highest concentration normally available. Dilute solutions of acids and alkalis are those usually available on the bench (approx. 2 N. or slightly more concentrated).

(4) Where theoretical considerations are provided, to assist an understanding of the practical work, they are given in smaller type.

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PART I

PHYSICAL CHEMISTRY

CHAPTER I

PROPERTIES OF DILUTE SOLUTIONS. OSMOTIC PRESSURE, DEPRESSION OF THE FREEZING POINT, ELEVATION OF THE BOILING POINT

THEORY

When a substance dissolves in a liquid, the substance is called a solute and the liquid a solvent. If a dilute solution of a given solute in a given solvent is separated from a concentrated solution of the same solute and solvent by a semipermeable membrane (i.e., a membrane permeable to the solvent but not permeable to the solute), solvent passes through the membrane from the dilute solution to the concentrated until the strengths are equalised. The pressure causing this movement of solvent is called *osmotic pressure*. When a pure solvent is separated by a semipermeable membrane from a solution of the same solvent, the pressure exerted by the solvent passing into the solution can be measured. The presence of a solute in a solvent also has the effect of lowering the freezing point of the solvent, and of raising the boiling point. The actual value of the osmotic pressure, or the number of degrees by which the freezing point is lowered or the boiling point raised, depends upon the concentration of the solution. Provided the solutions considered are sufficiently dilute, the laws governing these phenomena are accurate, the effects being directly proportional to the number of particles present in a fixed amount of solvent. "Particles" includes molecules of the solute and ions into which molecules have dissociated. Thus 2 gm.-molecules of the non-ionisable solute urea will have twice the effect of 1 gm.-molecule of urea in a given amount of a solvent, and 1 gm.-molecule of urea (60 gm.) will have the same effect as 1 gm.-molecule of cane-sugar (342 gm.). An ionisable substance, if fully ionised, will furnish as many particles (ions) as its constitution allows; thus 1 gm.-molecule of sodium chloride will give twice the number of ions as there were molecules:—

$$NaCl \rightarrow Na^+ + Cl^-$$

A molecule of barium chloride, when fully ionised, gives three ions:—

$$BaCl_2 \rightarrow Ba^{++} + 2Cl^-$$

A gm.-molecule of barium chloride will have three times the effect of 1 gm.-molecule of urea.

OSMOTIC PRESSURE

Osmotic pressure effects can be shown qualitatively in the laboratory by means of simple apparatus, but quantitative measurements are not usually possible because of difficulties of technique.*

Experiment 1. Copper ferrocyanide as a semipermeable membrane.

Apparatus: Glass tubing drawn out to form a capillary; 2 N. copper sulphate. *Material* (see also p. 370): potassium ferrocyanide.

Make a concentrated solution of potassium ferrocyanide and allow

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* 1 gm.-molecule of a non-electrolyte dissolved in water and made up to 22·4 litres of solution cause an osmotic pressure, at 0° C., of 760 mm. of mercury (1 atmosphere).

it to drop from a fine capillary into a dilute solution of copper sulphate (2N). The drop formed will be surrounded by a layer of copper ferrocyanide:—

$$2CuSO_4 + K_4Fe(CN)_6 \rightarrow 2K_2SO_4 + Cu_2Fe(CN)_6$$

ionically: $2Cu^{++} + Fe(CN)_6^{----} \rightarrow Cu_2Fe(CN)_6 \downarrow$

The drop, being denser than the copper sulphate solution, will sink but after a short time will rise by virtue of alteration in density caused by osmosis.

Experiment 2. Prussian blue as a semipermeable membrane.

**Material*: Solid ferric chloride.

Half fill an evaporating basin with a solution of potassium ferrocyanide (about 5 gm. in 100 c.c.), and drop in a small lump of ferric chloride. At the surface of the ferric chloride a layer of prussian blue will form and act as a semipermeable membrane. Inside the membrane there will be a highly concentrated solution of ferric chloride, and water will pass through from the dilute potassium ferrocyanide solution. The layer of prussian blue will swell, due to the dilution of the ferric chloride.

Experiment 3. Vegetable cells as a semipermeable membrane.

Material: Large potato.

Cut a large peeled potato into the shape shown in Fig. 1, and fill the cavity about half full of salt solution. Stand it in a vessel and add enough water to bring the level equal to that of the salt water. Note the level and leave until the following day. The salt solution will then have grown in bulk by passage of water molecules through the membrane.

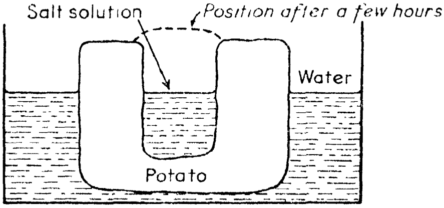

FIG. 1.

Experiment 4. Cellophane as a semipermeable membrane.

Apparatus: Short length of glass tube (diam. about $\frac{3}{4}$ in.); fine string; cellophane.

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* See also p. 370.

Take a piece of cellophane about 3 in. square, and fit round one end of the tube, tying it firmly in position with string. Fill the tube with sugar solution coloured with red ink, and close the other end of the tube with a well-fitted rubber bung fitted with a long piece of glass tubing. (Fig. 2.) Set up the tube in water and mark the level. The level rises appreciably after a few minutes and shows a considerable rise overnight.

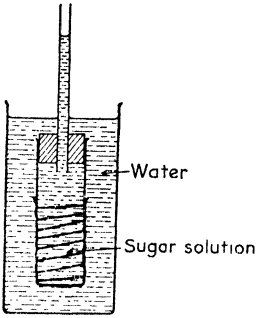

FIG. 2.

ELEVATION OF THE BOILING POINT

A solution has a lower vapour pressure than its pure solvent and will therefore boil at a higher temperature. The lowering of the vapour pressure can be shown to be proportional to the osmotic pressure, and, if the solution is dilute, the lowering of the vapour pressure is accompanied by a proportional elevation of the boiling point (and also a proportional lowering of the freezing point). The gm.-molecular weight of any non-ionisable solute when dissolved in 100 gm. of a solvent elevates the boiling point by a constant number of degrees, the number being specific for each solvent; thus, 1 gm.-molecular weight of any non-electrolyte when dissolved in 100 gm. of water elevates the boiling point by 5·2° C. i.e., the solution would boil at 105·2° C. Calculations of molecular weights of solutes are based on this statement, but it must be remembered that the experimental data must be obtained by using dilute solutions. It would be more accurate to state that if 'n' is a small fraction, then n gm.-molecules of a non-electrolyte in 100 gm. of water would elevate the boiling point by $5{\cdot}2 \times n°$ C.

Experiment 5. To determine the boiling point constant for water.

(Given that cane sugar is a non-electrolyte and has a molecular weight of 342.)

Apparatus: Landsberger (or modified Landsberger) apparatus; boiling cans; glazed paper. *Material*: cane sugar or urea.

The modified Landsberger apparatus consists of a boiling-tube with a small hole blown about half an inch from the top and fitted loosely with a bung which carries a glass tube and thermometer capable of being read accurately to $\frac{1}{10}°$ C. The whole fits into a gas-jar, a cork holding the boiling tube in place (see Fig. 3). With careful handling the apparatus will last for several determinations. Weigh accurately about 7 gm. of cane sugar

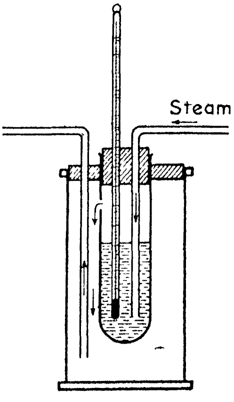

FIG. 3.

on a weighed piece of glazed paper. Half fill the boiling-tube with water and pass in steam. Note the temperature when the mercury has become steady; this is the boiling point of water at the pressure of the atmosphere. The bung in the boiling-tube must be loosely fitting throughout, or the tube will crack. Remove this bung, slide in the sugar, and determine the new boiling point. Weigh the solution immediately, and subtract the weight of solute to find the weight of water.

Example:

Weight of cane sugar = 6·9 gm.
Temperature of boiling solvent = 100·1° C.
Temperature of boiling solution = 100·4° C.
Weight of solution = 41·9 gm.
Weight of water = 35·0 gm.

6·9 gm. of cane sugar in 35 gm. of water caused an elevation of 0·3° C.

6·9 gm. of cane sugar in 100 gm. of water caused an elevation of

$$\frac{0{\cdot}3 \times 35}{100} \,^{\circ}\mathrm{C}.$$

342 gm. (gm. mol. wt.) of cane sugar in 100 gm. of water caused an elevation of

$$\frac{342 \times 0{\cdot}3 \times 35}{100 \times 6{\cdot}9} \,^{\circ}\mathrm{C} = 5{\cdot}2^{\circ}\,\mathrm{C}$$

Note: The error in the thermometer reading being large, the volume in c.c· of the final solution may be taken as the weight (in gms.) of the solvent, without serious additional error.

Experiment 6. To find the degree of ionisation* of potassium chloride at a given dilution.

(Given the elevation of boiling point constant for water to be 5·2 °C.)

Apparatus: As for Expt. 5. *Material*: Potassium chloride.

THEORY

If there were no ionisation, 1 gm.-molecule of potassium chloride would have an effect equal to that of 1 gm.-molecule of cane-sugar, i.e., 74·5 gm. of potassium chloride in 100 gm. of water would cause an elevation of the boiling point of 5·2° C. But ionisation does, in fact, occur and the observed elevation is therefore higher than this value.

$$\mathrm{KCl} \rightleftharpoons \mathrm{K}^{+} + \mathrm{Cl}^{-}$$

$$\frac{\text{Observed elevation}}{\text{Calculated elevation}} = \frac{\text{Number of particles of solute present}}{\text{Number of particles present if there had been no ionisation}}$$

Consider 1 gm.-molecule of a binary electrolyte (i.e., an electrolyte which

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* Assuming ionisation in accordance with Arrhenius's Theory.

can give two ions per molecule, e.g., potassium chloride). Let the degree of ionisation (i.e., the fraction of a gm.-molecule present as ions under the conditions of the experiment) be x. Then, in solution there would be $1-x$ gm.-molecules of undissociated potassium chloride, x gm.-ions of potassium, and x gm.-ions of chloride, giving a total number of gm.-molecules and gm.-ions of $1-x+2x$, or $1+x$. If ionisation had not occurred there would have been 1 gm.-molecule only. Hence:—

$$\frac{\text{Observed elevation}}{\text{Calculated elevation}} = \frac{1+x}{1}$$

In this expression the observed value is obtained experimentally, the calculated elevation is based on the constant obtained in Expt. 5, and x can therefore be determined.

Example:

Weight of potassium chloride	=	1·02 gm.
Boiling point of solvent	=	100·1° C.
Boiling point of solution	=	100·4° C.
Weight of water	=	42·8 gm.

Calculation of elevation if ionisation had not occurred:

74·5 gm. of potassium chloride in 100 gm. of water cause an elevation of 5·2° C.

1·02 gm. of potassium chloride in 42·8 gm. of water cause an elevation of $\frac{5\cdot 2 \times 1\cdot 02 \times 100}{74\cdot 5 \times 42\cdot 8}$

$$= 0\cdot 167^\circ \text{ C.}$$

Observed elevation was 0·30° C.

$$\frac{0\cdot 30}{0\cdot 167} = \frac{1+x}{1} \quad \therefore\ x = 0\cdot 8 \text{ (approx.) or } 80\% = \text{degree of ionisation.}$$

Experiment 7. To find the freezing point constant for water.

Apparatus: Accurate thermometers (50° C.); stirrers. *Material*: **ICE**; salt; urea.

Note: The constant for benzene may be found in a similar way to that described below, naphthalene being a suitable solute. In this case ice may be used in place of the freezing mixture.

Measure 30 c.c. (gm.) of water by means of a burette into a clean boiling-tube. Place this in a beaker and pack round alternate layers of ice and salt, making 5 or 6 layers of each (Fig. 4). Insert a thermometer (capable of being read accurately to $\frac{1}{10}$° C.) and a stirrer. Note the temperature when pure water begins to freeze. If the indicated temperature is much below 0° C. before freezing occurs there is probably supercooling and the true freezing point is the value

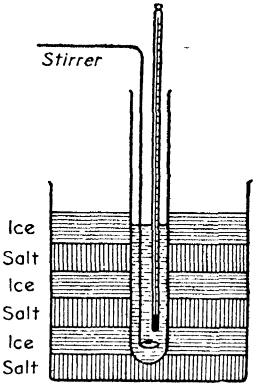

FIG. 4.

obtained when ice has separated out and the thermometer is steady. Have ready an accurately weighed quantity of urea (about 1 gm.) on a piece of glazed paper. Warm the boiling tube in the hand to melt the ice and then slide the urea into the water and stir to dissolve. Find the freezing point of the solution. Given that the gm.-molecular weight of urea is 60 gm., use the results to calculate the lowering of the freezing point when 1 gm.-molecule is dissolved in 100 gm. of water.

Note 1. Thorough stirring is necessary throughout the experiment to avoid supercooling.

Note 2. This experiment is capable of reasonably good results because of the much greater value of this constant than the corresponding boiling-point constant, and because the freezing point is much steadier during the period of observation than is the boiling point. The degree of ionisation of an electrolyte is found from freezing point data by a similar method to that given in Expt. 6 and a suitable variation would be to use the tertiary electrolyte barium chloride (about 1 gm. in 30 gm. of water).

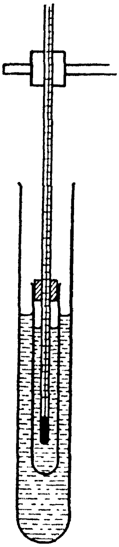

FIG. 5.

Experiment 8. To determine the molecular weight of naphthalene, given the freezing point constant for camphor as 400. *Rast's method.*

Apparatus: Ignition tubes; thermometer (360° C.); olive oil. *Material*: Camphor, naphthalene.

Note: The freezing point constant of camphor has a high value and this method is suitable for a small quantity of solute.

Weigh an ignition tube empty and then with about 0·5 to 1·0 gm. of camphor. Add about one-tenth of the camphor's weight of naphthalene, weigh and insert a thermometer with a piece of rubber tubing to act as a cork (Fig. 5). Place in a boiling tube containing olive oil and warm gently until the whole melts. Remove the ignition tube and adjust the thermometer so that it dips into the molten contents. Replace the tube and allow to cool while in the oil. Note the temperature when the camphor becomes cloudy and take this as the freezing point. Use another ignition tube to find the freezing point of pure camphor.

Example:

Freezing point of pure camphor	= 175° C.
Freezing point of solution	= 124° C.

Weight of ignition tube = 3·02 gm.
" " " " + camphor = 3·83 gm.
" " " " + camphor + naphthalene = 3·96 gm.

Calculation:

51° C. is the depression caused by 0·13 gm. naphthalene in 0·81 gm. camphor

51° C. is the depression caused by $\frac{0{\cdot}13 \times 100}{0{\cdot}81}$ gm. naphthalene in 100 gm. camphor

400° C. is the depression caused by $\frac{0{\cdot}13 \times 100 \times 400}{0{\cdot}81 \times 51}$ gm. naphthalene in 100 gm. camphor

= 126 gm. (correct value = 128)

CHAPTER II

REVERSIBLE REACTIONS AND THE LAW OF MASS ACTION

THEORY

A reversible reaction is one which can proceed in either direction by altering the conditions of the reaction. One of these conditions is the relative concentrations (or active mass) of the reactants. According to the Law of Mass Action the velocity of a chemical change is directly proportional to the "active mass" of the reactants, and active mass in a homogenous system is usually expressed in gm.-molecules of a substance per litre, or in the case of ions, in gm.-ions per litre. Other conditions which can influence the direction are temperature and pressure.

Experiment 9. Dependence of rate of reaction on concentration.

Apparatus: Measuring cylinder. *Material*: Magnesium ribbon; potassium iodate; starch; saturated solution of sulphur dioxide; measuring cylinder; 2 N. sulphuric acid.

(a) *Qualitative, using magnesium-acid reaction.* Measure into each of four beakers 10 c.c. of conc. hydrochloric acid. Leave the first beaker unaltered, but to the second, third and fourth add respectively 10 c.c., 30 c.c., and 70 c.c. of water, thus giving solutions of concentrations in the ratios $1 : \frac{1}{2} : \frac{1}{4} : \frac{1}{8}$. Measure four equal lengths (about 3 in. each) of magnesium ribbon, and drop one piece into each beaker simultaneously. Observe that the rate of reaction is approximately proportional to the concentrations of the acid.

(b) *Quantitative, using iodide-iodate reaction.* Make up solutions A and B as follows:—

A. 6 gm. potassium iodate + 2·5 c.c. 2 N. sulphuric acid made up to 1 litre with water.
B. 12·5 c.c. of a saturated solution of sulphur dioxide in water made up to 1 litre.

Add to each of two beakers the reagents in the order and quantities given, noting the time as the sulphurous acid solutions are simultaneously added. The time is noted again when the starch solution turns blue.

	Beaker I	Beaker II
	125 c.c. water, 50 c.c. A 2·5 c.c. starch	125 c.c. water, 50 c.c. A 2·5 c.c. starch
Finally	12·5 c.c. B diluted with 62·5 c.c. water	25 c.c. B diluted with 50 c.c. water
Time	*ca.* 12 secs.	*ca.* 6 secs.

ionically: $IO_3^- + 3HSO_3^- \rightarrow I^- + 3HSO_4^-$ (1)
$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 \downarrow + 3H_2O$ (2)

Reaction (1) is slow and (2) is rapid but does not take place until (1) is complete. Hence presence of iodine indicates the end of reaction (1).

THE LAW OF MASS ACTION

In many chemical reactions a point is reached where action apparently ceases in the forward direction although some of the reacting substances remain unchanged. If A and B represent the reacting substances, and C and D represent the resulting substances, an equilibrium is reached with some A and B unchanged and a definite quantity of C and D formed. The explanation, based on the Kinetic Theory, is that initially A and B react at a rate which depends on their concentrations (in gm.-molecules per litre) and since a change in the concentration of either A or B will produce a corresponding change in the rate of the reaction, the rate of the forward action is proportional to the product of the concentrations of A and B.

$$\begin{aligned}\text{Rate of reaction of A and B} &\propto \text{(Conc. of A) (Conc. of B)}\\ &= k_1 \text{ (Conc. of A) (Conc. of B)}\end{aligned}$$

As soon as A and B react, their concentrations will decrease, and the rate of reaction will progressively decrease. At the same time the reaction between A and B will have formed some of C and D, and the concentrations of these will progressively increase, and will in turn react to form A and B. The rate of reaction will be proportional to the product of their concentrations.

$$\begin{aligned}\text{Rate of reaction of C and D} &\propto \text{(Conc. of C) (Conc. of D)}\\ &= k_2 \text{ (Conc. of C) (Conc. of D)}\end{aligned}$$

When there is apparently no further action, an equilibrium has been reached with the rate of reaction of A and B forming C and D, equal to the rate of C and D forming A and B.

At equilibrium, k_1 (Conc. of A) (Conc. of B) $= k_2$ (Conc. of C) (Conc. of D)

$$\text{or, } \frac{\text{(Conc. of C) (Conc. of D)}}{\text{(Conc. of A) (Conc. of B)}} = \frac{k_1}{k_2} = K \text{ (called the equilibrium constant)}$$

The expression means that, at equilibrium, the product of the concentrations of C and D, divided by the product of the concentrations of A and B has a definite value. Hence, if at equilibrium the concentration of, say, A is increased by addition of more of it, the concentrations of B, C, and D will assume such new values that the value of the expression (K) will remain unchanged. Clearly this will involve the combination of some A and B to form more C and D, that is, the previous equilibrium concentration of B will be decreased and those of C and D will be increased. Examples of the effect of addition of one of the reacting substances are given in Expt. 10.

Experiment 10. To show the effect of alteration of concentration.

Material: Bismuth chloride; antimony chloride; saturated solutions of sodium chloride and barium chloride.

(a) *Hydrolysis of bismuth chloride.* Put a smear of bismuth chloride into a test-tube and add about 1 c.c. of water. A white substance bismuth oxychloride is formed.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl \downarrow + 2HCl$$

Add 1 drop of concentrated hydrochloric acid and further drops until the white precipitate disappears. Add a few more drops of water and notice the reappearance of the white oxychloride.

On first adding water, equilibrium was reached when definite concentrations of bismuth oxychloride and hydrochloric acid had been formed:—

$$\frac{[BiOCl]\,[HCl]^2}{[BiCl_3]\,[H_2O]} = K \text{ (Equilibrium constant)}$$

On adding concentrated hydrochloric acid, some bismuth oxychloride and some hydrochloric acid reacted to form more bismuth chloride and water. By these changes the value of the expression assumed the original mathematical value of K.

(b) *Hydrolysis of antimony chloride.* Repeat the above experiment using antimony chloride in the place of bismuth chloride. The reactions and the explanations are similar to those for bismuth.

$$SbCl_3 + H_2O \rightleftharpoons \underset{\text{antimony oxychloride.}}{SbOCl} \downarrow + 2HCl$$

(c) *Common ion effect to precipitate sodium chloride from solution.* To a saturated solution of common salt add a few drops of concentrated hydrochloric acid. (Hydrogen chloride may be passed in by means of an inverted funnel as an alternative method.) Sodium chloride comes down as a white crystalline precipitate.

$$\underset{\substack{\text{solid}\\\text{undissolved}}}{NaCl} \rightleftharpoons \underset{\substack{\text{dissolved}\\\text{but unionised}}}{NaCl} \rightleftharpoons Na^+ + Cl^-$$

$$HCl \rightarrow H^+ + Cl^-$$

Increase in the concentration of the chloride ion favoured the backward reaction with subsequent precipitation of common salt.

(d) *Common ion effect to precipitate barium chloride from solution.* The experiment is carried out in a similar manner to (c) above.

(e) *The increased concentration of ammonium ion from ammonium chloride reduces the (OH^-) concentration in ammonium hydroxide solution.* Add a drop of phenolphthalein to a dilute solution of ammonium hydroxide. The solution goes pink. Add solid ammonium chloride a little at a time when the colour will diminish and finally disappear.

$$\underset{\substack{\uparrow \\ \text{NH}_4\text{Cl produces NH}_4^+ \text{ ions which} \\ \text{increase the speed of the back reaction}}}{NH_4OH \rightleftharpoons NH_4^+ + OH^-}$$

Experiment 11. To show the effect of temperature on chemical equilibrium.

Apparatus: As shown in Fig. 6. *Material*: Lead nitrate.

(a) *Thermal dissociation of ammonium chloride.* Heat about a salt-spoonful of ammonium chloride in the bottom of a dry test-tube with a piece of damp litmus in the mouth. The solid will sublime and condense part of the way up the tube, leaving a clear space where the tube is hot. The litmus will turn blue. The clear space contains the products of decomposition of ammonium chloride, i.e. ammonia and hydrogen chloride—both colourless gases. The ammonia, being the lighter of the two gases, diffuses more rapidly, reaches the litmus first and turns it blue. In the cooler parts of the tube recombination to form ammonium chloride occurs.

$$NH_4Cl \underset{\text{cold}}{\overset{\text{hot}}{\rightleftharpoons}} HCl + NH_3$$

(b) *Action of heat on nitrogen tetroxide.* Fit up the apparatus shown (Fig. 6), and heat the tube containing the lead nitrate, and also the centre of the long horizontal tube. The colour of the gas in the hot part of the tube is a darker brown than in the cooler part because of the presence of more NO_2 molecules which are brown.

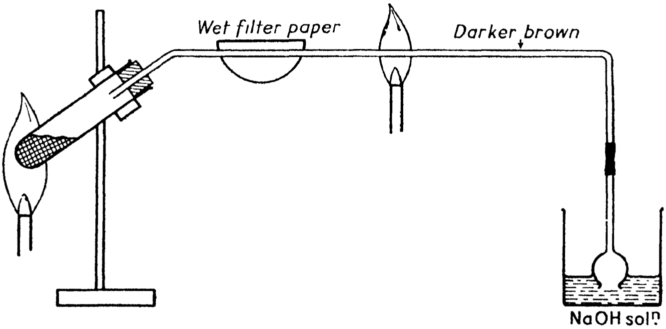

FIG. 6.

$$\underset{\text{pale yellow}}{N_2O_4} \underset{\text{cooling}}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\text{brown}}{2NO_2}$$

CHAPTER III

OXIDATION AND REDUCTION

THEORY

Oxidation may be regarded as:—

1. The chemical addition of oxygen to a substance.

e.g., $2Pb + O_2 \rightarrow 2PbO$ $\qquad S + O_2 \rightarrow SO_2$

$$\underset{\substack{\text{ferrous}\\ \text{oxide}}}{4FeO} + O_2 \rightarrow \underset{\substack{\text{ferric}\\ \text{oxide}}}{2Fe_2O_3}$$

2. The increase in the proportion of the non-metallic radical of a salt.

e.g., $2FeSO_4 + \underbrace{H_2SO_4 + O}_{\text{from oxidising agent}} \rightarrow Fe_2(SO_4)_3 + H_2O$

3. A chemical action removing hydrogen from a compound.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

4. A chemical action bringing about an increase in the valency of a metallic ion.

ionically: $\underset{\text{ferrous ion}}{2Fe^{++}} + 2H^+ + O \rightarrow \underset{\text{ferric ion}}{2Fe^{+++}} + H_2O$

Similarly reduction may be regarded as a chemical action in which

1. Oxygen is removed from a substance.
2. The proportion of the non-metallic radical of a salt is decreased.
3. Hydrogen is added to a substance.
4. There is a decrease in the valency of a metallic ion.

Experiment 12. To show bromine water, concentrated nitric acid and hydrogen peroxide are oxidising agents.*

Material: Solution of hydrogen sulphide.

Fill each of four test-tubes to a depth of half an inch with:

(a) acidified potassium iodide solution.
(b) ferrous sulphate solution acidified with dilute sulphuric acid.
(c) sulphuretted hydrogen water.
(d) concentrated hydrochloric acid.

Add two or three drops of bromine water to each of the test-tubes in turn. Observe and warm if no evidence of action is seen. Repeat the experiment using concentrated nitric acid and hydrogen peroxide in place of bromine water.

An oxidising agent will in

(a) turn the iodide solution brown and may precipitate black crystals of iodine, e.g.,

ionically: $2I^- + H_2O_2 \rightarrow I_2 \downarrow + 2OH^-$ (react with H^+ present)

---

* Other materials which may be used are chlorine water, manganese dioxide, potassium dichromate, potassium permanganate, lead dioxide, etc.

(b) form ferric sulphate solution which will be yellow or brown in colour, e.g.,

ionically: $2Fe^{++} + Br_2 \rightarrow 2Fe^{+++} + 2Br^-$

The presence of ferric iron may be shown by adding dilute caustic soda solution (in excess) when a reddish brown precipitate of ferric hydroxide will be seen.

(c) precipitate sulphur, giving the liquid a milky appearance, e.g.,

$$H_2S + 2HNO_3 \rightarrow 2H_2O + 2NO_2 + S\downarrow$$

A powerful oxidising agent in excess may oxidise the sulphur to sulphuric acid.

(d) liberate chlorine which may be tested for with a piece of damp litmus paper held in the mouth of the tube. The litmus will be bleached.

Note: The three reagents bromine water, nitric acid and hydrogen peroxide produce oxygen (for oxidation purposes) according to the equations:—

$$\begin{array}{lll} Br_2 + H_2O & \rightarrow & 2HBr + O \\ 2HNO_3 & \rightarrow & H_2O + 2NO_2 + O \\ H_2O_2 & \rightarrow & H_2O + O \end{array}$$

Experiment 13. To compare potassium chlorate and potassium persulphate as oxidising agents.

Material: Potassium chlorate; potassium persulphate.

Arrange in pairs in a test-tube rack, test-tubes containing approximately equal volumes of solutions (a) to (d) in Expt. 12 above. Perform the experiment with two of the test-tubes containing the same reagent, e.g., acidified potassium iodide, by adding approximately equal amounts (half a salt-spoonful) of potassium chlorate and potassium persulphate respectively. Note the action, warm if necessary, and observe in which case the reaction appears to take place the more readily. Repeat with pairs of test-tubes containing reagents (b) to (d) above. Both solids are powerful oxidising agents.

Note: Potassium persulphate produces oxygen (for oxidation purposes) according to the equation:—

$$K_2S_2O_8 + H_2O \rightarrow K_2SO_4 + H_2SO_4 + O$$

Experiment 14. To show that nitrous acid may act as either an oxidising or a reducing agent.

Material: Sodium nitrite.

(a) Make a solution of sodium nitrite in water and add it gradually to a solution of potassium iodide acidified with dilute sulphuric acid. Iodine will be liberated showing that the nitrous acid, produced by the action of the dilute acid on the sodium nitrite, has oxidised the potassium iodide. The nitrous acid has itself been reduced to nitric oxide (which on coming into contact with the oxygen of the air forms brown fumes of nitrogen dioxide).

$$\begin{array}{l} 2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2 \\ 2HNO_2 + 2KI + H_2SO_4 \rightarrow 2H_2O + 2NO + I_2 + K_2SO_4 \end{array}$$

i.e., to act as an oxidising agent the nitrous acid decomposes according to the equation:—

$$2HNO_2 \rightarrow H_2O + 2NO + \underbrace{\quad O \quad}_{\text{for oxidation.}}$$

(b) Acidify a solution of potassium permanganate with dilute sulphuric acid in a test-tube and pour in a solution of sodium nitrite until the colour of the permanganate is just discharged. Note the absence of brown fumes; the solution, which contains nitric acid, can be tested by the nitrate test (see p. 311). The potassium permanganate has oxidised the nitrous acid to nitric acid, itself being reduced to manganous salts. See Expt. 135 for explanation.

ionically: $2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{++} + 3H_2O + 5NO_3^-$

Experiment 15. To show hydrogen sulphide and sulphurous acid are reducing agents.

Apparatus: Sulphur dioxide syphon. *Material*: Potassium iodate.

(a) Bubble hydrogen sulphide from a Kipp's apparatus into an acidified potassium permanganate solution (very dilute) in a boiling tube. The colour of the permanganate is discharged but a milky precipitate of sulphur remains:

ionically: $2MnO_4^- + 6H^+ + 5H_2S \rightarrow 2Mn^{++} + 8H_2O + 5S\downarrow$

(b) Repeat (a) using sulphur dioxide from a syphon or sulphurous acid in place of hydrogen sulphide. The colour of the permanganate is discharged but no precipitate of sulphur is formed. The sulphurous acid has been oxidised to sulphuric acid:

ionically: $2MnO_4^- + 6H^+ + 5SO_3^{--} \rightarrow 2Mn^{++} + 3H_2O + 5SO_4^{--}$

(c) Bubble hydrogen sulphide for ten minutes through a dilute solution of ferric chloride acidified with a few drops of hydrochloric acid. The colour will change from yellow to green. Boil the solution in a dish for two minutes to expel hydrogen sulphide, filter through a double filter paper to remove sulphur, and add caustic soda solution in excess to the filtrate. A dirty green precipitate of ferr*ous* hydroxide will be obtained showing that the ferric iron has been reduced to ferrous iron:

ionically: $2Fe^{+++} + H_2S \rightarrow 2Fe^{++} + 2H^+ + S\downarrow$

(d) Bubble sulphur dioxide for some time through a dilute solution of ferric chloride. The liquid turns red (due to a complex sulphite). Transfer the solution to a dish and boil for a few minutes on a tripod and gauze. The resulting solution will be pale green or colourless. Add caustic soda solution in excess to a portion, when a dirty green precipitate of ferrous hydroxide will show that reduction is complete.

ionically: $2Fe^{+++} + SO_3^{--} + H_2O \rightarrow 2Fe^{++} + SO_4^{--} + 2H^+$

(e) *Reduction of iodate to iodine.* Dissolve a salt-spoonful of potassium iodate in water in a boiling-tube and pass a brisk stream of sulphur dioxide through it. Iodine will be deposited as black crystals.

ionically: $IO_3^- + 3SO_3^{--} \rightarrow I^- + 3SO_4^{--}$ followed by:

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 \downarrow + 3H_2O$$

If the stream of sulphur dioxide continues for a minute or two the solution goes clear due to the formation of hydrogen iodide.

ionically: $I_2 + SO_3^{--} + H_2O \rightarrow 2I^- + SO_4^{--} + 2H^+$

CHAPTER IV

HYDROGEN ION CONCENTRATION

Note: The theoretical considerations of pH value are set out in Chapter XXXIII.

Experiment 16. To make solutions of pH value 3 to 11 using buffer solutions.

Material: Universal indicator; N/10 acetic acid; N/10 sodium acetate; N/10 hydrochloric acid; N/10 caustic soda; M/10 disodium phosphate.

THEORY

A buffer solution is one whose pH value does not materially alter for small additions of acid or alkali. A typical buffer solution is one made up of a mixture of sodium acetate and acetic acid, the former being highly ionised, the latter only partially. If hydrogen ions are added to the solution the following reaction takes place

$$H^+ + Ac^- \rightarrow \underset{\text{undissociated}}{HAc}$$

thus removing H^+ from the solution. If an alkali is added more HAc dissociates to form hydrogen ions which combine with the hydroxyl ions to form water.

$$HAc \rightarrow H^+ + Ac^-$$
$$H^+ + OH^- \rightarrow H_2O$$

and again the OH^- ions are removed from the solution.

[Ac represents the radical CH_3COO]

The following figures are taken from the Science Masters' Book I, Part II, p. 65.

For preparing solutions of hydrion concentrations of 10^{-3} to 10^{-6} gm. ions per litre, the following are used:—

(1) 0·1 N acetic acid solution.

(2) 0·1 N sodium acetate solution (13·6 gm. of cryst. sodium acetate, $CH_3COONa.3H_2O$ per litre). The solutions are mixed as follows:—

C_H.	Volume. 0·1N acetic acid.	Volume. 0·1N sodium acetate.
10^{-3}	1 litre	18 c.c.
10^{-4}	1 litre	180 c.c.
10^{-5}	555 c.c.	1 litre
10^{-6}	55 c.c.	1 litre

For solutions with hydrion concentrations between 10^{-7} and 10^{-11}, the following are required.

(1) A solution of disodium phosphate (Na_2HPO_4), made by dis-

solving 0·1 gram molecule of the crystalline salt $Na_2HPO_4 . 12H_2O$ per litre. (35·8 gm.)

(2) 0·1N hydrochloric acid.

(3) 0·1N sodium hydroxide.

The mixtures are made as follows:

C_H	Na_2HPO_4 solution.	0·1N HCl.	0·1N NaOH.
10^{-7}	1 litre	322 c.c.	—
10^{-8}	1 litre	47 c.c.	—
10^{-9}	1 litre	5 c.c.	—
10^{-10}	1 litre	—	3·6 c.c.
10^{-11}	1 litre	—	36 c.c.

A convenient method of exhibiting the changes in colour shown by the indicator in solutions of various hydrion concentrations is to arrange three rows of nine 1-in. test-tubes or boiling-tubes in a wooden stand, covered with white paper, so that the three rows can be seen simultaneously one above the other, and to place in each tube the same volume of solution according to the following scheme:

	$C_H=10^{-3}$	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}
Top row	MO	MO*	MO	MO	—	PP	PP*	PP	PP
Second row	MR	MR	MR	MR*	MR	—	TP	TP	TP*
Third row	—	L	L	L	L*	L	L	—	—

Methyl orange, MO. Phenol Phthalein, PP. Litmus, L. Methyl red, MR. Thymol Phthalein, TP.

A few drops of the indicators are then added as shown above, and the colour changes observed. The asterisks in the table above show the hydrion concentrations at which the transition colours are most marked.

To show that the solutions are comparatively stable make a solution of N/1000 HCl ($pH = 3$) and N/1000 NaOH ($pH = 11$) and add a few drops of universal indicator to each. Pour out approximately the same volume of buffer solutions of $pH = 3$ and $pH = 11$ made as indicated above and add a few drops of universal indicator to these two solutions. Now add a drop of acid or alkali in turn to each of the four solutions and observe the change and estimate the alteration in pH value. It will be seen that there is a rapid change in case of the N/1000 acid and alkali but little change in the buffer solutions.

Experiment 17. To find the pH value of solutions of certain salts.

Material: Universal indicator; aluminium chloride; sodium sulphite.

THEORY

A normal salt is one in which the replaceable hydrogen atoms of an acid have been completely replaced by a metal. A normal salt is not necessarily a neutral salt since hydrolysis may occur. Thus, sodium carbonate, a normal salt, is alkaline in solution whereas ammonium chloride is acidic. The section on *hydrolysis*, Chapter XXXIII, explains this.

Arrange several test-tubes in a rack and half fill each with water and add a few drops of universal indicator. To the test-tubes add a salt-spoonful of one of the following salts: sodium carbonate, sodium sulphite, sodium chloride, ammonium chloride, aluminium chloride, borax, ferrous sulphate. (Use bench solutions of these reagents where available.) Note the pH value according to the colour produced and explain the reactions.

Warm the solutions. This increases the hydrolysis in some cases producing an even greater divergency from neutrality.

CHAPTER V

THERMOCHEMISTRY

THEORY

A chemical change is usually accompanied by an evolution or an absorption of heat, and the following definitions indicate how these heat changes are compared by specifying the quantities involved; certain physical changes also produce a heat change.

Heat of solution is the number of calories of heat evolved or absorbed when 1 *gm. molecule* of the substance is dissolved in such a volume of water that any increase in dilution brings about no further heat change.

Heat of neutralisation is the number of calories of heat evolved when *one gm. equivalent* of an acid is neutralised by *one gm. equivalent* of a base.

Experiment 18. To find the heat of solution of sodium thiosulphate crystals.

Apparatus: Calorimeter and stirrer; pestle and mortar; thermometer (100° C.) *Material*: Sodium thiosulphate crystals.

Into a calorimeter of known weight put a quantity of warm water (at a temperature 5–10° C. above that of the laboratory) and weigh again. Add finely powdered crystals of "hypo" stirring vigorously until the temperature falls approximately as far below the room temperature as the warm water was originally above it. When a batch of added crystals has just dissolved, take the temperature and weigh the calorimeter and contents.

Calculation.

Suppose:—
weight of copper calorimeter $= a$ gm.
weight of copper calorimeter + water $= b$ gm.
weight of copper calorimeter + water + "hypo" $= c$ gm.
hence, weight of water $= (b-a)$ gm.
weight of "hypo" $= (c-b)$ gm.
Suppose:—temperature of warm water $= t_1$° C.
final temperature of solution $= t_2$° C.

Assuming the specific heat of "hypo" solution to be unity, then the heat absorbed =

$$\underbrace{(t_1-t_2) \times a \times 0{\cdot}1}_{\text{heat given out by calorimeter}} + \underbrace{(t_1-t_2) \times (b-a) \times 1 \text{ calories}}_{\text{heat given out by water}}$$

$= A$ calories, say.

Then $(c-b)$ gm. of "hypo" absorbed A cals. of heat when dissolved.

Hence 248 gm. (Mol. Wt.) absorbed $\frac{A}{c-b} \times 248$ cals. when dissolved.

This value is the heat of solution (assuming further dilution causes no heat change).

Experiment 19. To determine the heat of neutralisation of caustic soda by hydrochloric acid.

Apparatus: Glass calorimeter; thermometer (150° C.) and stirrer; measuring cylinder; large dish. *Material*: N. caustic soda; N. hydrochloric acid; N. acetic acid.

Into a glass calorimeter (beaker, surrounded with non-conducting material) put 100 c.c. of Normal caustic soda solution, insert a thermometer (reading to 0·1° C.) and allow the beaker to stand in a large dish of cold water until the temperature is steady. Measure out 100 c.c. of Normal hydrochloric acid into a second beaker and allow to stand under the same conditions as the caustic soda when the steady temperature should be the same. Put the beaker containing the caustic soda into the container (see Fig. 7) and pour the acid quickly but without splashing into the caustic soda solution, stir and record the highest temperature reached. (A correction can be made for cooling during this time by recording subsequent cooling.) Assuming the specific heat of the solutions to be unity, calculate the heat which would be evolved if 1 litre of Normal caustic soda were neutralised by 1 litre of Normal hydrochloric acid. This value should be 13·7 Calories (= 13,700 calories).

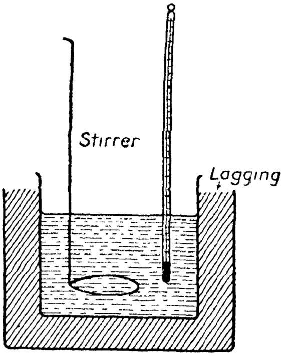

Fig. 7.

The experiment may be repeated using solutions of any strong acids and alkalis, when the value should be the same since the action:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O + Q \text{ calories}$$

is merely the ionic action in each case:—

$$OH^- + H^+ \rightarrow H_2O + Q \text{ calories.}$$

For accurate determinations the water equivalent of the stirrer and of the beaker containing the caustic soda solution should be determined in a separate experiment.

Repeat the above using Normal acetic acid in place of Normal hydrochloric acid and give the reason for the lower value obtained. See p. 223.

CHAPTER VI

PARTITION COEFFICIENT

THEORY

If a solid (or liquid) A dissolves in each of two immiscible liquids B and C then, providing A is in the same molecular state in each, and there is insufficient to saturate B or C, A will divide itself between B and C in a fixed proportion. This proportion is expressed as a ratio of the concentrations of A in the two layers and is termed the partition coefficient. The value of the partition coefficient, although constant at any one temperature, has a different value at different temperatures.

Experiment 20. Determination of partition coefficient of succinic acid between water and ether.

Apparatus: Measuring cylinder; pestle and mortar; separating funnel. *Material*: Succinic acid; ether; N/2 sodium hydroxide; N/10 sodium hydroxide.

Grind a little succinic acid in a mortar and weigh out quantities of 1½ gm., one gram, and half a gram (these weighings need only be roughly done). Pour into a separating funnel about 40 c.c. of water and add one quantity of succinic acid. Add about 40 c.c. of ether, shake until the acid has dissolved and allow to stand for a few minutes. Run off nearly all the water layer and titrate 20 c.c. of this against N/2 NaOH using phenolphthalein as an indicator (about 24 c.c. will be required for the initial addition of 1 gm. of succinic acid) Discard the boundary portion. Take 20 c.c. of the ether layer by means of a measuring cylinder and titrate this against the N/10 NaOH. Shake well after each addition of caustic soda. (The volume of N/10 caustic soda solution required will be approximately the same as the amount of N/2 caustic soda required for the water layer.) Obtain the distribution ratio:—

$$K = \frac{5 \times \text{Vol. of N/2 NaOH for 20 c.c. aqueous layer}}{\text{Vol. of N/10 NaOH for 20 c.c. ether layer}}$$

Repeat the process (simultaneously if three separating funnels are available) with the other quantities of the succinic acid.

NOTES ON EXTRACTION BY ETHER (AND OTHER LIQUIDS)

Extraction by ether is an application of the Distribution Law (or Partition Coefficient).

If a substance A is soluble in two liquids which are themselves immiscible, the substance distributes itself in a ratio of concentrations which is constant for the system.

Suppose that 11 gm. of A are dissolved in a litre of water, and that a litre of ether is available. The question to be discussed is whether it is more profitable to use all the ether in one extraction, or to take half of the litre for an extraction and then, after separating off the used ether, to add the remaining half litre for a further extraction. Let us assume that the solubility of A in ether is 10 times as great as its solubility in water, then,

$$\frac{\text{Solubility of A in ether}}{\text{Solubility of A in water}} = \frac{10}{1}$$

(a) On shaking 11 gm. of A in one litre of ether and one litre of water, 10 gm. of A will dissolve in ether and 1 gm. in water; *10 gm. of A will be extracted* and 1 gm. left in the water.

(b) On shaking 11 gm. of A in half a litre of ether and one litre of water let x gm. dissolve in the ether.

$$\frac{\text{Concentration of A in ether (in gm. per litre)}}{\text{Concentration of A in water (in gm. per litre)}} = \frac{2x}{11-x} = \frac{10}{1}.$$

From this, $x = 9{\cdot}16$ gm., i.e., 9·16 gm. of A extracted by the first half litre of ether.

1·84 gm. of A remain in the litre of water. Shake with the second half-litre of ether, and let y gm. of A dissolve in the ether.

$$\frac{\text{Concentration of A in ether (in gm. per litre)}}{\text{Concentration of A in water (in gm. per litre)}} = \frac{2y}{1{\cdot}84-y} = \frac{10}{1}$$

From this, $y = 1{\cdot}53$ gm., i.e., 1·53 gm. of A extracted by the second half-litre of ether.

Total of A extracted $= 9{\cdot}16 + 1{\cdot}53 = 10{\cdot}69$ *gm.*

It therefore follows that if the litre of ether were used in three or more portions the total extraction would approximate closely to the weight of A originally present.

Experiment 21. To determine the partition coefficient of iodine between water and carbon tetrachloride.

Apparatus: Separating funnels; weighing bottle; measuring cylinders.

Material: Carbon tetrachloride; iodine; N/100 sodium thiosulphate.

Weigh accurately (in a stoppered weighing bottle) 1 gm. of iodine, and add to 50 c.c. of carbon tetrachloride in a separating funnel. Add 50 c.c. of water and shake well. Leave to stand for some time and then run off the lower (carbon tetrachloride) layer. Take 25 c.c. of the water layer and titrate against N/100 sodium thiosulphate (see p. 273). Repeat the experiment with different weights of iodine.

Calculation.

Let the volume of sodium thiosulphate used for 25 c.c. of solution be 4·5 c.c.

$\therefore$ Iodine solution is $\frac{4{\cdot}5}{25} \times \frac{N}{100}$ and contains $\frac{4{\cdot}5}{25} \times \frac{127}{100}$ gm. of iodine per litre

$= 0{\cdot}0114$ gm. iodine in 50 c.c.

$\therefore$ weight of iodine in the 50 c.c. carbon tetrachloride

$= 1 - 0{\cdot}0114$ gm. $= 0{\cdot}9886$ gm.

$$\therefore \frac{\text{Concentration of iodine in carbon tetrachloride}}{\text{Concentration of iodine in water}} = \frac{0{\cdot}9886}{0{\cdot}0114} = \frac{87}{1}$$

The partition co-efficient will be found to be approximately constant over the range of experiments, showing that iodine is in the same molecular state in the two liquids.

Experiment 22. To find the partition coefficient of glacial acetic acid between water and carbon tetrachloride.

Apparatus: Separating funnels; 10 c.c. burette; measuring cylinder. *Material*: Carbon tetrachloride; Normal caustic soda; N/10 caustic soda.

Run from the burette 1 c.c. of glacial acetic acid into 20 c.c. of water and 20 c.c. of carbon tetrachloride in a separating funnel and shake for three minutes. Allow to settle and run off the lower layer of carbon tetrachloride, discarding the boundary layer. Titrate 10 c.c. of the aqueous layer with Normal caustic soda using phenolphthalein as an indicator. Titrate 10 c.c. of the carbon tetrachloride layer using N/10 caustic soda. Repeat the experiment using 2 c.c. and 3 c.c. of acetic acid. Allow plenty of time when titrating against the carbon tetrachloride solution and shake between each addition. You will observe from the figures for the titration that

$$\frac{\text{Concentration of acetic acid in carbon tetrachloride}}{\text{Concentration of acetic acid in water}}$$

is not constant.

Specimen readings and calculation. At 15° C.

	Vol. N/10 NaOH for 10 c.c. CCl_4 layer	Vol. N NaOH for 10 c.c. aqueous layer	$\frac{\sqrt{\text{Conc. in } CCl_4}}{\text{Conc. in } H_2O}$
I (1 c.c. acid added)	0·80 c.c. $\equiv$0·08 c.c. N	9·05 c.c.	0·031
II (2 c.c. acid added)	2·9 c.c. $\equiv$0·29 c.c. N	17·45 c.c.	0·031
III (3 c.c. acid added)	6·1 c.c. $\equiv$0·61 c.c. N	25·7 c.c.	0·030

THEORY

If the acetic acid exists in the carbon tetrachloride layer as double molecules then it can be deduced theoretically that:—

$$\frac{\sqrt{\text{Concentration in carbon tetrachloride}}}{\text{Concentration in water}} \text{ is a constant.}$$

The observed results from the above experiment do give a constant in accordance with this expression, proving the double-molecular condition of acetic acid in carbon tetrachloride.

CHAPTER VII

CATALYSIS

Experiment 23. To show manganese dioxide is a catalyst.

Apparatus: Deep sand tray. *Material*: Potassium chlorate.

Mix a little manganese dioxide with about four times its bulk of potassium chlorate and place in an ignition tube. Into each of two other tubes put an approximately equal bulk of manganese dioxide and potassium chlorate respectively. Surround each with sand on the sand tray so that they are close together and vertical. Commence to heat. After about one minute oxygen is tested for by means of a glowing splint and found to be coming off steadily from the mixture. The other two compounds do not decompose for some considerable time.

To show the weight of manganese dioxide remains unchanged, the original mixture may be made by weighing 0·500 gm. of manganese dioxide and 2 gm. of potassium chlorate. When the reaction is complete wash contents into a beaker, filter, wash, dry and weigh the residue and show there is no loss in weight. Both potassium chloride and potassium chlorate are soluble in water.

Experiment 24. Catalytic decomposition of hydrogen peroxide.

Material: 20 vol. hydrogen peroxide.

(a) Fill a test-tube with hydrogen peroxide to a depth of about half an inch and add a pinch of manganese dioxide. Test for oxygen with a glowing splint. There is a rapid evolution of oxygen and the manganese dioxide suffers no discernible loss.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(b) Take two test-tubes and fill each approximately 1 in. deep with hydrogen peroxide (20 vol. solution). Make one alkaline with a little caustic soda solution and the other acid with approximately an equal volume of dilute sulphuric acid. Immerse both in a beaker half full of hot water. The alkaline solution rapidly begins to decompose and the oxygen can be tested for by means of a glowing splint. The acidic solution remains unaffected.

Experiment 25. Catalytic oxidation of methyl alcohol and ammonia.

Apparatus: Platinum spiral; oxygen cylinder. *Material*: Methyl alcohol.

Fill a beaker to the depth of about half an inch with methyl alcohol and warm it gently by means of a small flame. Prepare a platinum spiral by winding it round a glass rod leaving a length above the spiral so that it will be just above the alcohol when lowered into it.

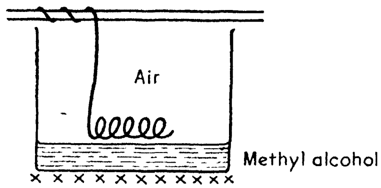

FIG. 8.

Heat the spiral strongly in the bunsen burner and transfer the glowing spiral to the beaker (Fig. 8). It will continue to glow and the smell of formaldehyde is quickly apparent. Have ready a piece of cardboard to place over the beaker in the event of the alcohol catching fire.

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$$

The experiment may be repeated with ·880 ammonia in place of methyl alcohol and a current of oxygen from a cylinder sent through the mixture when brown fumes of nitrogen dioxide or white fumes of ammonium nitrate and nitrite will be seen:

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$$

See also Expt. 172.

Experiment 26. To show carbon monoxide will not burn in dry air.

Apparatus: Large flask; carbon monoxide apparatus fitted with calcium chloride tube.

Take a flask with wide neck and pour 20–30 c.c. of concentrated sulphuric acid into it, close the mouth with a cork and swill the acid round. Allow to stand for 10 minutes. Meanwhile set up a carbon monoxide apparatus as shown in Fig. 9 with a long jet so that the jet will pass into the interior of the flask. *After all the air has been expelled from the apparatus*, light the jet and slide the flask towards the carbon monoxide apparatus allowing the burning jet to pass into the flask. The flame is extinguished. A similar experiment using a flask containing undried air may be set up. In this latter case the jet of carbon monoxide will continue to burn. In this reaction moisture is acting as a catalyst.

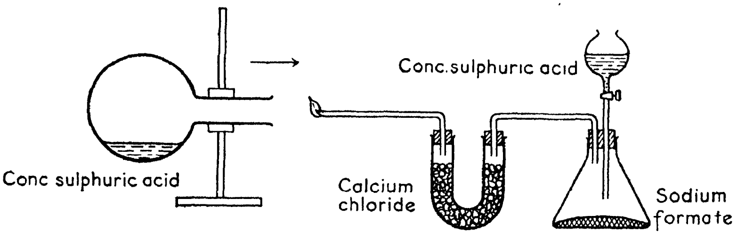

FIG. 9.

Experiment 27. To show that dry hydrogen sulphide and dry sulphur dioxide will not react.

Apparatus: Sulphur dioxide syphon; gas-jars; Woulfe's bottle; calcium chloride tube.

Collect sulphur dioxide in a dry gas-jar after passing the gas slowly through a wash-bottle containing concentrated sulphuric acid to dry it. Collect a gas-jar of sulphuretted hydrogen, after drying with a calcium chloride tube (phosphorus pentoxide is the correct, but rather inconvenient, drying agent). Invert the jar containing sulphur dioxide over the jar containing the sulphuretted hydrogen and remove the covers. No reaction takes place. Leave for a minute or two and then pour a few drops of water into the lower gas-jar and quickly replace the upper. Sulphur is precipitated at once:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \downarrow$$

Experiment 28. To show that bromine catalyses the oxidation of sulphur to sulphuric acid.

Material: Bromine.

Put a salt-spoonful of flowers of sulphur into each of two dishes and add approximately 5 c.c. of concentrated nitric acid to each but to one also add one drop of bromine (care!). The whole reaction is best performed in the fume chamber. Warm each for 2–3 minutes, decant the solution from each into a test-tube, add hydrochloric acid followed by barium chloride. In the case of the solution to which bromine has been added there is a copious deposit of barium sulphate.

One explanation of catalysis is that intermediate compounds are formed which are more readily decomposed. In this example an explanation is given by the equations:—

$$2S + Br_2 \rightarrow \underset{\text{sulphur monobromide,}}{S_2Br_2}$$

$$2S_2Br_2 + 2H_2O \rightarrow SO_2 + 4HBr + 3S$$

$$SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO_2$$

$$2HBr + 2HNO_3 \rightarrow 2H_2O + 2NO_2 + Br_2$$

Experiment 29. To show brucine retards the oxidation of sulphites to sulphates (negative catalysis).

Material: Brucine (care! very poisonous); sodium sulphite.

Measure out equal volumes of a solution of sodium sulphite into two beakers. To one add a crystal of brucine. Expose both to the air for one week. Test for sulphate at the end of a week by adding dilute hydrochloric acid followed by barium chloride. The solution not containing the brucine has been oxidised whereas the one containing the brucine remains almost unaffected.

Experiment 30. Catalytic decomposition of hypochlorites.

Materials: Sodium hypochlorite; cobalt salt.

Warm a test-tube half full of sodium hypochlorite solution and notice that there is no decomposition. Add a few drops of a cobaltous solution, e.g. cobalt sulphate, and there is an immediate evolution of oxygen which will rekindle a glowing splint.

$$2NaOCl \rightarrow 2NaCl + O_2$$

CHAPTER VIII

ATOMIC AND MOLECULAR WEIGHTS (INCLUDING VAPOUR DENSITY)

THEORY

$$\text{Atomic Weight} = \frac{\text{Weight of 1 ATOM of an element}}{\text{Weight of 1 ATOM of hydrogen.}}$$

(i) Equivalent weight = number of parts by weight of an element which will combine with or displace one part by weight of hydrogen.

(ii) Valency = number of hydrogen atoms which one atom of the element will combine with or displace.

Let Atomic weight of an element be A and valency V, and Equivalent E.
Let the weight of one atom of hydrogen be x gm.
$\therefore$ Weight of 1 atom of element $= Ax$ gm.

From (ii) 1 atom of element combined with V atoms of hydrogen.
$\therefore$ Ax gm. ,, ,, ,, ,, Vx gm. ,, ,,
From (i) E gm. ,, ,, ,, ,, 1 gm. ,, ,,
$\therefore$ VEx gm. ,, ,, ,, ,, Vx gm. ,, ,,

$$\therefore Ax = VEx$$

i.e., Atomic weight = Valency × Equivalent.

For determination of molecular weight by elevation of B.P., etc., see Chapter 1.

Experiment 31. To find the atomic weight of copper, given specific heat of copper = 0.1.

Apparatus: Reduction tubes; desiccator. *Material*: Sample of *dry* copper oxide.

THEORY

Dulong and Petit's Law states that the atomic heat of a solid element (i.e., the atomic weight multiplied by the specific heat) is approximately equal to 6·4. The approximate atomic weight using this law will be used in conjunction with the experimentally determined equivalent to find the valency (which must be a whole number).

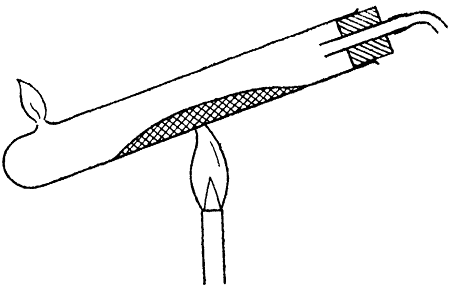

Fig. 10.

Heat some black copper oxide in a dish for five minutes stirring all the while and allow it to cool in a desiccator. Weigh a clean dry test-tube (a light copper boat may be used to contain the oxide) in which a hole has been blown at one end and introduce about 2 gm. of black copper oxide and weigh again. Fit up the apparatus as shown in Fig. 10 and warm the oxide gently in a stream of coal gas taking care to have the black copper oxide near the centre of the tube and a gentle stream of coal gas (the flame should not be green—this indicates that particles of copper are being carried over mechanically.) When reduction is complete, allow the copper to cool in a current of coal gas and weigh the test-tube and copper when cold. The reduction, cooling and weighing must be repeated until the weight is constant.

From the weighings find the weight of copper which had combined with 8 gm. of oxygen and assuming a specific heat of 0·1 for copper return a value for the accurate atomic weight from your experiment.

Experiment 32. To find the atomic weight of mercury from first principles.

Apparatus: Specific heat determination apparatus. *Material*: Mercuric chloride; hypophosphorous acid or sodium hypophosphite; industrial spirit; ether.

Determine the specific heat of mercury by the usual physical calorimetric method and hence find the approximate atomic weight.

(It is assumed that Dulong and Petit's Law applies to the non-solid element mercury.)

Weigh a clean dry boiling-tube and weigh again with approximately 3 gm. of mercuric chloride crystals. Half fill the boiling-tube with water and immerse in a beaker of water and warm the latter on a tripod and gauze. Add one third of the total volume of hypophosphorous acid, or a tea-spoonful of sodium hypophosphite. A grey precipitate of mercury is thrown down which soon settles out as globules of mercury. When the mercury is all in the form of globules in the boiling-tube, wash by decantation with water several times, dry with alcohol followed by ether (care!). Weigh the boiling tube and contents and from your result calculate the weight of mercury which would have combined with 35·5 gm. of chlorine. Using this value as the accurate value for the equivalent find the accurate atomic weight.

N.B. Valency must be a whole number.

$$2HgCl_2 + H_3PO_2 + 2H_2O \rightarrow 2Hg + 4HCl + H_3PO_4$$

Hypophosphorous acid and its salts are very powerful reducing agents.

Experiment 33. To find the atomic weights of potassium, silver and chlorine. Method of Stas.

Material: N/25 silver nitrate containing free nitric acid; potassium chlorate.

THEORY

These determinations are really equivalent weight determinations but since the valency of each of the above elements is unity, the atomic weight is obtained.

Stas knew that potassium perchlorate, potassium hypochlorite and potassium chlorate possessed weights of oxygen in the proportion of 4 : 1 : 3 combined with equal weights of potassium chloride and he assumed that potassium chlorate contained six equivalents of oxygen.

(a) *Determination of equivalent weight* of potassium chloride.*

Weigh out accurately in a clean dry weighed crucible 1·225 gm. of potassium chlorate. Replace the lid and heat gently at first and finally strongly for five minutes. Allow to cool and weigh. Repeat to constant weight. Assuming six equivalents of oxygen have been evolved calculate the equivalent weight (which is also the molecular weight) of potassium chloride.

Specimen weighings:

Weight of crucible and lid = 10·200 gm.
,, ,, ,, ,, + potassium chlorate = 11·425 gm.
,, ,, ,, ,, + potassium chloride = 10·945 gm.

∴ 0·48 gm. of oxygen was combined with 0·745 gm. potassium chloride.
∴ 48 gm. ,, ,, ,, ,, 74·5 gm. ,, ,,
i.e. Equivalent and molecular weight of potassium chloride.

(b) *Determination of equivalent weight (atomic weight) of silver.*

Transfer the residue from experiment (a) completely to a 250 c.c. flask by putting a short-necked funnel in the flask and emptying the solid into the funnel and washing out the crucible with distilled water, allowing all the washings to flow into the 250 c.c. flask. Shake at intervals and make up to the mark. Take 25 c.c. of this solution (it should be accurately N/25 if Experiment (a) was accurately performed) and run in the silver nitrate solution from a burette. The silver nitrate solution contains 4·32 gm. of silver dissolved in nitric acid and made up to 1 litre. The latter is exactly N/25 and therefore equivalent (approximately) to the chloride solution volume for volume. Run in 22 c.c. of the N/25 silver nitrate and then warm over the bunsen burner to coagulate the precipitate of silver chloride. Allow more silver nitrate solution to run in a little at a time, repeating the boiling, and the titration is complete when one drop of silver nitrate no longer produces a cloudy precipitate of silver chloride. Repeat the titration by adding a further 25 c.c. of potassium chloride solution to the titration just completed and running in more N/25 $AgNO_3$ until the end point is reached.

---

* This is the equivalent weight required for (b) and (c).

Specimen titration:

25 c.c. KCl containing (0·0745 gm. KCl) required 25·0 c.c. $AgNO_3$ containing 4·32 gm. Ag. per litre.

$$\therefore\ 0{\cdot}0745 \text{ gm. KCl} \equiv \frac{4{\cdot}32 \times 25{\cdot}0}{1000} \text{ gm. Ag.}$$

$$\begin{aligned} \therefore\ 74{\cdot}5 \text{ gm. KCl} &\equiv 4{\cdot}32 \times 25{\cdot}0 \text{ gm. Ag.} \\ &= 108 \\ &= \text{Equivalent weight (Atomic Weight) of Ag.} \end{aligned}$$

(c) *Determination of equivalent weight (atomic weight) of chlorine and potassium.*

Filter the precipitate of silver chloride obtained in the last experiment and wash three or four times with a little hot water. Dry the precipitate by allowing the air from a small flame to rise on to the filter paper suspended in a ring, Fig. 11.

Open the dried filter paper on a sheet of glazed paper (alternatively, the paper may be ignited in the crucible, a little concentrated nitric acid added, followed by a little concentrated hydrochloric acid and ignition) and remove all the silver chloride by means of a feather. Transfer the silver chloride to a weighed crucible, warm gently, allow to cool and weigh.

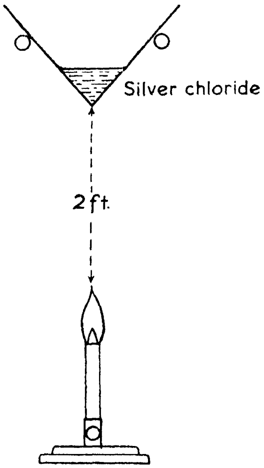

FIG. 11.

Specimen weighings: Weight of silver chloride = 0·287 gm.

The silver was precipitated from 50·0 c.c. of the silver nitrate solution by 50·0 c.c. of the potassium chloride solution.

$$\text{Hence weight of silver} = \frac{50}{1000} \times 4{\cdot}32 = 0{\cdot}216 \text{ gm.}$$

$$\therefore\ 0{\cdot}216 \text{ gm. Ag has combined with } 0{\cdot}071 \text{ gm. chlorine}$$

$$\therefore\quad 1 \text{ gm. Ag has combined with } \frac{0{\cdot}071}{0{\cdot}216} \text{ gm. chlorine.}$$

$$108 \text{ gm. silver has combined with } \frac{{\cdot}071}{{\cdot}216} \times 108 \text{ gm. of chlorine}$$

$$\begin{aligned} &= 35{\cdot}5 \text{ gm. of chlorine} \\ &= \text{Equivalent weight (atomic weight of chlorine).} \end{aligned}$$

But weight of potassium chloride in 50 c.c. was 0·149 gm.

∴ weight of potassium united with 0·071 gm. chlorine was (0·149—0·071) gm. = 0·078 gm.

∴ 0·071 gm. chlorine had combined with 0·078 gm. potassium.
35·5 gm. chlorine had combined with 39 gm. potassium.
= equivalent weight (atomic weight) of potassium.

Experiment 34. To find the molecular weight of carbon dioxide.[*]

Apparatus: 500 c.c. flask fitted as shown in Fig. 12; Kipp's apparatus for carbon dioxide; washing bottle.

THEORY

By definition, Vapour density $= \dfrac{\text{Wt. of 1 volume of carbon dioxide}^{\dagger}}{\text{Wt. of 1 volume of hydrogen}}$

(by Avogadro) $= \dfrac{\text{Wt. of 1 molecule of carbon dioxide}}{\text{Wt. of 1 molecule of hydrogen}}$

But the molecular weight of carbon dioxide $= \dfrac{\text{Wt. of 1 molecule of carbon dioxide}}{\text{Wt. of 1 atom of hydrogen}}$

But the molecule of hydrogen contains two atoms

∴ Vapour Density $= \dfrac{\text{Wt. of 1 molecule of carbon dioxide}}{\text{Wt. of 2 atoms of hydrogen}}$

Hence 2 V.D. = M.Wt.

Weigh the flask (full of air) and cork and clips and then pass a stream of dry carbon dioxide through the apparatus for 5–10 minutes. Close the clips—the one nearer the apparatus first or an increase in pressure might be obtained—and weigh again. Note the temperature and pressure. Now fill the flask with water by connecting the apparatus to a water supply (gently controlled) and empty the water into a measuring cylinder and so find the volume of the flask. Correct this volume to N.T.P. (*V* c.c.) and hence calculate:

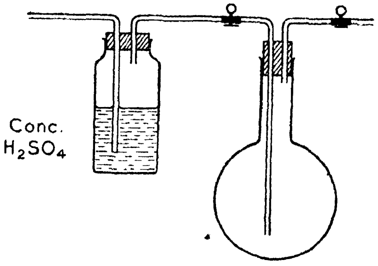

FIG. 12.

(a) the weight of air in the flask.
(b) ,, ,, ,, the flask.
(c) ,, ,, ,, carbon dioxide.
(d) ,, ,, ,, an equal volume of hydrogen.

By definition, the V.D. of carbon dioxide $= \dfrac{(c)}{(d)}$

Hence the molecular weight $= \dfrac{2(c)}{(d)}$

Note: 1 litre of dry air at N.T.P. weighs 1·293 gm.
1 litre of dry hydrogen at N.T.P. weighs 0·090 gm.

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[*] Alternatively, sulphur dioxide may be used direct from a syphon.

[†] Measured under the same conditions of temperature and pressure.

Experiment 35. To find the vapour density of chloroform by Dumas' method.

Apparatus: Dumas bulb; water-bath to fit; thermometer (100° C.). *Material*: chloroform.

This method will give a good degree of accuracy but requires a comparatively large volume of the liquid, the vapour density of which is to be determined.

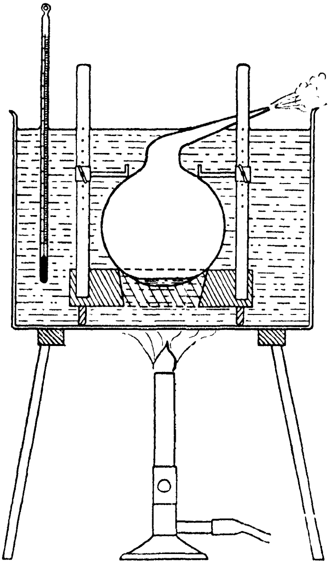

FIG. 13.

A glass bulb of about 150 c.c. capacity is weighed and about 10 c.c. of chloroform is introduced into the bulb by warming the bulb slightly and allowing it to cool with the neck under the surface of chloroform. The bulb is fixed in a bath of water (Fig. 13) which is heated until the temperature is about 25° C. above the boiling point of the chloroform (B.P. 61° C.). The chloroform vaporises and expels the air as it fills the bulb. Allow the vapour to impinge on a small flame so that the rate of issue of vapour can be estimated. (The flame can subsequently be used for sealing off.) Just as the vapour ceases to issue, seal off the bulb and record the temperature of the water bath and the barometric pressure. Weigh the bulb again. Break off the neck under water and allow the bulb to fill completely with water. Weigh the bulb (also the piece broken off) full of water.

Readings:

Weight of bulb and air	27·56 gm.
„ „ „ „ vapour after sealing	28·28 gm.
„ „ „ full of water (and piece broken off)	205·6 gm.
Temperature of laboratory	17° C.
„ „ bath	75° C.
Pressure of atmosphere	750 mm.
1 litre of dry air at N.T.P. weighs	1·293 gm.
1 litre of hydrogen at N.T.P. weighs	0·09 gm.

Calculations:

Approximate volume of bulb = (205·6—27·56) c.c.
= 178 c.c.

178 c.c. of air at 17° C. and 750 mm. weigh at N.T.P.

$$\frac{178}{1000} \times \frac{273}{290} \times \frac{750}{760} \times 1{\cdot}293 \text{ gm.}$$

$$= 0{\cdot}213 \text{ gm.}$$

$\therefore$ True weight of bulb = 27·347 gm.

$\therefore$ weight of vapour = 0·936 gm.

but 178 c.c. of vapour at 75° C. and 750 mm. would occupy at 0°C and 760 mm. a volume of

$$178 \times \frac{273}{348} \times \frac{750}{760} \text{ c.c.}$$

$$= 137{\cdot}5 \text{ c.c.}$$

$\therefore$ 137·5 c.c. of vapour weigh 0·936 gm.

1 litre ,, ,, weighs $0{\cdot}936 \times \frac{1000}{137{\cdot}5}$ gm.

$\therefore$ V.D. $= \frac{0{\cdot}936 \times 1000}{137{\cdot}5 \times {\cdot}09}$

$$= 59{\cdot}2$$

Experiment 36. To find the vapour density of ether by Victor Meyer's method.

Apparatus: Victor Meyer's apparatus. *Material*: Ether.

THEORY

This method is much less accurate than Dumas' method, but is very rapid and is sufficiently accurate when it is necessary merely to decide what relation exists between the empirical and molecular formulæ.

Note that the volume measured is that of an equal volume of air expelled as the liquid vaporises. If the vapour diffuses rapidly and enters the measuring tube it will condense to a liquid and so cause an error.

The apparatus consists (Fig. 14) of a long glass tube with a bulb at one end, into which can be dropped a small cylindrical bottle (A). The long glass tube fits into an outer casing, usually of copper, which contains water (or a liquid boiling above the boiling point of the liquid whose vapour density is being determined) which is raised to boiling point. When the temperature is steady no more bubbles of air will emerge from the side tube (cork inserted in top). The small bottle is meanwhile weighed empty, then filled with ether and weighed again, and the stopper is loosely inserted. The measuring tube is filled with water, placed in position and the cork is removed, the small bottle dropped in and the cork rapidly and firmly replaced. The pressure of the vapour formed in the small bottle blows off the stopper and the vapour displaces its own volume of air. When no more bubbles of air are seen to come off, the volume of air is measured*

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* The volume of air may be measured at atmospheric pressure by transferring the tube to a gas-jar containing water.

and the temperature and pressure of the air in the room are measured.

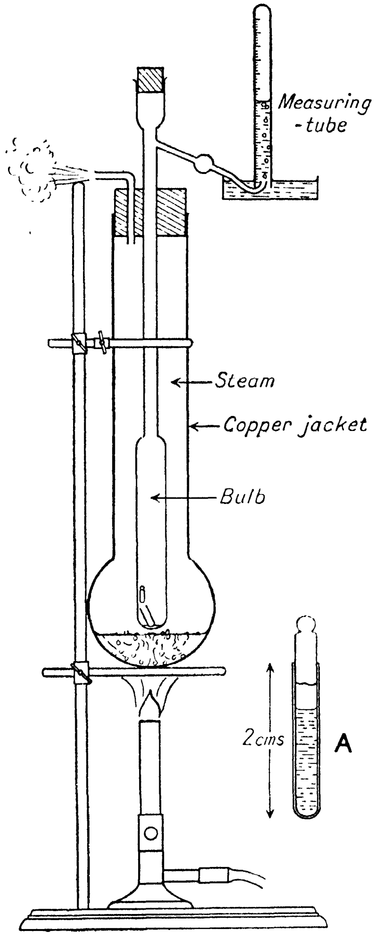

FIG. 14.

Calculation:

Weight of small bottle = W_1 gm.
Weight of small bottle + liquid = W_2 gm.
Volume of displaced air = V_1 c.c.
Temperature of laboratory = $T°$ C.
Pressure of laboratory = P mm.
Maximum water vapour pressure at $T°$ C. = p mm.

Then V_1 c.c. of air at $T°$ C. and $(P-p)$ mm. pressure would occupy at 0° C. and 760 mm. a volume of

$$V_1 \times \frac{273}{273+T} \times \frac{(P-p)}{760} \text{ c.c.}$$
$$= V_2 \text{ c.c. (say)}$$

1 litre of vapour would weigh at N.T.P. $\frac{1000}{V_2} \times (W_2 - W_1)$ gm.

$$\therefore \text{ V.D. } = \frac{1000\,(W_2 - W_1)}{V_2 \times 0{\cdot}09}$$

CHAPTER IX

SOLUTIONS

THEORY

A solution is a homogeneous mixture of two (or more) substances the proportions of which may vary between certain limits.

The following types of mixtures will be mentioned:—

1. Gas in gas.
2. Gas in liquid.
3. Liquid in liquid.
4. Solid in liquid.

Experiment 37. To show the solution of bromine in air.

Apparatus: Gas-jar. *Material*: Bromine.

Gases are miscible in all proportions. Thus air contains numerous gases and under no circumstances does one gas become "insoluble" in air.

Take a gas-jar and allow one drop of bromine to fall to the bottom of it (*care!*) and replace the lid. The bromine can be seen rapidly to diffuse until the mixture is homogeneous. This is in spite of a very large difference in density since bromine vapour is nearly six times as dense as air.

Experiment 38. To determine the composition of the gas boiled out of water.

Apparatus: Apparatus shown in Fig. 15.; absorption cup. *Material*: pyrogallol.

Set up the apparatus shown in Fig. 15, using a burette to collect the gas, and making sure that all air is excluded from the apparatus.

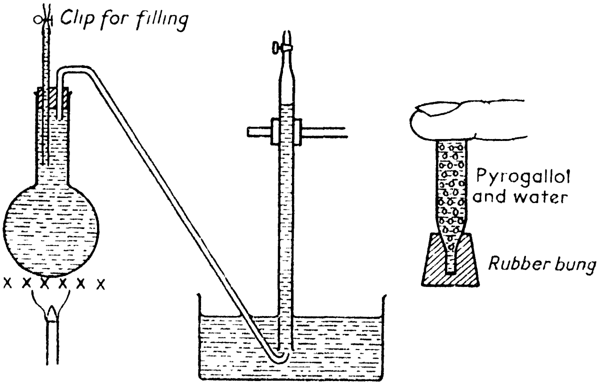

FIG. 15.

Boil the water in the flask until all air has been expelled, allow to cool and note the volume of gas. The alkaline pyrogallol is best introduced by means of an absorption cup (G. Fowles), which is inserted in a rubber bung which will fit the burette. Fill the cup with crystals of pyrogallic acid, add a few drops of water to fill the air spaces and close the end with the finger. Have ready a piece of caustic soda (make certain it will go up into the burette) and insert this into the burette (which is *in situ*) followed quickly by the absorption cup. Invert the tube several times and release the cup under water and note the volume of gas absorbed. This will be found to be approximately one third of the total volume of air boiled out of the water. Now the volume of oxygen dissolved (and therefore boiled out) will vary directly with the partial pressure of oxygen in the air (20% approximately) and directly with the coefficient of absorption of oxygen by water. Similarly with nitrogen which occupies 80% (approximately) by volume of the air.

$$\therefore \frac{\text{Coefficient of abs. for } N_2 \times 80}{\text{Coefficient of abs. for } O_2 \times 20} = \frac{\text{Vol. of gas remaining in tube}}{\text{Vol. of gas absorbed by pyrogallol (approx.).}}$$

If the volume of the flask is known the coefficients can be estimated in terms of volume of gas (oxygen or nitrogen) absorbed by 1 volume of water at the temperature of the laboratory.

Experiment 39. To determine the solubility of a very soluble gas in water.

Apparatus: Ammonia apparatus; test-tube fitted as in Fig. 16; gas-jar; string. *Material*: 2N hydrochloric acid; 2N caustic soda.

Fit a test-tube with a rubber bung through which is a heavy glass rod. Tie a piece of string round the mouth of the test-tube to facilitate weighing. See Fig. 16. Weigh the test-tube with bung and glass rod. Into the test-tube put about 15 c.c. of 0·880 ammonia and pass ammonia gas into it for a few minutes to ensure maximum solubility at the temperature of the laboratory. Cork the tube firmly with the rubber bung

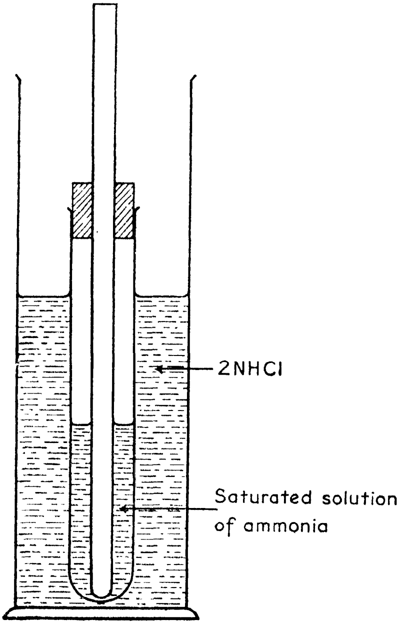

FIG. 16.

(with the glass rod in position touching the bottom of the test-tube) and weigh again. Put 250 c.c. of 2N hydrochloric acid into a gas-jar and in it place the test-tube containing the ammonia. Strike the rod to break the bottom of the test-tube and stir. Use the rod and broken tube as stirrer throughout the operation. Add methyl orange and withdraw by means of a pipette about 10 c.c. of the solution. Run in the 2N caustic soda fairly rapidly with stirring until the solution turns yellow, add the 10 c.c. (with washings) which had been withdrawn and proceed to obtain an accurate end-point.

Specimen readings:

Temperature of laboratory 15° C.
Wt. of test-tube, bung and glass rod = 21·75 gm.
Wt. of test-tube, bung, rod and ammonia solution = 37·00 gm.
Volume of 2N hydrochloric acid taken = 250 c.c.
Volume of 2N caustic soda used to neutralise excess acid = 100·3 c.c.
149·7 c.c. 2N acid ≡ ammonia in 15·25 gm. of solution.

$$\begin{array}{ccccc} NH_3 & + & HCl & \rightarrow & NH_4Cl \\ 17 \text{ gm.} & & 1 \text{litre} & & \\ & & \text{Normal} & & \end{array}$$

∴ 149·7 c.c. 2N ammonia contain $\dfrac{17 \times 149{\cdot}7 \times 2}{1000}$ gm.
= 5·09 gm. ammonia

∴ 10·16 gm. water dissolved 5·09 gm. ammonia

∴ 100 gm. water would dissolve $\dfrac{5{\cdot}09 \times 100}{10{\cdot}16}$ gm.
= 50·2 gm. at 15° C.

Experiment 40. To effect a partial* separation of water and alcohol by distillation.

Apparatus: Distillation apparatus fitted with thermometer (100° C.)
Material: Industrial alcohol.

Mix 25 c.c. of water and 25 c.c. of methylated spirit and introduce into a distilling flask in which there are some pieces of porous pot. Allow the flask to rest on gauze whilst being heated—this minimises the risk of fracture at the end of the distillation. Fit the flask with a thermometer dipping into the liquid and distil, separating the fractions which pass over through successive ranges of about 4° C. With care, almost the whole of the liquid can be distilled and the fractions are arranged in order in a test-tube rack. Warm the first fraction and apply a light to the mouth of the test-tube. The alcohol

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* Alcohol and water form a constant boiling point mixture (96% alcohol). The final traces of water, therefore, cannot be removed by distillation.

vapour-burns and this fraction will burn away almost completely. The final fraction shows no tendency to produce an inflammable gas on heating. Now add a salt-spoonful of anhydrous copper sulphate to each fraction and shake. There is a gradation of colour from very pale blue to a deep blue solution.

Experiment 41. Preparation of a supersaturated solution.

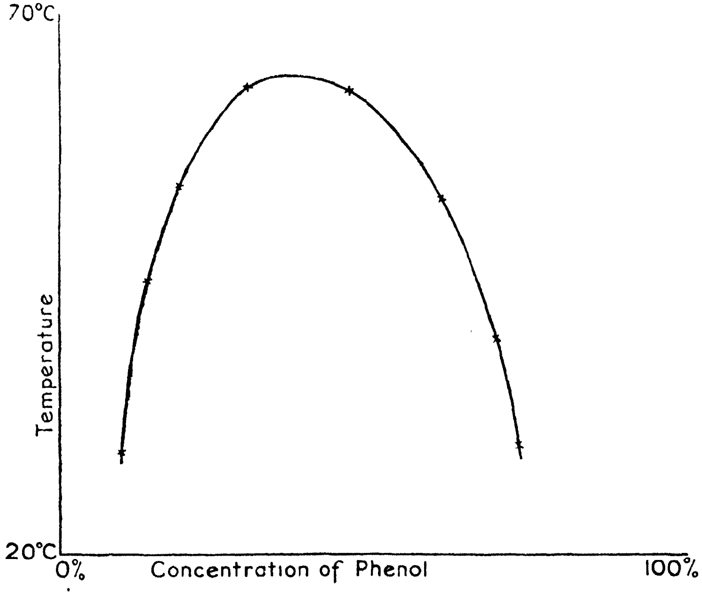
Material: "Hypo."

Two thirds fill a boiling-tube with crystals of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and warm carefully until all dissolved. Cool under the tap, avoiding undue agitation, for three to five minutes. When cold, hold in the hand whilst dropping in one small crystal of hypo. As the crystal grows the tube gets warm and finally the contents are almost completely solid.

Experiment 42. To obtain a solubility curve for phenol in water.

Apparatus: Corked test-tubes; thermometer (100° C.). *Material*: Phenol.

About 7 gm. of phenol is weighed accurately into a corked test-tube. 3 c.c. of water are added from a burette. The test-tube is gradually warmed in a beaker of water with continual shaking until the two layers disappear. It is allowed to cool slowly with shaking until the contents suddenly go cloudy. The temperature of the solution is then read off. The contents of the test-tube then represent a saturated solution in phenol at this temperature. One c.c. of water



is added from the burette and the same procedure is repeated. By continuing in this manner the solubility of water in phenol at various temperatures can be determined. When a temperature of 66° C. is reached a second test-tube is taken and about 10 c.c. of water measured out into it. A weighed quantity of phenol is then added (about 1 gm.) and the temperature at which this mixture just becomes a saturated solution is found as above. A further weighed amount of phenol is added and the experiment repeated until a temperature of about 66° C. is again reached. Plot the values on squared paper. (See the diagram.) Care is taken throughout the experiment to avoid contact between phenol and the skin.

Experiment 43. To obtain a solubility curve for potassium chlorate.

Apparatus: Thermometer (100° C.); stirrers; pestle and mortar.
Material: Potassium chlorate.

This experiment may be performed as a class experiment by different students finding the solubility at different temperatures.

Grind some potassium chlorate to a fine powder in a mortar and add it to water in a boiling-tube fitted up as shown in Fig. 17. Heat the water to about 5° C. above the temperature at which the solubility is to be found (say 40° C.) and allow to cool. Stir continuously

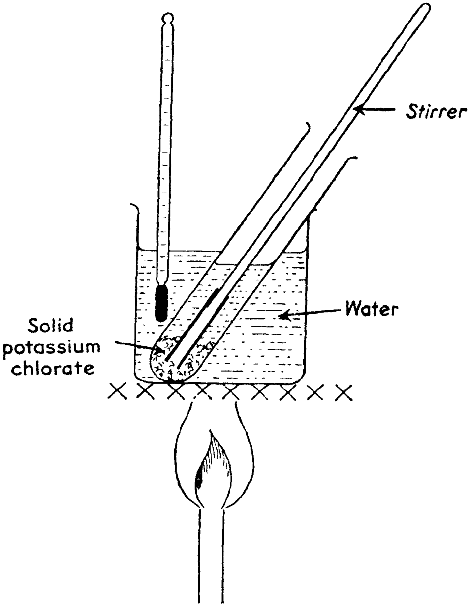


FIG. 17.

and maintain the presence of solid in the bottom of the boiling-tube. At the required temperature, decant quickly a portion (about 5 c.c.) of the solution into a weighed dish. Weigh again and evaporate to dryness on the water-bath. When apparently dry transfer the dish to a tripod and gauze and gently warm with a flame 3 or 4 inches away from the dish for a minute. Allow to cool and weigh. Repeat the warming process until the weight is constant. Calculate the weight of potassium chlorate necessary to saturate 100 gm. of water at the temperature. Collect values from other students and construct a graph.

Whilst waiting for the potassium chlorate solution to evaporate on the water bath, show that calcium hydroxide is *less* soluble in hot water than in cold by warming a test-tube containing lime-water when a slight precipitate of the hydroxide will be obtained.

Experiment 44. Solubility of potassium chlorate (*alternative method*).

Apparatus: Thermometers (100° C.); 10 c.c. pipette; stirrers. *Material*: Potassium chlorate.

Note: This method will not give accurate results with solids which exhibit supersaturation.

Weigh out into a series of test-tubes the following weights of potassium chlorate:—

0·7 gm.; 1·0 gm.; 1·5 gm.; 2·0 gm.; 3·0 gm.

Run in exactly 10 c.c. (gm.) of water from a pipette into each. Use the apparatus of Fig. 17 and heat, with constant stirring, until the solid has just dissolved. Allow to cool and note the temperature at which crystals can be seen forming in the test-tube. This temperature can be taken as the temperature at which the solution was just saturated. Proceed in a similar manner with each of the other test-tubes and plot the solubility curve.

Note. The above experiment will usually be carried out as a class experiment each student making one observation. If a student must obtain all the necessary data for the graph he should proceed in a slightly different manner. Weigh out 3·0 gm. of the salt into a boiling tube and add 10 c.c. of water from a burette. Proceed as above to find one point on the curve. Now add 5 c.c. of water and continue to find points on the curve until a total of 40 or 45 c.c. of water has been added.

Experiment 45. Preparation of potassium perchlorate as an example of fractional crystallisation.

Material: Potassium chlorate.

Half fill a crucible with potassium chlorate and arrange it firmly in a pipe-clay triangle. Heat gently until it melts and then stir the liquid (just molten) continuously until it becomes pasty (15 minutes). During the period supply sufficient heat to keep the mass just molten. Allow to cool, add an equal bulk of water and heat gently until all has dissolved. Pour the solution on to a clock-glass

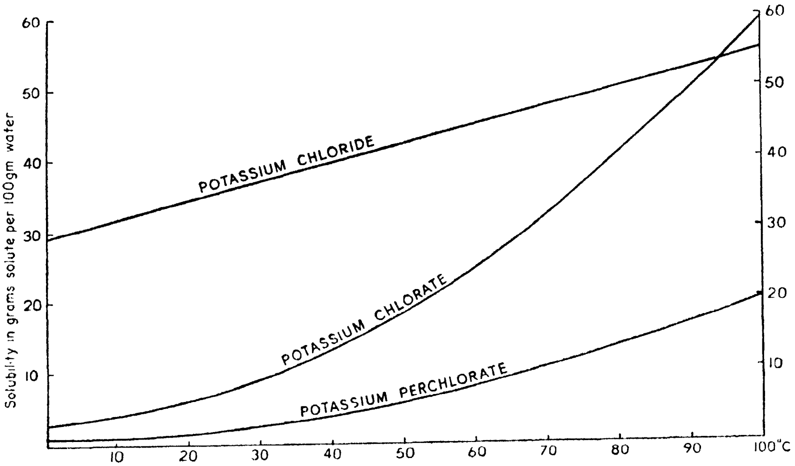


Fig. 18.

and allow to cool. The crystals which come out first are almost pure potassium perchlorate and can be purified further by dissolving in the minimum of hot water and recrystallising.

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

The solubility curve, Fig. 18, explains the separation.

CHAPTER X

THE COLLOIDAL STATE

THEORY

True solutions contain particles of solute of approximately molecular size. The solution is transparent to the ultramicroscope and the particles diffuse rapidly. There is a gradation in size from the molecule through colloidal sizes to such large aggregates of particles that they settle out under the action of gravity (suspensions).

By careful control of the size of the particles of a substance most materials can be prepared in the colloidal state.

Experiment 46. The ultramicroscope—Brownian movement.

Apparatus: Microscope; square cover slips; lantern.

Construct a small cubical box made of cover slips and on it mount a microscope as shown in the diagram, Fig. 19. Arrange for a narrow lantern beam to strike the box at right angles to the field of view. Puff a little smoke (cigarette smoke works perfectly) into the box and view the field by means of the high power. The particles are seen to be in constant irregular motion and even if a convection current is present the relative motion of the particles (seen as small circles of light) shows the Brownian movement clearly.

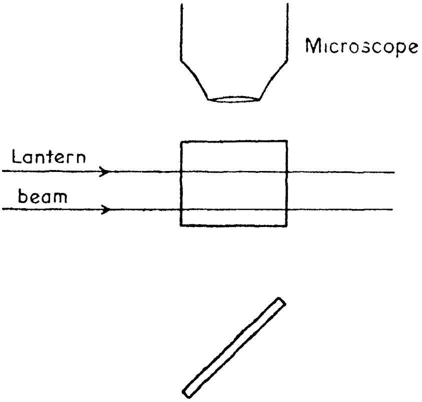


FIG. 19.

Experiment 47. To show dialysis.

Apparatus: "Cut-down" test-tube; string. *Material*: Cellophane.

Fit up a cellophane membrane round the test-tube as described in Expt. 4 and arrange it in a boiling-tube containing water as shown in Fig. 20. Add potassium ferrocyanide solution in excess to two or three c.c. of ferric chloride solution and pour the mixture into the test-tube. After five minutes, test for the presence of ferrocyanide in the boiling-tube by pouring off a little of the solution and adding ferric chloride. It will be found that the ferrocyanide ions have passed easily through the membrane, whereas the Prussian blue (which is colloidal) obviously remains in the inner tube.

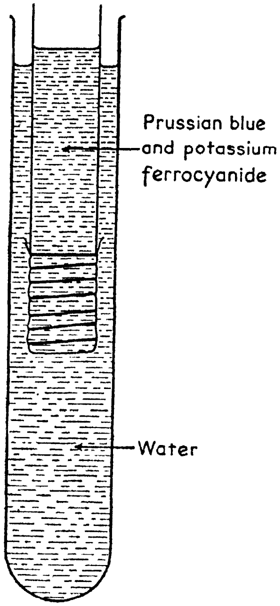


FIG. 20.

Experiment 48. Preparation of a colloidal solution of antimony sulphide.

Material: Tartar emetic; starch solution.

Pour about 20 drops of yellow ammonium sulphide into a boiling-tube nearly full of water. Put enough tartar emetic to cover the bottom of a test-tube in another boiling-tube and fill with water. The colloidal solution can be made by adding equal volumes of the two solutions. Carry out the following experiments with portions of the solution:

(a) Show that the solution filters unchanged.

(b) Boil some of the sol in a test-tube. After a while coagulation takes place.

(c) Add a small quantity of common salt. Precipitation takes place.

(d) Add some ferric hydroxide sol prepared as in Expt. 51.

Coagulation takes place because the particles in the two sols are oppositely charged: ferric hydroxide sol being positively charged and antimony sulphide negatively charged.

(e) Add 2 c.c. of starch solution to 2 c.c. of the antimony sulphide sol. Dilute 2 c.c. of the antimony sulphide sol with 2 c.c. of water to act as "control". Add a solution of common salt to both. The salt solution coagulates the "control" but no effect is observed in the solution where the sol is protected by the starch.

Experiment 49. Preparation of an olive oil emulsion.

Material: Olive oil; soap solution; gelatine solution.

In three separate test-tubes shake 5–10 drops of olive oil with

(a) Water.
(b) Soap solution.
(c) Soap solution and gelatine solution.

The final volume of liquid in each of the three cases should be approximately the same. Leave them to settle and note that the oil separates out from the water very quickly, from the soap solution slowly, and from the soap solution with gelatine very slowly or not at all.

The soap solution acts as an emulsifier, whilst the gelatine protects the colloid from coagulation.

Experiment 50. Preparation of colloidal arsenious sulphide.

Apparatus: 500 c.c. flask. *Material*: Arsenious oxide.

Add about half a salt-spoonful of arsenious oxide* to the flask two-thirds full of distilled water, and boil. Allow to cool. Remove approximately 20 c.c. of the solution and pass washed hydrogen sulphide through the remainder for ten minutes. The colloidal solution is a deep golden yellow. Now add the 20 c.c. of arsenious oxide solution to remove the excess of hydrogen sulphide. The solution will pass unchanged through a filter paper. Pour out two portions. To one add dilute hydrochloric acid and to the other sodium chloride. In each case precipitation of arsenious sulphide takes place.

Experiment 51. Preparation of colloidal ferric hydroxide.

Material: Solid ferric chloride.

Prepare a fresh solution of ferric chloride by dissolving a salt-spoonful of the solid in a test-tube half full of water. Divide into two parts. Add two or three drops of ammonium hydroxide to one and notice the reddish brown liquid which contains colloidal ferric hydroxide. The ferric chloride serves to show the contrast. Show the liquid will pass through a filter paper. Add more ammonia to the test-tube containing the ferric hydroxide and the hydroxide is precipitated.

Experiment 52. Preparation of colloidal sulphur.

Apparatus: Syphon of sulphur dioxide; Woulfe's bottle.

Sulphur dioxide is much more soluble in water than is hydrogen sulphide. To obtain suitable solutions for producing a sulphur sol proceed as follows:—Saturate some distilled water with hydrogen sulphide which has been washed by passing it through water in a

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* Care! Very poisonous.

Woulfe's bottle. Saturate a smaller quantity of distilled water with sulphur dioxide from a syphon. Dilute this solution approximately 25 times with distilled water and add an equal volume of the hydrogen sulphide water. A clear yellow colloidal solution of sulphur is formed. This will easily pass through the pores of a filter paper and is coagulated by solutions of electrolytes, e.g., sodium chloride or alum.

Experiment 53. Preparation of resin sol by dispersion.

Material: Powdered resin; industrial alcohol.

Weigh about 2·5 gm. of resin and dissolve in about 50 c.c. of alcohol on a water-bath. Filter into a 100 c.c. flask and fill to the mark with alcohol. This is a true solution of resin in alcohol.

Mix 25 c.c. of solution with about 500 c.c. of water to obtain an opalescent colloidal solution. This is a very stable colloidal solution and may be used to show the simpler properties of colloids, thus:

(a) A portion of the solution when treated with an electrolyte, e.g., sodium chloride, or better, the trivalent ion in alum, gives an immediate precipitate of the coagulated colloid.

(b) The solution shows dispersion of light when a beam is focused into it (Tyndall effect).

(c) The solution can be used to demonstrate the Brownian movement; and

(d) To show that colloids pass readily through filter paper.

PART II

INORGANIC CHEMISTRY

With each group of elements in the periodic table is given a table comparing the properties of the elements in that group.

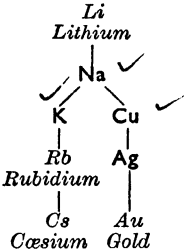
The student is advised to use the experimental work as a basis for showing these similarities and gradations in properties as well as for noting the chief differences.

The elements and their more important compounds are considered in the order of the periodic table. The properties of hydrogen should be looked for under the various headings, e.g., reduction, diffusion, hydrogen chloride, hydrogen sulphide, etc.

CHAPTER XI

GROUP I

GENERAL



Elements in italics are not usually studied in an elementary course. Sodium and potassium show a very close similarity, and their corresponding compounds are alike both in appearance and in their reactions; these points have already been noted in elementary work. Their electronic structure and the positions they occupy at the beginning of periods in the Periodic Table account for this close resemblance.

Copper and silver are not first members of periods but lie in the middle of long periods, and although conveniently included in Group I are not related to sodium and potassium. General similarity between the four elements does not exist, but as copper and silver occupy corresponding positions in the long periods, points of similarity between these two elements are to be expected and, in fact, do occur. These general remarks apply *mutatis mutandis* to the other groups, and it is usual to divide the elements in each case into a main and a sub-group.

COMPARISON OF PROPERTIES OF ELEMENTS IN GROUP I

	Sodium.	Potassium.	Cupric copper.	Cuprous copper.	Silver.
Metal	Very reactive and strongly metallic. Attacks water.	as for sodium.	metallic.	metallic.	metallic.
	← All form stable salts →				
Oxides	oxide strongly basic.	oxide strongly basic.	basic.	basic.	unstable. Sol. in ammonia.
Hydroxide	alkaline.	alkaline.	basic.	not formed.	not formed.
Chloride	sol. in water.	sol. in water.	sol. in water. With ammonia gives deep blue solution.	insol. in water. Sol. in conc. hydrochloric acid. Sol. in conc. ammonium hydroxide.	insol. in water. Sol. in conc. hydrochloric acid. Sol. in conc. ammonium hydroxide.
Iodide	v. soluble	v. soluble.	unstable forms cuprous iodide and iodine.	stable. Insol. in water.	stable. Insol. in water.
Flame coloration.	golden yellow, invisible through blue glass.	lilac, visible through blue glass.	green with blue zone.	—	—

Experiment 54. Reactions of solid copper compounds.

Material: Black copper oxide.

(a) Mix intimately a little copper oxide with fusion mixture and heat on a charcoal block in the reducing flame of the blowpipe. Brown scales of copper are formed.

(b) Moisten a little copper oxide with conc. hydrochloric acid on a watch glass, dip a platinum wire in the mixture and perform the flame test. An intense bluish green flame is obtained.

(c) Obtain a borax bead on a platinum wire, dust on a little copper oxide and re-heat in the oxidising flame. A blue bead is seen (green when hot).

Experiment 55. Reactions of cupric ions.

Material: Potassium cyanide solution.

(a) Pass hydrogen sulphide into copper sulphate solution and obtain a dark brown precipitate of cupric sulphide.

ionically: $Cu^{++} + S^{--} \rightarrow CuS \downarrow$

Wash the precipitate by decantation, add excess of dilute nitric acid and boil in a dish. The cupric sulphide readily dissolves.

ionically: $CuS + 2H^{+} \rightarrow Cu^{++} + H_2S \uparrow$

(b) Take some copper sulphate solution in a test-tube and add a solution of potassium iodide. A white precipitate of cuprous iodide is thrown down and iodine is liberated.

ionically: $2Cu^{++} + 4I^{-} \rightarrow Cu_2I_2 \downarrow + I_2 \downarrow$

Add sodium thiosulphate solution to dissolve the iodine when the cuprous iodide is observed as a white precipitate. See p. 277 for use of this reaction in the estimation of copper.

(c) Add caustic soda solution to a solution of copper sulphate in a boiling-tube. Note the blue gelatinous precipitate of cupric hydroxide.

ionically: $Cu^{++} + 2OH^{-} \rightarrow Cu(OH)_2 \downarrow$

Pour some of the suspension into a test-tube. Boil the portion remaining in the boiling-tube. The black precipitate is copper oxide.

$$Cu(OH)_2 \rightarrow CuO \downarrow + H_2O$$

Add ammonium hydroxide to the portion in the test-tube and show that the blue precipitate dissolves to form a deep blue solution. This solution contains the cuprammonium ion $[Cu(NH_3)_4]^{++}$

Note the similarity of the action of ammonia on silver, cuprous and cupric compounds.

(d) Dilute two or three drops of copper sulphate solution with water and add potassium cyanide solution (Care! It is very poisonous.) A brownish green precipitate of cupric cyanide is first obtained:—

ionically: $Cu^{++} + 2CN^{-} \rightarrow Cu(CN)_2 \downarrow$

This quickly decomposes by loss of cyanogen gas into white cuprous cyanide:—

$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 \downarrow + (CN)_2 \uparrow$$

On the addition of more potassium cyanide solution, the colourless complex ion $[Cu(CN)_2]^-$ is obtained.

(e) Add a solution of potassium ferrocyanide to a solution of copper sulphate to obtain a brown precipitate of copper ferrocyanide.

ionically: $2Cu^{++} + [Fe(CN)_6]^{----} \rightarrow Cu_2Fe(CN)_6 \downarrow$

Experiment 56. Preparation of cupric ammonium sulphate, $(NH_4)_2SO_4.CuSO_4.6H_2O$.

Material: Ammonium sulphate.

Weigh 5 gm. of copper sulphate and dissolve in 50 c.c. of boiling water. Weigh 2·6 gm. of ammonium sulphate and dissolve in 10 c.c. of water. Mix the solutions and evaporate until crystallisation begins, then set aside to cool. This is a "double salt".

Experiment 57. Preparation of cuprammonium sulphate, $Cu(NH_3)_4SO_4.H_2O$.

Apparatus: corked flask. *Material*: Industrial alcohol.

Dissolve 10 gm. of copper sulphate by boiling in 50 c.c. of water in a 200 c.c. flask and cool to room temperature. Carefully add conc. ammonium hydroxide until the precipitate which forms redissolves. Cool to room temperature. Add 20 c.c. of alcohol from a pipette so that it forms a layer on top of the blue solution. Cork the flask loosely and leave undisturbed for a week. Filter off the crystals and transfer at once to a stoppered bottle. This compound is fundamentally different from the double salt, cupric ammonium sulphate, which behaves in solution as would its constituent sulphates. Cuprammonium sulphate is a "complex salt" in which the copper ion and ammonia form a single divalent ion:—$[Cu(NH_3)_4]^{++}$

Experiment 58. Preparation of Cuprous Oxide.

Material: Rochelle salt; glucose.

Fill a boiling-tube to the depth of about 1 in. with copper sulphate solution and add a salt-spoonful of Rochelle salt (sodium potassium tartrate). When the salt has dissolved, add caustic soda solution* followed by a salt-spoonful of glucose and boil. An orange-red

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* This is now Fehling's solution. See p.

precipitate of cuprous oxide is formed by the reducing action of glucose on the cupric copper in solution. See also Expt. 176 (b).

$$2Cu(OH)_2 \underset{\text{(Reduction by glucose)}}{-\ O} \rightarrow Cu_2O + 2H_2O.$$

Show that the precipitate (which readily settles) is soluble in concentrated hydrochloric acid, but gives free copper and the cupric salt with dilute sulphuric or dilute nitric acid. (In the latter case the copper is acted upon by any excess nitric acid.)

$$Cu_2O + 2HCl \rightarrow Cu_2Cl_2 + H_2O$$
$$Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O$$

Experiment 59. Preparation of cuprous chloride.

Apparatus: Buchner funnel. *Material*: glass wool.

Take sufficient cupric oxide to cover the bottom of a test-tube and add five times that bulk of concentrated hydrochloric acid. Warm to obtain a clear green solution of cupric chloride.

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O$$

Add copper filings of about equal bulk to the copper oxide used, and boil for about 2 mins. Filter the mixture through glass wool into a beaker full of water. The white precipitate is cuprous chloride.

$$Cu + CuCl_2 \rightarrow Cu_2Cl_2$$

Decant the supernatant liquid and show that the cuprous chloride is soluble:—

(a) in ammonium hydroxide, due to the formation of a complex ion

ionically: $Cu_2Cl_2 + 4NH_3 \rightarrow 2[Cu(NH_3)_2]^+ + 2Cl^-$

(b) in concentrated hydrochloric acid, due to the formation of another complex ion, this time with the chloride ion:—

ionically: $Cu_2Cl_2 + 4Cl^- \rightarrow 2[CuCl_3]^{--}$

This ion is unstable and decomposes on dilution with water. If it is desired to prepare a pure dry specimen of the cuprous chloride, filter off the white solid using a filter pump and Buchner funnel, wash the solid with sulphurous acid followed by glacial acetic acid, and finally dry quickly by heating the solid on a water-bath. The product is kept in a bottle out of contact with the air.

Experiment 60. Reactions of cuprous compounds.

Material: Cuprous oxide; cuprous chloride in concentrated hydrochloric acid.

(a) Add a few drops of potassium iodide solution to the solution of cuprous chloride. The white precipitate is cuprous iodide.

$$Cu_2Cl_2 + 2KI \rightarrow Cu_2I_2 \downarrow + 2KCl$$

(b) Pour a little of the solution of cuprous chloride in concentrated hydrochloric acid into water. The white precipitate is cuprous chloride which, although soluble in a high concentration of chloride ions, is insoluble in water.

ionically: $Cu_2Cl_2 + 4Cl^- \rightleftharpoons 2[CuCl_3]^{--}$

(c) To a salt-spoonful of cuprous oxide in a test-tube, add some dilute hydrochloric acid and warm. A white precipitate of cuprous chloride is seen.

$$Cu_2O + 2HCl \rightarrow Cu_2Cl_2 + H_2O$$

(d) To a salt-spoonful of cuprous oxide in a test-tube, add some dilute sulphuric acid. The solution turns blue, and red metallic copper is thrown down.

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu \downarrow + H_2O$$

(e) Repeat Expt. 60d, using dilute nitric acid. A similar reaction takes place, but the liberated copper reacts with any excess dilute nitric acid. The products are, therefore, a green or blue solution of copper nitrate, nitric oxide (turning brown on exposure to air) and water.

$$Cu_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O + Cu$$
$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Experiment 61. Reactions of silver compounds.

Material: Silver nitrate crystals.

(a) Grind a little solid silver nitrate with twice its bulk of anhydrous sodium carbonate in a mortar and heat on charcoal in the reducing flame of the blowpipe. The white bead, which will not mark paper (cf. lead), but which will dissolve in dilute nitric acid (cf. tin) is metallic silver.

(b) Fill a test-tube half full of silver nitrate solution and add three or four drops of concentrated hydrochloric acid. The white precipitate is silver chloride. Shake the mixture to coagulate the silver chloride, decant, wash with water and allow to settle.

ionically: $Ag^+ + Cl^- \rightarrow AgCl \downarrow$

Pour off the water and divide the solid into three parts. Leave one part exposed to light and it will turn violet. To another, add ammonium hydroxide solution when the solid will readily dissolve. Warm the third portion with concentrated hydrochloric acid which will dissolve the silver chloride. The explanations of the solubility of silver chloride in ammonia and concentrated hydrochloric acid are similar to the explanations for the solubility of cuprous chloride in the same reagents (see Expt. 59). For the reaction of silver halides with sodium thiosulphate see Expt. 117.

(c) Add a few drops of potassium chromate solution to a solution of silver nitrate. A brick-red precipitate of silver chromate, soluble in both dilute nitric acid and caustic soda, is obtained.

ionically: $2Ag^+ + CrO_4^{--} \rightarrow Ag_2CrO_4 \downarrow$

(d) Add sodium phosphate solution to silver nitrate solution to obtain a yellow precipitate of silver phosphate.

ionically: $3Ag^+ + PO_4^{---} \rightarrow Ag_3PO_4 \downarrow$

(e) Dilute bench ammonium hydroxide solution to four or five times its bulk with water. Add this gradually to silver nitrate solution in a test-tube. A brown precipitate of silver oxide is first formed which dissolves in excess of ammonia to form a complex ion $[Ag(NH_3)_2]^+$.

$$2AgNO_3 + 2NH_4OH \rightarrow Ag_2O \downarrow + 2NH_4NO_3 + H_2O$$

Similarly, silver oxide is precipitated by caustic soda solution but is not soluble in excess of the reagent.

(f) Add potassium cyanide solution carefully to a solution of silver nitrate. The white precipitate of silver cyanide dissolves in excess to form a complex ion $[Ag(CN)_2]^-$.

Experiment 62. Recovery of silver from silver chloride.

Material: Glucose; fusion mixture; laboratory residues of silver chloride.

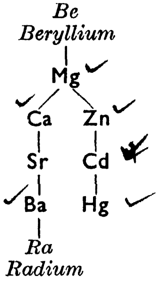
Method (*a*) Wash the residues with water several times by decantation, dry them and mix well with twice the bulk of a mixture of anhydrous sodium and potassium carbonates. Transfer the mixture to a crucible and heat strongly in a furnace. On cooling a button of silver is left in the bottom of the crucible.

Method (*b*) Transfer the residues after washing by decantation to a dish and add caustic soda solution and glucose and warm the mixture. When a portion of the solid dissolves completely in dilute nitric acid, decant the liquid from the grey silver which remains in a finely divided condition. After washing, it can easily be taken up in dilute nitric acid.

CHAPTER XII

GROUP II

GENERAL



Elements in italics are not usually studied in an elementary course.

Magnesium links the alkaline earths (calcium, strontium and barium) with zinc, which in turn is similar in many respects to cadmium. The sub-group, zinc, cadmium, and mercury do not show many points of similarity but calcium, strontium and barium are more closely related.

The properties of mercury will be considered separately.

COMPARISON OF THE PROPERTIES OF SOME OF THE ELEMENTS OF GROUP IIA

Note that zinc and mercury do not show properties analagous to those given below.

	Magnesium.	Calcium.	Strontium.	Barium.
Metallic character	———— Activity increases ————→ All strongly metallic forming divalent compounds.			
Metal on water	burns in steam.	reacts in cold.	reacts in cold.	reacts in cold.
Carbonate	decomposes at 750° C.	decomposes at 825° C.	decomposes at 1150° C.	decomposes at 1842° C.
Oxide	Slight action with water.	slakes on addition of water with evolution of heat.	as for calcium but with greater evolution of heat	as for calcium but much greater evolution of heat.
Hydroxide	Slightly alkaline.	slightly soluble and alkaline.	more alkaline.	even more alkaline.
Halides Nitrates Sulphates Chromates	solubility in water decreases with increasing Atomic Weight of metal.			
Flame coloration	—	brick red.	crimson.	green.

Experiment 63. Reactions of magnesium and its compounds.

Apparatus: As indicated in (f). *Material*: Magnesium ribbon; magnesium sulphate; sodium nitrite.

(a) Burn three or four inches of magnesium ribbon in the air over a piece of paper. The white solid is the oxide. Transfer the oxide to some water in a beaker, put in a piece of red litmus paper and boil. The litmus paper gradually turns blue showing the oxide to be feebly alkaline.

(b) Add ammonium carbonate solution to a solution of magnesium sulphate in water. A white precipitate is obtained which is a basic carbonate.

(c) Add ammonium hydroxide to a solution of magnesium sulphate in water. A white precipitate of magnesium hydroxide is obtained.

If (b) and (c) are repeated after the addition of ammonium chloride to the magnesium sulphate solution there is no precipitate. Hence magnesium does not appear in either Group III or V of the analytical tables. The reason is that the increased concentration of ammonium ion, due to the presence of ammonium chloride, suppresses the ionisation of, for example, the ammonium hydroxide leaving insufficient hydroxyl ions to attain the solubility product of magnesium hydroxide.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(d) Add ammonium chloride and ammonia to a solution of magnesium sulphate in water. Add a solution of sodium phosphate (disodium hydrogen phosphate). There is a white crystalline precipitate of magnesium ammonium phosphate.

ionically: $Mg^{++} + HPO_4^{--} + NH_3 \rightarrow MgNH_4PO_4 \downarrow$

(e) Heat a few magnesium sulphate crystals on charcoal and allow to cool. Moisten the white mass with cobalt nitrate solution and heat again. A pink mass is obtained on allowing to cool.

(f) Take a 250 c.c. flask fitted with a cork and delivery tube which in turn is connected to a "U" tube and the latter to a piece of combustion tube. Mix about a level tea-spoonful each of ammonium chloride and sodium nitrite in the flask and add 30 c.c. of water. Place a length of magnesium ribbon loosely in the combustion tube. Heat the flask cautiously until action begins, then remove the flame, and heat the combustion tube. Nitrogen is formed (see Expt. 88h) which combines with magnesium to form magnesium nitride, Mg_3N_2. The purpose of the "U" tube is to condense steam and prevent it passing into the combustion tube. Transfer the white nitride to a test-tube, add water and boil. Test for ammonia with litmus paper.

$$Mg_3N_2 + 6H_2O \rightarrow 2NH_3 + 3Mg(OH)_2$$

Experiment 64. Reactions of calcium and its compounds.

Material: Calcium; calcium chloride.

(a) Put a flake of calcium on gauze on a tripod and direct a bunsen flame on to it. It will burn brilliantly with a red flame and leave a white product, calcium oxide. Allow the solid to cool, transfer it to a test-tube and add a few drops of water. There is a vigorous exothermic reaction and on dipping a piece of red litmus paper into the solution it turns blue immediately. Note that the solid is not very soluble in water.

$$2Ca + O_2 \rightarrow 2CaO$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$

(b) Add ammonium carbonate solution to a solution of calcium chloride in water. The white precipitate is calcium carbonate.

ionically: $Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \downarrow$

(c) Add ammonium oxalate solution to a solution of calcium chloride. A white precipitate of calcium oxalate (soluble in dilute hydrochloric acid but insoluble in acetic acid) is obtained.

ionically: $Ca^{++} + C_2O_4^{--} \rightarrow CaC_2O_4 \downarrow$

Note: Solutions of calcium salts give no precipitate with potassium chromate (cf. barium) and no precipitate with calcium sulphate solution (cf. strontium).

(d) Add sodium phosphate solution to a solution of calcium chloride. White calcium phosphate is precipitated.

ionically: $3Ca^{++} + 2PO_4^{---} \rightarrow Ca_3(PO_4)_2 \downarrow$

This precipitate is soluble in dilute hydrochloric, nitric or acetic acid, as also are the corresponding phosphates of strontium and barium.

(e) Moisten a little calcium chloride with concentrated hydrochloric acid and perform the flame test. Note the brick-red flame and observe the green colour when seen through blue glass.

Experiment 65. Reactions of strontium compounds.

Material: Strontium nitrate.

(a) Perform reactions given in Expt. 64(b), (c), and (d) with strontium nitrate solution instead of calcium chloride. Precipitates of strontium carbonate, strontium oxalate and strontium phosphate, are obtained under similar conditions to those in which the corresponding compounds of calcium are obtained.

(*b*) Add calcium sulphate solution to a solution of strontium nitrate in water. Warm and allow to stand. A white precipitate of strontium sulphate (which is much more insoluble than calcium sulphate) is thrown down.

ionically: $Sr^{++} + SO_4^{--} \rightarrow SrSO_4 \downarrow$

(c) Perform the flame test with strontium nitrate and observe the crimson coloration of the flame. Viewed through blue glass there is no change.

Experiment 66. Reactions of barium compounds.

Material: Barium chloride crystals.

(a) Perform reactions given in Expt. 64(b), (c), and (d) with barium chloride solution instead of calcium chloride. Precipitates of barium carbonate, barium oxalate and barium phosphate, are obtained under similar conditions to those in which the corresponding compounds of calcium are obtained. Expt. 65 (b) performed with barium chloride in place of strontium nitrate also shows barium sulphate to be very insoluble in water.

(b) Add potassium chromate solution to a solution of barium chloride. A yellow precipitate of barium chromate is obtained.

ionically: $Ba^{++} + CrO_4^{--} \rightarrow BaCrO_4 \downarrow$

(c) Perform the flame test and show that barium compounds colour the flame with flashes of green.

Experiment 67. Reactions of zinc and its compounds.

Material: Zinc sulphate; zinc foil.

(a) Hold a piece of zinc foil by means of crucible tongs in the bunsen flame. The powder, yellow when hot and white when cold, is zinc oxide.

(b) Add sodium carbonate solution to a solution of zinc sulphate. A white precipitate of basic zinc carbonate is thrown down: $ZnCO_3.2Zn(OH)_2.H_2O$. (Sodium *bi*carbonate gives the normal carbonate.)

(c) Add caustic soda solution a drop at a time to a solution of zinc sulphate in water. A white precipitate of zinc hydroxide is formed which dissolves in excess of caustic soda solution to form sodium zincate. Zinc hydroxide is amphoteric.

$$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

If hydrogen sulphide is bubbled through the solution of sodium zincate, zinc sulphide is precipitated as a white solid.

(d) Add a few drops of ammonium sulphide solution to a solution of zinc sulphate. A white precipitate of zinc sulphide is obtained. (This precipitate is often discoloured.)

(e) Dip a rolled filter paper into a *concentrated* solution of zinc sulphate to which some cobalt nitrate solution has been added. Burn the filter paper on gauze on a tripod. A green ash (Rinmann's green) remains. (See p. 325.)

(f) Add ammonium hydroxide, drop by drop, to a solution of zinc sulphate. The precipitate of zinc hydroxide dissolves in excess, due to the formation of a complex ion, $[Zn(NH_3)_2]^{++}$.

Experiment 68. Reactions of cadmium salts.

Material: Cadmium chloride or sulphate; potassium cyanide solution.

(a) Pass hydrogen sulphide into a solution of cadmium sulphate. The bright yellow precipitate is cadmium sulphide.

ionically: $Cd^{++} + S^{--} \rightarrow CdS \downarrow$

(b) Add to a test-tube one quarter full of cadmium sulphate solution an equal bulk of concentrated hydrochloric acid, and pass hydrogen sulphide. No precipitate appears in acid of this concentration (approximately 5N). Dilute the solution until the yellow precipitate appears. Cadmium sulphide is sometimes incompletely precipitated in Group II of the analysis tables if the solution is too strongly acidic. (See p. 316.) Filter off some of the yellow cadmium sulphide and show that it is soluble in dilute nitric acid.

ionically: $CdS + 2H^+ \rightarrow Cd^{++} + H_2S \uparrow$

(c) Add caustic soda solution to a solution of cadmium sulphate. Cadmium hydroxide (insoluble in excess) appears as a white precipitate.

ionically: $Cd^{++} + 2OH^- \rightarrow Cd(OH)_2 \downarrow$

(d) Add ammonium hydroxide, drop by drop, to a solution of cadmium sulphate. The white cadmium hydroxide is precipitated but dissolves in excess (*cf.* 67f). If the potassium cyanide solution is added to the ammino cadmium solution and hydrogen sulphide passed, the cadmium is precipitated (unlike copper). The equations for these reactions are given on p. 318.

THE PROPERTIES OF MERCURY

The properties of mercury do not show any marked agreement with those of other members of the main group or sub-group. It forms two series of salts: mercurous and mercuric.

Mercury is very low in the electrochemical series and is therefore precipitated from solution by nearly all metals. Its hydroxide, carbonate and oxide are unstable and if heat is applied mercury is obtained.

Mercurous salts give, in solution with water, the unusual ion Hg_2^{++}; mercuric salts on the other hand are ionised only to a very slight extent.

Experiment 69. General reaction of mercury compounds.

Material: Mercuric chloride or any compound of mercury.

Grind a salt-spoonful of mercuric chloride in a mortar with two or three times its bulk of anhydrous sodium carbonate. Introduce the mixture into an ignition tube and heat gently. A grey deposit of mercury is obtained which if scraped together will give globules of mercury

$$HgCl_2 + Na_2CO_3 \rightarrow \underset{\text{unstable}}{HgCO_3} + 2NaCl$$

$$2HgCO_3 \rightarrow 2Hg + 2CO_2 + O_2$$

Experiment 70. Reactions of mercurous compounds.

Material: Mercurous nitrate solution (acidified with dilute nitric acid).

(a) Add a few drops of dilute hydrochloric acid to a little of the mercurous nitrate solution. A white precipitate of mercurous chloride (calomel) is seen.

ionically: $Hg_2^{++} + 2Cl^- \rightarrow Hg_2Cl_2 \downarrow$

Filter off the precipitate and pour ammonia on to the filter paper. A black precipitate of a mixture of mercury and mercuric aminochloride is obtained.

$$Hg_2Cl_2 + 2NH_3 \rightarrow NH_2HgCl + Hg + NH_4Cl$$

(b) Add caustic soda solution (excess) to a little of the mercurous nitrate solution. A black precipitate of mercurous oxide is produced.

ionically: $Hg_2^{++} + 2OH^- \rightarrow Hg_2O \downarrow + H_2O$

(c) Add a few drops of potassium iodide solution to a little of the mercurous nitrate solution. A yellowish green precipitate of mercurous iodide is obtained. The mercurous iodide (yellow) decomposes readily into mercuric iodide and mercury. This mixture is green

ionically: $Hg_2^{++} + 2I^- \rightarrow Hg_2I_2 \downarrow$

(d) Shake two or three crystals of mercurous nitrate with two of three c.c.s. of water and boil. In common with many oxysalts or mercury, hydrolysis occurs and the white precipitate is the basic nitrate.

(e) Add a solution of stannous chloride to a little of the mercurous nitrate. A grey precipitate of mercury is obtained by reduction and the stannous salt is oxidised to a stannic salt.

Experiment 71. Reactions of mercuric compounds.

(a) Add caustic soda solution to a little of the mercuric chloride solution. A yellow precipitate of mercuric oxide is obtained.

ionically: $Hg^{++} + 2OH^- \rightarrow HgO \downarrow + H_2O$

(b) Add potassium iodide solution drop by drop to a little of the mercuric chloride solution. A brilliant red precipitate of mercuric iodide is obtained, soluble in excess. The latter solution when made alkaline with caustic soda solution is Nessler's solution (see p. 66).

ionically: $Hg^{++} + 2I^- \rightarrow HgI_2 \downarrow$
$HgI_2 + 2I^- \rightarrow \underset{\text{soluble}}{HgI_4^{--}}$

(c) Pour a little stannous chloride solution into a solution of mercuric chloride. The latter is reduced to mercurous chloride which comes down as a characteristic "silky" white precipitate. If excess stannous chloride is added the precipitate turns grey due to a further reduction to metallic mercury.

ionically: $2Hg^{++} + Sn^{++} + 2Cl^- \rightarrow Hg_2Cl_2 \downarrow + Sn^{++++}$

(d) Bubble hydrogen sulphide slowly into a solution of mercuric chloride. Finally a black precipitate of mercuric sulphide is obtained. (The colour range is white—yellow—brown—black. See p. 318.)

ionically: $Hg^{++} + S^{--} \rightarrow HgS \downarrow$

(e) Add a little dilute hydrochloric acid to a solution of mercuric chloride in a test-tube. Drop in a piece of bright copper foil and warm. The foil is soon coated with a bright deposit of mercury.

ionically: $Hg^{++} + Cu \rightarrow Hg \downarrow + Cu^{++}$

Experiment 72. To illustrate the relation between mercurous and mercuric compounds.

Apparatus: Pestle and mortar. *Material*: Mercury; iodine; industrial alcohol.

Generally speaking, mercur**ous** compounds are produced with mercury in excess and mercur**ic** compounds if the acid radical is in excess.

Grind a little mercury (excess) with a small crystal of iodine in a mortar to which has been added a drop or two of alcohol. The yellowish green mercurous iodide is formed. Add more iodine and grind again when finally the red mercuric iodide is produced.

$2Hg + I_2 \rightarrow Hg_2I_2$ mercury in excess.
$2Hg + 2I_2 \rightarrow 2HgI_2$ iodine in excess.

Experiment 73. To show the relation between the two forms of mercuric iodide.

Material: Mercuric iodide.

Heat a few of the red crystals gently in an ignition tube; yellow crystals form as a sublimate in the cooler parts of the tube. Set aside for some time—the red variety is gradually formed.

Red	$\rightleftharpoons$	Yellow
Stable below 126° C.		Stable above 126° C.

Alternatively put two or three grams of the red variety into a dish, cover with a clock glass and heat gently until all has sublimed. Allow to cool. Remove the clock glass and notice the yellow crystals adhering to it. On touching any of them with a glass rod, they immediately revert to the red variety.

Experiment 74. Preparation of mercuric iodide and Nessler's solution.

Apparatus: Measuring cylinder. *Material*: Mercuric chloride solution (5 gm. in 100 c.c.); potassium iodide solution (10 gm. in 100 c.c.).

Take 20 c.c. of mercuric chloride solution in a measuring cylinder. Pour 10 c.c. of this into a beaker and add potassium iodide solution until the salmon-red precipitate which first forms just redissolves, then add the second 10 c.c. of mercuric chloride. Filter off the mercuric iodide.

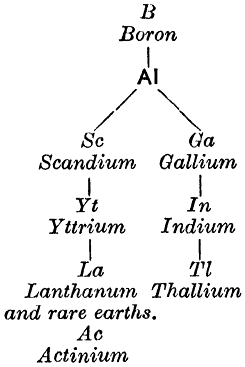
Take a little of the mercuric iodide in a test-tube and add potassium iodide solution until the solution is clear. For equations, see Expt. 71 (b).

Make alkaline with sodium hydroxide solution; this is *Nessler's solution*. Make a very dilute solution of an ammonium salt and add a drop of Nessler's solution to obtain a brown precipitate. Repeat with a still more dilute solution of ammonium salt and demonstrate the delicacy of the test.

CHAPTER XIII

GROUP III

GENERAL



Elements in italics are not usually studied in an elementary course.

We see that this group is somewhat unsatisfactory from the point of view of comparison with other elements in the group. It will be remembered that the properties of gallium (eka-aluminium) were predicted by Mendeléeff before the element was discovered.

Experiment 75. The reactions of aluminium.

Material: Aluminium foil.

(a) Show that aluminium readily dissolves in warm dilute hydrochloric acid with the production of hydrogen.

ionically: $2Al + 6H^+ \rightarrow 2Al^{+++} + 3H_2 \uparrow$

Hot concentrated sulphuric acid will attack it with the evolution of sulphur dioxide whilst nitric acid, dilute or concentrated, acts only very slowly on the metal.

(b) Add a little caustic soda solution to aluminium powder in a test-tube. The reaction is extremely rapid, hydrogen being evolved.

ionically: $2Al + 2OH^- + 2H_2O \rightarrow \underset{\text{aluminate ion}}{2AlO_2^-} + 3H_2 \uparrow$

Experiment 76. The reactions of aluminium salts.

Material: Aluminium sulphate solution; aluminium powder; flowers of sulphur.

(a) Add ammonia to a solution of aluminium sulphate. A white precipitate of aluminium hydroxide is thrown down.

ionically: $Al^{+++} + 3OH^- \rightarrow Al(OH)_3 \downarrow$

Show that the precipitate is insoluble in excess ammonia.

(b) Repeat (a) using a solution of caustic soda and adding the alkali drop by drop. The white precipitate is obtained but is readily dissolved in excess forming sodium aluminate. Aluminium hydroxide is amphoteric.

ionically: $Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O$

(c) Add blue litmus solution to a solution of aluminium sulphate in water. The litmus turns red. Add sodium carbonate solution and there is a rapid evolution of carbon dioxide. Aluminium salts in solution frequently act as acids due to hydrolysis:—

ionically: $Al^{+++} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

(d) Make a mixture of dry aluminium powder with twice its bulk of dry flowers of sulphur and introduce into a test-tube enough of the mixture to cover the bottom. (Care! Larger quantities may explode.) Clamp the tube vertically, place a bunsen burner under it and stand aside. There is a vigorous action in which aluminium sulphide is synthesised. Add a few drops of water when the contents of the tube have cooled. Hydrogen sulphide is at once evolved due to the hydrolysis of the sulphide.

$$2Al + 3S \rightarrow Al_2S_3$$
$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3H_2S \uparrow$$

Similarly, the effect of bubbling hydrogen sulphide through a solution of aluminium sulphate is to produce the hydroxide, not the sulphide.

(e) Mix a little aluminium sulphate with twice its bulk of anhydrous sodium carbonate and heat on the charcoal block. A white infusible mass is left, which, if moistened with cobalt nitrate solution and again heated, forms a bright blue solid.

Experiment 77. Oxidation of aluminium when in form of amalgam.

Material: Aluminium foil.

Aluminium is high in the electro-chemical series and therefore should be extremely reactive. Many of its actions, e.g., effect on exposure to air, suggest that there is a protective layer of oxide on the top. The following experiment shows that aluminium is readily oxidised. Dip a piece of aluminium foil in a solution of mercuric chloride and rub the foil with the finger three or four times. Take the foil out and expose it to the air. In a few moments it will be too hot to hold, and a feathery growth of alumina will be observed.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

ALUMS

Aluminium sulphate has the property of forming a double salt with the sulphate of a monovalent metal. Thus with potassium sulphate it forms potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, and, where Na or (NH_4) is denoted by X, similar compounds of formula, $X_2SO_4.Al_2(SO_4)_3.24H_2O$. All these alums crystallise as octahedra. The general method of preparation is to mix equi-molecular quantities of the constituent sulphates in solution and allow to crystallise. An extension of the term 'alum' includes similar compounds in which the sulphate of other trivalent metals have been substituted for aluminium sulphate, and if Y denotes one of these metals, the general formula of an alum becomes $X_2SO_4.Y_2(SO_4)_3.24H_2O$. For the above reasons, preparations of various alums are given at this point, and the important consequence of isomorphism—the formation of overgrowths—is appropriately included here.

Experiment 78. Preparation of potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

Material: Potassium sulphate; aluminium sulphate crystals.

The molecular weight of potassium sulphate is 174: and of hydrated aluminium sulphate $Al_2(SO_4)_3.18H_2O$ is 666 (check these figures). Equi-molecular weights of the sulphates will be as 174: 666 or, e.g., 1·45 gm. to 5·6 gm. Weigh 1·45 gm. of potassium sulphate and dissolve it in 15 c.c. of distilled water. Weigh 5·6 gm. of aluminium sulphate crystals and dissolve in another 15 c.c. of water, warming to dissolve. Mix the solutions and leave over-night. From the crystals choose a well-formed specimen and allow it to grow in the solution. Dissolve the rest of the crystals in the minimum of water and re-crystallise.

Experiment 79. Preparation of ferric ammonium alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$.

Material: Ammonium sulphate.

Find the molecular weight of this alum by substitution of atomic weights, and the molecular weights of (a) ammonium sulphate (which is anhydrous) and (b) ferrous sulphate ($FeSO_4.7H_2O$) needed to make the corresponding weight of ferric sulphate. Then calculate the weights of these needed to make 20 gm. of the alum.

Take 11·5 gm. of ferrous sulphate, dissolve in 30 c.c. of dilute sulphuric acid, add 5 c.c. of conc. nitric acid and evaporate the solution to about half of its original volume. Meanwhile dissolve 2·7 gm. of ammonium sulphate in 10 c.c. of water. Mix the solutions and set aside to crystallise. Choose a good crystal and allow it to grow in the solution. Ferric alum crystals have an amethyst colour but deteriorate on standing in air for a long period due to the formation of basic ferric sulphate.

Experiment 80. Preparation of chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$.

Apparatus: Thermometer. *Material*: Potassium dichromate; industrial alcohol.

Instead of weighing equi-molecular weights of potassium sulphate and chromium sulphate, advantage is taken of the reducing action of ethyl alcohol on potassium dichromate in acid solution.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5.OH \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + \underset{\text{(acetaldehyde)}}{3CH_3.CHO}$$

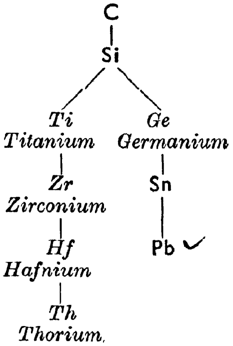
Heat 7·5 gm. of potassium dichromate in 50 c.c. of water and cool the solution to room temperature. Add 6 c.c. of conc. sulphuric acid, stir with a thermometer and cool to 25° C. Add, drop by drop, 5 c.c. of alcohol keeping the temperature below 50° C., and when all has been added, set aside to cool over-night. Choose a good crystal to grow, and place another crystal in the solution of potash alum (from Expt. 78) to form an overgrowth.

Alternatively, sulphur dioxide may be used to reduce the dichromate.

CHAPTER XIV

GROUP IV

GENERAL



Elements in italics are not usually studied in an elementary course.

The properties of the series carbon, silicon, tin and lead, show a rising value in the metallic character at the end of the series and an increasing importance of the lower oxide. Thus carbon and silicon are non-metallic and exhibit a fairly close analogy, whereas tin and lead are metallic and therefore resemble one another more closely than they resemble the parent element.

	C.	Si.	Sn.	Pb.
Metallic character	non-metal.	non-metal.	metal.	metal.
Oxide	acidic.	acidic.	acidic and basic.	acidic and basic.
Hydrides	many hydrides known.	several hydrides known.	very unstable.	—
Halides of form XCl_4	stable, not ionised.	unstable, not ionised.	unstable, not ionised.	very unstable, not ionised.
Halides of form XCl_2	—	—	ionised and reducing agent.	ionised, non-reducer.

Experiment 81. Preparation and properties of silica and silicon.

Material: Water glass; magnesium powder; pure silica.

(a) To a dilute solution of water-glass in water add a few c.c. of dilute hydrochloric acid and warm. A white precipitate of hydrated silica is thrown down.

ionically: $SiO_3^{--} + 2H^+ \rightarrow SiO_2\downarrow + H_2O$

cf. $CO_3^{--} + 2H^+ \rightarrow CO_2\uparrow + H_2O$

(b) Remove some of the precipitated silica* obtained in Expt. (a) to a test-tube and add caustic soda solution and warm. It dissolves forming sodium silicate in solution.

ionically: $SiO_2 + 2OH^- \rightarrow SiO_3^{--} + H_2O$

cf. $CO_2 + 2OH^- \rightarrow CO_3^{--} + H_2O$

(c) Mix together approximately 3 gm. of dry silica and 1 gm. of dry magnesium powder. Introduce the mixture into a *dry* test-tube, clamp at an angle, place a bunsen underneath and stand aside. A violent reaction ensues and on allowing to cool, brown pieces of silicon may be picked out.

$SiO_2 + 2Mg \rightarrow 2MgO + Si$

cf. $CO_2 + 2Mg \rightarrow 2MgO + C$

(d) Put one or two pieces of silicon on a crucible lid and play on the solid from above with a bunsen burner. Silicon oxidises to form silica.

$Si + O_2 \rightarrow SiO_2$ (compare carbon)

(e) Add caustic soda solution to amorphous silicon in a test-tube and warm. Hydrogen is evolved and sodium silicate remains in solution.

ionically: $Si + H_2O + 2OH^- \rightarrow SiO_3^{--} + 2H_2 \uparrow$

Experiment 82. Preparation of silico-methane.

Material: Silica; magnesium powder.

Repeat Expt. 81(c) using equal bulks of magnesium powder and silica to fill a test-tube to the depth of about one inch. When cold transfer the contents of the tube to a beaker and add bench dilute hydrochloric acid. Silicon hydride is formed, which ignites to form a fine fog of silica. Compare the preparation and combustion of methane.

$2Mg + Si \rightarrow Mg_2Si$

ionically: $Mg_2Si + 4H^+ \rightarrow SiH_4 + 2Mg^{++}$

$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$

Experiment 83. Reactions of tin and its compounds.

(a) Bubble hydrogen sulphide through a solution of stannous chloride. A precipitate is observed which is insoluble in dilute hydrochloric acid.

ionically: $Sn^{++} + S^{--} \rightarrow SnS \downarrow$

Filter off the precipitate and wash with distilled water. Transfer

---

* Anhydrous silica may not easily dissolve in alkalis. Its acidic properties may be shown by heating with a small piece of solid caustic soda in a crucible. Lixiviation with water, when cool, will give a solution of sodium silicate.

it to a dish and digest with a little yellow ammonium sulphide solution. The precipitate readily dissolves.

$$(NH_4)_2S + SnS + \underset{\text{from ammonium sulphide}}{S} \rightarrow \underset{\text{ammonium thiostannate}}{(NH_4)_2SnS_3}$$

(*Note that there has been oxidation by the free sulphur in the ammonium sulphide. On the addition of a dilute acid to the thiostannate, stannic sulphide* SnS_2 *is precipitated.*)

(b) Add caustic soda solution drop by drop to a solution of stannous chloride. A white precipitate of stannous hydroxide appears but dissolves in excess to form sodium stannite.

ionically:

$$Sn^{++} + 2OH^- \rightarrow Sn(OH)_2 \downarrow$$

$$Sn(OH)_2 + 2OH^- \rightarrow \underset{\text{stannite ion}}{SnO_2^{--}} + 2H_2O$$

An exactly parallel reaction occurs if lead nitrate is used in place of stannous chloride.

(c) Repeat Expt. (b) with stannous chloride using ammonium hydroxide in place of caustic soda solution. A white precipitate of the hydroxide is obtained but is not soluble in excess of ammonium hydroxide.

(d) Stannous chloride is a powerful reducing agent. Add stannous chloride solution to solutions of the following reagents. Reduction occurs readily in each case.

Ferric chloride.	Pale green ferrous ions formed
Potassium permanganate.	Manganous ions formed
Potassium dichromate.	Green chromic ions formed
Mercuric chloride.	White mercurous chloride or grey mercury precipitate formed.

See also Expts. 71 (c) and 247.

Experiment 84. Preparation and properties of stannic chloride.

Apparatus: as in Fig. 21; supply of dry chlorine. *Material*: Tin.

Into the retort put a little sand (to protect the glass during heating) followed by about a tea-spoonful of tin (granulated). Insert the delivery tube and connect to a chlorine apparatus. The experiment should be carried out in a fume chamber. Warm the retort while chlorine passes over and note: (i) ignition of the tin, (ii) fine white crystals in the upper part of the retort, and (iii) the yellow distillate of stannic chloride. The white crystals are $SnCl_4.5H_2O$, due to traces of moisture in the apparatus.

$$Sn + 2Cl_2 \rightarrow SnCl_4$$

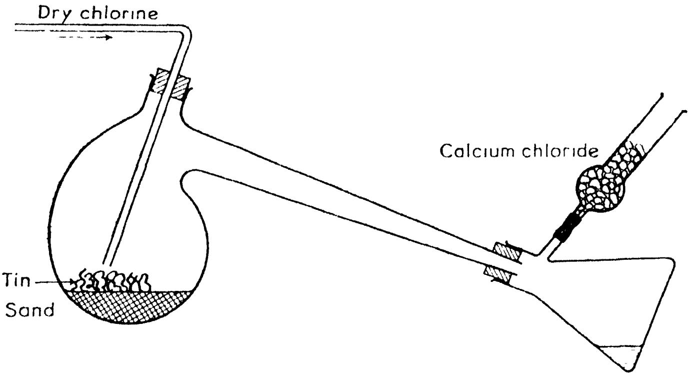


FIG. 21.

Perform the following reactions with small portions of the liquid:—

(a) Add a few drops of water and warm the mixture. Test for hydrogen chloride evolved. The white precipitate is hydrated stannic oxide (or α-stannic acid).

$$SnCl_4 + 4H_2O \rightarrow SnO_2.2H_2O + 4HCl$$

(b) Add a little ammonium hydroxide and warm. Divide the suspension of hydrated stannic oxide into two parts and show its amphoteric nature by dissolving one part in sodium hydroxide solution and the other part in hydrochloric acid.

$$\begin{array}{lll} SnO_2.2H_2O + 4HCl & \rightarrow & SnCl_4 + 4H_2O \\ SnO_2.2H_2O + 2NaOH & \rightarrow & \underset{\text{(sodium stannate)}}{Na_2SnO_3} + 3H_2O \end{array}$$

Experiment 85. Equivalent of tin by preparation of stannic oxide, SnO_2.

Material: Tin.

Weigh an evaporating basin. Add about 1·5 gm. of tin and weigh again. Add not more than 5 c.c. of conc. nitric acid and warm very gently on a gauze until action is proceeding moderately, then remove the flame. From time to time add a few drops of conc. nitric acid until there is no further evolution of nitrogen dioxide. The pale yellow mass is metastannic acid of formula $SnO_2.xH_2O$, the value of x being uncertain. Heat the metastannic acid, gently while it appears to be moist, and later to red heat, to convert it to stannic oxide. When cool, weigh the basin and oxide and from the results calculate the equivalent of tin. As in all gravimetric estimations, re-heating and re-weighing should continue until the final weight is constant. The experiment is best performed in a fume-chamber.

Experiment 86. Reactions of lead and its compounds.

Material: Lead nitrate.

(a) To two portions of solution of lead nitrate add respectively dilute hydrochloric acid and dilute sulphuric acid. In each case a white insoluble precipitate is thrown down.

ionically:
$$Pb^{++} + 2Cl^- \rightarrow PbCl_2 \downarrow$$
$$Pb^{++} + SO_4^{--} \rightarrow PbSO_4 \downarrow$$

Wash the lead chloride by decantation, add about four times its bulk of water and heat. The solid dissolves and is re-precipitated on cooling.

Wash the lead sulphate by decantation, add a strong solution of ammonium acetate and warm. The lead sulphate dissolves.

(*b*) Add a little potassium chromate solution to 2 or 3 c.c. of lead nitrate solution in a test-tube and observe the curdy yellow precipitate of lead chromate thrown down.

ionically:
$$Pb^{++} + CrO_4^{--} \rightarrow PbCrO_4 \downarrow$$

Repeat, using a little potassium iodide solution in the place of potassium chromate. The yellow precipitate is lead iodide (soluble in hot water).

ionically:
$$Pb^{++} + 2I^- \rightarrow PbI_2 \downarrow$$

(c) Add caustic soda solution a drop at a time to a solution of lead nitrate in water. The white precipitate is lead hydroxide. This precipitate is soluble if excess caustic soda solution is added.

ionically:
$$Pb^{++} + 2OH^- \rightarrow Pb(OH)_2 \downarrow$$
$$Pb(OH)_2 + 2OH^- \rightarrow \underset{\text{plumbite ion}}{PbO_2^{--}} + 2H_2O$$

(d) Bubble hydrogen sulphide through a solution of lead nitrate in water. A black precipitate of lead sulphide is thrown down.

ionically:
$$Pb^{++} + S^{--} \rightarrow PbS \downarrow$$

Wash the precipitate by decantation, transfer to a dish, add dilute nitric acid and boil. Some of the sulphide dissolves forming lead nitrate solution, whilst some is oxidised to lead sulphate.

(e) Add dilute caustic soda solution to a solution of lead acetate in a test-tube until the precipitate at first formed disappears. Add hydrogen peroxide solution and warm. A brown precipitate of lead dioxide is formed.

Experiment 87. Experiments with tetravalent lead.

(a) Add a salt-spoonful of red lead to a test-tube filled to a depth of one inch with glacial acetic acid. Warm the mixture and the red lead will dissolve. (If a brown precipitate occurs at this stage, commence again using less red lead.) On cooling under the tap, white crystals of lead tetracetate come down.

$$Pb_3O_4 + 8CH_3COOH \rightarrow Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 4H_2O$$

Add two or three times the bulk of water to the mixture and warm. The tetracetate is hydrolysed and a brown precipitate of lead dioxide is formed.

$$Pb(CH_3COO)_4 + 2H_2O \rightarrow PbO_2 \downarrow + 4CH_3COOH$$

(b) Add a salt-spoonful of lead dioxide to a test-tube filled to a depth of one inch with concentrated hydrochloric acid and cool under the tap. There is little evolution of chlorine at this temperature and on filtering, a golden yellow liquid containing the tetrachloride is obtained.

$$PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O$$

Warm a portion of the yellow solution and test for chlorine. Cool the remaining solution under the tap, when white crystals of plumbous chloride are obtained.

$$PbCl_4 \rightarrow PbCl_2 + Cl_2 \uparrow$$

To another portion of the yellow plumbichloride solution, add 0·880 ammonium hydroxide drop by drop. Fine yellow crystals of ammonium chloroplumbate are readily obtained.

$$PbCl_4 + 2NH_3 + 2HCl \rightarrow (NH_4)_2PbCl_6$$

To a third portion, add a few drops of caustic soda solution. A red gelatinous precipitate (very similar to ferric hydroxide in appearance) is obtained, which, if heated, forms the well-known brown powder, lead dioxide.

$$PbCl_4 + 2H_2O \rightarrow PbO_2 \downarrow + 4HCl$$

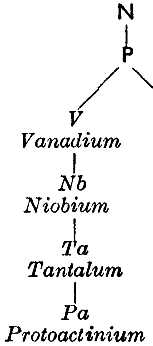
(c) Warm a little dilute nitric acid in a beaker and add red lead a little at a time (avoid excess). The brown precipitate is lead dioxide which can be filtered off, washed and dried. The solution contains lead nitrate.

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2 \downarrow$$

CHAPTER XV

GROUP V

GENERAL



Elements in italics are not usually studied in an elementary course.

The elements in Group V form a good example of the gradation of properties to be found in the elements of the groups. The following table sums up these properties.

Property.	Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
Metallic character	non-metal.	non-metal.	metalloid.	metalloid.	typical metal.
Hydrides	very stable. Alkaline.	fairly stable. Feebly alkaline.	unstable at 200° C.	more unstable.	very unstable.
Oxides	N_2O_3, N_2O_5 both acidic.	P_2O_3, P_2O_5 both acidic.	As_2O_3 amphoteric. As_2O_5 acidic.	Sb_2O_3 amphoteric. Sb_2O_5 acidic.	Bi_2O_3 basic. Bi_2O_5 acidic.
Halides	explosive	not true salts.	Few As^{+++} ions. Hydrolysed	More Sb^{+++} ions. Hydrolysed to some extent.	Salts hydrolysed a little.
Acids	Nitrous acid reducing agent, also oxidising agent. Nitric acid vigorous oxidising agent.	phosphorous acid reducing agent. Phosphoric acid no oxidising properties.	arsenites feeble reducing agent.	antimonites easily oxidised to antimonates.	
Sulphides	—	P_4S_3	As_2S_3,As_2S_5	Sb_2S_3,Sb_2S_5	Bi_2S_3

Ammonia and the ammonium ion.

The properties of ammonia and the ammonium ion are summarised below together with a reference to experimental work illustrating these properties:—

(a) Ammonia gas when hot is a reducing agent, e.g., hot black copper oxide is reduced to copper by a stream of the gas.

(b) Ammonia tends to form complex ions with a number of metallic ions (see p. 54 *et seq.*).

(c) Ammonia with water gives ammonium hydroxide which is mainly undissociated, but which does contain sufficient hydroxyl ions to behave as a weak alkali (see p. 220).

(d) The ammonium ion, NH_4^+, is a stable ion which is metallic in character. When warmed with a high concentration of hydroxyl ions, it yields ammonia gas (see pp. 241, 307).

ionically: $NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$

By hydrolysis, ammonium salts may react acidic (see p. 20).

ionically: $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

(e) Ammonium salts sublime when heated (see p. 13).

Experiment 88. The reactions of the nitrites.

Material: Sodium nitrite solution approximately normal.

THEORY

Nitrous acid, HNO_2 (which gives rise to the nitrites), may be considered as the acid formed from the lower oxide N_2O_3:—

$$2HNO_2 \equiv H_2O.N_2O_3$$
$$2NaNO_2 \equiv Na_2O.N_2O_3$$

The oxide itself is unstable at temperatures above −21° C. decomposing into nitric oxide and nitrogen dioxide.

$$N_2O_3 \rightarrow NO + NO_2$$

Note: Fumes of nitrogen dioxide are poisonous, and preferably the actions given below should be performed in a fume chamber. If it is necessary to perform them on the open bench, add water and pour away as soon as the observations have been made.

In reactions (c), (d) and (e) the nitrous acid acts as an oxidising agent according to the equation:—

$$2HNO_2 \rightarrow H_2O + 2NO + \underset{\text{for oxidation}}{(O)}$$

In reactions (f) and (g) the nitrous acid acts as a reducing agent being oxidised to nitric acid:—

$$HNO_2 + \underset{\substack{\text{from oxidising}\\\text{agent.}}}{O} \rightarrow HNO_3$$

When nitrous acid acts as a reducing agent there is no evolution of gas. Care must be taken not to have the free nitrous acid in excess, otherwise decomposition occurs as in Expt. (a).

(a) Add some dilute hydrochloric acid to a little sodium nitrite solution in a test-tube. The liquid turns pale blue, effervescence and brown fumes are observed. The explanation is that with acids, nitrites liberate nitrous acid which is unstable and decomposes into nitric oxide and oxygen. The latter oxidises nitrous acid to nitric acid.

$$\begin{aligned} 3NaNO_2 + 3HCl &\rightarrow 3HNO_2 + 3NaCl \\ 2HNO_2 &\rightarrow H_2O + 2NO + [O] \\ HNO_2 + [O] &\rightarrow HNO_3 \end{aligned}$$

Adding, $3NaNO_2 + 3HCl \rightarrow HNO_3 + 3NaCl + H_2O + 2NO$

ionically: $3NO_2^- + 2H^+ \rightarrow NO_3^- + H_2O + 2NO$

This nitric oxide finally reacts with the oxygen of the air to form nitrogen dioxide.

$$2NO + O_2 \rightarrow 2NO_2$$

(b) Make solutions of ferrous sulphate and sodium nitrite and mix them. Add a few drops of dilute sulphuric acid when the whole solution turns brown due to the formation of the loose compound which ferrous sulphate makes with nitric oxide (see p. 311). This test serves to distinguish between a nit*rite* and a nit*rate*.

(c) Add a few drops of concentrated hydrochloric acid to a few c.c. of potassium iodide solution and pour the mixture into a solution of sodium nitrite. Iodine forms as a brown coloration or black precipitate due to the oxidation of potassium iodide to iodine.

ionically: $2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO\uparrow + 2H_2O + I_2\downarrow$

The gas liberated is nitric oxide which forms brown fumes with the oxygen of the air.

(d) Pass hydrogen sulphide into a solution of sodium nitrite acidified with dilute hydrochloric acid. There is a rapid action, sulphur being deposited. Brown fumes are observed.

ionically: $2NO_2^- + S^{--} + 4H^+ \rightarrow 2H_2O + 2NO\uparrow + S\downarrow$

(e) Add a piece of copper to the solution of sodium nitrite acidified with dilute sulphuric acid. The copper is rapidly attacked (much more rapidly than with nitric acid of similar concentration) giving a blue solution.

(f) Add a solution of sodium nitrite to bromine water acidified with dilute sulphuric acid. The bromine water is decolorised due to its reduction to hydrobromic acid.

ionically: $Br_2 + NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2Br^-$

Note there is no evolution of gas when nitrous acid acts as a reducing agent until excess nitrous acid is present in solution.

(g) Add a solution of sodium nitrite to a solution of potassium permanganate acidified with dilute sulphuric acid. The colour of the permanganate is discharged.

ionically: $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{++} + 3H_2O$

(h) Add ammonium chloride solution to a solution of sodium nitrite and warm. Effervescence takes place and a colourless odourless gas is given off which gives negative results on testing with lime water, litmus, and a lighted splint. The gas is nitrogen.

ionically: $NH_4^+ + NO_2^- \rightarrow 2H_2O + N_2\uparrow$

See also Expt. 63f.

Experiment 89. The reactions of the nitrates.

Material: Sodium nitrate; aluminium powder.

Nitric acid and the nitrates correspond to the higher acidic oxide of nitrogen N_2O_5:—

$$\begin{aligned} 2HNO_3 &\equiv H_2O.N_2O_5 \\ 2NaNO_3 &\equiv Na_2O.N_2O_5 \end{aligned}$$

The oxide is difficult to prepare and is unstable at temperatures above 0° C. forming nitrogen dioxide and oxygen.

(a) To a little sodium nitrate in a test-tube add concentrated sulphuric acid just to cover it (Care!), and warm gently. Nitric acid vapours are evolved with some decomposition giving rise to brown fumes of nitrogen dioxide. The nitric acid condenses as oily drops on the cooler parts of the tube.

$$\begin{aligned} NaNO_3 + H_2SO_4 &\rightarrow NaHSO_4 + HNO_3 \\ 4HNO_3 &\rightarrow 2H_2O + 4NO_2 + O_2 \end{aligned}$$

For the action of heat on nitrates consult an elementary text-book. See also p. 305.

(b) Add two or three small pieces of copper to a little sodium nitrate in a test-tube and just cover with concentrated sulphuric acid (Care!) and warm gently. Brown fumes of nitrogen dioxide are readily evolved.

$$Cu + 2NaNO_3 + 3H_2SO_4 \rightarrow 2NaHSO_4 + CuSO_4 + 2H_2O + 2NO_2$$

(c) *Brown ring test.* Make a *cold* solution of ferrous sulphate by shaking a few crystals with a little water in a boiling-tube and add a little sodium nitrate and again shake until it dissolves. The depth of liquid should be about one inch. Pour concentrated sulphuric acid carefully down the side until it has formed a layer about half an inch deep under the ferrous sulphate solution. A brown ring is observed at the junction of the two liquids (see p. 311).

(d) *Reduction of nitrate to ammonia.* Take two or three small crystals of sodium nitrate in a test-tube. Fill the tube about one quarter full of dilute caustic soda solution. When dissolved, add a small quantity of either aluminium or zinc powder. Warm gently and test for ammonia. If Devarda's alloy* is available use this in preference to the metal powder.

For the oxidising action of nitric acid, see experiments, p. 14.

Experiment 90. Reactions of Phosphites.

Material: Disodium hydrogen phosphite.

Phosphorous acid H_3PO_3 behaves as a dibasic acid and may be regarded as the acid corresponding to the lower oxide:—

$$2H_3PO_3 \equiv 3H_2O.P_2O_3 \equiv \underset{\substack{\uparrow \\ \text{acidic hydrogen}}}{H_2}(HPO_3)$$

sodium phosphite Na_2HPO_3

(a) Add silver nitrate solution to a neutral solution of sodium phosphite. A white precipitate of silver phosphite is formed which if warmed or allowed to stand darkens due to reduction to metallic silver.

ionically: $HPO_3^{--} + 2Ag^+ + H_2O \rightarrow 2Ag\downarrow + HPO_4^{--} + 2H^+$

(b) Add mercuric chloride solution to a neutral solution of sodium phosphite. A white precipitate of mercurous chloride is formed which if warmed darkens due to further reduction to metallic mercury.

ionically: $Hg^{++} + HPO_3^{--} + H_2O \rightarrow Hg\downarrow + HPO_4^{--} + 2H^+$

Experiment 91. Reactions of phosphorus and the phosphates.

Apparatus: Carbon dioxide apparatus; measuring cylinder; corks.
Material: Disodium hydrogen phosphate solution; yellow and red phosphorus; iodine; phosphoric acid.

Phosphoric acid, H_3PO_4, behaves as a tribasic acid although the normal salts are considerably hydrolysed in solution.

$$2H_3PO_4 \equiv 3H_2O.P_2O_5$$

(a) Add two or three drops of the sodium phosphate solution to a test-tube half full of ammonium molybdate acidified with concentrated nitric acid. (The ammonium molybdate must be in considerable excess.) Gently warm (the heat of the hand is sufficient) and a yellow precipitate of ammonium phosphomolybdate of composition $(NH_4)_3PO_4.12MoO_3$ is produced (cf. Expt 97 (d)).

(b) Add a few drops of sodium phosphate solution to a neutral solution of silver nitrate. A canary yellow precipitate of silver

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* Devarda's alloy is 45% Al, 50% Cu, 5% Fe.

phosphate is produced. This precipitate is soluble in dilute nitric acid and also in ammonium hydroxide.

ionically: $3Ag^+ + PO_4^{---} \rightarrow Ag_3PO_4 \downarrow$

(c) Add a few drops of sodium phosphate to a solution containing magnesia mixture (magnesium sulphate, ammonia and ammonium chloride—the latter to prevent the precipitation of magnesium hydroxide) when a white crystalline precipitate of magnesium ammonium phosphate is produced.

ionically: $Mg^{++} + NH_4^+ + PO_4^{---} \rightarrow Mg.NH_4.PO_4 \downarrow$

(d) Add ferric chloride solution a drop at a time to a solution of sodium phosphate. A buff precipitate of ferric phosphate is formed.

ionically: $HPO_4^{--} + Fe^{+++} \rightarrow FePO_4 \downarrow + H^+$

This precipitate is soluble in dilute mineral acids and also in excess of ferric chloride.

(e) *Conversion of orthophosphate to pyrophosphate.* Heat about a quarter of a test-tube full of disodium hydrogen phosphate to red heat.

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

Make a solution of the residual sodium pyrophosphate and compare its action on silver nitrate solution (white precipitate) with that of disodium hydrogen phosphate (yellow precipitate).

(f) *Preparation of orthophosphoric acid.* Take a little red phosphorus in an evaporating basin and add a few c.c. of concentrated nitric acid. Warm gently (in a fume chamber preferably) and note the vigorous evolution of nitrogen dioxide Add more nitric acid if some phosphorus remains undissolved and again heat. The liquid left is a solution of orthophosphoric acid, which may be evaporated to a thick syrup.

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 \uparrow + 4H_2O$$

(g) *Preparation of sodium salts of orthophosphoric acid.* Titrate a dilute solution of phosphoric acid against bench caustic soda solution using litmus as an indicator. Suppose *a* c.c. of the acid neutralised 25 c.c. of the alkali. Repeat the titration without litmus. This solution contains mainly disodium hydrogen phosphate from which crystals may be obtained by evaporation to small bulk and allowing to cool. Filter off the crystals, wash with a little cold distilled water and dry between filter papers.

To obtain sodium dihydrogen phosphate add *a* c.c. of the same phosphoric acid solution to 12·5 c.c. of the caustic soda solution.

To obtain trisodium phosphate add *a* c.c. of the same phosphoric acid solution to 37·5 c.c. of the caustic soda solution.

Proceed in both cases to obtain crystals as indicated above.

$$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H\ O$$
$$2NaOH + H_3PO \rightarrow Na_2HPO_4 + 2H_2O$$
$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$$

(h) *Inter-conversion of red and yellow phosphorus* (*G. Fowles*). Drop a small piece of yellow phosphorus (the size of a small pea) into a dry test-tube and sweep out the air by means of carbon dioxide. Insert a *loose* cork and heat over a low flame. Allow to cool. The phosphorus vapour condenses to small droplets of yellow phosphorus once again.

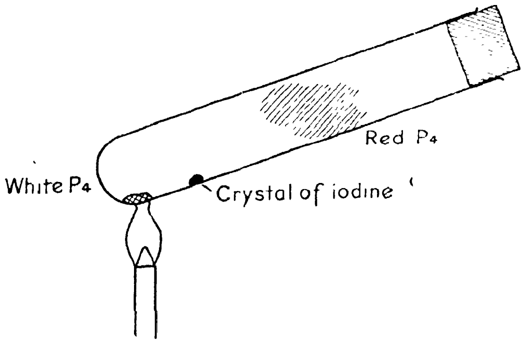


FIG. 22.

Repeat the experiment but insert a small crystal of iodine by means of a glass rod placing it about one quarter of an inch away from the yellow phosphorus. (See Fig. 22.) On this occasion the red variety is obtained on the cooler side of the tube.

Repeat the experiment using red phosphorus (no iodine) and the yellow variety is obtained on cooling.

Experiment 92. Preparation of phosphorus pentachloride.

Apparatus: Chlorine apparatus; apparatus as shown. (All parts carefully dried.) *Material*: Phosphorus trichloride.

Fit up the apparatus of Fig. 23. Pass a stream of chlorine (well dried by passage through wash bottles containing concentrated sulphuric acid) into the flask, and allow the trichloride to drop slowly into the atmosphere of chlorine. The pentachloride collects as a yellow crystalline solid on the bottom of the flask.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

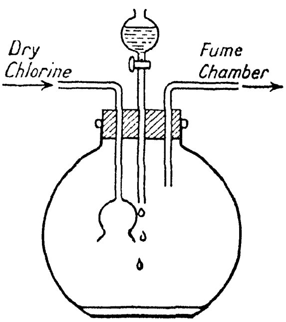


FIG. 23.

The funnel prevents blocking of the inlet tube by solid. The pentachloride should be transferred to a storage bottle.

Experiment 93. Action of water on the chlorides of phosphorus.

Material: Phosphorus tri- and penta-chlorides.

(a) Take a test-tube about one eighth full of water and add one drop of phosphorus trichloride. Hold a rod moistened with silver nitrate near the mouth of the test-tube. The hydrolysis is vigorous and hydrogen chloride is evolved.

$$PCl_3 + 3H_2O \rightarrow 3HCl\uparrow + H_3PO_3$$

(b) Repeat as with (a) but use a small piece of solid phosphorus pentachloride. This reaction is also vigorous.

$$PCl_5 + 4H_2O \rightarrow 5HCl\uparrow + H_3PO_4$$

See also p. 140.

Experiment 94. Preparation of microcosmic salt, $Na.NH_4.H.PO_4.4H_2O$.

Material: Disodium hydrogen phosphate.

Take 14 gm. of sodium phosphate and 2·2 gm. of ammonium chloride in separate beakers and dissolve each in 10 c.c. of water, heating to dissolve. Mix the solutions while hot and leave to crystallise. Recrystallise with the minimum of water.

$$Na_2HPO_4 + NH_4Cl \rightarrow Na(NH_4)HPO_4 + NaCl$$

When heated, microcosmic salt decomposes into ammonia, water and sodium metaphosphate.

$$Na(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3\uparrow + H_2O$$

Make a loop on a platinum wire, make the wire red hot, and dip it into microcosmic salt. Heat to obtain a glassy bead of sodium metaphosphate, then dust the bead with manganese dioxide and heat again. The amethyst colour is due (probably) to the formation of manganese orthophosphate.

Experiment 95. Reactions of arsenic.

Material: Arsenious oxide. (*Care*! very poisonous.)

(a) Mix a little of the arsenic compound with anhydrous sodium carbonate (or fusion mixture or powdered potassium cyanide) and heat on the charcoal block with the mouth blowpipe—a smell of garlic (poisonous!) characteristic of arsenic is observed.

$$As_2O_3 + 3C \rightarrow 2As + 3CO$$

(b) Mix a little of the arsenic compound with anhydrous sodium carbonate and charcoal and heat in a dry tube. A black ring of the element arsenic is observed in the cooler parts of the tube.

(c) *Marsh's test.* (Modified.) Fit up the apparatus shown in Fig. 24 and pour dilute hydrochloric acid on to the zinc in the tube. After *testing that all air has been driven out*, add a solution of the arsenic compound in hydrochloric acid, and warm the delivery tube. A black deposit of arsenic (soluble in sodium hypochlorite solution or bleaching powder solution) forms on the cooler parts. The nascent hydrogen has reduced the arsenic in the arsenic compound to arsine, AsH_3, which is readily decomposed by heat into the element. (As an alternative a filter paper soaked in mercuric chloride or bromide gives a yellow stain if held in the gas containing arsine.)

In Marsh's test proper, the gas must pass over lead acetate paper to remove hydrogen sulphide and through anhydrous calcium chloride to dry it before reaching the hot part of the tube.

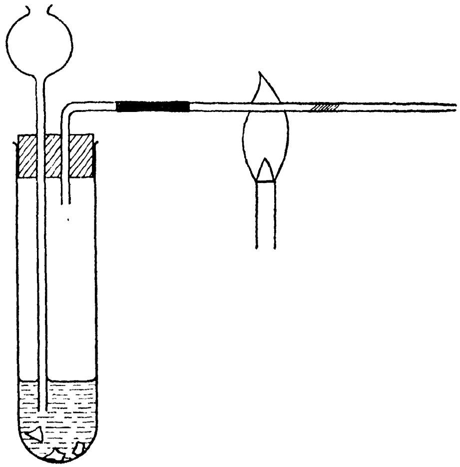


FIG. 24.

(d) *Reinsch's test.* Dissolve a little of the arsenic compound by warming with dilute hydrochloric acid and immerse a clean strip of copper in the solution. A grey deposit of copper arsenide, Cu_3As_2, is formed.

Experiment 96. Reactions of arsenious compounds.

Material: Arsenious oxide (*Care!* Very poisonous); iodine-potassium iodide solution.

(a) Arsenious oxide is amphoteric in character and although only very slightly soluble in water readily dissolves in either alkalies or acids:—

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$
$$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O$$

(b) Pass hydrogen sulphide into a solution of arsenious oxide in dilute hydrochloric acid. A yellow precipitate of arsenious sulphide is readily obtained. Filter this off and warm with ammonium carbonate and caustic soda solution respectively. In both solutions the sulphide readily dissolves. It is also soluble in yellow ammonium sulphide with the production of a thioarsenate [$(NH_4)_3AsS_4$], from which arsenic pentasulphide may be precipitated by adding dilute hydrochloric acid.

Arsenic trisulphide is insoluble in hydrochloric acid, even when hot and concentrated. It can readily be obtained in the colloidal form (see p. 49).

(c) Dissolve a little of the arsenious oxide in dilute ammonia solution and add to each of three portions respectively

(i) silver nitrate solution, which gives a pale yellow precipitate of silver arsenite.

ionically: $AsO_3^{---} + 3Ag^+ \rightarrow Ag_3AsO_3 \downarrow$

(ii) iodine in solution in potassium iodide, when the iodine coloration disappears due to the oxidation of the arsenite to arsenate. (Oxidising agents generally produce this effect.)

ionically: $AsO_3^{---} + I_2 + H_2O \rightarrow AsO_4^{---} + 2H^+ + 2I^-$

(iii) copper sulphate solution, which produces a bright green precipitate of cupric hydrogen arsenite (Scheele's green).

ionically: $AsO_3^{---} + Cu^{++} + H_2O \rightarrow CuHAsO_3 \downarrow + OH^-$

Experiment 97. Reactions of arsenic compounds.

Material: Sodium arsenate Na_2HAsO_4

Note: In pentavalent arsenic compounds the element is always in the anion.

(a) Pass hydrogen sulphide into a solution of sodium arsenate in dilute hydrochloric acid. There is no effect. Warm the solution and continue to pass the gas for some time. A yellow precipitate of arsenious sulphide is obtained. The hydrogen sulphide first reduces the arsenate to arsenite and then precipitates the sulphide.

(b) Add silver nitrate solution to a solution of sodium arsenate. A brick red precipitate of silver arsenate (soluble in dilute acid or ammonium hydroxide) is produced:—

ionically: $HAsO_4^{--} + 3Ag^+ \rightarrow Ag_3AsO_4 \downarrow + H^+$

(c) Add ammonium chloride and ammonia solution to a solution of sodium arsenate and finally add magnesium sulphate solution. A white crystalline precipitate of magnesium ammonium arsenate is obtained.

ionically:

$HAsO_4^{--} + Mg^{++} + NH_4^+ + OH^- \rightarrow MgNH_4AsO_4 \downarrow + H_2O$

(d) Add a few drops of sodium arsenate solution to half a test-tube full of ammonium molybdate solution acidified with concentrated nitric acid and boil. A yellow precipitate of ammonium arseno molybdate is formed. (Cf. Expt. 91 (a).)

Experiment 98. Reactions of Antimony.

Material: Antimonious oxide (Care! very poisonous).

(a) Mix a little of the antimony compound with anhydrous sodium carbonate and heat on a charcoal block with the mouth blowpipe. Grey metallic globules of antimony with a white incrustation of antimonious oxide are seen.

(b) Perform Marsh's test (see Expt. 95(c)) using antimonious oxide in place of arsenious oxide. A similar result is obtained but the black metallic residue of antimony is not soluble in a solution of sodium hypochlorite or bleaching powder.

(c) Perform Reinsch's test (see Expt. 95(d)) using antimonious oxide in place of arsenious oxide. A grey deposit is likewise obtained.

Experiment 99. Reactions of antimonious compounds.

Material: Antimony trichloride; antimonious oxide; tartar emetic.

(a) Antimonious oxide is insoluble in water but readily soluble in hydrochloric acid and in alkalis. Like arsenious oxide it is therefore amphoteric. See Expt. 96 (a).

(b) Pass hydrogen sulphide into a solution of antimony chloride in hydrochloric acid. An orange precipitate of antimonious sulphide is obtained.

ionically: $2Sb^{+++} + 3S^{--} \rightarrow Sb_2S_3\downarrow$

Filter this precipitate off and warm with caustic soda solution or yellow ammonium sulphide. It is readily soluble in these solutions and on acidifying, antimony sulphide is partially reprecipitated (see similar action in Expt. 96(b)). Show that antimony sulphide will dissolve if warmed with concentrated hydrochloric acid but it is not affected by ammonium carbonate solution (as is arsenic sulphide).

ionically: $Sb_2S_3 + 6H^{+} \rightarrow 2Sb^{+++} + 3H_2S\uparrow$

(c) Add sodium hydroxide solution to a solution of antimony trichloride in dilute hydrochloride acid until the white precipitate just dissolves. On the addition of silver nitrate solution a black precipitate of metallic silver is obtained, whilst the antimonious compound is oxidised to sodium antimonate.

(d) Dissolve a little tartar emetic (potassium antimonyl tartrate, $K(SbO).C_4H_4O_6$) in water and add a little sodium bicarbonate. Shake until the bicarbonate is dissolved and then add iodine solution in potassium iodide. The latter is decolorised being reduced to hydrogen iodide whilst the antimonite becomes antimonate (see Expt. 96(c) ii.)

(e) Dissolve a little antimony trichloride in dilute hydrochloric acid and pour the clear solution into a boiling-tube full of water. A white precipitate of antimony oxychloride is formed.

$$SbCl_3 + 2H_2O \rightleftharpoons SbOCl\downarrow + 2HCl$$

If concentrated hydrochloric acid is now added to a little of the white precipitate, it redissolves. The reaction is a good example of the Law of Mass Action. (See Expt. 10(b).)

Experiment 100. Reactions of antimonic compounds.

Material: Potassium antimonate, $2KSbO_3 \equiv K_2O.Sb_2O_5$.

(a) Pass hydrogen sulphide into a solution of a little potassium antimonate in dilute hydrochloric acid. An orange precipitate of antimonic sulphide, Sb_2S_5, is obtained. This precipitate is, like arsenic sulphide and antimony trisulphide, soluble in solutions of either caustic soda or yellow ammonium sulphide. The addition of acid to the solution brings about a reprecipitation of the sulphide.

(b) Add silver nitrate solution to a neutral solution of potassium antimonate. A white precipitate of silver antimonate (soluble in either ammonia or nitric acid) is formed.

ionically: $SbO_3^- + 3Ag^+ + H_2O \rightarrow Ag_3SbO_4\downarrow + 2H^+$

Note that with magnesium sulphate in the presence of ammonium chloride and ammonia, no precipitate forms with an antimonate.

Experiment 101. The reactions of bismuth compounds.

Material: Bismuth nitrate; bismuth chloride.

(a) Mix a little solid bismuth nitrate with anhydrous sodium carbonate and heat on the charcoal block with the mouth blowpipe. A pink globule of bismuth is obtained surrounded by a brown incrustation of bismuth oxide Bi_2O_3.

(b) Pass hydrogen sulphide into a solution of bismuth nitrate acidified with dilute hydrochloric acid. A dark brown precipitate of bismuth sulphide (insoluble in yellow ammonium sulphide or in caustic soda) is obtained.

ionically: $2Bi^{+++} + 3S^{--} \rightarrow Bi_2S_3\downarrow$

Filter the precipitate off and wash a little into a dish with dilute nitric acid and warm. The precipitate readily dissolves.

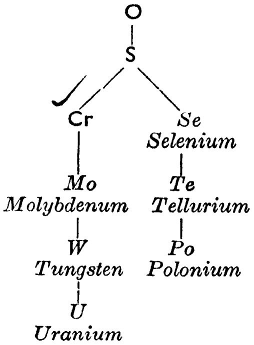
(c) Dissolve a little bismuth chloride in dilute hydrochloric acid and then pour it into a boiling-tube full of water. A white precipitate of bismuth oxychloride is formed. If a little of this is poured off into a test-tube and a few drops of concentrated hydrochloric acid added the precipitate redissolves. (See Expt. 10(a).)

$$BiCl_3 + H_2O \rightleftharpoons BiOCl\downarrow + 2HCl$$

CHAPTER XVI

GROUP VI

GENERAL



Elements in italics are seldom studied in an elementary course.

CHARACTERISTICS OF ELEMENTS IN GROUP VI

Oxygen, sulphur, selenium, and telurium are more related to each other than to chromium, molybdenum, tungsten and uranium, although sulphur has points of similarity with chromium in a few corresponding compounds.

Chromium is a metal and some of its compounds resemble corresponding sulphur compounds, e.g., the sulphates and chromates of potassium are isomorphous and sulphuryl chloride and chromyl chloride show similarities. The reactions of chromium and its compounds also show points of similarity with aluminium (Group III) and trivalent iron (Group VIII).

Generally, it may be said that the elements show a tendency to become more metallic with increase in atomic weight, and the maximum valency exhibited is six.

OXYGEN

Experiment 102. Preparation of oxides by direct oxidation.

Apparatus: Gas-jars; deflagrating spoons. *Material*: Supply of oxygen; sulphur; carbon; phosphorus; calcium; iron wire; magnesium.

Take seven jars of the gas and introduce, respectively, a little of each element listed, in a deflagrating spoon, heating sufficiently to promote action; iron will need to be heated to red heat, or dipped into a little sulphur when warm.

Note the nature of the oxide and test with litmus. Divide the oxides into (a) acidic, (b) alkaline, and (c) metal oxides. Show that both (b) and (c) dissolve in hydrochloric acid and are therefore bases.

Experiment 103. Preparation of oxides by indirect oxidation.

Material: Copper foil; lead.

Take a small piece of copper foil in a test-tube and add concentrated nitric acid to fill the tube about one-eighth full. Add more acid if the action dies down before the copper dissolves to complete the solution of the metal. Transfer to a dish and cautiously evaporate the nitrate solution until crystals are formed and then heat strongly to complete the decomposition of the nitrate to oxide. When cool, show that the oxide is a base by dissolving it in diluted sulphuric acid.

Repeat the experiment, using lead, but finally dissolve the oxide in acetic acid instead of sulphuric acid.

Experiment 104. Preparation of hydrogen peroxide solution.

Material: Barium peroxide; phosphoric acid.

Dilute about 5 c.c. of syrupy phosphoric acid with its own volume of water in a test-tube. Gradually add barium peroxide (cooling under the tap) until on filtering and testing by reaction of Expt. 105(a) a rapid evolution of oxygen is obtained. Filter and use the solution for the tests described in Expt. 105.

$$2H_3PO_4 + 3BaO_2 \rightarrow Ba_3(PO_4)_2 \downarrow + 3H_2O_2$$

Note. The solution may contain, in addition to hydrogen peroxide, a little excess phosphoric acid and some barium ions.

Experiment 105. Properties of hydrogen peroxide.

Material: Platinised asbestos; ether.

(a) To about 5 c.c. of hydrogen peroxide in a test-tube add a small piece of platinised asbestos or manganese dioxide. Test the oxygen evolved. The action is catalytic.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$$

(b) Moisten a piece of filter paper with lead acetate solution and hold it in a stream of hydrogen sulphide until it is stained black with lead sulphide. Leave standing in a test-tube containing hydrogen peroxide. The restoration of whiteness is due to oxidation of lead sulphide to lead sulphate:—

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

(c) To a test-tube filled to a depth of about one inch with potassium permanganate solution acidified with diluted sulphuric acid, add a few drops of hydrogen peroxide. Note the evolution of gas and the decoloration of the permanganate; retain the gas in the tube and test for oxygen:—

ionically: $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$

(d) To a test-tube filled to a depth of one inch with potassium iodide solution acidified with dilute sulphuric acid, add a few drops of hydrogen peroxide. The brown coloration of iodine may then be tested with a drop of starch solution.

ionically: $2I^- + H_2O_2 \rightarrow I_2 + \underset{\text{reacts with acid.}}{2OH^-}$

(e) Fill a test-tube to a depth of about one inch with silver nitrate solution and add a slight excess of caustic soda solution to form silver oxide; decant the supernatant liquid. Add a few drops of hydrogen peroxide to the silver oxide. Note the evolution of oxygen and the change of colour as brown silver oxide becomes black metallic silver.

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2\uparrow$$

Add a few more drops of hydrogen peroxide and show that the finely divided silver acts catalytically as did platinised asbestos in (a).

(f) Fill a test-tube to a depth of about one inch with potassium dichromate solution and acidify with dilute sulphuric acid. Cover the solution with a layer of ether about one inch deep, and add a drop of well diluted hydrogen peroxide. The blue coloration in the ether layer is probably due to a perchromic acid ($HCrO_5$) and this reaction serves as a delicate test for hydrogen peroxide.

OZONE, O_3

When oxygen is passed through a silent electric discharge, the issuing gas contains a small amount of ozone (5–10%). Even this small percentage is higher than is stable with oxygen at room temperature:—

$$3O_2 \rightarrow 2O_3 - 69{,}000 \text{ calories.}$$

Consequently, when ozonised oxygen, obtained as above, is heated much of the ozone dissociates into oxygen until true equilibrium is reached for the given temperature. Chemically, ozone is an oxidiser, each molecule losing an atom of oxygen to the reducer and leaving a molecule of oxygen.

$$O_3 \rightarrow O_2 + O \text{ (combining with reducer).}$$

Experiment 106. Preparation of ozonised oxygen.

Apparatus: As shown in Fig. 25. *Material*: Supply of oxygen; mercury; starch iodide solution.

The outside of the outer tube, and the inside of the inner tube, are coated with tin-foil (marked T). Dry oxygen is passed through the space between the two tubes while the tin-foil surfaces are kept at a high electrical tension by connecting them to the output terminals of a secondary coil. The supply of oxygen is conveniently stored in a siphon bottle and the flow regulated to a moderate rate.

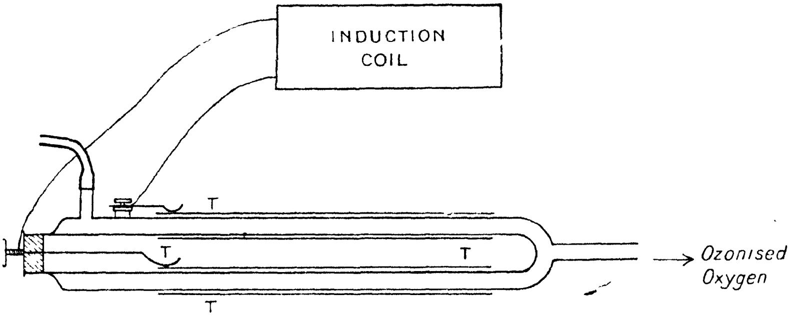


FIG. 25.

Ozonised oxygen attacks rubber tubing, but connections can now be made with P.V.C. (poly-vinyl-chloride) tubing, which is unaffected.

Reactions

(a) Soak a piece of filter paper in a solution of starch-potassium iodide and hold in the issuing gas. The blue colour indicates free iodine.

ionically: $2I^- + O_3 + H_2O \rightarrow I_2\downarrow + O_2 + 2OH^-$

(b) Take a small drop of mercury in a clean, dry test-tube. Pass ozonised oxygen into the tube for a short time. Note the "tailing" of the mercury. Heat the tube strongly and show that the mercury regains its usual mobility.

(c) Moisten a piece of filter paper with lead acetate solution and hold it in a stream of hydrogen sulphide to form black lead sulphide. Put the piece in a test-tube and pass in ozonised oxygen for two or three minutes. Note the lighter colour as lead sulphide is oxidised to lead sulphate.

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$

SULPHUR

The preparation of allotropes of sulphur will have been demonstrated in the elementary course. For revisionary purposes rhombic, plastic, and amorphous sulphur may readily be prepared as follows:—

Experiment 107. Preparation of forms of sulphur.

Material: Flowers of sulphur; carbon disulphide.

Fill a dry test-tube three-quarters full of sulphur and heat gradually to boiling (using a holder for safety). Pour the boiling sulphur into a beaker half full of water. Immerse any floating sulphur by stirring with a rod, and then remove and examine the plastic sulphur. Note the gradual loss of elasticity as the plastic form changes to rhombic.

Take enough sulphur to cover the bottom of a test-tube, add about 5 c.c. of carbon disulphide, and stand the tube in hot water in a beaker. (*Carbon disulphide inflammable.*) When the liquid has boiled for two or three minutes, filter the liquid into a dish, cover with a filter paper held in position with an elastic band and pierce a few holes in the filter paper with a pin, and leave to crystallise. The residue in the original filter paper is amorphous sulphur and the crystals separating from the filtrate, rhombic sulphur.

Experiment 108. Preparation of sulphides.

Material: Flowers of sulphur; sheet copper.

(a) Take an ignition tube a third full of flowers of sulphur and heat until melted. Take a strip of copper and hook it over the rim of the tube so that its lower edge is a little above the surface of the sulphur. Heat to boil the sulphur and note the glow as the copper forms copper sulphide (a mixture of cupric and cuprous sulphides).

(b) Mix approximately equal parts of iron filings and sulphur and take a test-tube about half-full of the mixture. Heat until the action begins and note the glow of the mixture as combination to form ferrous sulphide continues. (Compare with direct oxidation of metals.)

(c) Into a solution of copper sulphate pass hydrogen sulphide. Filter off the precipitated cupric sulphide.

ionically: $Cu^{++} + S^{--} \rightarrow CuS \downarrow$

The precipitation of sulphides in both acid and alkaline solutions is important in the separation of metallic ions and is fully discussed in Qualitative Analysis, Chapter XLIV.

Experiment 109. Preparation of chlorides and oxychlorides of sulphur.

Apparatus: Distilling flasks (150 c.c.): condenser; water bath.
Material: Siphon of sulphur dioxide; phosphorus pentachloride; supply of chlorine; natural camphor.

(a) Take about two tea-spoonfuls of sulphur in a distilling flask. Fit the flask with a one-holed cork fitted with a tube to reach the level of the sulphur, and connect the tube to a supply of dry chlorine. Heat the sulphur on a gauze and pass in chlorine. Collect the liquid product (sulphur monochloride, S_2Cl_2) in a dry test-tube. Warm a few drops of the product in a little water and test for sulphur dioxide and hydrochloric acid and note the deposit of sulphur.

$$2S_2Cl_2 + 2H_2O \rightarrow 4HCl + 3S \downarrow + SO_2$$

(b) Take about two tea-spoonfuls of phosphorus pentachloride in a dry distilling flask which is attached to a sloping condenser (Fig. 26). Fit the flask with a cork and delivery tube, the latter reaching well

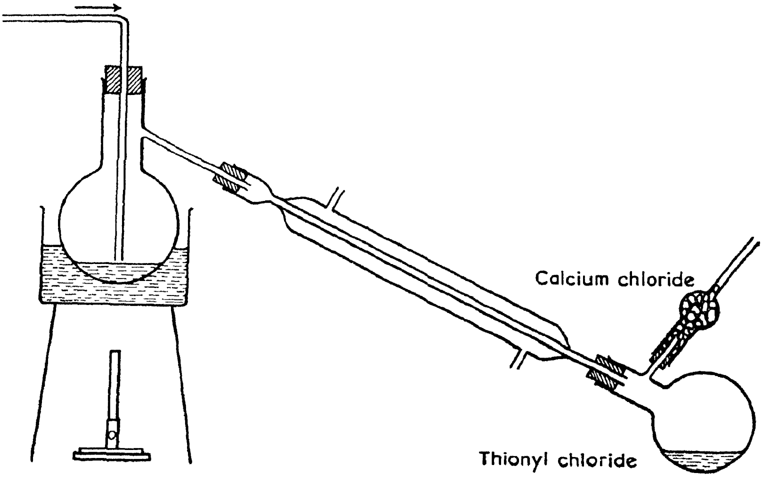


FIG. 26.

down into the flask. Stand the flask in a water-bath (cold water). Pass sulphur dioxide into the phosphorus pentachloride until it has completely liquefied. Heat the water-bath and collect the distillate of thionyl chloride, $SOCl_2$. The liquid still remaining in the flask is phosphorus oxychloride and this serves as a method of preparing the compound.

$$PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$$

Add a few drops of the thionyl chloride to a little water and test for sulphurous acid and hydrochloric acid.

$$SOCl_2 + 2H_2O \rightarrow H_2SO_3 + 2HCl$$

(c) Fit up the apparatus as for Expt. 109(b). Cut a cube of camphor into pieces and place in the dry flask. Pass sulphur dioxide until the camphor liquefies and then disconnect the sulphur dioxide siphon and substitute a supply of dry chlorine. Pass in chlorine until it is no longer absorbed. Heat the water-bath and collect the distillate of sulphuryl chloride:—

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

Add a few drops of the product to a little water and show that the resulting solution contains sulphuric and hydrochloric acids.

$$SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

Experiment 110. Properties of sulphur dioxide.

Material: Magenta; magnesium ribbon.

As these properties have been studied at an earlier stage, it will be sufficient to give brief instructions:—

(a) Pass the gas into a test-tube about half-full of water and use the stock solution to show that it is acid, decolorises potassium permanganate, reduces potassium dichromate, decolorises magenta, and gives a deposit of sulphur with hydrogen sulphide. Write appropriate equations.

The above experiments may be performed in a simpler way by heating a little sulphur in an evaporating basin and testing the sulphur dioxide formed by drops of the various reagents on a glass rod.

(b) Prepare sodium sulphite and sodium bisulphite (in solution) as follows:—

Take two equal volumes of caustic soda solution in test-tubes. Saturate one volume with sulphur dioxide to form sodium bisulphite. Add the second volume to the product to form sodium sulphite.

$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O$$

(c) Collect two gas-jars full of the gas. Hold a piece of magnesium ribbon in a pair of crucible tongs, heat until ignited and hold the burning metal in the gas. Note the decomposition of the gas into sulphur and oxygen (magnesium oxide formed).

$$2Mg + SO_2 \rightarrow 2MgO + S$$

Place a jar of hydrogen sulphide mouth to mouth with the second jar of sulphur dioxide. (See Expt. 27.)

Experiment 111. Reactions of sodium sulphite and the sulphites.

Apparatus: Bellows. *Material*: Sodium sulphite; iodine in potassium iodide.

(a) Make a hot solution of sodium sulphite and blow in air from the bellows. Test the solution for sulphate.

ionically: $2SO_3^{--} + O_2 \rightarrow 2SO_4^{--}$

(b) Make a solution of about a tea-spoonful of sodium sulphite crystals in 50 c.c. of water in a small flask. Add half a teaspoonful of crushed roll sulphur and boil for at least an hour, adding water as required to replace that lost by evaporation. Transfer to an evaporating basin and heat to a small bulk. Test the concentrated solution for sodium thiosulphate by (i) iodine solution, and (ii) addition of acid.

The absorption of oxygen in the first experiment and of sulphur

Note again the precipitate of chromium hydroxide (like aluminium, the carbonate and sulphide of chromium are rapidly hydrolysed in solution).

(c) *Reactions of dichromates.* Make a stock solution of potassium dichromate. Use a test-tube about a quarter full of the solution for each test.

(i) Add one drop of sodium hydroxide solution. Note the change of colour from orange to yellow, due to the formation of the chromate ion.

ionically: $Cr_2O_7^{--} + 2OH^- \rightarrow 2CrO_4^{--} + H_2O$

To the yellow solution add two or three drops of dilute acid. The orange colour is due to the formation of the dichromate ion.

ionically: $2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O$

(ii) Add a few drops of dilute sulphuric acid, then pass sulphur dioxide through the solution. The change of colour to green is due to the reduction of potassium dichromate to chromium sulphate, the sulphurous acid being oxidised to sulphuric acid.

ionically: $Cr_2O_7^{--} + 8H^+ + 3SO_3^{--} \rightarrow 2Cr^{+++} + 3SO_4^{--} + 4H_2O$

Reduce acidified solutions of potassium dichromate by hydrogen sulphide and by alcohol (see Expt. 80). Show that the relevant equations depend on the ionic equation,

$$Cr_2O_7^{--} + 8H^+ + 3X \rightarrow 2Cr^{+++} + 3XO + 4H_2O$$

(iii) Acidify a solution of potassium dichromate, add enough ether (Care!) to give a layer about an inch deep above the solution. Add a drop of a dilute aqueous solution of hydrogen peroxide. The blue colour is due to perchromic acid (see Expt. 105).

Note. For the preparation of chromyl chloride see Expt. 118.

(d) *Reactions of chromates.* Make a stock solution of potassium chromate, and use small portions for each of the following experiments.

(i) Add a drop of silver nitrate solution. The brick-red precipitate is silver chromate (see p. 58).

(ii) Add to three portions of the solution, solutions of lead acetate, barium chloride, and mercurous nitrate respectively. The precipitates are the chromates of the metals.

(iii) Acidify a portion of the solution. Pass hydrogen sulphide into the solution to reduce the chromate to a chromium salt.

$$2CrO_4^{--} + 10H^+ + 3H_2S \rightarrow 2Cr^{+++} + 8H_2O + 3S \downarrow$$

(iv) Acidify a portion of the solution and pass in sulphur dioxide. Sulphurous acid has reduced the solution of chromate (yellow) to the chromium salt (green).

$$2CrO_4^{--} + 10H^+ + 3SO_3^{--} \rightarrow 2Cr^{+++} + 5H_2O + 3SO_4^{--}$$

(e) *Oxidation of chromium compounds to chromates.* Prepare a dilute solution of chrome alum. Add about half a salt-spoonful of sodium peroxide, then boil the solution. The yellow colour of the solution indicates the presence of sodium chromate.

Test for the chromate ion by acidifying the solution with acetic acid and adding a solution of lead acetate (see p. 317).

Experiment 114. Preparation of chromium trioxide, CrO_3.

Apparatus: Measuring cylinder; glass wool; water-bath. *Material*: Finely ground potassium dichromate.

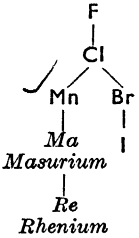
Dissolve 25 gm. of potassium dichromate in 50 c.c. of boiling water. Cool the solution to room temperature, and *when cold add very gradually* 35 c.c. of conc. sulphuric acid. Leave for a few hours, then decant the liquid from the potassium hydrogen sulphate crystals. Heat the liquid to 85° C. and add 25 c.c. of dilute sulphuric acid. Evaporate on a water-bath until crystals form on the surface, then set aside to crystallise. Filter through glass wool, preferably with suction and evaporate the filtrate for a further crop of crystals. To remove traces of sulphuric acid wash the crystals while still in the filter with concentrated nitric acid, in which the chromium trioxide is not soluble. Transfer the crystals to a dry evaporating basin and heat in an air oven at 130° C.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

CHAPTER XVII

GROUP VII

GENERAL



Elements in italics are not usually studied at this standard.

TABLE OF PROPERTIES OF THE HALOGENS

	Fluorine.	Chlorine.	Bromine.	Iodine.
Element.	yellow gas. Irritating smell.	yellowish-green gas. Irritating smell.	red liquid. Irritating smell.	black solid. Irritating smell.
Preparation.	electrolysis of KHF_2	heat on mixture of chloride, manganese dioxide and conc. H_2SO_4.	heat on mixture of bromide, manganese dioxide and conc. H_2SO_4.	heat on mixture of iodide, manganese dioxide and conc. H_2SO_4.
Activity.	very reactive. Combines with most metals and non-metals.	very reactive. Combines with most metals and many non-metals.	very reactive. Combines with most metals and many non-metals.	reactive. Combines with most metals and a few non-metals.
Replacing action.	replaces all halogens from combination in simple salts.	replaces bromine and iodine from bromides and iodides.	replaces iodine from iodides.	—
Oxidising action.	very powerful oxidising agent.	very powerful oxidising agent.	powerful oxidising agent.	weak oxidising agent.
Action with alkalis.	forms the fluoride and displaces oxygen.	forms hypochlorite with cold dilute, and chlorate with hot conc.	similarly forms hypobromite and bromate.	similarly forms hypoiodite and iodate (more readily).
Halogen acid.	fuming gas, very soluble, weakly acidic. Reacts with silica. Does not dissociate into elements.	fuming gas. Dissociates only at high temperature. Very soluble forming strong acid.	fuming gas. Dissociation begins at red heat. Very soluble forming strong acid.	fuming gas. Readily dissociates and is powerful reducing agent. Very soluble forming strong acid.

FLUORINE

The study of fluorine is complicated by its extreme activity—it combines with nearly all known elements.

Experiment 115. Preparation of hydrogen fluoride and to show its effect on glass.

Apparatus: Lead dish; waxed microscope slide. *Material*: Calcium fluoride.

Place a little powdered calcium fluoride in the bottom of a lead dish and pour over it some concentrated sulphuric acid. A microscope slide has been previously coated with wax and part of the wax removed by writing on the slide with a pin. Place the slide face downwards over the dish and warm gently. Whilst the reaction is in progress the similarity of hydrogen fluoride to the other halogens may be shown by (a) blowing across an ammonia bottle in the directions of the gas, (b) placing a piece of damp blue litmus paper in the gas. The action of silver nitrate on fluorides in solution is not typical as silver fluoride is soluble in water. *Steamy fumes* (Care!) of hydrogen fluoride are observed and if after two or three minutes the wax is removed from the slide the writing will be seen to be etched on the glass. This is due to the formation of silicon fluoride.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$
$$\underset{\text{from glass}}{SiO_2} + 4HF \rightarrow SiF_4 + 2H_2O$$

This reaction may be performed in a test-tube when the etching takes the form of a greasy appearance in the tube.

Note. It is advisable to perform the reaction in a fume chamber.

Experiment 116. Preparation of silicon tetrafluoride and to show its action on water (pure silica from sand).

Apparatus: As shown in Fig. 27. All the apparatus must be dry. *Material*: Mercury; sand; calcium fluoride.

Mix together equal bulks of fine dry sand and powdered calcium fluoride (one tea-spoonful of each will be sufficient) and introduce into a small flask (250 c.c.). See Fig. 27. Place the delivery tube in a gas-jar and pour in about half an inch deep of mercury. (It is essential to keep the delivery tube dry.) Pour concentrated sulphuric acid on to the mixture in the flask, and shake to moisten the whole mass. Pour water to a depth of 3 or 4 inches on to the mercury, and then warm the contents of the flask. The silicon tetrafluoride, which is a gas, passes into the water via the mercury, and hydrolyses to form a white precipitate of hydrated silica and a solution of hydrofluosilicic acid.

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + \underset{\text{hydrofluosilicic acid.}}{2H_2SiF_6}$$

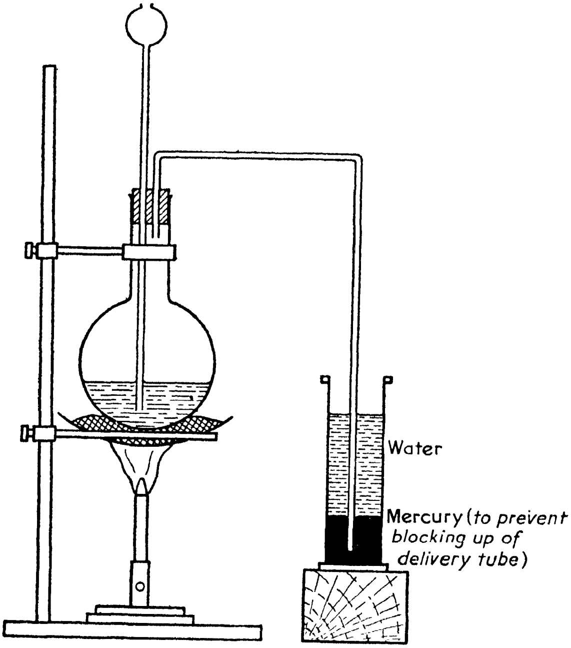


FIG. 27.

The precipitate may be regarded as silicic acid (with a formula H_2SiO_3 or H_4SiO_4) or as hydrated silica ($SiO_2.xH_2O$). Some of the water (1 or 2 molecules per molecule of silica) may be combined and some occluded.

To obtain a specimen of pure silica from sand.

Filter off the solution with suspended silica obtained above, and wash the hydrated silica well with three or four washings of hot distilled water. Transfer the silica to a crucible and heat (finally to redness). Allow to cool. The product is pure silica.

CHLORINE

Experiment 117. To compare and contrast the chloride, bromide and iodide of silver.

Material: Potassium chloride; potassium iodide; potassium bromide.

Fill each of three test-tubes in a rack, to a depth of about an inch, with solutions of potassium chloride, bromide and iodide respectively. (If the solids are supplied, dissolve a crystal of the size of a match head in about 5 c.c. of water.) Add a solution of silver nitrate to each. The silver chloride is white, the silver bromide slightly yellow, and the iodide yellow. Divide each into two parts. Add dilute nitric acid to one portion and dilute ammonium hydroxide drop by drop to the other in each case. All three precipitates are insoluble in nitric acid; silver chloride is soluble in ammonia, silver bromide slightly soluble, silver iodide insoluble.

ionically:
$$\begin{aligned} Ag^+ + Cl^- &\rightarrow AgCl \downarrow \\ Ag^+ + Br^- &\rightarrow AgBr \downarrow \\ Ag^+ + I^- &\rightarrow AgI \downarrow \\ AgCl + 2NH_3 &\rightarrow \underset{\text{soluble complex ion}}{[Ag(NH_3)_2]^+} + Cl^- \end{aligned}$$

Repeat the experiment (or divide the original precipitate into three parts instead of two) and show that all three precipitates are soluble in "hypo" solution.

$$AgCl + Na_2S_2O_3 \rightarrow \underset{\text{sodium silver thiosulphate}}{NaAgS_2O_3} + NaCl$$

Experiment 118. Some reactions of chlorides.

Material: Sodium chloride; solid potassium dichromate.

(a) Add 1 c.c. of conc. sulphuric acid to a salt-spoonful of sodium chloride in a test-tube. Hydrogen chloride is liberated.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$$

(b) Grind one salt-spoonful of sodium chloride with twice its bulk of manganese dioxide, transfer the mixture to a boiling-tube, add 2 or 3 c.c. of conc. sulphuric acid and warm. Chlorine is evolved (bleaches litmus) and some hydrogen chloride.

$$2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow$$

(c) *Preparation of chromyl chloride, CrO_2Cl_2.*

Heat a dry test-tube in the bunsen flame to soften the glass in the region about a quarter to a third from the open end. Draw out the glass to reduce the diameter of the tube to about a quarter of an inch at the heated part and at the same time bend the open end slightly downwards. The apparatus will then serve as a small retort. When cold introduce into the tube a mixture of not more than a salt-spoonful of finely ground potassium dichromate and half that amount of sodium chloride. Add just enough conc. sulphuric acid to cover the mixture. Grasp the tube in one holder and in another hold a dry test-tube to act as a receiver. Heat the mixture *gently* and collect a few drops of the reddish-brown liquid, chromyl chloride.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \rightarrow K_2SO_4 + 2Na_2SO_4 + 2CrO_2Cl_2 + 3H_2O$$

Add a few drops of water to the compound. Test the gas (hydrogen chloride) with litmus paper and with silver nitrate solution on a glass rod. The yellow solution contains chromic acid. Add sodium hydroxide solution until neutral, then acidify with acetic acid and add a solution of lead acetate. The yellow precipitate confirms the presence of chromate ion.

$$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl$$

(d) For the action of silver nitrate see Expt. 117.

Experiment 119. Preparation of chlorine.

Apparatus: As in Fig. 28. Woulfe's bottles. *Material*: Solid potassium permanganate.

The following is the most convenient method of preparing chlorine since it is easily controlled. Fit up the apparatus as shown in Fig. 28 and put one or two tea-spoonfuls of potassium permanganate into the flask. Fill the dropping funnel with concentrated hydrochloric acid and allow the acid to run on to the permanganate to produce chlorine at the required speed.

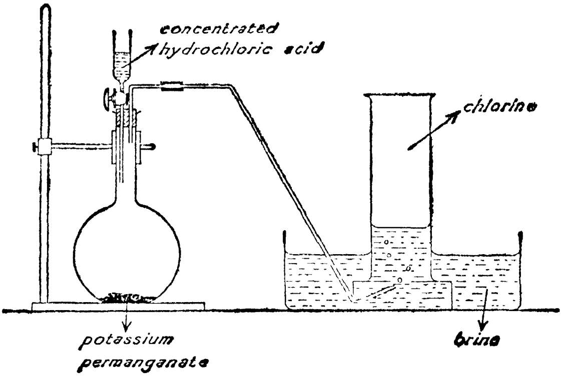


FIG. 28.

ionically: $2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2\uparrow$

If required dry, pass the gas through a little water to remove hydrogen chloride and through conc. sulphuric acid to dry it.

Experiment 120. Preparation of anhydrous ferric chloride.

Apparatus: As shown in Fig. 29; chlorine generator. *Material*: Iron wire; solid potassium permanganate.

THEORY

Anhydrous ferric chloride (similar remarks apply to other chlorides, e.g., ferrous, magnesium, zinc, aluminium, antimony, etc.) cannot be prepared by evaporating a solution of the salt to dryness because hydrolysis takes place and the final product is ferric oxide. See p. 120.

Fit up the apparatus as shown in Fig. 29, coil two feet of thin iron wire by winding it round a pencil and put it in the combustion tube. Pass dry chlorine over for a minute to displace the air and then heat by means of a bunsen burner. As soon as the iron wire commences to burn remove the flame and the wire will continue to burn if the supply of chlorine is sufficient. Most of the ferric chloride will condense as a mass of black crystals in the cool part of the tube. A trap (thistle funnel dipping into caustic soda solution) may be used to absorb excess chlorine, or the gas may be led into the fume chamber.

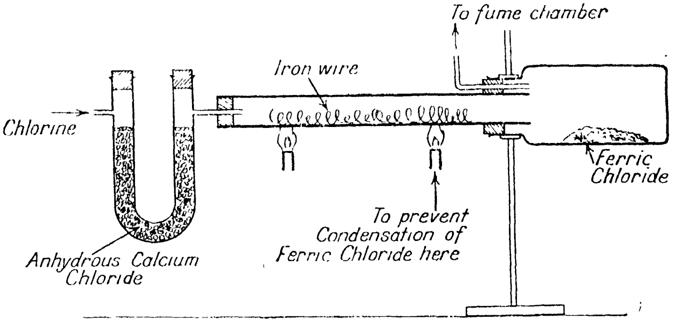


FIG. 29.

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

Note. Anhydrous ferrous chloride may be prepared in a similar apparatus. Dry hydrogen chloride is used in place of chlorine and the small colourless scales of ferrous chloride are much less volatile and frequently adhere to the unattacked iron.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Experiment 121. Action of concentrated sulphuric acid on potassium chlorate.

Apparatus: Clean dry test-tube. *Material*: Potassium chlorate.

Drop a crystal (or crystals) of potassium chlorate *the size of a match head* into a clean dry test-tube and clamp in a position nearly horizontal. By means of a dropping tube drop *two* or *three drops* of concentrated sulphuric acid in the mouth of the tube. Adjust the slant so that the acid runs slowly down on to the solid, the mouth of the tube pointing in a safe direction. As the two meet, a yellow gas (chlorine peroxide or dioxide) is seen. Holding a burner at arm's length, warm the tube. A violent explosion takes place as the chlorine dioxide decomposes.

$$3KClO_3 + 2H_2SO_4 \rightarrow KClO_4 + 2KHSO_4 + 2ClO_2 + H_2O$$

Note: For the preparation of potassium perchlorate from potassium chlorate see Expt. 45.

BROMINE

(Care! Liquid bromine will cause sores if it comes in contact with the flesh, and bromine vapour is painful to the eyes.)

A gas-jar full of bromine may be obtained by warming a gas-jar, dropping 1 or 2 c.c. of bromine into it, leaving the lid two-thirds on. After a little while the bromine will evaporate and fill the jar.

Experiment 122. Reactions of bromine.

Apparatus: Hydrogen generator. *Material*: Gas-jars of bromine vapour obtained from liquid bromine as described above; alcoholic solution of fluorescein.

(a) Invert a gas-jar of hydrogen over bromine, remove cover plates and mix. On applying a flame there is a feeble explosion.

$$H_2 + Br_2 \rightarrow 2HBr$$

(b) Invert a gas-jar of hydrogen sulphide over bromine. A deposit of sulphur is obtained and the colour of bromine is replaced by the misty fumes of hydrogen bromide.

$$Br_2 + H_2S \rightarrow 2HBr + S \downarrow$$

(c) Dip a filter paper in an alcoholic solution of fluorescein and allow to dry. Place it in a gas-jar of bromine vapour, when the paper turns red due to the formation of eosin.

(d) See Expt. 131 Part II.

Experiment 123. Reactions of bromine water.

Material: Red phosphorus; sulphurous acid.

Bromine dissolves to a slight extent in water forming a red solution of concentration approximately 4%. Note the presence of the red vapour above the saturated solution.

(a) Add a pinch of iron filings to a test-tube one quarter filled with bromine water. Shake. According to which element is in excess a pale green solution of ferrous bromide (iron in excess), or a yellow solution of ferric bromide (bromine in excess) will be obtained.

$Fe + Br_2 \rightarrow FeBr_2$ or *ionically*: $Fe + Br_2 \rightarrow Fe^{++} + 2Br^-$
$2Fe + 3Br_2 \rightarrow 2FeBr_3$ or *ionically*: $2Fe + 3Br_2 \rightarrow 2Fe^{+++} + 6Br^-$

The presence of ferrous or ferric iron may be shown by the addition of caustic soda solution (a mixture of the two will give a black precipitate of Fe_3O_4).

(b) Hold a piece of blue litmus paper in the vapour above bromine water. It turns red and is bleached.

(c) Add a few drops of bromine water to a test-tube one quarter filled with sulphurous acid. Test the solution for sulphate by adding dilute hydrochloric acid followed by barium chloride.

ionically: $SO_3^{--} + Br_2 + H_2O \rightarrow SO_4^{--} + 2Br^- + 2H^+$

(d) Add caustic soda solution drop by drop to a test-tube one quarter filled with bromine water until the colour is just discharged. The solution contains the hypobromite ion.

ionically: $2OH^- + Br_2 \rightarrow OBr^- + Br^- + H_2O$

This hypobromite solution will precipitate manganese dioxide from a solution of manganese sulphate and lead dioxide from a solution of lead nitrate.

(e) Add a salt-spoonful of red phosphorus* to a test-tube one quarter filled with bromine water. Shake and allow to stand. The colour of the bromine water disappears. The bromine and phosphorus have combined and the resulting bromide of phosphorus has been decomposed to give phosphorous or phosphoric acids.

$$\begin{aligned} P_4 + 6Br_2 &\rightarrow 4PBr_3 \\ P_4 + 10Br_2 &\rightarrow 4PBr_5 \\ 2PBr_3 + 6H_2O &\rightarrow 2H_3PO_3 + 6HBr \\ PBr_5 + 4H_2O &\rightarrow H_3PO_4 + 5HBr \end{aligned}$$

(f) Add a little bromine water to a solution of potassium iodide in water. Iodine is displaced.

ionically: $2I^- + Br_2 \rightarrow I_2 + 2Br^-$

Note: See Expt. 198 for the action of bromine on the unsaturated hydrocarbons.

Experiment 124. Preparation and properties of hydrogen bromide.

Apparatus: Boiling-tube fitted with cork and tube bent at right angles. *Material*: Potassium bromide; chlorine water.

For class purposes hydrogen bromide may readily be prepared by the action of fairly concentrated sulphuric acid on potassium bromide. If the acid is concentrated there is considerable oxidation.

Dilute a quantity of sulphuric acid with water by pouring two volumes of concentrated sulphuric acid into one volume of water, adding the acid a little at a time. If each experimenter is preparing his own acid it will be sufficient if 2 c.c. of acid are poured two to

---

* This reaction gives a suitable method of disposing of phosphorus residues.

three drops at a time into 1 c.c. of water in a boiling-tube. Into the diluted acid put a salt-spoonful of potassium bromide and warm gently. (Care!)

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr \uparrow$$

Test the misty fumes by carefully lowering a drop of the following reagents on the end of a glass rod into the gas:—

(a) Silver nitrate solution. A pale yellow precipitate of silver bromide is formed.

ionically: $$Ag^+ + Br^- \rightarrow AgBr \downarrow$$

(b) 0·880 ammonia. Fumes of ammonium bromide are observed.

$$NH_3 + HBr \rightarrow NH_4Br$$

(c) Litmus solution. It is turned red.

(d) Chlorine water. Yellow coloration due to bromine.

ionically: $$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

(e) A drop of water. This may be removed and tested by dipping the rod into, e.g., a few drops of silver nitrate solution in a test-tube. The positive reaction shows the high solubility of the gas in water.

(f) Concentrated nitric acid. The hydrogen bromide is rapidly oxidised to bromine.

$$2HNO_3 + 2HBr \rightarrow 2H_2O + 2NO_2 + Br_2$$

(g) Attach a cork with tube bent at right angles and heat the tube strongly, having a piece of white paper ready to hold behind the tube. The hydrogen bromide is decomposed by strong heat into bromine and hydrogen. If the bromine is not easily visible its presence may be shown by the fluorescein test (Expt. 122(c)).

Experiment 125. Preparation of hydrogen bromide (Demonstration).

Apparatus: As in Fig. 30. *Material*: Bromine; red phosphorus.

Make a paste of 5–10 gm. of red phosphorus with water and sand (to moderate the action) and introduce this into the flask. Bromine is dropped in gradually from the tap funnel, the first few drops reacting with a flash of light. The bromine volatilised by the heat of the reaction is removed by passing the gases through a U-tube containing beads smeared with damp red phosphorus. (Do not have this material too wet or much of the hydrogen bromide will be absorbed here.) The hydrogen bromide, which is very similar in appearance to hydrogen chloride, is collected by displacement of air. Alternatively, if a solution is wanted, it may be collected by passing it through an inverted funnel over water. (Equations in Expt. 123(e)).

The reactions of Expt. 124(a) to (g) may be repeated, using gas-jars of hydrogen bromide and correspondingly larger quantities of reactants. The action of heat on hydrogen bromide is best shown by filling a boiling-tube with hydrogen bromide, inserting a loose cork, and heating strongly in the flame of a bunsen burner with a piece of white paper held at the back as soon as decomposition begins.

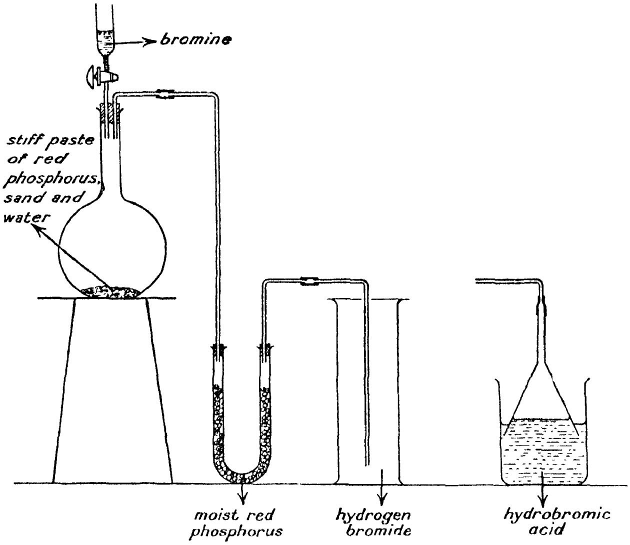


FIG. 30.

$$2HBr \rightleftharpoons H_2 + Br_2$$

Experiment 126. Preparation of potassium bromide, KBr.

Apparatus: 250 c.c. flask; measuring cylinder; Buchner funnel; water-bath. *Material*: Bromine; potassium carbonate.

Take 100 c.c. of distilled water in the flask. Measure 5 c.c. of bromine in a measuring cylinder which already contains 2 or 3 c.c. of water. Pour the bromine and water into the flask (and wash out the cylinder at once). Weigh 8 gm. of iron filings and add to the solution in portions of about 0·5 gm., shaking well on each addition. If this operation of adding the iron is hurried, much heat is generated and some ferric bromide is formed and persists throughout the preparation. Heat the flask on a water-bath for ten minutes and filter quickly.

$$Fe + Br_2 \rightarrow FeBr_2$$

Prepare a solution of 20 gm. of potassium carbonate in 50 c.c. of water. Add this solution to the green solution of ferrous bromide, mix well and heat on the water-bath for ten minutes. The white (later green) precipitate is ferrous carbonate.

$$FeBr_2 + K_2CO_3 \rightarrow 2KBr + FeCO_3$$

Filter quickly and evaporate the colourless solution to crystallisation. Examine a drop of solution under a microscope for cubic crystals of the bromide.

Experiment 127. Reactions of bromides.

Material: Use one crystal the size of a match-head or 1 c.c. of 10% potassium bromide for each experiment; chlorine water; carbon tetrachloride.

(a) Grind the bromide with a small quantity of manganese dioxide, add 1 c.c. of concentrated sulphuric acid to the mixture in a test-tube and warm gently. The red vapour of bromine may condense to small drops of liquid bromine on the sides of the test-tube.

$$MnO_2 + 2KBr + 2H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + 2H_2O + Br_2 \uparrow$$

(b) Add a few drops of silver nitrate solution to a solution of potassium bromide. The pale yellow precipitate of silver bromide is insoluble in dilute nitric acid but dissolves in excess ammonium hydroxide (sparingly soluble).

ionically: $Ag^+ + Br^- \rightarrow AgBr \downarrow$

(c) Add a little chlorine water, a drop at a time, to a solution of potassium bromide. Bromine is liberated which turns the solution light brown or red. If two drops of carbon tetrachloride are added (cf. Expt. 130(c)) the bromine dissolves forming a brown or red solution.

ionically: $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$

IODINE

Experiment 128. Class preparation of hydrogen iodide.

Apparatus: As in Fig. 31; mortar and pestle. *Material*: Red phosphorus; iodine.

Grind a salt-spoonful each of dry red phosphorus and iodine in a mortar and introduce into a boiling-tube. Add three or four drops of water and fit the boiling-tube up as shown in Fig. 31.

$$P_4 + 6I_2 \rightarrow 4PI_3$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI \uparrow$$

The boiling-tube may be warmed to generate further quantities of hydrogen iodide. The following reactions of the gas may be shown:—

(a) Pass the gas into silver nitrate solution in a test-tube. A yellow precipitate of silver iodide is seen.

(b) Pass the gas into a test-tube containing a few drops of ·880 ammonia. White fumes of ammonium iodide are produced.

$$HI + NH_3 \rightarrow NH_4I$$

(c) Pass the gas into a test-tube containing a few drops of concentrated nitric acid. The hydrogen iodide is easily oxidised to iodine and the nitric acid reduced to nitrogen dioxide.

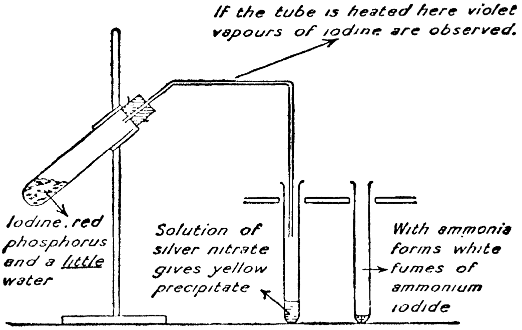


Fig. 31.

$$2HNO_3 + 2HI \rightarrow 2H_2O + 2NO_2 + I_2$$

(d) Pass the gas for a little time into a test-tube containing a few c.c. of concentrated sulphuric acid. The acid is reduced to sulphur dioxide, hydrogen sulphide or sulphur, showing that hydrogen iodide is a powerful reducing agent.

(e) Action of heat. Warm the delivery tube with a bunsen burner. The violet vapours of iodine will be observed.

$$2HI \rightleftharpoons H_2 + I_2$$

Experiment 129. Preparation of hydrogen iodide. (Demonstration.)

Apparatus: As in Fig. 30; mortar and pestle. *Material*: Red phosphorus; iodine.

Grind 2 gm. of dry red phosphorus with 10 gm. of iodine and introduce the mixture into a dry flask fitted up as shown in the diagram (Fig. 30). Run in water from the dropping funnel drop by drop until the flashing ceases. Be sure not to add too much water as the gas is very soluble. 10–15 drops will be sufficient as a rule. Warm the flask gently and after a little while the gas comes off readily and may be collected.

The experiments of Expt. 128(a) to (e) may be repeated using larger quantities.

Experiment 130. Reaction of iodides.

Material: Use one crystal the size of a match-head or 1 c.c. of a 10% solution for each reaction; chlorine water; carbon tetrachloride.

(a) Grind the iodide with a small quantity of manganese dioxide and add 1 c.c. of concentrated sulphuric acid to the mixture in a test-tube. Warm gently and observe the violet vapours of iodine.

$$MnO_2 + 2KI + 2H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + 2H_2O + I_2$$

With concentrated sulphuric acid alone iodine is also obtained on heating because hydrogen iodide is a powerful reducing agent.

(b) Add a little silver nitrate solution to a solution of potassium iodide. The yellow precipitate of silver iodide obtained is insoluble in both dilute nitric acid and in ammonium hydroxide.

ionically: $Ag^+ + I^- \rightarrow AgI \downarrow$

(c) Add a little chlorine water a drop at a time to a solution of potassium iodide. Iodine is liberated which turns the solution brown whilst black crystals can usually be seen at the surface of the liquid by careful inspection.

ionically: $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$

Add two drops of carbon tetrachloride. The iodine dissolves on shaking, giving an intense violet coloration.

(d) Add a few drops of lead acetate solution to a solution of potassium iodide. A yellow precipitate of lead iodide is obtained.

ionically: $Pb^{++} + 2I^- \rightarrow PbI_2 \downarrow$

(e) Add potassium iodide solution, a drop at a time, to three or four drops of mercuric chloride solution. A brilliant scarlet precipitate of mercuric iodide is obtained which will dissolve in excess of the iodide to form a complex ion. If caustic soda solution is added at this stage, Nessler's solution is formed. This solution is used as a very delicate test for ammonia (see Expt. 74). (Equations for reactions given in Expt. 71(b).)

Note: See Expt. 55 (b) for reaction of potassium iodide solution with cupric ions.

Experiment 131. Preparation of iodic acid, HIO_3 and potassium iodate.

Apparatus: Retort; small flask; sand-tray; water-bath; measuring cylinder. *Material*: iodine; fuming nitric acid; caustic potash.

Iodic acid.

Take 5 gm. of iodine in a retort and add a measured 40 c.c. of fuming nitric acid. Heat the retort on a sand-tray, keeping the temperature just high enough to promote action. Collect any nitric acid which distils over and return it to the retort. When the iodine has all been oxidised to white crystals of iodic acid, pour the contents of the retort into an evaporating basin and heat almost to dryness on a water-bath. Collect the crystals and dry between filter paper.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Heat some of the crystals in a dry test-tube, gently at first, and later strongly. Note the formation of moisture to leave iodine pentoxide:—

$$2HIO_3 \rightarrow I_2O_5 + H_2O$$

This is followed by decomposition to iodine and oxygen. (Test with glowing splint.)

$$2I_2O_5 \rightarrow 2I_2 + 5O_2$$

✓

Potassium iodate.

Put a small piece (2 gm.) of potassium hydroxide into a test-tube and fill to a depth of two inches with water. When dissolved add, a little at a time, three saltspoonfuls (4·5 gm.) of iodine to the warm solution. Pour the solution into a clock-glass and allow to cool.

ionically: $6OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$

Decant the solution from the crystals, wash the latter with a *little* water and dry them on a filter paper. Heat a few crystals in a dry tube and show oxygen is evolved. (Potassium bromate may be made by a similar experiment using 30 drops (1 c.c.) of bromine in place of the iodine.)

MANGANESE

REACTIONS OF MANGANESE

It will be seen that manganese appears in the same group of the periodic table as the halogens but it is not in the same sub-group. Manganese is typically metallic in character and the similarity between it and the halogens is almost entirely confined to the heptoxide, Mn_2O_7, which shows similarities to Cl_2O_7 in the corresponding perchlorates and permanganates.

We shall investigate the properties of manganous salts, manganates and permanganates.

Manganous salts (e.g., $MnCl_2$ manganous chloride)
correspond to MnO — Manganese divalent.
Manganates (e.g., K_2MnO_4 potassium manganate)
correspond to MnO_3 — manganese hexavalent.
Permanganates (e.g., $KMnO_4$ potassium permanganate)
correspond to Mn_2O_7 — Manganese heptavalent.

Manganese also forms some unstable manganic salts (e.g., manganic sulphate $Mn_2(SO_4)_3$) corresponding to Mn_2O_3.

Experiment 132. Reactions of manganous salts.

Material: Use 1 c.c. of a solution of manganous chloride for each test. Note that solutions of manganese salts are pink.

(a) Add a few drops of yellow ammonium sulphide solution to a solution of manganous chloride. A flesh coloured precipitate (cf. No. 9 grease paint) of manganous sulphide is obtained.

ionically: $Mn^{++} + S^{--} \rightarrow MnS \downarrow$

This same precipitate is obtained if hydrogen sulphide is bubbled into an *alkaline* solution of a manganous salt but no precipitate is obtained with an acidic solution.

(b) Add caustic soda solution a drop at a time (using a dropping tube) to a solution of manganous chloride. A white precipitate (rapidly turning brown due to atmospheric oxidation) of manganous hydroxide is obtained. Keep on adding the caustic soda solution and note that the precipitate is *not* soluble in excess (cf. zinc hydroxide, p. 62).

ionically: $Mn^{++} + 2OH^{-} \rightarrow Mn(OH)_2 \downarrow$

(c) Repeat (b) using ammonium hydroxide with same observations.

(d) Repeat (b) after first adding one salt-spoonful of solid ammonium chloride to the manganous chloride solution. No precipitate occurs. The ammonium ion introduced depresses the ionisation of the hydroxide (see p. 332).

(e) Add 1 c.c. of caustic soda solution followed by 2 c.c. of bromine water (many oxidising agents will do, e.g., sodium peroxide, hypochlorite or hypobromite) and warm. The divalent oxide or hydroxide is oxidised to the higher quadrivalent oxide, manganese dioxide, which comes down as a dark brown precipitate. If the manganous salt is warmed with excess of the oxidising agent or a powerful oxidising agent is used, then the permanganate is obtained. Boil a little of the manganous chloride solution with a salt-spoonful of lead dioxide and 1 c.c. of concentrated nitric acid. Dilute with water and filter—the solution comes through showing the pink permanganate colour.

Experiment 133. Preparation and reaction of manganates.

Material: Solid caustic potash; potassium nitrate.

Heat on a crucible lid a piece of caustic potash, a few crystals of potassium nitrate and a little manganese dioxide until the whole mass has fused. Allow to cool and add a little water and filter. A deep green solution of potassium manganate is obtained.

$$4KOH + 2MnO_2 \underbrace{+ \; O_2}_{\text{from } KNO_3} \rightarrow 2K_2MnO_4 + 2H_2O$$

The solution is unstable and is readily hydrolysed by dilute acids and even by largely diluting the solution into a permanganate.

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$$

Dilute the green solution about ten times with water and boil—the pink colour of the permanganate is observed on allowing the solution to settle.

Experiment 134. Preparation of potassium permanganate, $KMnO_4$.

Apparatus: Clean sand-tray; 500 c.c. flask; glass-wool; mortar and pestle. *Material*: Potassium hydroxide (powder); potassium chlorate; supply of carbon dioxide.

Take 10 gm. of potassium hydroxide on the tray and warm gently to melt. Add 1 gm. of potassium chlorate, mixing with a glass rod. Add 7·5 gm. of manganese dioxide very gradually and continuing to stir. When all has been added heat to bright red heat for about fifteen minutes. Allow to cool, break off the melt and grind to a fine powder in a mortar. Transfer the powder to a 500 c.c. flask, add 200 c.c. of water and heat on a gauze. During the boiling pass carbon dioxide into the solution. At first the solution is green and contains potassium manganate:—

$$6KOH + 3MnO_2 + KClO_3 \rightarrow 3K_2MnO_4 + KCl + 3H_2O$$

Later it becomes purple potassium permanganate:—

$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

After boiling for ten minutes allow to cool and decant through glass-wool in a filter. Wash the flask and return the filtrate to it. Boil for a further ten minutes while carbon dioxide passes through, withdraw a drop of solution and place on a filter paper. If the drop has a green centre continue the process until complete. Finally cool and filter. Transfer the solution to a large evaporating basin and evaporate until crystals appear, then set aside to crystallise.

Experiment 135. Reactions of the permanganate ion.

Material: Materials mentioned in section (c).

Permanganates are very powerful oxidising agents, especially in acidic solution. When the permanganate ion oxidises in acid solution, the negatively charged permanganate ion becomes the positively charged manganese ion, the charges necessary to do this coming from the hydrogen ions:—

$$\textit{ionically}: \; 2MnO_4^- + 6H^+ \rightarrow 2Mn^{++} + 3H_2O + \underset{\text{for oxidation}}{5O}$$

In neutral or alkaline solution the reaction is represented by:—

ionically: $2MnO_4^- + H_2O \rightarrow 2MnO_2 + 2OH^- + 3O$
for oxidation

The quantitative oxidising actions of potassium permanganate are given in Chapter XXXV.

(a) To a solution of potassium permanganate add 1 c.c. of dilute sulphuric acid followed by 1 or 2 c.c. of hydrogen peroxide. The oxygen evolved may be recognised by the rekindling of a glowing splint. If the permanganate has not been in excess the solution will be decolorised.

ionically: $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{++} + 8H_2O + 5O_2$

(b) Add 1 c.c. of concentrated hydrochloric acid to a solution of potassium permanganate. There is an evolution of chlorine which can be recognised by its smell or by its bleaching action on damp litmus.

ionically: $2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2 \uparrow$

(c) Try the effect of potassium permanganate solution on acidic solutions of any of the following materials:—Ferrous sulphate, stannous chloride, sulphurous acid or sodium sulphite, sodium nitrite, sodium thiosulphate, sodium phosphite or hypophosphite, sodium arsenite. Oxidation occurs in all these cases as well as in many others not listed.

CHAPTER XVIII

GROUP VIII

(*or* TRANSITION GROUP)

GENERAL

The elements in this group occur in the middle of long periods. Thus iron, nickel and cobalt link manganese with copper; ruthenium, rhodium and palladium link masurium with silver; osmium, iridium and platinum link rhenium with gold. In an elementary course only iron, nickel and cobalt are considered. The order of atomic weights does not show the gradation of properties of the three metals quite as well as the order in which they are considered below, namely, iron, cobalt and nickel.

	Iron.	Cobalt.	Nickel.
Appearance	←—— All tough metals, grey colour ——→		
Atomic weight	55·84	58·97	58·68
Melting point	1500°	1460°	1452°
Specific gravity	7·8	8·5	8·8
Magnetic susceptibility	high	less	least
Valency	2 and 3	2 and 3	usually 2 but sometimes 3

COMPOUNDS.

	Iron.	Cobalt.	Nickel.
Oxides	FeO. Basic. Easily oxidised to Fe_2O_3	CoO. Basic. Stable but oxidised when heated to Co_3O_4.	NiO. Basic. Stable but oxidised when heated to Ni_2O_3.
	Fe_2O_3. Basic	Co_2O_3. Basic	Ni_2O_3. Not basic but forms salts corresponding to NiO.
	Fe_3O_4. Mixed base	Co_3O_4. Mixed base	
Sulphates MSO_4	←—— All isomorphous. With ammonium sulphate they form double salts. ——→		
Sulphates $M_2(SO_4)_3$	$Fe_2(SO_4)_3$	None	None.
Sulphides MS	←—— All black in colour and soluble in hot acids. ——→		
Chloride MCl_2	Hydrated salt oxidised and hydrolysed to ferric oxide on heating	Hydrated salt pink and becomes blue (anhydrous) on heating	Stable.
Hydroxide $M(OH)_2$	Green. Oxidised to brown $Fe(OH)_3$ in air	Pink. Oxidised to brown $Co(OH)_3$ in air	Stable.

Experiments with iron salts have probably been done in an earlier course, and the following brief instructions are included for revision purposes.

Experiment 136. Revisionary experiments with ferrous and ferric salts.

Make a stock solution of a ferrous salt and one of a ferric salt. Take about 5 c.c. of the required solution for each of the following tests:—

(a) Add caustic soda solution.
(b) Add ammonium hydroxide.
(c) Add acidified potassium permanganate solution.
(d) Add potassium ferrocyanide solution.
(e) Add potassium ferricyanide solution.
(f) Add potassium (or ammonium) thiocyanate solution. If the ferrous sulphate is not fresh, a trace of ferric salt will give a result here; ferrous ammonium sulphate should show a negative result.

The following table summarises the results:—

	Ferrous salt.	Ferric salt.
(a) Caustic soda	Green ppt. of ferrous hydroxide, $Fe(OH)_2$	Foxy-red ppt. of ferric hydroxide $Fe(OH)_3$.
(b) Ammonium hydroxide	As for caustic soda solution.	
(c) Acidified potassium permanganate	Decolorises the permanganate. Ferrous salts are reducers (see p. 14)	Does not reduce.
(a) Potassium ferrocyanide $K_4[Fe(CN)_6]$	Light blue ppt. of no special importance	Deep blue ppt. Prussian blue.
(e) Potassium ferricyanide $K_3[Fe(CN)_6]$	Deep blue ppt. "Turnbull's" blue	Brown coloration of no special importance.
(f) Potassium thiocyanate KCNS	No action	Blood-red coloration of ferric thiocyanate $Fe(CNS)_3$.

Experiment 137. Conversion of ferrous salt to ferric salt and vice versa.

Oxidation of ferrous salt. Take a test-tube filled to a depth of about one inch with a solution of a ferrous salt (e.g., ferrous sulphate). Add excess (about an equal volume) of dilute sulphuric acid, two or three drops of concentrated nitric acid and boil. Cool, and add caustic soda solution until a red precipitate of ferric hydroxide is formed. This indicates that oxidation has taken place.

$$2FeSO_4 + H_2SO_4 + 2HNO_3 \rightarrow Fe_2(SO_4)_3 + 2NO_2 + 2H_2O$$

Other oxidising materials such as chlorine, bromine, potassium permanganate or hydrogen peroxide may be substituted for nitric acid in the above experiment.

Reduction of ferric salt. Fill a test-tube to a depth of about one inch with a ferric salt solution (e.g., ferric chloride). Pass hydrogen sulphide into it until there is no further precipitate of sulphur, and on filtering a pale green solution is obtained.

Test the filtrate with potassium ferricyanide for proof of ferrous salt.

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S \downarrow$$

Take a test-tube one-quarter full of ferric salt solution. Add an equal volume of conc. hydrochloric acid and a few pieces of granulated zinc. Leave for half an hour. Filter. Test the filtrate with excess of sodium hydroxide solution to show that reduction to the ferrous condition is complete. Hydrogen generated *in situ* (nascent hydrogen) was the reducer.

ionically: $Fe^{+++} + H \rightarrow Fe^{++} + H^+$

Experiment 138. Preparation of ferrous oxide, FeO.

Material: Ferrous oxalate; glass-wool.

Take a dry test-tube about a quarter full of ferrous oxalate, and close it with a plug of glass-wool. Heat, gently at first, and finally strongly enough to convert all the yellow oxalate to black ferrous oxide. Remove the glass-wool and pour the oxide in small portions so that it sprinkles into an evaporating basin. Note the spontaneous ignition of the ferrous oxide as it oxidises to red ferric oxide.

$$FeC_2O_4 \rightarrow FeO + CO + CO_2$$

Dissolve any particles still in the test-tube in hydrochloric acid. Test the solution for ferrous ions. Ferrous oxide is a base, but, for convenience, ferrous salts are prepared from metallic iron and acid.

Experiment 139. Preparation of ferric oxide, Fe_2O_3.

Material: Solution of any iron salt.

If the salt is a ferrous salt, oxidise to the ferric condition as described in Expt. 137. Add excess ammonium hydroxide to the ferric salt and filter off the ferric hydroxide. Heat the paper and contents in a crucible to leave red ferric oxide. Boil a little of the oxide in conc. hydrochloric acid and show that it is a base.

Experiment 140. To show that ferroso-ferric oxide is a mixed base.

Material: Black (magnetic) oxide of iron.

Take enough of the oxide to cover the bottom of a test-tube and fill the tube a quarter full of conc. hydrochloric acid. Warm gently and then filter. Divide the filtrate and test one part for ferric ions and the other for ferrous ions. Both ions will be found present.

$$Fe_3O_4 + 8HCl \rightarrow 2FeCl_3 + FeCl_2 + 4H_2O$$

Experiment 141. Action of heat on hydrated iron chlorides.

Material: solid hydrated ferric chloride.

Prepare a solution of ferrous chloride by dissolving iron (filings) in a small quantity of conc. hydrochloric acid. Evaporate in the test-tube until crystals appear. Heat strongly and test the vapour for hydrogen chloride (silver nitrate on a glass rod). Note the residue of *ferric* oxide, due to the ferrous oxide which first formed, being oxidised by air.

$$FeCl_2 + H_2O \rightarrow FeO + 2HCl\ ;\ 2FeO + O\ (\text{air}) \rightarrow Fe_2O_3$$

Heat a little ferric chloride in a test-tube. Test the gas for hydrogen chloride and note the residue of ferric oxide. Again hydrolysis has occurred.

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$$

Experiment 142. Preparation of ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$.

Apparatus: Measuring cylinder. *Material*: Ammonium sulphate.

Take 30 c.c. of distilled water in a conical flask and add 4 c.c. of conc. sulphuric acid from the measuring cylinder. Add 5 gm. of iron gradually and then heat to boiling. Add 10 gm. of ammonium sulphate and evaporate to about two-thirds of its original volume. Cork loosely and set aside to crystallise. This salt is not an alum, but a double salt. An interesting fact is that it contains one-seventh of its weight of iron.

Experiment 143. Properties of cobalt salts.

Material: Cobalt chloride and carbonate; bleaching powder.

(a) Heat a little cobalt carbonate in a small hard-glass tube. The brown residue is cobaltous oxide.

$$CoCO_3 \rightarrow CoO + CO_2$$

Transfer the oxide to a crucible and heat to redness. The black residue is cobalto-cobaltic oxide, Co_3O_4. Compare the stability of cobaltous oxide with ferrous oxide and also the products of oxidation of the lower oxides.

(b) Take a test-tube one-quarter full of a solution of a cobalt salt. Add excess of hot caustic soda. The pink ppt. is cobaltous hydroxide.

ionically: $Co^{++} + 2OH^{-} \rightarrow Co(OH)_2 \downarrow$

Note the change to brown cobaltic oxide, Co_2O_3, on exposure to air and compare with ferrous hydroxide in this respect. Show that cobaltous hydroxide is soluble in ammonium hydroxide due to the formation of the complex ion $[Co(NH_3)_6]^{++}$.

(c) Add a suspension of bleaching powder to a test-tube containing a solution of a cobaltous salt. The black ppt. is cobaltic hydroxide (the bleaching powder having acted as an alkaline hydroxide and an oxidiser). Divide the precipitate into two parts. Add excess hydrochloric acid to one part to obtain a brown solution of the unstable cobaltic chloride, and heat the second part to obtain oxygen and a residue containing cobaltous oxide. Hence cobaltic hydroxide behaves as a weak base, and differs from ferric hydroxide in acting as a hydrated peroxide.

(d) Evaporate some cobaltous chloride solution to dryness. Note the blue colour of the anhydrous salt. Cobalt chloride is stable. (Compare with hydrated ferrous chloride.) The action of heat may be shown in a picturesque manner by writing on a piece of paper with cobalt chloride solution and allowing to dry. If the solution is fairly dilute the writing becomes invisible. On warming the writing appears bright blue due to dehydration of the salt.

Experiment 144. Properties of nickel salts.

Material: Nickel sulphate and carbonate.

(a) Heat some nickel carbonate in a hard-glass test-tube. The greenish brown residue is nickelous oxide, which on transference to a crucible and further heating goes to the black nickelic oxide Ni_2O_3. This is a close resemblance to ferrous oxide although the action is less rapid. Show that nickelic oxide dissolves in dilute sulphuric acid to give green nickel*ous* salt.

$$2Ni_2O_3 + 4H_2SO_4 \rightarrow 4NiSO_4 + 4H_2O + O_2$$

(b) Add caustic soda solution to a solution of nickel sulphate. The light green ppt. is nickelous hydroxide.

ionically: $Ni^{++} + 2OH^{-} \rightarrow Ni(OH)_2 \downarrow$

It is stable in air. (Contrast with ferrous and cobaltous hydroxides.) Show that the hydroxide is soluble in ammonium hydroxide to give a blue solution (due to the complex ion $[Ni(NH_3)_6]^{++}$) and compare this action with that of cobaltous hydroxide.

(c) Heat a solution of nickel chloride, made by dissolving the carbonate in hydrochloric acid. Note that the chloride crystals are stable when heated. Neither nickel chloride nor cobalt chloride resembles ferrous chloride in this respect.

Experiment 145. To prepare sulphides of iron, cobalt and nickel.

Material: Nickel sulphate.

Make solutions of ferrous, cobalt and nickel salts. Pass hydrogen sulphide into each. A slight ppt. of ferrous sulphide may be seen as a dark coloration, but neither of the other salts shows a ppt.

Now add ammonium hydroxide, and pass more hydrogen sulphide. All three give a black ppt. of the metallic sulphide.

Show that ferrous sulphide alone dissolves in dilute hydrochloric acid. The sulphides of cobalt and nickel will dissolve in conc. hydrochloric acid in the presence of potassium chlorate or in aqua regia. Transfer the sulphides to evaporating basins, add conc. hydrochloric acid and a crystal of potassium chlorate. Heat until dissolved. The cobalt salt is pink in solution, the nickel salt greenish yellow.

PART III

ORGANIC CHEMISTRY

CHAPTER XIX

INTRODUCTION TO PRACTICAL ORGANIC CHEMISTRY

So many organic compounds are important, either as essential ingredients of biological processes or as desirable supplements to civilised life, that a course of practical chemistry must include the study of some of them. Food, fuel, clothing, drugs, paper and dyes are, in the main, organic compounds; all are either necessary, or desirable, for civilised existence. Many organic compounds of biological importance are, however, of complex structure, and it would be unprofitable to attempt their study at this stage. The scientific method of approach is to study the structure and behaviour of the simpler compounds, and later to apply the knowledge so gained to a study of more complex compounds.

The aim of the present course is to select a comparatively few compounds, chiefly derived from either ethyl alcohol or benzene, and study their reactions. Many of these reactions will be carried out on a test-tube scale since the essential reactions can equally well be studied with a small quantity as with a large quantity of material, but in order to give opportunities for handling the types of apparatus used in preparative organic work, a number of preparations on a larger scale are included. The compounds which are to be considered contain one, or in some cases, two, **characteristic groups.** Thus, all primary alcohols contain the characteristic $-CH_2.OH$ group which has specific properties independent of the rest of the molecule; consequently, as a class, alcohols have a large number of reactions common to all of them. Similarly the properties of an acid depend very largely on the presence of the $-COOH$ group in the molecule and many of the properties of acetic acid ($CH_3.COOH$) are common properties of all such acids. The importance of a thorough knowledge of the properties associated with these characteristic groups cannot be exaggerated, since upon it depends the approach to advanced work in the subject.

GENERAL INSTRUCTIONS

1. Many organic compounds are easily oxidised and some are highly inflammable. Care should always be taken to guard against fire, especially when handling liquids. Remove winchesters containing inflammable liquids to a safe place before lighting bunsens. When distilling ether, lead away any vapour to the waste pipe of the sink. The distilling flask containing the ether should be heated over water brought to boiling point elsewhere, to avoid using a naked flame near the flask.

2. Apparatus must be dry as well as clean. The presence of moisture may lower the yield and cause unwanted products to be formed. For quick drying of apparatus, wash it first with methylated spirits, drain as well as possible, wash with the minimum of ether to dissolve traces of alcohol, and finally dry off the ether with a jet of air from the bellows.

3. Liquids containing moisture are usually dried by adding pieces of calcium chloride.

Exceptions:

- Alcohols (use quick lime).
- Amines (use caustic potash, anhydrous sodium sulphate, or potassium carbonate).
- Phenols (use anhydrous sodium sulphate).

4. When using distillation apparatus see that corks are well fitted to avoid losses. Introduce liquids into the flask through a thistle-funnel to prevent them running down the side tube. Add fragments of porous pot to minimise "bumping" during boiling. See that the bulb of the thermometer is just below the side tube to ensure that the temperature of the *vapour* is being recorded.

5. It is often necessary to boil liquids for a considerable time to complete a reaction. To prevent loss by vaporisation the flask is fitted with an upright condenser, which, in the case of liquids of high boiling points, need not be water-jacketed. This method of retaining a volatile liquid is called "refluxing". (See Expt. 191, Fig. 49.)

6. Note that organic preparations differ from inorganic preparations in being slower; this is because organic compounds are not usually ionised and reactions are therefore molecular instead of ionic. Note also that yields of products are usually less than the expected. This is not a contradiction of accepted laws, but is due to the simultaneous formation of products other than those required. Thus, ethyl alcohol and conc. sulphuric acid give the gas ethylene, but also give ether and ethyl hydrogen sulphate. The quantities and conditions given in preparations are chosen to favour the highest yield of the required product, and instructions should, therefore, be closely followed.

7. Approximate yields have been given. This will enable a decision to be made where considered advisable to use smaller apparatus and a fractional quantity of materials. For example, in the preparation of aniline (Expt. 206(b)), a suitable modification would be to arrange for the reduction of nitrobenzene to be performed using fractional quantities, merging the products at the steam distillation stage.

Where the term "yield is small" is given it is not advisable to attempt the experiment on a smaller scale.

CHAPTER XX

PURITY OF COMPOUNDS

DETERMINATION OF THE MELTING POINT

If a compound is pure it will melt at a specific temperature and the change from solid to liquid will be sharp. If the temperature is raised gradually this sudden change of state allows the melting point to be observed with accuracy.

The presence of an impurity has two effects on the melting point:—

(a) it causes it to be lower than that of the pure compound, and

(b) it prolongs the period of melting, so that, instead of a sharp change, melting proceeds slowly over a range of temperature.

A sharp melting point is therefore a criterion of purity of a solid compound.

Experiment 146. To find the melting point of meta-dinitrobenzene.

Apparatus: Thermometer (100° C or 360° C.); 4 in. length of glass tubing; boiling-tube; stirrer; rubber rings. *Material*: Meta-dinitrobenzene; olive oil (or glycerol or medicinal paraffin).

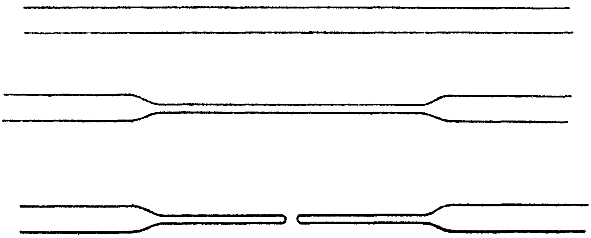


FIG. 32 (a).

Take a piece of glass tubing and rotate it in the hottest part of a bunsen flame until the golden-yellow flame has persisted for some time and the glass has become very soft. Remove from the flame and draw out the tube to the diameter of a match-stalk. Allow to cool, break at about the centre of the drawn portion, and seal off the small ends to form tubes as shown in Fig. 32(a).

Grind a small quantity of the given solid (with the flat side of a knife blade) and introduce a little into the narrow part of the tube. Set up the apparatus as shown and heat gradually, stirring the olive oil (or glycerol or medicinal paraffin) to keep its temperature uniform (see Fig. 32(b)). Watch the solid closely until it appears to collapse as it suddenly melts. Record the temperature. (Pure meta-dinitrobenzene melts at 90° C.)

Note (*i*). Do not read the temperature of solidification as some solids decompose at temperatures above their melting points.

Note (*ii*). Many compounds melt above 100° C. If melting has not occurred at 95° C., interrupt the experiment and replace the 100° C. thermometer by one graduated for higher temperatures.

Note (*iii*). Other suitable compounds for determination of the melting point are naphthalene, urea, and meta-nitraniline.

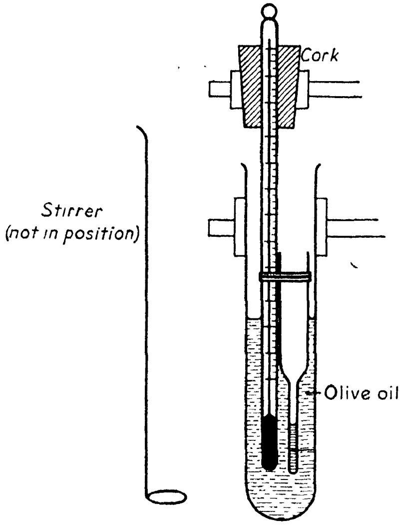


FIG. 32 (b).

Note (*iv*). The presence of an impurity always lowers the M.P. (see Expts. 7 and 8). If two substances have the same M.P. they may or may not be identical. If they are identical a mixture of them will still have the same M.P., but if they are different each will act as an impurity to the other and the M.P. will be lowered. This "mixed melting point" test is used as a final test when the identity of a substance has been established almost to the point of certainty.

DETERMINATION OF THE BOILING POINT

If a liquid is pure it will boil at a specific temperature provided the pressure remains constant, and will distil off without appreciable change of temperature.

If a mixture of two liquids is distilled it usually happens that, at the boiling point of the more volatile liquid, the mixture begins to boil, and the temperature remains fairly constant until the more volatile liquid has passed off. The temperature then rises sharply to the boiling point of the second liquid, when it, too, vaporises. This is the principle of fractional distillation which is used extensively in the purification of liquid products in organic chemistry. Where there is a considerable difference between the boiling points of the two liquids in a mixture, ordinary apparatus is sufficient to effect a fairly complete separation, but otherwise a fractionating column must be employed. It should also be noted that a number of mixtures of two or more liquids behave as if they were pure liquids, having a constant boiling point and a constant composition of distillate. These are 'constant-boiling mixtures'. In inorganic chemistry, hydrochloric acid containing 20·24% of hydrogen chloride boils at a constant temperature of 110° C., and similar mixtures occur with hydrogen bromide and hydrogen iodide in aqueous solution. In organic chemistry certain aqueous or alcoholic mixtures of liquids form constant-boiling mixtures, e.g., a mixture of 13·5% ethyl alcohol and 86·5% ethyl iodide boils, and distils over unchanged, at 63° C. The occurrence of these mixtures should not, however, raise doubts about the efficacy of fractional distillation, which has wide industrial and laboratory application.

The separation of liquids by steam distillation is considered later (Expt. 206).

Experiment 147. To find the boiling point of benzene.

Apparatus: Distilling flask (150 c.c.); condenser; thermometer (100° C.); flask (100 c.c.); fragments of porous pot. *Material*: Pure benzene.

Arrange the apparatus as in Fig. 33. Take about 50 c.c. of benzene in the distilling flask and add a few fragments of porous pot. Attach the side tube of the flask to the condenser by a bored cork, and close the neck of the flask with a bored cork and thermometer, adjusting the thermometer so that its bulb is below the side tube. Heat the flask and note the temperature when boiling begins. Record this temperature at half minute intervals for a period of five minutes and take the average as the boiling point. The boiling point of benzene is 80° C.

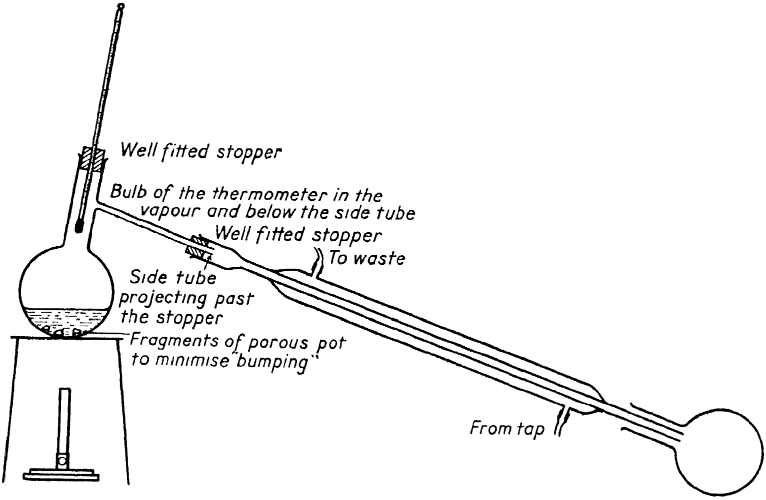


FIG. 33.

Experiment 148. Separation of a mixture of ether and aniline.

Apparatus: As in Expt. 147, but with a distilling flask as a receiver as in Fig. 34; thermometer (360° C.). *Material*: Mixture of about 50 c.c. each of ether and aniline.

Set up the apparatus as described in Expt. 147, using the mixture in place of benzene. Ether is very inflammable and care must be taken to lead away any vapour which might otherwise be ignited.

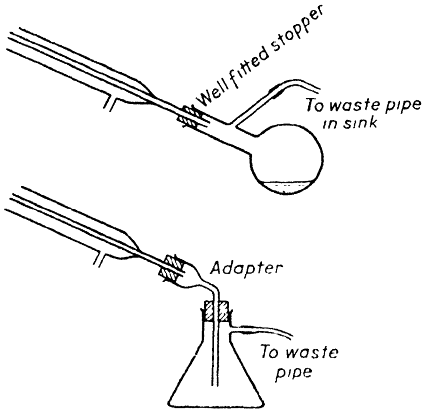


FIG. 34.

Heat the flask on a water-bath containing water which has been brought to boiling point elsewhere. When the temperature reaches 40° C., detach the receiver and replace with a similar one. Discard the distillate collected between this temperature and 180° C., and at 180° C. begin to collect the distillate of aniline in an ordinary flask (at about 130° C. allow the water to run out of the condenser). The receiver which was first used will contain almost pure ether (B.P. 35° C.) and the last receiver will contain almost pure aniline (B.P. 184° C.).

CHAPTER XXI

DETECTION OF ELEMENTS IN AN ORGANIC COMPOUND

THEORY

Organic compounds contain carbon, and usually contain hydrogen. They may contain one or more of the elements oxygen, chlorine, bromine, iodine, nitrogen, sulphur, phosphorus; a metal may also be present. The detection of these elements is based on the following considerations:—

When the compound is heated with copper oxide, *carbon* is oxidised to carbon dioxide and *hydrogen* is oxidised to water.

When a compound containing a *halogen* is heated with copper, it gives a green flame; heated with quick lime, and then acidified with nitric acid, gives a precipitate with silver nitrate; heated with sodium, and then acidified with nitric acid, gives a precipitate with silver nitrate.

Many compounds containing *nitrogen* evolve ammonia when heated with soda lime. All organic compounds which contain nitrogen form sodium cyanide on fusion with sodium. If ferrous sulphate solution is then added, sodium ferrocyanide is left in solution.

$$2NaCN + FeSO_4 \rightarrow Fe(CN)_2 + Na_2SO_4$$
$$4NaCN + Fe(CN)_2 \rightarrow Na_4Fe(CN)_6$$

This solution with a ferric salt gives Prussian blue.

Compounds containing *sulphur*, when fused with sodium, give sodium sulphide, which, with acid, gives hydrogen sulphide.

Phosphorus is rarely present. When a compound containing phosphorus is heated with magnesium, the phosphorus combines to form magnesium phosphide, which, with water, gives phosphine.

$$Mg_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Mg(OH)_2$$

If an organic compound contains a *metal*, the metal, metallic oxide or carbonate will be left as the final product on ignition, and the residue after solution in acid may be treated by the usual methods of qualitative analysis.

There is no general method of detecting *oxygen*. In some cases it will appear as water when the organic compound is heated alone, but in general its presence is inferred, its percentage being found by difference after the percentages of all other detected elements have been determined. Thus if the total percentages of elements known to be present were 80%, it would be assumed that oxygen accounted for the remaining 20%.

Experiment 149. Detection of carbon and hydrogen.

Apparatus: Cork fitted with a bent delivery tube. *Material*: Glucose (or other organic compound); anhydrous copper sulphate.

Heat a crucible about half full of copper oxide to redness to ensure its complete dryness and cool in a desiccator. Fit a dry test-tube with a bent tube as shown (Fig. 35). Mix about a salt-spoonful of the given compound with about three times that quantity of dry copper oxide and heat the mixture in the test-tube. Hold a test-tube half filled with lime-water so that any gas evolved may bubble through it. Note the cloudy suspension of chalk. Note also that the copper oxide has been reduced to copper.

$$2CuO + C \text{ (in the compound) } \rightarrow 2Cu + CO_2$$

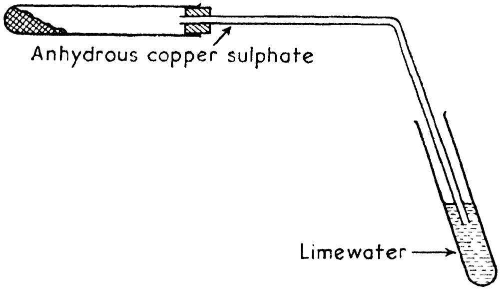


FIG. 35.

Repeat the experiment, again with dry apparatus. Introduce a little anhydrous copper sulphate into the horizontal part of the bent tube, and omit the lime-water. After heating, note the hydration of the anhydrous salt by the water formed.

$$CuO + 2H \text{ (in the compound) } \rightarrow Cu + H_2O$$

Experiment 150. Detection of nitrogen.

Material: Urea (solid methyl orange, acetanilide); soda lime; sodium.

Method (*a*). Take enough of the given solid to cover the bottom of a test-tube and add about twice that quantity of soda lime. Heat the mixture and test the issuing gas for ammonia (red litmus paper). Many nitrogenous compounds do not give their nitrogen as ammonia, and a negative test must not be taken as a proof that nitrogen is absent.

Method (*b*). Take a small dry test-tube (about 4 in. × ½ in.) Take a piece of clean sodium no larger than a small pea and cut into fine shavings. Put half of the sodium into the tube, add about four times that quantity of the compound, and then add the rest of the sodium. Have ready a dish containing about 25 c.c. of distilled water.

Hold a piece of *wire gauze to guard the eyes* and proceed as follows:—Take the test-tube in a test-tube holder and heat gently until the first (sometimes vigorous) action has moderated, then heat strongly, concentrating the heat on the tip of the tube. The bottom of the test-tube must be kept red-hot for *a full minute*. Still guarding the eyes, plunge the red-hot end of the test-tube into the distilled water and stir with the broken part of the tube.

Filter the solution and take about 10 c.c. in a test-tube. Add a few drops of a freshly prepared solution of ferrous sulphate and boil to complete the formation of sodium ferrocyanide (see equation on p. 131). Cool the solution under the tap, add a few drops of a solution of ferric chloride, and acidify with conc. hydrochloric acid. A greenish-blue coloration, or precipitate, of Prussian blue indicates that the given compound contained nitrogen. After leaving to stand for a few minutes, filter, and examine the paper for particles of Prussian blue.

Experiment 151. Detection of halogens.

Material: Ethyl bromide; ethyl iodide; bromo-benzene; copper foil; sodium: calcium oxide.

Method (*a*). Hold a strip of copper in a holder and heat in a clear bunsen flame until the flame is no longer coloured. Allow the copper to cool, then add a drop of the given compound. Heat again. A green flame indicates either chlorine, or bromine or iodine in the compound.

Method (*b*). Take enough calcium oxide to cover the bottom of a test-tube and add a drop of the given compound. Heat the mixture until the tube gives a yellow coloration to the flame. Allow to cool and then add dilute nitric acid. Warm gently to obtain a clear solution and add a drop of silver nitrate solution.

> White precipitate indicates chlorine in the given compound.
> Pale yellow precipitate indicates bromine in the given compound.
> Deep yellow precipitate indicates iodine in the given compound.

Method (*c*). Heat the compound with sodium* (see Expt. 150). After filtering, the solution (which contains sodium halide) is treated in one of the following ways, according to whether nitrogen is known to be present or absent.

(i) If nitrogen is known to be absent, acidify the filtrate with dilute nitric acid and add silver nitrate solution. Note the colour of the silver halide.

(ii) If nitrogen is known to be present, sodium cyanide (as well as the expected sodium halide) will be in the solution, and this, with acidified silver nitrate solution, will give a white precipitate of silver cyanide. The cyanide must, therefore, be removed before adding silver nitrate. Take an evaporating basin about a quarter full of the solution, add a slight excess of dilute nitric acid and evaporate (in a fume chamber) to about one-third of the total volume; the

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* It is dangerous to use either chloroform or carbon tetrachloride in sodium fusion experiments.

cyanide group is thus expelled as hydrogen cyanide. Cool the solution and test with silver nitrate as before.

Experiment 152. Detection of sulphur.

Material: Sodium benzene sulphonate (or sulphanilic acid, solid methyl orange, etc.); sodium; sodium nitroprusside.

Fuse the compound with sodium as described in Expt. 150, method (b). Filter the solution and pour a drop of it on a silver coin. A brown stain of silver sulphide indicates sulphur present in the given compound. Divide the rest of the solution into two parts.

Part (*i*). Acidify with conc. hydrochloric acid, heat, and test the vapour with lead acetate solution on a filter paper. A brown stain of lead sulphide indicates sulphur.

Part (*ii*). Add a few drops of a freshly prepared (and very dilute) solution of sodium nitroprusside. A purple coloration indicates the presence of sulphur in the given compound.

Experiment 153. Middleton's method for detecting nitrogen, halogens, and sulphur in organic compounds.

Material: Zinc dust.

In this method the use of sodium is avoided by using a mixture of the purest zinc dust and sodium carbonate. The reagent is made by mixing pure anhydrous sodium carbonate with twice its weight of zinc dust as intimately as possible in a mortar.

(a) If the given compound is a solid, take enough to give a depth of about 0·5 cm. in the bottom of a *hard-glass* test-tube (3 in. × $\frac{3}{8}$ in.) and add the reagent to bring the depth to 1 cm., mixing as well as possible. Now add more reagent, without mixing, until the depth is about 4 cm.

(b) If the given compound is a liquid, take enough of the reagent to give a depth of 1 cm. and add two or three drops of the compound. When the liquid has soaked the reagent, add more of the latter to give a total depth of 4 cm.

Use a test-tube holder and hold the tube *horizontally*. Heat the tube gently near the exposed surface of the mixture and gradually raise the temperature until the tube is red-hot there. *Very gradually* progress with the heating towards the closed end until the whole is red-hot, and finally turn the tube vertical and keep it red-hot for a full minute. Have ready an evaporating basin containing about 20 c.c. of distilled water, and plunge the red-hot tube, closed end down, into it. Boil the contents of the basin, allow to cool, then decant through a filter. Retain the residue.

Test for nitrogen. Take about half of the filtrate, add 2 or 3 c.c. of sodium hydroxide solution, and then ferrous sulphate solution.

Proceed as described in Expt. 150, remembering, however, that carbonate is present when acidifying. In Middleton's method, as in the sodium-fusion method, nitrogen becomes sodium cyanide during ignition.

Test for halogens. Take the remaining part of the filtrate and proceed as described in Expt. 151, method (c). If nitrogen is known to be present the same procedure will be followed as in the sodium-fusion method.

Test for sulphur. Transfer the residue from the evaporating basin to a test-tube. Add about 10 c.c. of dilute hydrochloric acid and test the issuing gas with lead acetate paper.

Experiment 154. Estimation of nitrogen in urea. Kjeldahl's method.

Apparatus: Long-necked boiling flask (250 c.c.); flask (500 c.c.); conical flask; measuring cylinder; steam trap; tap-funnel. The 500 c.c. flask and distilling apparatus are fitted as in Fig. 36. *Material*: Urea; potassium hydrogen sulphate; standard (N) acid and alkali.

The method depends upon the decomposition of organic nitrogen compounds by conc. sulphuric acid to give ammonium sulphate. When the resulting solution is treated with excess of alkali the ammonia is expelled and absorbed in standard acid; the ammonia is estimated by back-titration of the standard acid. Some nitrogen compounds do not give satisfactory results, and among these, nitro-compounds are notable examples; they may, however, be reduced first to amines and then the estimation is satisfactory.

Weigh accurately about 0·5 gm. of urea and transfer to the long-necked flask. Add 10 c.c. of conc. sulphuric acid and add about a salt-spoonful of potassium hydrogen sulphate (to raise the boiling point of the acid and make the decomposition of the nitrogen compound complete). Heat to boiling and continue to boil until the slight charring has cleared, then allow to cool to room temperature. Dilute by adding about 200 c.c. of water. Transfer the solution to the distilling flask and add fragments of porous pot (to prevent bumping during boiling). Fit up the apparatus as in Fig. 36. Take exactly 25 c.c. of N. acid in the conical flask and arrange

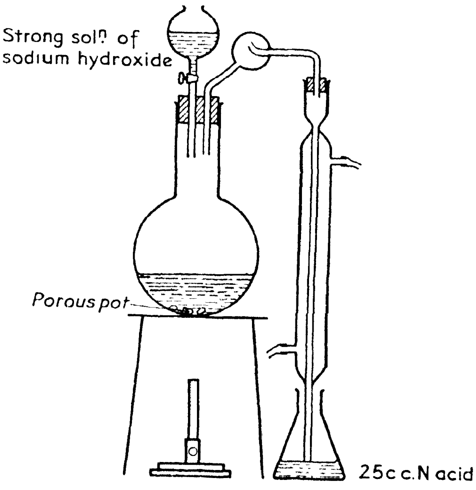


FIG. 36.

to keep the end of the condenser just below the surface of the acid throughout the period of distillation.

Dissolve a stick of caustic soda (about 20 gm.) in 100 c.c. of water and transfer to the tap funnel. Run this solution into the flask and heat to boiling. Ammonia is evolved and passes into the standard acid. Continue distillation until half the solution has distilled over, by which time all the ammonia has been expelled. Titrate the contents of the conical flask against standard alkali in the burette, using methyl orange as indicator.

Example.

Weight of urea = 0·48 gm.
Volume of N. acid in receiver = 25 c.c.
Volume of N. alkali to neutralise acid after absorption of ammonia = 9·15 c.c.
Volume of acid used by ammonia = (25 – 9·15) c.c. = 15·85 c.c.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$$

1000 c.c. of N. acid ≡ 17 gm. of ammonia ≡ 14 gm. of nitrogen

$$15{\cdot}85 \text{ c.c. of N. acid} \equiv \frac{14 \times 15{\cdot}85}{1000} \text{ gm. nitrogen}$$

$$\% \text{ of nitrogen in urea} = \frac{14 \times 15{\cdot}85 \times 100}{1000 \times 0{\cdot}48} \%$$

$$= 46{\cdot}2\% \text{ (Theoretical value } 46{\cdot}7\text{)}$$

CHAPTER XXII

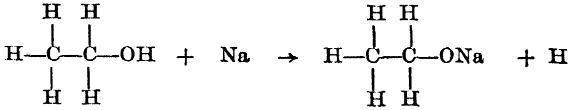
PROPERTIES OF ALCOHOLS

Experiment 155. Preparation of sodium ethoxide, $C_2H_5.ONa$.

Apparatus: Water-bath. *Material*: Ethyl alcohol (or industrial spirit); sodium.

THEORY

Primary alcohols contain the characteristic $-CH_2.OH$ group. Of all the hydrogen atoms present in a molecule of an alcohol, only the one directly attached to the oxygen atom can be replaced by sodium. Thus ethyl alcohol when treated with sodium gives a solid, sodium ethoxide, and gives off hydrogen.



$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH + Na \rightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}ONa + H$$

$$\text{or,} \quad 2C_2H_5.OH + 2Na \rightarrow 2C_2H_5.ONa + H_2$$

Similarly, methyl alcohol gives sodium methoxide ($CH_3.ONa$), and hydrogen. These sodium compounds are readily hydrolysed, even by atmospheric moisture, to regenerate the alcohol:—

$$C_2H_5.ONa + H_2O \rightarrow C_2H_5.OH + NaOH$$

Take about 12 c.c. of alcohol in an evaporating basin and add a piece of sodium about 0·5 c.c. in volume. Note the immediate effervescence (hydrogen). When the sodium has dissolved, evaporate the solution on a water-bath, stirring to break the crust of solid as it forms. Transfer the dry solid to a dry test-tube and seal off to exclude moisture. If industrial spirit has been used, the product will contain sodium methoxide as an impurity. (Industrial spirit consists of 85% of ethyl alcohol, the remainder being impure methyl alcohol.) Yield about 1 gm. (almost theoretical).

Experiment 156. Determination of the equivalent of sodium, using the sodium-alcohol reaction.

Apparatus: Siphon apparatus (as in Fig. 37); measuring cylinder. *Material*: Industrial alcohol; sodium.

Arrange the apparatus as shown and fill the siphon tube with water. Take about 15 c.c. of alcohol in the (dry) flask. Weigh a piece of clean sodium (about 0·5 c.c.) in a weighing bottle. Remove the flask, add the sodium, and replace the flask immediately. Open the clip on the siphon tube as quickly as possible and collect the water displaced by the hydrogen. Make the usual adjustments of levels after the gas has cooled and correct the volume of hydrogen for temperature and pressure.

Find the weight of sodium required to displace 11·2 litres of hydrogen at N.T.P.

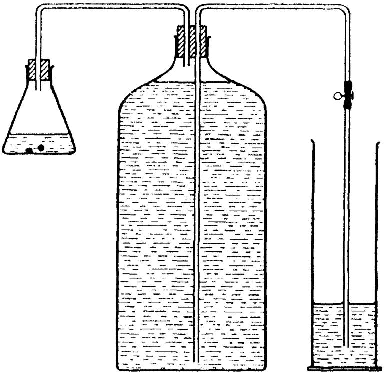


FIG. 37.

The remaining solution may be evaporated to give solid sodium ethoxide as in the previous experiment.

REACTIONS OF ALCOHOL WITH ACIDS

Alcohols react in some respects as bases. When an alcohol reacts with an acid (organic or inorganic), water is eliminated between the —OH of the alcohol and the displaceable hydrogen of the acid, e.g.,

$$\underset{}{C_2H_5.OH} + HBr \rightarrow \underset{\text{(ethyl bromide)}}{C_2H_5.Br} + H_2O$$

Organic acids, with rare exceptions (see p. 185), contain the characteristic carboxyl (—COOH) group, and it is the hydrogen of this group which reacts with the hydroxyl of the alcohol, e.g.,

$$C_2H_5.OH + CH_3.COOH \rightarrow \underset{\text{(ethyl acetate)}}{CH_3.CO.OC_2H_5} + H_2O$$

The products of both of the above reactions are called esters to distinguish them from the salts of inorganic chemistry, with which they have a superficial similarity. Salts and esters differ both in the speeds of their formation and in their properties.

Experiment 157. Reaction of ethyl alcohol with hydrogen bromide. *Apparatus*: Boiling-tube fitted with cork and bent tube. *Material*: Ethyl alcohol (or industrial spirit); potassium bromide.

Take enough alcohol to fill the boiling-tube to a depth of 1 in. Add about one-third of that volume of conc. sulphuric acid, cooling and shaking the mixture during the addition. Add crystals of potassium bromide until the total volume is about twice that of the liquid. Fit the delivery tube and immerse the end of it deeply in water in a test-tube (Fig. 38). Warm the mixture in the boiling-tube and note the oily drops of a heavy liquid (ethyl bromide) collecting below the water.

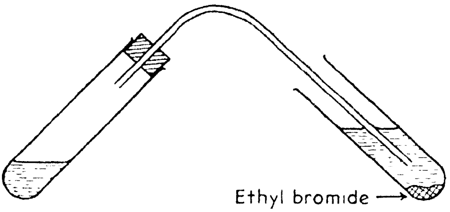


FIG. 38.

The preparation of this compound on a larger scale is given in Expt. 162.

Experiment 158. Reaction of ethyl alcohol with acetic acid.

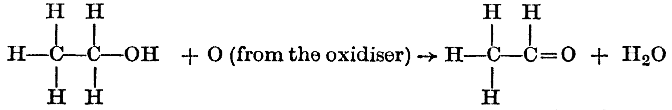
Material: Industrial spirit; glacial acetic acid.

Make a mixture of about ten drops of alcohol, five drops of glacial acetic acid and three drops of conc. sulphuric acid. Warm gently. Pour the liquid into a test-tube half full of water (in which the ester is insoluble), and note the fruity smell of ethyl acetate.

The preparation of ethyl acetate on a larger scale is given in Expt. 187.

OXIDATION OF ALCOHOLS

Primary alcohols are readily oxidised to give aldehydes. In every case the hydrogen atom of the —OH group and a hydrogen atom attached to the same terminal carbon atom are removed by an atom of oxygen from the oxidiser, e.g.,



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH} + \mathrm{O}\ (\text{from the oxidiser}) \rightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}O} + H_2O$$

(acetaldehyde)

Experiment 159. Oxidation of ethyl alcohol.

Material: A saturated solution of sodium (or potassium) dichromate; ethyl alcohol (or industrial spirit).

Take approximately 5 c.c. of the dichromate solution. Add five drops of alcohol and five drops of conc. sulphuric acid. Warm gently. Note the irritating smell of acetaldehyde, and also the change in colour of the dichromate as it is reduced to chromium sulphate.

$$Na_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5.OH \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3.CHO$$

The preparation of acetaldehyde on a larger scale is given in Expt. 173, and the oxidation of methyl alcohol by atmospheric oxygen is described in Expt. 172.

Experiment 160. Specific test for ethyl alcohol.

Material: A strong solution of iodine in aqueous potassium iodide; ethyl alcohol (or industrial spirit).

To about 5 c.c. of the iodine solution add five drops of ethyl alcohol. Add sodium hydroxide solution carefully until the colour has almost gone. Stand the test-tube in water at about 70° C. for two or three minutes, then remove and leave to cool. The yellow crystals are iodoform, and the smell is reminiscent of antiseptics.

This reaction does not occur with methyl alcohol or other alcohols and serves as a specific test for *ethyl* alcohol. The reaction does, however, occur with acetaldehyde and with acetone (see p. 150).

Experiment 161. Reaction between ethyl alcohol and phosphorus pentachloride.

Material: Industrial spirit; phosphorus pentachloride.

To about 1 c.c. of ethyl alcohol add a few crystals of phosphorus pentachloride. The action is vigorous and hydrogen chloride is evolved.

$$C_2H_5.OH + PCl_5 \rightarrow C_2H_5.Cl + HCl + POCl_3$$

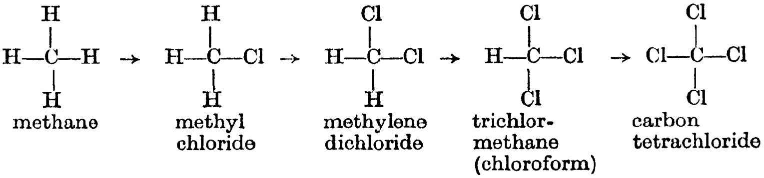
This action is typical of a great many reactions between phosphorus pentachloride (or trichloride) and compounds containing an hydroxyl group.

CHAPTER XXIII

ALKYL HALIDES

THEORY

When the paraffin hydrocarbon methane is mixed with chlorine and the mixture exposed to sunlight, hydrogen atoms are slowly, and progressively, displaced by chlorine.



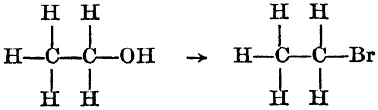
$$\overset{H}{\underset{H}{H-C-H}} \rightarrow \overset{H}{\underset{H}{H-C-Cl}} \rightarrow \overset{Cl}{\underset{H}{H-C-Cl}} \rightarrow \overset{Cl}{\underset{Cl}{H-C-Cl}} \rightarrow \overset{Cl}{\underset{Cl}{Cl-C-Cl}}$$

Methyl chloride, chloroform and carbon tetrachloride are compounds of considerable importance and although none of them are actually made by direct chlorination of methane but by various alternative methods, the above shows how they are related.

Methyl chloride, the first product of chlorination, is an example of an alkyl halide. Other compounds of similar structure may be prepared, by various means, having bromine or iodine in place of chlorine, and having the ethyl, propyl or other alkyl radical in place of methyl. All such compounds are known as alkyl halides.

There are two suitable general methods of preparation, both starting with the corresponding alcohol, and the essential reaction in both is the replacement of the hydroxyl (—OH) group of the alcohol by an atom of the halogen:—

e.g.,



$$\overset{H\ H}{\underset{H\ H}{H-C-C-OH}} \rightarrow \overset{H\ H}{\underset{H\ H}{H-C-C-Br}}$$

Method (*i*). The hydracid of the halogen is prepared *in situ* with the appropriate alcohol. This is a suitable method of introducing —Cl or —Br, but not —I.

Method (*ii*). Phosphorus and the halogen (functioning as the phosphorus halide) react with the alcohol. This method is usually used for introducing —Br or —I.

Experiment 162. Preparation of ethyl bromide.

Formula: $C_2H_5.Br$. *Physical properties*: colourless liquid, immiscible with water. *B.P.* 39° C. *Sp.G.* 1·5.

Apparatus: Distilling flask (500 c.c.); condenser; adapter; conical flask (200 c.c.); measuring cylinder; separating funnel; distilling flask (150 c.c.); thermometer (100° C.); water-bath; sand-tray. *Material*: Ethyl alcohol (or industrial spirit); potassium bromide; calcium chloride.

Arrange the apparatus as shown in Fig. 39. Take 40 c.c. of alcohol in the large distilling flask, and add 50 c.c. of conc. sulphuric acid slowly and with shaking, from the measuring cylinder (using a thistle-funnel). Allow the mixture to cool to room temperature.

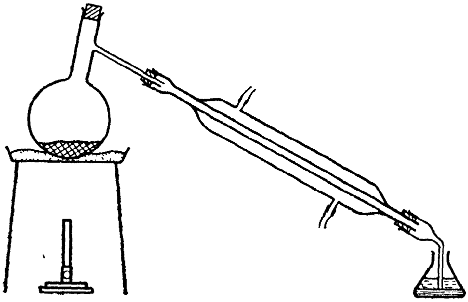


FIG. 39.

Add 50 gm of potassium bromide, cork the flask, and gently heat on the sand-tray. The oily liquid which falls to the bottom of the water in the receiver is ethyl bromide. When no more oily drops can be seen in the condenser, remove the bunsen and transfer the contents of the receiver into the separating funnel.

Run off the lower layer temporarily into a flask and discard the upper (aqueous) layer. Return the lower layer to the funnel and add approximately an equal volume of a sodium carbonate solution which has been prepared by dissolving about 5 gm. in 100 c.c. Shake the liquids, taking care to remove the stopper at frequent intervals to avoid a high pressure of carbon dioxide (formed by the action of acid impurity on the carbonate). Remove the lower layer as before, discard the aqueous layer and return the lower layer to the funnel. Wash with water and then run off the lower layer into a flask. Add enough granulated calcium chloride to cover the bottom of the flask, cork and leave overnight to dry.

Decant the clear liquid into a small distilling flask and attach the flask to a sloping condenser. Close the neck of the flask with a bored cork and thermometer and adjust the latter so that its bulb is below the level of the side tube. Use a small dry flask as a receiver. Heat the liquid over a water-bath at a moderate temperature so that distillation proceeds steadily. Collect the fraction between 35° C. and 43° C. If the product is to be kept for some time it should be transferred to an amber-coloured bottle and stored out of direct sunlight. Yield 35 gm.

$$C_2H_5.OH + KBr + H_2SO_4 \rightarrow C_2H_5.Br + KHSO_4 + H_2O$$

Experiment 163. Preparation of methyl iodide.

Formula: $CH_3.I$. *Physical properties*: colourless immiscible liquid. *B.P.* 45° C. *Sp.G.* 2·27.

Apparatus: Flask (250 c.c.); condenser; water-bath; separating funnel; thermometer (100° C.); measuring cylinder; small corked flask; adapter; distilling flask (150 c.c.). *Material*: Methyl alcohol; dry red phosphorus; iodine; calcium chloride.

Measure 25 c.c. of methyl alcohol into the flask and add 3 gm. of red phosphorus. Attach a condenser in an upright position as shown in Fig. 40. The purpose of the condenser here is to condense vapour that otherwise would escape and return it, as liquid, to the reaction mixture in the flask; it is therefore referred to as a "reflux" condenser.

Weigh 30 gm. of iodine in a small corked flask. Detach the condenser and add a small portion of the iodine, then attach the condenser again. Proceed in this way until the whole of the iodine has been added (half an hour).

Heat on a water-bath for half an hour, then leave overnight.

Transfer the liquid to a distilling flask connected to a sloping condenser as in Fig. 33. Distil over a water-bath and collect the distillate under water in the receiver.

Shake the distillate with caustic soda solution until the lower layer is no longer coloured with excess iodine. Run off the lower layer into a flask and add pieces of granulated calcium chloride and leave to dry.

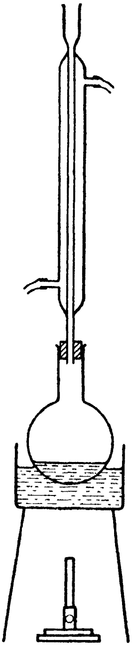


FIG. 40.

Distil the clear liquid in a small distilling flask fitted with a thermometer and attached to a sloping condenser. Collect the fraction distilling between 43° C. and 46° C. and store in a coloured bottle. Yield 20 gm.

$$3CH_3.OH + PI_3 \rightarrow 3CH_3.I + H_3PO_3$$

Note 1. Ethyl iodide may be prepared by the same method (using 35 c.c. of absolute alcohol) but the yield is less satisfactory.

Note 2. The red phosphorus must be dry. It is advisable to use fresh stock.

Experiment 164. Reactions of alkyl halides.

Apparatus: Cork with bent tube. *Material*: Methyl iodide; ethyl iodide; ethyl bromide; sodium ethoxide; alcoholic potash; zinc dust.

(a) *Reaction with silver nitrate*. Add about 1 c.c. of silver nitrate solution to two drops of methyl iodide. Note the precipitate of silver iodide (yellow). Methyl iodide readily hydrolyses in aqueous silver nitrate. Repeat with ethyl iodide in place of the methyl compound. Compare the incomplete precipitation with the former case. Now add a few drops of dilute nitric acid and heat. The more complete precipitation of silver iodide is due to hydrolysis of the alkyl halide by the acid. Repeat using ethyl bromide in place of ethyl iodide.

$$C_2H_5.I + H.OH \rightarrow C_2H_5.OH + HI$$

(b) *Reaction with sodium ethoxide.* Take a test-tube one-eighth full of sodium ethoxide. Add about five drops of ethyl bromide and allow it to soak into the solid. Warm gently. Recognise the smell of di-ethyl ether. (See also Expt. 166.)

(c) *Reaction with alcoholic potash.* Take ten drops of ethyl iodide in a test-tube. Add about 5 c.c. of alcoholic potash and fit the tube with a cork and bent delivery tube. Arrange to collect any gas evolved over water in a test-tube. Warm the mixture. Show that the gas collected burns with a smoky flame. The gas is ethylene, but contains some ethyl iodide as impurity.

$$C_2H_5.I + KOH \rightarrow C_2H_4 + KI + H_2O$$

(d) *Reduction.* Prepare zinc-copper couple by sprinkling about a tea-spoonful of zinc dust into a beaker half full of copper sulphate solution. Leave for a minute, then decant and wash by decantation. Wash with alcohol and filter. Take about 4 c.c. of ethyl iodide in a test-tube, add an equal volume of alcohol, then the zinc-copper couple. Close the test-tube with a cork and delivery tube and collect the gas (ethane) over water. Burn the gas. Note the slightly luminous flame (tinged with green due to ethyl iodide as impurity).

$$C_2H_5.I + 2H \text{ (nascent)} \rightarrow C_2H_6 + HI$$

CHAPTER XXIV

ETHERS

THEORY

The best known member of this group of compounds is the liquid di-ethyl ether, usually called simply 'ether'. A lower member, di-methyl ether, is a gas. The structural formula of any ether contains two alkyl radicals attached to an oxygen atom:—

$$\begin{array}{ll} C_2H_5—O—C_2H_5 & \text{di-ethyl ether} \\ CH_3—O—CH_3 & \text{di-methyl ether} \end{array}$$

or, generally, $R_1—O—R_2$ where R_1, R_2 are alkyl radicals which may be either the same or different.

Two methods are available for preparing these compounds:—

1. By distilling a mixture of an alcohol and conc. sulphuric acid. When the distillation has begun it is (theoretically) only necessary to add more alcohol to obtain a continuous supply of ether. The process falls short of the ideal through the dilution of the acid by the water formed in the action, but it is still known as Williamson's Continuous Process. The action takes place in two stages as shown in the equations:—

$$C_2H_5.OH + H_2SO_4 \rightarrow C_2H_5.HSO_4 + H_2O$$
$$C_2H_5.HSO_4 + C_2H_5.OH \rightarrow C_2H_5—O—C_2H_5 + H_2SO_4$$

The method could not be used to make a mixed ether, i.e., an ether containing two different alkyl radicals.

2. By the reaction of an alkyl halide with the sodium compound of an alcohol. Here the alkyl radical in the halide may be the same as, or different from, the alkyl radical of the alcohol, and the method could therefore be used for making any ether. For the preparation of ethers the first method is to be preferred where possible both because of its simplicity and the higher yield obtained.

$$RONa + IR_1 \rightarrow R-O-R_1 + NaI$$

Experiment 165. Preparation of di-ethyl ether. Continuous process.

Formula: $C_2H_5.O.C_2H_5$. *Physical properties*: volatile, inflammable liquid. *B.P.* 35° C. *Sp.G.* 0·72.

Apparatus: Distilling flask (500 c.c.); condenser; adapter; Buchner flask; tap funnel; thermometer (360° C.); sand-tray; **ICE.** *Material*: Industrial alcohol; sodium chloride; calcium chloride.

Arrange the apparatus as shown in Fig. 41. Note that the bulb of the thermometer dips into the liquid and also that a rubber tube leads any ether vapour to the waste pipe away from the region of the flame.

Pour 50 c.c. of alcohol into the distilling flask and gradually add with shaking 40 c.c. of conc. sulphuric acid. Attach the flask to the apparatus and pour 100 c.c. of alcohol into the funnel.

Heat on the sand-tray, and when the thermometer records 140° C.

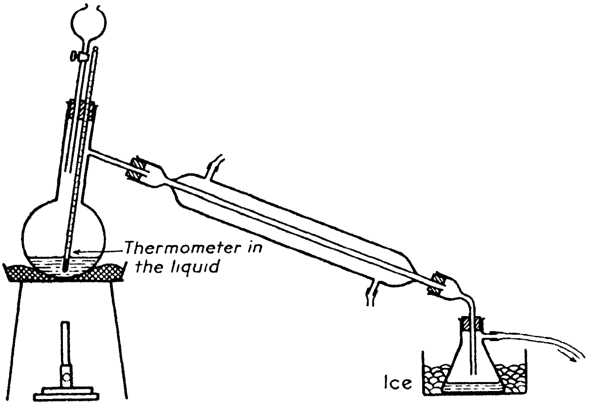


FIG. 41.

allow alcohol to drip into the flask at about the speed at which the liquid is distilling. Adjust the bunsen to maintain the temperature within two or three degrees of 140° C. and continue distilling until all the alcohol has been added from the funnel.

Note. A smoother flow of alcohol into the liquid in the flask is obtained by using a thistle funnel dipping below the surface. A tap-funnel and bung is inserted in the mouth of the thistle funnel to control the entry of alcohol into the flask.

Transfer the distillate to the separating funnel and shake cautiously with 50 c.c. of bench caustic soda solution to absorb sulphurous acid which has been formed by some reduction of sulphuric acid. When shaking the mixture, the volatile nature of ether should be remembered and care taken to avoid a high pressure in the funnel by frequently opening the stopper. At all times the high inflammability of ether requires precautions against fire.

Run off the lower layer of aqueous solution and retain the ether layer. Add a saturated solution of salt to remove traces of alcohol, and after shaking, run off the lower layer and discard. Run the ether layer into a flask and add enough granulated calcium chloride to cover the bottom of the flask. Leave, loosely corked, in a cool place overnight to dry.

Arrange a distilling flask attached to a sloping condenser which is fitted with an adapter dipping into a dry Buchner-flask as before. Transfer the dry ether to the flask and close the neck with a bored cork and thermometer. Heat the flask on a water-bath containing water which has been brought to boiling point elsewhere, so avoiding a flame near ether during distillation. Collect the fraction when the temperature is steady at 35° C. Yield 30 gm.

Experiment 166. Preparation of di-ethyl ether from ethyl iodide.

Apparatus: Flask (150 c.c.); condenser; distilling flask (100 c.c.); Buchner flask; adapter; measuring cylinder; water-bath; weighing bottle. *Material*: Industrial alcohol; sodium; ethyl iodide.

Take 50 c.c. of alcohol in the 150 c.c. flask. Weigh 3 gm. of sodium in a weighing bottle and add it in small pieces to the alcohol allowing half-minute intervals between additions.

Fit the flask with a reflux condenser and then place it on a water-bath. Measure 10 c.c. of ethyl iodide and pour it down the condenser tube (see Fig. 40).

Heat the flask until crystals of sodium iodide are formed, then transfer the liquid to a distilling flask and distil over a water-bath, collecting the fraction distilling at 35° C.

The yield is small, but the action is important because it enabled Williamson to establish the formula of ether.

$$C_2H_5.ONa + C_2H_5.I \rightarrow C_2H_5.O.C_2H_5 + NaI$$

Experiment 167. Reactions of ether.

Apparatus: Bellows. *Material*: Di-ethyl ether; iodine.

Generally speaking, ethers are chemically very stable and inert. It requires the drastic action of hydrogen iodide, prepared *in situ* by moist yellow phosphorus and iodine, to decompose an ether, e.g.,

$$C_2H_5.O.C_2H_5 + 2HI \rightarrow 2C_2H_5.I + H_2O$$

(a) *Volatility of di-ethyl ether.* Take about 20 c.c. of ether in a beaker, and stand the beaker in a pool of water on a piece of wood. Blow a rapid stream of air from bellows into the ether. Note the ice, which on occasions is sufficient to bind the beaker to the wood. The vapour pressure of ether is high because it is near to its boiling point (35° C.).

(b) *Solvent action.* Add a crystal of iodine to about 5 c.c. of di-ethyl ether. Note how easily the iodine dissolves. Pour the solution into a test-tube half full of water. Note that the ether is immiscible in water, and that the iodine remains to a large extent in the ether.

(c) *Inflammability.* Take about 5 c.c. of ether in a test-tube. Dip a glass-rod into the liquid and hold the rod near a flame. Care must always be exercised when ether is being used.

CHAPTER XXV

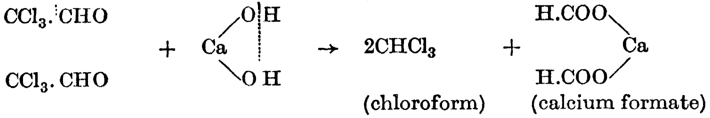
CHLOROFORM AND IODOFORM

Chloroform ($CHCl_3$) and iodoform (CHI_3) are halogenated compounds of methane. They are both prepared from either *ethyl* alcohol or acetone by the action of a hypochlorite or hypobromite. The action in both cases probably takes place in three stages, involving, (a) oxidation (when the alcohol is used) by the halogen, (b) halogenation of the oxidised product, (c) alkaline hydrolysis of the compound so formed.

(a) $$CH_3.CH_2.OH + Cl_2 \rightarrow \underset{\text{(acetaldehyde)}}{CH_3.CHO} + 2HCl$$

(b) $$CH_3.CHO + 3Cl_2 \rightarrow \underset{\text{(chloral)}}{CCl_3.CHO} + 3HCl$$

(c)



$$\begin{matrix}CCl_3.CHO\\ CCl_3.CHO\end{matrix} + Ca\begin{matrix}OH\\ OH\end{matrix} \rightarrow \underset{\text{(chloroform)}}{2CHCl_3} + \underset{\text{(calcium formate)}}{\begin{matrix}H.COO\\ H.COO\end{matrix}Ca}$$

When acetone is used, the intermediate compound in (b) is tri-chloracetone, $CH_3.CO.CCl_3$.

Experiment 168. Preparation of chloroform.

Formula: $CHCl_3$. *Physical properties*: sweet-smelling liquid, *B.P.* 61° C. *Sp.G.* 1·5.

Apparatus: Large (1 litre) flask; condenser and adapter; mortar and pestle; sand-tray; separating funnel; distilling flask (100 c.c.); water-bath; thermometer (100° C.); measuring cylinder. *Material*: Ethyl alcohol or acetone*; bleaching powder; calcium chloride.

Arrange the apparatus as shown in Fig. 42. Make sure that all connections are well made.

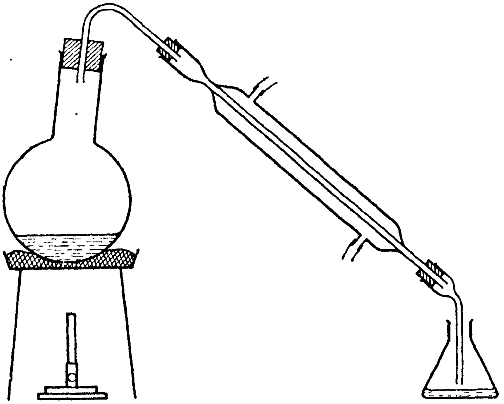


FIG. 42.

Weigh 100 gm. of bleaching powder and grind it with water taken from a measured 300 c.c. to make a cream. Decant the mixture into a large flask and use the rest of the water to rinse the mortar and add the washings to the flask. Add either 35 c.c. of ethyl alcohol or 40 c.c. of acetone,* then connect the flask to the condenser, and gently

---

* Acetone gives a better yield.

shake to mix thoroughly. The reaction usually begins spontaneously, and a bath of cold water should be ready to moderate the action if it is too vigorous. If, however, the action is slow in starting, warm the flask on a water-bath until action begins. When the first action has proceeded for about ten minutes, heat the flask on a sand-tray and distil until no more oily drops can be seen in the condenser.

Transfer the contents of the receiver to a separating funnel, allow to settle, then run off the lower layer temporarily into a flask. Discard the aqueous layer and return the chloroform layer to the funnel. Shake with an equal volume of a solution made by diluting bench caustic soda with about three times its own volume of water to remove free chlorine or hydrogen chloride. Allow to settle and run off the lower layer into a flask. Add enough granulated calcium chloride to cover the bottom of the flask, cork the flask and leave until the liquid is clear.

Decant the dry liquid into a distilling flask connected to a sloping condenser. Close the neck of the flask with a bored cork and thermometer and distil over a water-bath, collecting the fraction between 60° C. and 62° C. Yield 30 gm.

Experiment 169. Reactions of chloroform.

Material: Alcoholic potash; iodine; ether; industrial alcohol; resorcinol; aniline.

(a) *Reaction with silver nitrate*. Add a few drops of silver nitrate solution to a test-tube about one quarter full of chloroform. Shake well. Silver chloride is *not* precipitated, chloroform being un-ionised. Add a few drops of alcohol to give a solution, and show that even when aqueous silver nitrate is in solution with chloroform, silver chloride is not precipitated. Chloroform is a covalent compound.

(b) *Hydrolysis of chloroform.* Boil a few drops of chloroform with about ten times that volume of alcoholic potash. Acidify with dilute nitric acid and add silver nitrate solution. A white precipitate of silver chloride is obtained. Under these conditions, chloroform has been hydrolysed to potassium chloride and potassium formate.

$$CHCl_3 + 4KOH \rightarrow H.COOK + 3KCl + 2H_2O$$

(c) *Carbylamine (or iso-cyanide) test.* Mix in a test-tube, *one drop each* of chloroform and aniline. Add five drops of alcoholic potash and warm gently, preferably in a fume chamber. The sickly smell is due to phenyl iso-cyanide, and similar products are obtained when any other primary amine is substituted for aniline.

$$CHCl_3 + C_6H_5.NH_2 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$$

(d) *Solvent action.* Take a few drops of chloroform in a test-tube and add a crystal of iodine. Note the ease with which iodine dissolves. Add water to show the immiscibility of chloroform, then add a solution of iodine in ether to show (i) the relative densities of ether and chloroform, and (ii) the different colours of the two iodine solutions.

(e) *Reaction with resorcinol.* Dissolve a few crystals of resorcinol in the minimum of sodium hydroxide solution. Add a few drops of chloroform and warm the mixture gently. Note the red fluorescence in the aqueous layer.

Experiment 170. Preparation of iodoform.

Formula: CHI_3. *Physical properties*: yellow crystalline solid. *M.P.* 119° C.

Apparatus: Small flask; water-bath; thermometer (100° C.); measuring cylinder. *Material*: Ethyl alcohol or industrial spirit; iodine.

Make a solution of 10 gm. of sodium carbonate in 50 c.c. of distilled water. Keep about 5 c.c. of the solution for use later, and to the remainder add 7 c.c. of ethyl alcohol.

Warm the solution on a water-bath at about 60° C. and add 10 gm. of iodine gradually, with continual stirring until the solution is permanently brown. Discharge the colour by adding a few drops of the sodium carbonate solution kept back for this purpose.

Heat for a few minutes in the water-bath at 70° C., then set aside to cool. Filter to isolate the crystals of iodoform. Yield 5 gm.

$$C_2H_5.OH + 2I \rightarrow CH_3.CHO + 2HI$$
$$CH_3.CHO + 6I \rightarrow CI_3CHO + 3HI$$
$$2CI_3.CHO + Na_2CO_3 + H_2O \rightarrow 2CHI_3 + 2H.COONa + CO_2$$

Compare these equations with those given for the preparation of chloroform, p. 148.

Experiment 171. Reactions of iodoform.

Material: Iodoform; alcoholic potash; aniline; industrial alcohol.

(a) *Reaction with silver nitrate.* Repeat Expt. 169(a), using a few crystals of iodoform in place of the chloroform. Show that iodoform does not react with silver nitrate solution.

(b) *Hydrolysis of iodoform.* Repeat Expt. 169(b), using a few crystals of iodoform in place of chloroform. Write the appropriate equation.

(c) *Carbylamine test.* Repeat Expt. 169(c), using a crystal of iodoform in place of the drop of chloroform. Note the same sickly smell of phenyl iso-cyanide. Write the equation.

(d) *Decomposition of iodoform.* Heat a few crystals of iodoform in a dry test-tube. Note the violet vapour of iodine as the compound decomposes.

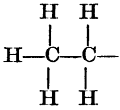
CHAPTER XXVI

ALDEHYDES AND KETONES

THEORY

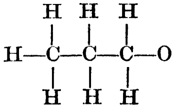
The oxidation of alcohols has been considered briefly under 'Properties of alcohols—Oxidation'. It is now necessary to distinguish between two types of alcohols.

Primary alcohols consist of an alkyl radical linked to a hydroxyl group, and the structural formula shows the —OH group attached to a terminal carbon atom, e.g.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

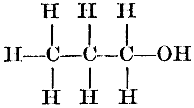
ethyl alcohol



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

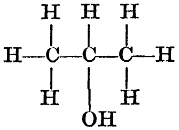
propyl alcohol

Secondary alcohols contain a $>$ CH.OH group, linked to two alkyl radicals, i.e., the —OH group is not attached to a terminal carbon atom. Since ethyl alcohol contains only two carbon atoms, it is immaterial to which carbon atom the —OH group is attached. In the case of propyl alcohol, however, the —OH group may be attached either to a terminal carbon atom or to the middle one and it is necessary to distinguish the two compounds; the former is called normal propyl alcohol and the latter, secondary or iso-propyl alcohol:—



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

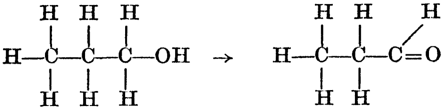
normal propyl alcohol, a primary alcohol.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & | & & H & & \\ & & & & OH & & & & \end{array}$$

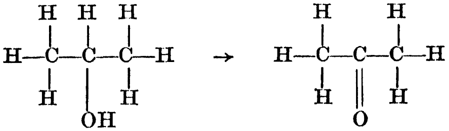
iso-propyl alcohol, a secondary alcohol.

Oxidation. Whether an alcohol is primary or secondary, the first product of oxidation is formed by the removal of two hydrogen atoms, one of them being the hydrogen of the —OH group and the other a hydrogen attached to the same carbon as the —OH group:—



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array} \rightarrow \begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & / & \\ H & - & C & - & C & - & C{=}O \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

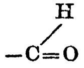
propionaldehyde, an aldehyde

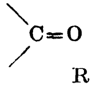


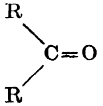
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & | & & H & & \\ & & & & OH & & & & \end{array} \rightarrow \begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & \| & & | & & \\ & & H & & \| & & H & & \\ & & & & O & & & & \end{array}$$

acetone, a ketone.

An aldehyde is thus the first product of oxidation of a primary alcohol.
A ketone ,, ,, ,, ,, ,, a secondary alcohol.

An aldehyde, therefore, contains the characteristic  $-\overset{H}{C}=O$ group attached to an alkyl radical.

A ketone contains the group  $>C=O$ attached to *two* alkyl radicals, i.e.,



$R_2C=O$

Preparation of aldehydes and ketones. It is usual to prepare aldehydes by simple oxidation of primary alcohols as described below. Ketones may be prepared by a similar method using secondary alcohols, but an alternative method is available, namely, by heating the calcium salt of the appropriate acid; this method is described and explained later (Expt. 175).

Experiment 172. Preparation of formaldehyde by oxidation with air.

Formula: H.CHO. *Physical properties*: gas with an irritating smell. *B.P.* −21° C. Soluble in water to give the solution formalin.

Apparatus: As in Fig. 43. *Material*: Methyl alcohol; platinised asbestos.

Arrange the apparatus as shown. Fill the siphon tube and warm the methyl alcohol in flask A gently so that a steady stream of alcohol vapour and air is carried through the combustion tube containing the catalyst (platinised asbestos). At the same time heat the combustion tube, gently at first, and then strongly. Note the glow of the platinum, indicating that oxidation of alcohol is exothermic. Continue to heat for about ten minutes. The aqueous solution of formaldehyde which collects in flask B may be tested with ammoniacal silver oxide as described in Expt. 176.

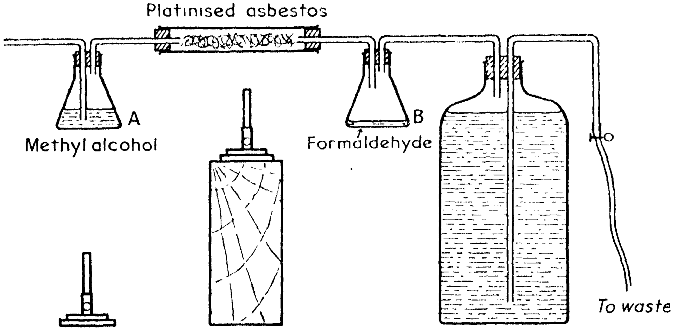


FIG. 43.

$$CH_3.OH + O \text{ (from the air) } \rightarrow H.CHO + H_2O$$

Experiment 173. Preparation of acetaldehyde.

Formula: $CH_3.CHO$. *Physical properties*: colourless liquid with pungent smell. *B.P.* 21° C. *Sp.G.* 0·8.

Apparatus: Large flask (one litre); cork with tap funnel and bent tube; condenser; sand-tray; flask (250 c.c.); measuring cylinder. *Material*: Ethyl alcohol (industrial spirit); sodium dichromate. **ICE.**

Arrange the apparatus as shown in Fig. 44. Connections must be well-made to avoid losses.

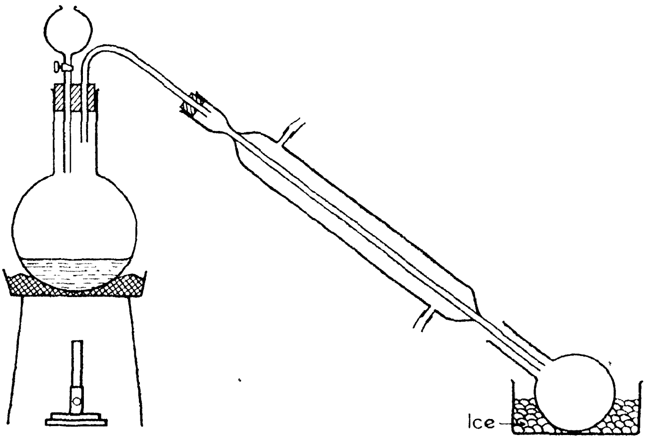


FIG. 44.

Weigh 75 gm. of sodium* dichromate and place in the large flask together with 100 c.c. of water. Fit the flask to the rest of the apparatus.

Mix 30 c.c. of conc. sulphuric acid and 60 c.c. of alcohol, adding the acid to the alcohol slowly and with shaking, in the 250 c.c. flask, and cool the mixture. Transfer the mixture to the funnel.

Heat the dichromate solution to a moderate temperature and then allow the mixture in the funnel to run in slowly. When action begins remove the flame until the first vigorous action has moderated, then continue heating until about 60 c.c. of distillate has been collected. By that time practically all the aldehyde will have distilled. The product will contain aldehyde, alcohol and water.

Note. During the addition of the acid-alcohol mixture it is advisable to shake the flask frequently.

Experiment 174. Purification of acetaldehyde.

Apparatus: Flask (250 c.c.); two absorption bottles; condenser; delivery tube; apparatus being arranged as in Fig. 45; water-bath;

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* Sodium dichromate is much more soluble than the potassium salt.

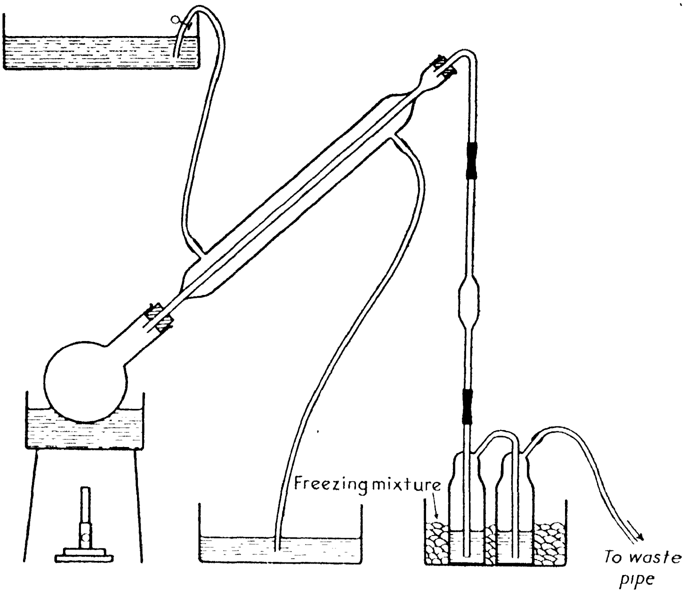


FIG. 45.

measuring cylinder; apparatus for preparing dry ammonia. Buchner funnel. *Material:* Distillate from Expt. 173; ether; **ICE**; salt.

Acetaldehyde forms an addition compound with ammonia, and this is the basis of the separation of the aldehyde from its mixture with alcohol and water.

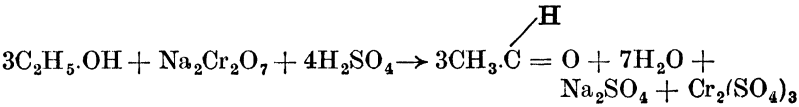
Take the distillate in the 250 c.c. flask and attach it to the condenser. Pass water at 35° C. through the condenser and maintain it at this temperature by siphoning water slightly above this temperature from a trough elevated above the apparatus. The waste-flow from the condenser can be warmed with a little boiling water and returned to the trough.

Heat the flask on the water-bath. The temperature of the condenser allows the volatile aldehyde to pass into the cold ether, where it dissolves, but condenses the alcohol and water which return into the flask. After half an hour detach the tube connecting the condenser to the absorption bottles.

Prepare ammonia and dry it by passing through a tower filled with quick lime. Pass the dry ammonia into the aldehyde-ether solution for half an hour to ensure that the solution is saturated. The crystals are acetaldehyde-ammonia. Yield 15 gm. Filter in a Buchner funnel and keep in a dry corked test-tube. The regeneration of pure aldehyde from the crystals is tedious, but if required the procedure is as follows:—

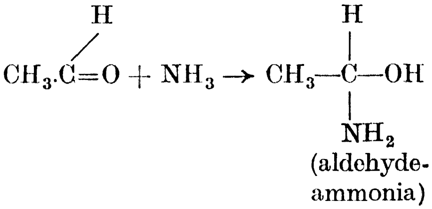
Transfer the crystals to a distilling flask attached to a sloping condenser. Fit an adapter to the lower end of the condenser leading to a flask cooled in ice. To the crystals add about four times the bulk of a mixture of equal parts of water and conc. sulphuric acid. Close the neck of the flask with a cork and heat on a water-bath, starting with cold water and stopping distillation when the water boils. Dry the distillate with calcium chloride and re-distil on a water-bath maintained at about 30° C.

Preparation.



$$3C_2H_5.OH + Na_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3CH_3.\overset{H}{C} = O + 7H_2O + Na_2SO_4 + Cr_2(SO_4)_3$$

Purification.



$$CH_3.\overset{H}{C}=O + NH_3 \rightarrow CH_3-\underset{NH_2}{\overset{H}{C}}-OH$$

(aldehyde-ammonia)

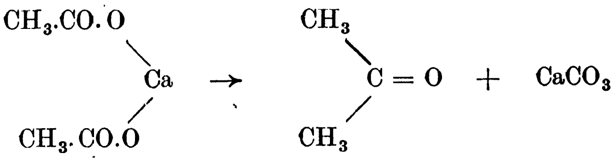
Experiment 175. Preparation of acetone.

Formula: $CH_3.CO.CH_3$. *Physical properties*: colourless liquid with a characteristic odour. *B.P.* 56° C. *Sp.G.* 0·8.

Apparatus: Two or three small (100 c.c.) distilling flasks or hard glass tubes; condenser; small flask. *Material*: Calcium acetate.

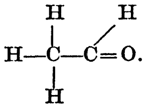
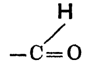
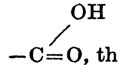
Fill a small distilling flask (or hard glass tube) about half full of calcium acetate. Attach the flask to a condenser and close the neck of the flask with a cork.

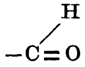
Heat with a small luminous flame which is kept moving to heat as much of the bulb as possible. The yield of acetone is small and a second and possibly a third flask should be prepared and the action repeated. It is better to proceed in this way rather than attempt to use a larger quantity in one operation. If required purer, distil the total distillate and collect the fraction between 54° C. and 58° C. The yield is small.

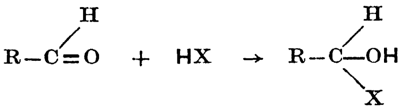


$$\begin{matrix} CH_3.CO.O & \\ & Ca \\ CH_3.CO.O & \end{matrix} \rightarrow \begin{matrix} CH_3 & \\ & C = O \\ CH_3 & \end{matrix} + CaCO_3$$

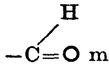
THEORY

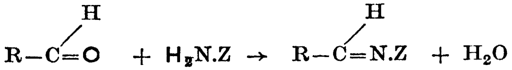
Properties of aldehydes. The formula of acetaldehyde (a typical aldehyde) is . The hydrogen atom of the  group is readily oxidised to —OH to give the group , the characteristic group of acids. For this reason aldehydes are *reducers.*

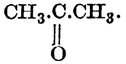
The double bond of the  group readily breaks in presence of certain hydrogen compounds, the hydrogen atom attaching to the oxygen to form a —OH group and the rest of the compound attaching itself to the spare valency bond:—



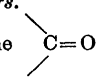
The resulting compound, having been formed by 'adding on' to the aldehyde, is called an *addition* compound.

In rare cases the oxygen atom of  may be removed by the hydrogen of compounds containing the amino group ($-NH_2$) to form water, and the resulting compound is called a '*condensation*' compound:—



Properties of ketones. The formula of a typical ketone is  $CH_3.\underset{\underset{O}{\|}}{C}.CH_3$.

The molecule does not contain a hydrogen atom favourably placed for oxidation, and consequently ketones are *not reducers.*

The molecule does, however, contain the  group and the formation of *addition* compounds and *condensation* compounds would be expected: this in fact is the case.

Experiment 176. Aldehydes as reducing agents.

Material: Fehling's solution; formaldehyde; acetone.

(a) *Reduction of silver oxide.* Take a test-tube one-quarter filled with silver nitrate solution. Add an excess of bench caustic soda to precipitate silver oxide. Decant the liquid and add ammonium hydroxide drop by drop and with continuous shaking until the precipitate has almost dissolved. Divide the solution into two portions and add respectively two drops of formaldehyde solution (formalin) and one drop of acetaldehyde. Leave in a beaker of hot water and observe the mirror of silver in both cases.

$$Ag_2O + CH_3.CHO \rightarrow 2Ag + CH_3.COOH$$

(b) *Reduction of Fehling's solution.* Fehling's solution is prepared as follows:—Dissolve 17 gm. of copper sulphate crystals in water and make up to 250 c.c. This is referred to as "Solution A". Dissolve 30 gm. of sodium hydroxide and 87 gm. of sodium potassium tartrate (Rochelle salt) in water and make up to 250 c.c. This is "Solution B". Mix equal volumes of solution A and solution B as required for an experiment; the resulting Fehling's solution is a clear, deep-blue solution.

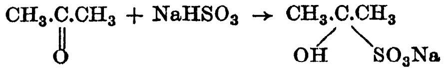
Take a test-tube about a quarter full of the deep-blue solution. Add a few drops of formalin and boil the mixture. Note the appearance of a yellow, orange, and finally red precipitate of cuprous oxide. The copper in the salt has been reduced from the divalent to the monovalent condition. Repeat the experiment, substituting acetaldehyde for formaldehyde and note the similarity of the reactions. In both cases the aldehyde has been oxidised to the corresponding acid.

Repeat both the above reactions using a ketone, acetone, in place of an aldehyde and show that neither silver oxide nor Fehling's solution is reduced.

Experiment 177. Preparation of an addition compound; the bisulphite compound of acetone.

Material: Acetone; washing soda crystals; siphon of sulphur dioxide.

Crush some washing soda crystals and take enough to form a layer about a quarter of an inch deep in a conical flask. Add just enough water to cover the crystals. Pass a steady stream of sulphur dioxide into the mass, using the delivery tube as a stirrer. Carbon dioxide is displaced, the solution effervesces and becomes a light-green colour; this is a saturated solution of sodium bisulphite. Add about 2 c.c. of acetone, shake well, and leave to stand, preferably in ice. The crystals are the bisulphite compound of acetone.*



$$CH_3.\underset{\underset{O}{\|}}{C}.CH_3 + NaHSO_3 \rightarrow CH_3.\underset{OH\quad SO_3Na}{\underset{/\ \ \backslash}{C}}.CH_3$$

Note: All aldehydes and ketones form bisulphite compounds.
All aldehydes and ketones form addition compounds with hydrogen cyanide.
Aldehydes (except formaldehyde) form addition compounds with ammonia.
Ketones do *not* form addition compounds with ammonia.

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* Difficulty may be experienced in obtaining these crystals, which are very soluble in water. Benzaldehyde may be substituted for acetone for the purpose of illustration (Expt. 218).

Experiment 178. Action of ammonia on formaldehyde.

Apparatus: Water-bath. *Material*: Formalin.

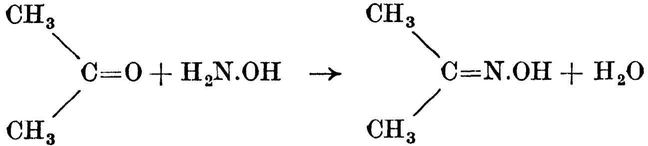
Mix a test-tube one-quarter full of formalin with an equal volume of conc. ammonium hydroxide. Pour into a watch-glass and leave to evaporate to dryness on a water-bath. The white solid is not an addition compound, but the complex condensation compound, hexamethylene tetramine, $(CH_2)_6N_4$, used in medicine as a diuretic under the name urotropine or hexamine.

Experiment 179. Preparation of condensation compounds of acetaldehyde and acetone.

(a) *Condensation with hydroxylamine.*

Apparatus: Small corked flask; measuring cylinder. *Material*: Hydroxylamine hydrochloride; sodium hydroxide; acetone.

Make a solution containing 3 gm. of sodium hydroxide in 10 c.c. of water. This is simply done by weighing rather more than one-eighth of a stick of sodium hydroxide in a corked test-tube. On the basis of 3 gm. of the solid to 10 c.c. of water, calculate the volume of water needed and use this to make a solution. Measure 10 c.c. of the resulting solution and pour it into a flask. Dissolve 5 gm. of hydroxylamine hydrochloride in 10 c.c. of water and add this to the sodium hydroxide solution. Add 7·6 c.c. of acetone, gradually and with shaking, cork the flask, and leave overnight. The colourless needles are crystals of the oxime of acetone, acetoxime.



$$(CH_3)_2C{=}O + H_2N.OH \rightarrow (CH_3)_2C{=}N.OH + H_2O$$

Note: Any aldehyde or ketone may be used.

(b) *Condensation with phenyl hydrazine.*

Material: 2.4.dinitrophenyl hydrazine.

Phenyl hydrazine itself is not suitable, as the compounds formed with either acetone or acetaldehyde do not crystallise readily, but the substituted nitro-compound of phenyl hydrazine gives excellent results.

Take enough of the dinitrophenyl hydrazine to cover the bottom of a test-tube. Add dilute hydrochloric acid, gradually and with shaking, until the solid is almost dissolved. Filter to obtain a clear solution. Add one drop of either acetaldehyde or acetone to a few drops of the prepared solution. The crystals formed are the hydrazones (actually, the dinitrophenyl hydrazones).

$$CH_3.CHO + H_2N.NHC_6H_3(NO_2)_2 \rightarrow CH_3.CH{=}N.NHC_6H_3(NO_2)_2 + H_2O$$

$$(CH_3)_2CO + H_2N.NHC_6H_3(NO_2)_2 \rightarrow (CH_3)_2C{=}N.NHC_6H_3(NO_2)_2 + H_2O$$

Note: Any aldehyde or ketone may be used.

THEORY

Polymerisation. Aldehydes readily polymerise, i.e., two or more molecules unite to form a complex molecule having the same percentage composition but two or more times the molecular weight of the aldehyde. Aldehydes polymerise in presence of acid or alkali; formaldehyde polymerises when its solution is evaporated or even when left to stand for some time. Polymers of aldehydes will, in general, dissociate into the simpler molecules when distilled, but this is not possible when the polymer has been made by the action of caustic soda (see below).

Experiment 180. Preparation of polymers of formaldehyde and acetaldehyde.

Material: Formalin; acetaldehyde; sodium hydroxide.

(a) *Preparation of paraformaldehyde.* Fill a watch-glass with formalin and leave to evaporate on a water-bath. The white solid is paraformaldehyde.

$$3H.CHO \rightarrow (CH_2O)_3$$

(b) *Preparation of paraldehyde.* Take ten drops of acetaldehyde in a dry test-tube. Add one drop of conc. sulphuric acid and cool to room temperature. Add enough water to treble the volume. The suspension is the immiscible liquid, paraldehyde.

$$3CH_3.CHO \rightarrow (C_2H_4O)_3$$

Heat the contents of the tube. The oily liquid dissolves as it changes back to acetaldehyde.

(c) *Preparation of aldehyde resin.* To a test-tube a quarter full of acetaldehyde add half that volume of water, and then a piece of sodium hydroxide about the size of a pea. Warm gently. The yellow resinous suspension is a polymer of unknown composition; it cannot be changed back to acetaldehyde.

Note: Formaldehyde differs from other aldehydes in its action with caustic soda. Instead of polymerising, it forms a mixture of methyl alcohol and sodium formate. As an aldehyde on reduction gives an alcohol, and on oxidation gives an acid, it appears that half of the formaldehyde is oxidised at the expense of the other half, which is reduced.

$$2H.CHO + NaOH \rightarrow CH_3.OH + H.COONa$$

A similar action occurs with aldehydes of the aromatic series (see p. 203) and is known as Cannizzaro's Reaction.

Experiment 181. Further reactions of aldehydes and ketones.

Material: Schiff's reagent; acetaldehyde; acetone; aqueous iodine-potassium iodide solution.

(a) *Reaction with Schiff's reagent.* Schiff's reagent is made by passing sulphur dioxide into a solution of magenta dye until the solution is colourless. Add a drop of acetaldehyde; the colour is restored. *Any aldehyde restores the colour.*

Repeat using acetone in place of the aldehyde. The colour is slowly restored, but other ketones *do not* react in this way.

(b) *Iodoform reaction.* Repeat Expt. 160, but using either acetaldehyde or acetone in place of ethyl alcohol. Show that both these compounds give iodoform. Other aldehydes and ketones *do not* react in this way.

CHAPTER XXVII

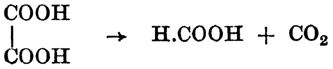
ACIDS

THEORY

The name "fatty acids" is given to the series of which formic and acetic acids are the first members, although it is only among higher members that the term 'fatty' is appropriate. Natural fat contains the glyceryl esters of palmitic and stearic acids, from which the acids themselves may be obtained by hydrolysis (see Expt. 293).

Acetic acid may be obtained in the laboratory by hydrolysing its ester (Expt. 188), acyl chloride (Expt. 190), nitrile (Expt. 193) or amide (Expt. 192).

Formic acid is usually prepared by removing the elements of carbon dioxide from oxalic acid:—



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \rightarrow H.COOH + CO_2$$

Experiment 182. Preparation of formic acid.*

Formula: H.CO.OH. *Physical properties*: colourless liquid. *B.P.* 101° C. *Sp.G.* 1·2.

Apparatus: Distilling flask (250 c.c.); condenser; sand-tray; thermometer (360° C.). *Material*: Oxalic acid; glycerol.

Weigh 30 gm. of glycerol in an evaporating basin, and dehydrate by heating on a sand-tray until a thermometer, which is used as a stirrer, indicates a temperature of 175°–180° C.

Weigh three portions (30 gm. each) of oxalic acid.

Pour the glycerol into the distilling flask and connect it to a sloping condenser. Add one of the portions of oxalic acid and close the neck of the flask with a cork and thermometer, adjusting the latter so that it dips *into* the liquid.

Heat the mixture gradually on the sand-tray to 110° C. and maintain it at that temperature until the evolution of gas (carbon dioxide) has moderated, and collect the distillate of formic acid. Allow the temperature to fall to 80° C. and add a second portion of oxalic acid. Heat as before and when the action again slackens, allow to cool and add the third portion.

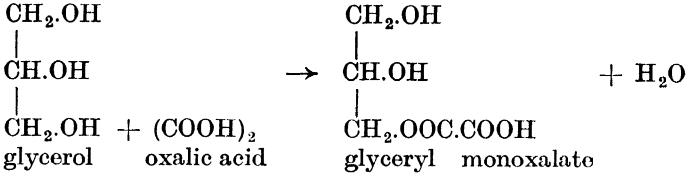
The distillate is an aqueous solution of formic acid (about 50%) and may be used as formic acid for most purposes.

Use the product for the preparation of lead formate and for reactions of the acid.

* The relation between the preparation and the purification of formic acid is conveniently shown by groups of students performing Expts. 182, 183 and 184 simultaneously.

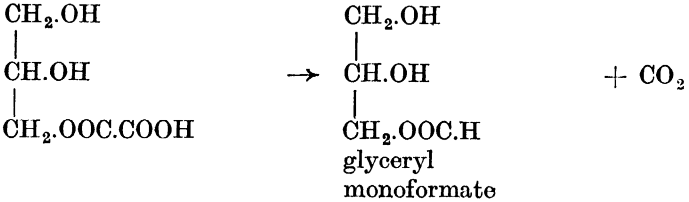
The reaction probably takes place in three stages:—

(a)



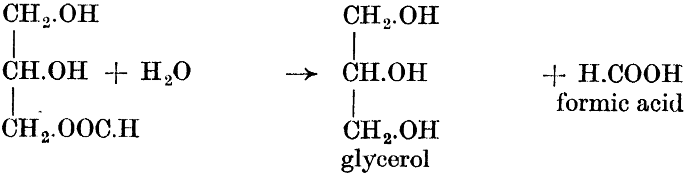
$$\underset{\text{glycerol}}{\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array}} + \underset{\text{oxalic acid}}{(COOH)_2} \rightarrow \underset{\text{glyceryl monoxalate}}{\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OOC.COOH\end{array}} + H_2O$$

(b) at about 110° C.



$$\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OOC.COOH\end{array} \rightarrow \underset{\text{glyceryl monoformate}}{\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OOC.H\end{array}} + CO_2$$

(c) hydrolysis then occurs:—



$$\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OOC.H\end{array} + H_2O \rightarrow \underset{\text{glycerol}}{\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array}} + \underset{\text{formic acid}}{H.COOH}$$

Experiment 183. Preparation of lead formate.

Formula: $(H.COO)_2Pb$. *Physical properties*: white needle crystals.

Apparatus: Water-bath; filter-funnel (in steam jacket for preference); crystallising dish. *Material*: Formic acid; lead carbonate.

Take an evaporating basin half full of formic acid (either pure formic acid or the product from Expt. 182) and heat on a water-bath. Add lead carbonate in small portions, stirring continuously, until some of the solid remains undissolved. Filter the hot solution into a crystallising dish and leave to crystallise. Filter and dry.

$$2H.COOH + PbCO_3 \rightarrow (H.COO)_2Pb + CO_2 + H_2O$$

(i) Heat a little of the product in an ignition tube. Ignite the gas (carbon monoxide) and note the residue of lead oxide.

(ii) Warm a little of the formate with conc. sulphuric acid. Test for carbon monoxide. The solid left is lead sulphate.

Write equations for both these reactions.

Experiment 184. Preparation of pure formic acid from lead formate.

Apparatus: As shown in Fig. 46; glass-wool. *Material*: Lead formate.

Place the powdered lead formate in the tube, holding the compound loosely in position by a plug of glass-wool at each end. Clamp the tube in a sloping position and connect the upper end to a supply of hydrogen sulphide. Place a receiver at the lower end. Pass a stream of hydrogen sulphide through the tube and warm the tube with a luminous flame. (The temperature should be maintained at about 100° C.) Formic acid is liberated and collects in the receiver. The yield is small.

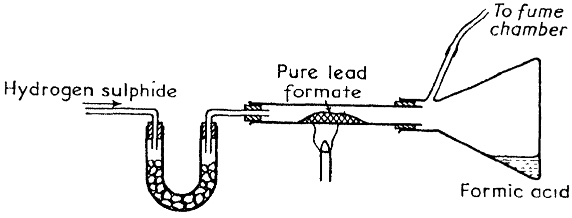
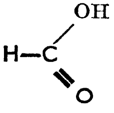


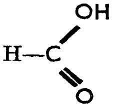
FIG. 46.

$$(H.COO)_2Pb + H_2S \rightarrow 2H.COOH + PbS$$

THEORY

Reactions of formic acid and acetic acid. Formic acid, H.COOH, and acetic acid, CH_3.COOH, contain the characteristic carboxyl group, —COOH. Purely acid properties depend on the terminal hydrogen atom of this group. Both of these acids in aqueous solution turn litmus red and neutralise bases to form salts, and although weaker (i.e., less ionised) than mineral acids, they are stronger than carbonic acid and displace carbon dioxide from carbonates. Formic acid differs from acetic acid in being a reducing agent. This property is accounted for by the structural formula which shows that formic acid is both an aldehyde and an acid.


(aldehyde)


(acid)

When acting as a reducing agent, it is oxidised to carbon dioxide and water.

Experiment 185. Reactions of formic acid.

Material: Formic acid; sodium formate; ethyl alcohol (industrial spirit).

(a) Mix about five drops each of formic acid and ethyl alcohol, add three drops of conc. sulphuric acid, and warm gently. The pleasant smelling volatile liquid is ethyl formate.

$$H.COOH + C_2H_5.OH \rightarrow H.COOC_2H_5 + H_2O$$

(b) Add a few drops of formic acid to a test-tube a quarter full of an acidified solution of potassium permanganate, and warm gently. The permanganate is reduced.

$$2KMnO_4 + 3H_2SO_4 + 5H.COOH \rightarrow K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O$$

(c) Add five drops of formic acid to five drops of mercuric chloride solution and warm. Mercuric chloride is reduced to mercurous chloride. Add ammonium hydroxide to test for mercurous chloride (black precipitate obtained).

$$2HgCl_2 + H.COOH \rightarrow Hg_2Cl_2 + 2HCl + CO_2$$

(d) Prepare a test-tube about a quarter full of ammoniacal silver oxide (Expt. 176(a)). Add two or three drops of formic acid and warm gently. Silver is formed as a black powder by reduction of the oxide.

$$Ag_2O + H.COOH \rightarrow 2Ag + H_2O + CO_2$$

(e) To a test-tube about one-eighth full of formic acid add about half that volume of conc. sulphuric acid. Heat gently, and light the gas at the mouth of the tube. The formic acid has been dehydrated to give carbon monoxide.

$$H.COOH + (H_2SO_4) \rightarrow CO + (H_2SO_4.H_2O)$$

(f) Repeat Expt. (e), using sodium formate in. place of formic acid. Note the formation of carbon monoxide as before.

(g) Ferric chloride test. Add caustic soda solution, drop by drop, to a test-tube one-quarter full of ferric chloride solution until a permanent precipitate of ferric hydroxide is obtained. Filter off the precipitate. The filtrate is called "neutral" ferric chloride. Add ammonium hydroxide to about 10 c.c. of formic acid until just alkaline to litmus and then boil for a minute or two to remove excess ammonia, and cool the solution. Add "neutral" ferric chloride. A deep red coloration is obtained, which, on boiling, gives a red-brown precipitate of basic formate.

Experiment 186. Reactions of acetic acid.

Material: Acetic acid; sodium acetate; reagents as in Expt. 185.

(a) Mix five drops each of acetic acid and ethyl alcohol, add three drops of conc. sulphuric acid and warm gently. Pour the product into a test-tube about half-full of water. The pleasant smelling ester is ethyl acetate.

$$CH_3.COOH + C_2H_5.OH \rightarrow CH_3.COOC_2H_5 + H_2O$$

(b) Repeat Expt. 185(b), using acetic acid in place of formic acid, and show that potassium permanganate is not reduced.

(c) Show that acetic acid does not reduce mercuric chloride.

(d) Show that acetic acid does not reduce ammoniacal silver oxide.

(e) Show that acetic acid is not dehydrated by conc. sulphuric acid.

(f) Show that the product of the action of conc. sulphuric acid on sodium acetate is acetic acid.

(g) Show that a neutral solution of an acetate with neutral ferric chloride gives similar results to those obtained in Expt. 185(g).

Note: Acetic acid is typical of a series of acids. Formic acid is the only fatty acid which shows reducing properties.

CHAPTER XXVIII

ESTERS, ACYL CHLORIDES, AMIDES AND NITRILES

THEORY

1. The hydrogen atom of the carboxyl (—CO.OH) group may be replaced by an alkyl radical to give *an ester.* Thus acetic acid, $CH_3CO.OH$ forms $CH_3.CO.OC_2H$. ethyl acetate.

2. The —OH group of the —CO.OH group may be replaced by:

(a) —Cl to form an *acyl chloride,* $CH_3.CO.Cl$

or (b) —NH_2 to form *an amide,* $CH_3.CO.NH_2$

Experiment 187. Preparation of an ester. Ethyl acetate.

Formula: $CH_3CO.OC_2H_5$. *Physical properties*: Pleasant smelling immiscible liquid. *B.P.* 77° C. *Sp.G.* 0·9.

Apparatus: Distilling flask (500 c.c.); tap funnel; adapter; oil-bath; flask (250 c.c.); measuring cylinder; thermometer (200° C.). *Material*: Glacial acetic acid; ethyl alcohol (industrial alcohol); calcium chloride.

The apparatus is arranged as in Fig. 47. Prepare two solutions, as follows:—

(a) To 25 c.c. of alcohol add gradually 25 c.c. of conc. sulphuric acid with shaking. Pour this mixture into the distilling flask.

(b) Mix 50 c.c. of alcohol with 50 c.c. of glacial acetic acid. Pour this mixture into the funnel.

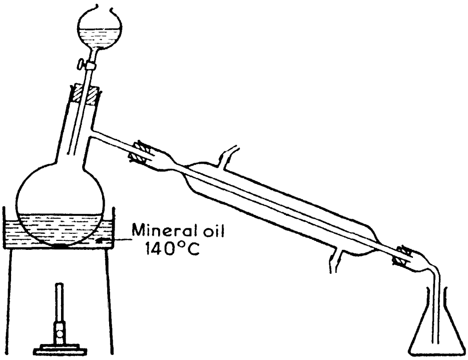


FIG. 47.

Raise the temperature of the oil-bath to 140° C. and maintain it at that temperature throughout. Allow the mixture in the funnel to drip into the flask at the same rate at which the distillate collects in the receiver. Transfer the distillate to a separating funnel and shake with a fairly saturated solution of sodium carbonate, taking care to avoid a high pressure of carbon dioxide by inverting the funnel and leaving the stop-tap open. Test the upper layer with litmus paper to make sure that all traces of acetic acid and sulphurous acid (present as impurities) have been removed. Run off the lower layer and discard it.

To the ester in the funnel, add a solution of 50 gm. of calcium chloride in 50 c.c. of water. Shake well; this removes the alcohol remaining as an impurity.

Discard the lower layer and run the ester into a flask. Add enough anhydrous calcium chloride to cover the bottom of the flask, and leave it corked overnight.

Distil and collect the fraction between 74° C. and 79° C. Yield 45 gm.

$$CH_3CO.OH + C_2H_5.OH \rightarrow CH_3.CO.OC_2H_5 + H_2O$$

Experiment 188. Hydrolysis of an ester. Saponification.

Apparatus: 250 c.c. flask; condenser; porous pot; water-bath; measuring cylinder; distilling flask. *Material*: ethyl acetate; solid caustic soda.

THEORY

Hydrolysis of an ester. An ester may be hydrolysed either by:—

(1) the action of an acid, in which case the H^+ of the acid catalyses the hydrolysis,

$$CH_3CO.OC_2H_5 + HOH \rightarrow CH_3CO.OH + C_2H_5.OH$$

or (2) the action of an alkali, in which case the products are the alcohol and the sodium salt of the acid,

$$CH_3.CO.OC_2H_5 + NaOH \rightarrow CH_3.CO.ONa + C_2H_5.OH$$

This method is known as saponification because of its application to soap manufacture when fats are the esters hydrolysed. (See p. 363.)

Dissolve a stick of caustic soda (about 20 gm.) in 50 c.c. of water in the flask and add some fragments of porous pot. Attach a reflux condenser. Pour 25 c.c. of ethyl acetate down the inner tube of the condenser. Boil gently on a gauze until the ester has gone into solution (about ¾ hour).

Transfer to a distilling flask connected to a sloping condenser and distil off half of the liquid: this consists of alcohol and water. Confirm by the iodoform reaction (Expt. 160).

Transfer the remaining liquid from the flask to an evaporating basin and heat to dryness on the water-bath. Powder the solid and distil with concentrated sulphuric acid to obtain acetic acid.

$$CH_3.CO.OC_2H_5 + NaOH \rightarrow CH_3.CO.ONa + C_2H_5.OH$$
$$2CH_3.CO.ONa + H_2SO_4 \rightarrow 2CH_3.CO.OH + Na_2SO_4$$

Experiment 189. Preparation of an acyl chloride, e.g., acetyl chloride.

Formula: $CH_3.CO.Cl$. *Physical properties*: colourless fuming liquid. *B.P.* 55° C. *Sp.G.* 1·1.

Apparatus: Two 250 c.c. distilling flasks; condenser; tap funnel; calcium chloride tube; water-bath; thermometer (100° C.). *Material*: Phosphorus trichloride; calcium chloride.

Arrange the apparatus as shown in Fig. 48.

Take 50 c.c. of glacial acetic acid in the distilling flask, and 25 c.c. of phosphorus trichloride in the tap funnel, which should be stoppered immediately.

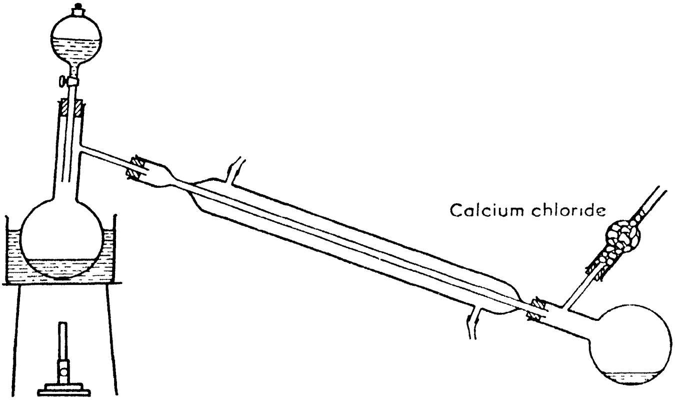


FIG. 48.

Immerse the bulb of the flask in the water in the bath and allow the phosphorus trichloride to drip slowly into the acid.

When all has been added, raise the temperature of the bath to 40° C. until the evolution of hydrogen chloride has subsided and then heat to boiling.

When nothing further distils over attach the receiver-distilling flask and its contents to the condenser in place of the first distilling flask. Close the neck with a thermometer and cork and heat as before. Collect the portion distilling between 53° C. and 56° C., and store in a stoppered bottle. Yield 40 gm.

$$3CH_3.CO.OH + 2PCl_3 \rightarrow 3CH_3.CO.Cl + P_2O_3 + 3HCl$$

Experiment 190. Reactions of acetyl chloride.

Material: Acetyl chloride; industrial spirit; sodium chloride; aniline. Use three or four drops of acetyl chloride for each reaction.

(a) To the acetyl chloride add five drops of alcohol. Allow to cool and add about a quarter of a test-tube full of a strong solution of sodium chloride. The immiscible liquid which rises to the surface is ethyl acetate, recognised by its fragrant smell. This is a useful method of making esters, no dehydrating agent being needed.

$$CH_3.CO.Cl + C_2H_5.OH \rightarrow CH_3CO.OC_2H_5 + HCl$$

(b) Add about five drops of water to the second portion and place the test-tube in a stand. Note the accelerating action as the temperature rises due to hydrolysis. Test the gas with silver nitrate solution on a glass rod.

$$CH_3CO.Cl + HOH \rightarrow CH_3.CO.OH + HCl$$

(c) Reaction with ammonia. (Care!) This vigorous reaction should be carried out exactly as stated. Take the third test-tube containing acetyl chloride and place the tube in a stand. Take three or four drops of conc. ammonium hydroxide in another test-tube and empty this small quantity into the acetyl chloride. The thick white fumes are ammonium chloride and the solid residue acetamide.

$$CH_3.CO.Cl + 2NH_4OH \rightarrow CH_3.CO.NH_2 + NH_4Cl + 2H_2O$$

(d) To the fourth portion add three drops of aniline. The solid formed is acetanilide. When cool, add enough water to fill the tube one-third full, boil for a few minutes and allow to cool. Acetanilide crystallises as colourless flakes.

$$CH_3.CO.Cl + C_6H_5.NH_2 \rightarrow \underset{\text{(acetanilide)}}{C_6H_5.NH.CO.CH_3} + HCl$$

Experiment 191. Preparation of an amide. Acetamide.

Formula: $CH_3.CO.NH_2$. *Physical properties*: white solid with an odour of mice. *M.P.* 82° C.

Apparatus: Flask (250 c.c.); condenser; thermometer (360° C.); measuring cylinder. *Material*: Ammonium acetate.

THEORY

The decomposition of ammonium acetate by heat is shown by the equation:—

$$CH_3.CO.ONH_4 \rightarrow CH_3.CO.NH_2 + H_2O$$

The water formed, however, hydrolyses ammonium acetate (salt of a weak acid and a weak base) and this would become the main action unless a method were designed to control it:—

$$\begin{array}{l} CH_3CO.ONH_4 + H_2O \rightarrow CH_3.CO.OH + NH_4OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NH_3 + H_2O \end{array}$$

There are two such methods,

(a) by heating ammonium acetate in a sealed tube. Here the pressure of ammonia and acetic acid vapour favours their re-combination to form ammonium acetate,

(b) by adding excess acetic acid and heating the mixture for some time under ordinary pressure. Here the increased concentration of acetic acid has the same effect as in (a).

In either case the ammonium acetate is prevented from hydrolysing appreciably, and the main action becomes the formation of acetamide as shown in the first equation. Both (a) and (b) are good examples of the application of the Law of Mass Action. (See Chapter II.)

Add 70 c.c. of glacial acetic acid to 50 gm. of ammonium acetate in the 250 c.c. flask. Attach a reflux condenser and boil gently on a gauze for four hours (see Fig. 49).

After cooling transfer the mixture to a distilling flask attached to a sloping condenser and close the neck of the flask with a cork and thermometer. Raise the temperature to 130° C. and discard the distillate (chiefly water and acetic acid).

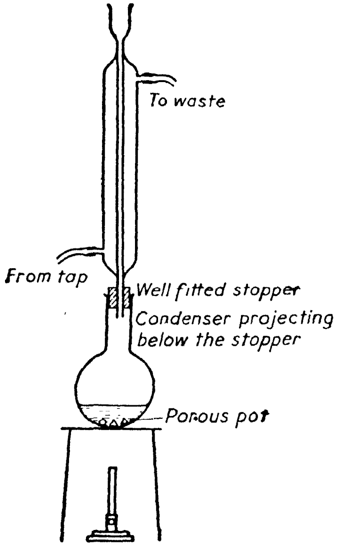


FIG. 49.

Distillation must be controlled at a very slow rate to make as complete as possible the removal of excess acetic acid and water.

Replace the condenser by the inner tube of a condenser, and continue distillation, collecting the distillate in beakers (Fig. 50). Take separate fractions first up to 180° C. and then in 10 c.c. portions. When crystallisation has occurred in one portion use a small crystal to seed the rest. Dry the crystals between filter papers and keep in a dry stoppered flask. Note the peculiar smell. Yield 25 gm.

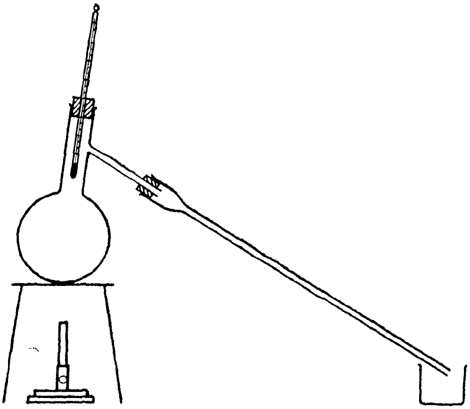


FIG. 50.

Experiment 192. Reactions of acetamide.

Material: Acetamide; sodium nitrite.

(a) Take about half a salt-spoonful of acetamide and add about 5 c.c. of caustic soda solution. Warm gently and recognise ammonia.

Evaporate the solution to dryness and warm the crystals (sodium acetate) with a drop or two of conc. sulphuric acid. Confirm acetic acid by its smell.

$$CH_3.CO.NH_2 + NaOH \rightarrow CH_3.COONa + NH_3$$

(b) Dissolve about a salt-spoonful of sodium nitrite in the minimum of water. Keep the test-tube cold under the tap and add enough dilute hydrochloric acid to double the volume. Immediately add about half a salt-spoonful of acetamide. The effervescence is due to nitrogen.

$$CH_3.CO.NH_2 + HNO_2 \rightarrow CH_3.CO.OH + N_2 + H_2O$$

Nitrous acid has thus replaced the $-NH_2$ group by a $-OH$ group, an action which occurs generally to compounds containing the $-NH_2$ group.

(c) Boil about a salt-spoonful of acetamide with about 5 c.c. of dilute hydrochloric acid, and recognise the smell of acetic acid in the vapour. Ammonium chloride is also formed, and to show this add an excess of caustic soda solution and boil. Note the ammonia in the vapour. Compare this action with test (a). Hydrolysis has occurred in both cases.

$$CH_3.CO.NH_2 + HCl + H_2O \rightarrow CH_3.CO.OH + NH_4Cl$$

(d) When acetamide is dehydrated, aceto-nitrile (methyl cyanide) is formed (see Expt. 193).

Experiment 193. Preparation of aceto-nitrile (methyl cyanide).

Formula: $CH_3.CN$. *Physical properties*: pleasant smelling liquid. *B.P.* 82° C. *Sp.G.* 0·8.

Apparatus: Retort (150 c.c.). *Material*: Acetamide; phosphorus pentoxide.

Into a small retort introduce 10 gm. of acetamide. Make a paper funnel and use it to introduce about twice the weight of phosphorus pentoxide. Mix as well as possible and heat moderately, using a large luminous flame. Collect the aceto-nitrile as a slightly discoloured liquid (see Fig. 51). Yield very small.

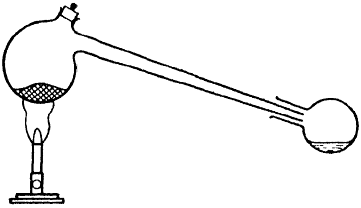


FIG. 51.

$$CH_3.CO.NH_2 + P_2O_5 \rightarrow CH_3.C{\equiv}N + 2HPO_3$$

Divide the liquid into two portions.

(a) To one portion add caustic soda solution and heat. Test for ammonia with litmus paper.

$$CH_3.C \equiv N + NaOH + H_2O \rightarrow CH_3.CO.ONa + NH_3$$

It is because the compound hydrolyses to acetic acid (which is neutralised to sodium acetate) that the name aceto-nitrile is given as an alternative to methyl cyanide.

(b) Add to the other portion a piece of granulated zinc and about 1 c.c. of conc. hydrochloric acid. Leave until effervescence has almost ceased. Add caustic soda solution until the solution is alkaline and then heat. The fishy ammoniacal smell is due to ethylamine. The reduction of a nitrile by nascent hydrogen is known as Mendius' Reaction and is used as a preparation of amines.

$$CH_3.C \equiv N + 4H \rightarrow \underset{\text{(ethylamine)}}{CH_3.CH_2.NH_2}$$

CHAPTER XXIX

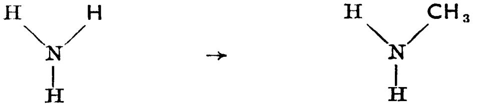
AMINES

THEORY

The structure of a primary amine shows an alkyl radical united with an amino ($-NH_2$) group, e.g., $CH_3.NH_2$, methylamine or $C_2H_5.NH_2$, ethylamine.

A primary amine may be considered as ammonia in which one atom of hydrogen in the molecule has been displaced by an alkyl group:—

e.g.,



In Expt. 193 (b), ethylamine was obtained by reducing methyl cyanide.

The usual method of preparing amines is to treat the appropriate amide with bromine and caustic potash (Hofmann's Reaction).

The sum total of the reaction is:—

$R.CO.NH_2 \rightarrow R.NH_2$, where R is an alkyl radical. The stages of the reaction may be shown by the equations:—

$$\begin{aligned}
CH_3.CO.NH_2 + Br_2 + KOH &\rightarrow \underset{\text{(brom-acetamide)}}{CH_3CO.NHBr} + KBr + H_2O \\
CH_3.CO.NHBr + KOH &\rightarrow \underset{\text{(methyl iso-cyanate)}}{CH_3N:C:O} + KBr + H_2O \\
CH_3.N:C:O + 2KOH &\rightarrow \underset{\text{(methylamine)}}{CH_3.NH_2} + K_2CO_3
\end{aligned}$$

Experiment 194. Preparation of methylamine and its hydrochloride.

Formula: $CH_3.NH_2$. *Physical properties*: alkaline gas with a smell resembling ammonia. Soluble in water.

Apparatus: 250 c.c. flask; large distilling flask (500 c.c.); tap-funnel; adapter; condenser; measuring cylinder; pieces of porous pot; water-bath; thermometer (100° C.) *Material*: Acetamide; bromine; potassium hydroxide; industrial spirit.

Make a solution of 15 gm. of caustic potash in 150 c.c. of water.

Take 15 gm. of acetamide in the 250 c.c. flask and add 13·5 c.c. of bromine, taking care to avoid bromine vapour reaching the eyes. Add the caustic potash solution in portions of about 20 c.c., keeping the flask cool under the tap and shaking the mixture at intervals. The reddish-brown liquid changes gradually to yellow, and contains brom-acetamide.

Transfer the liquid to a tap-funnel fitted to a 500 c.c. distilling flask. Prepare a solution of 40 gm. of caustic potash in 75 c.c. of water and pour this into the flask. Add a few fragments of porous pot. Attach the flask to a sloping condenser fitted with an adapter which dips into a conical flask. Make a solution of 25 c.c. of conc. hydrochloric acid and 75 c.c. of water and pour this into the conical flask. Adjust the apparatus so that the end of the adapter is just under the surface of the acid, and throughout the preparation make periodical adjustments to keep it so.

Heat the distilling flask on a water-bath maintained at 60° C. and allow the liquid in the tap-funnel to drip in slowly, and after all has been added continue to heat at this temperature until the yellow colour disappears (about ½ hour).

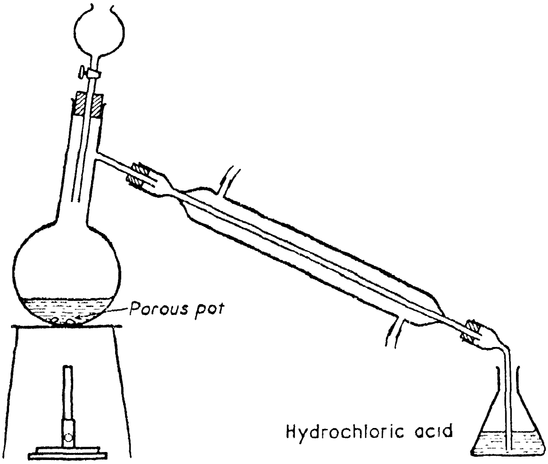


FIG. 52.

Replace the water-bath by a gauze and boil the liquid (Fig. 52). Water and methylamine distil into the hydrochloric acid. When about two-thirds of the liquid has distilled, detach the apparatus, transfer to a dish and evaporate the total distillate (methylamine hydrochloride) first on a gauze and, when crystals appear, on a water-bath. The crystals contain a little ammonium chloride. Transfer the crystals to a dry flask and dissolve the methylamine hydrochloride by adding five successive portions of 20 c.c. of alcohol and warming each time on a water-bath. Pour each extraction into an evaporating basin and heat the total solution on a water-bath until crystals form, then set aside to crystallise. Yield 7 gm.

Experiment 195. Reactions of methylamine.

Material: Methylamine hydrochloride; sodium nitrite.

(a) Warm a few crystals of methylamine hydrochloride with caustic soda solution. Note the fishy smell of the free amine.

$$CH_3.NH_2.HCl + NaOH \rightarrow \underset{\text{(methylamine)}}{CH_3.NH_2} + NaCl + H_2O$$

(b) In one test-tube make about 5 c.c. of a weak (light blue) solution of copper sulphate. In another test-tube take about half a salt-spoonful of methylamine hydrochloride and add about 10 c.c. of caustic soda solution. Add the second solution to the first until the precipitate which forms re-dissolves to form a deep blue solution. This action is similar to the action of ammonia on copper salts, and is a reminder of the close structural relationship of ammonia and methylamine.

(c) Dissolve about a salt-spoonful of sodium nitrite in the minimum of water. Keep the test-tube cool under the tap and add enough dilute hydrochloric acid to double the volume. Pour this solution into a test-tube containing enough methylamine hydrochloride to cover the bottom. The effervescence is nitrogen and the test recalls a similar one with acetamide. In both cases the $-NH_2$ group is replaced by the $-OH$ group.

$$CH_3.NH_2.HCl + HNO_2 \rightarrow CH_3.OH + N_2 + HCl + H_2O$$

(d) Methylamine will give the isocyanide test with chloroform. See Expt. 169(c).

CHAPTER XXX

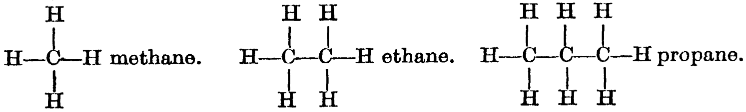
HYDROCARBONS

THEORY

Hydrocarbons of the aliphatic series are divided into three classes:—

1. Paraffins: examples methane CH_4, ethane C_2H_6, propane C_3H_8
2. Olefines: examples ethylene C_2H_4, propylene C_3H_6
3. Acetylenes: examples acetylene C_2H_2, allylene C_3H_4

1. *The paraffins* are fully saturated hydrocarbons, i.e., each carbon atom is exerting its full tetravalency:—

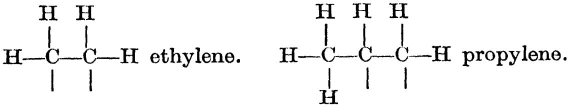


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \text{ methane.} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \text{ ethane.} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \text{ propane.}$$

They are (a) unaffected by almost all reagents, and

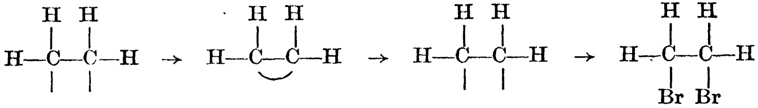
(b) form compounds by substitution; a hydrogen atom must be displaced to allow another monovalent atom or group to enter the molecule.

2. *Olefines* are not saturated: the molecular formula shows two atoms of hydrogen less than would be required for full saturation:—



$$H-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}-H \text{ ethylene.} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}-H \text{ propylene.}$$

The free valencies link to form a 'double bond' which readily breaks in the presence of a reagent with which the free valencies can unite:—

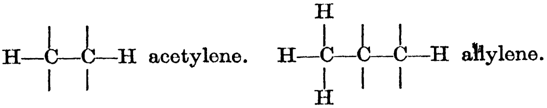


$$H-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}-H \rightarrow \underset{\smile}{H-\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-H} \rightarrow H-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}-H \rightarrow H-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}-H$$

(in presence of bromine)

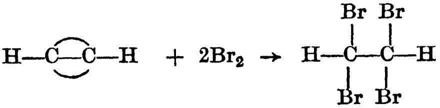
This property of forming "*addition*" compounds is the chief characteristic of olefines. The formation of "addition" compounds by other unsaturated groups has been noted previously. (See Expts. 177 and 193 (b).)

3. *Acetylenes* are still less saturated: the molecular formula shows four hydrogen atoms less than required for saturation:—



$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H \text{ acetylene.} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H \text{ allylene.}$$

The free valencies form a 'triple bond', which breaks to form addition compounds. Thus with bromine acetylene forms tetrabrom-ethane:—



$$H-\overset{\frown}{\underset{\smile}{C-C}}-H + 2Br_2 \rightarrow H-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-H$$

Acetylene forms metallic derivatives which still retain the triple bond. They are very unstable and explosive.

Experiment 196. Preparation of the paraffin methane.

Apparatus: As in Fig. 53; mortar and pestle. *Material*: Fused sodium acetate*; soda lime; bromine.

About 20 gm. of sodium acetate and an equal weight of soda lime are mixed intimately in a mortar and transferred to the hard glass tube (wrapped with gauze). The tube is heated, care being taken that water is not sucked back through variations of temperature. Collect three jars full of methane.

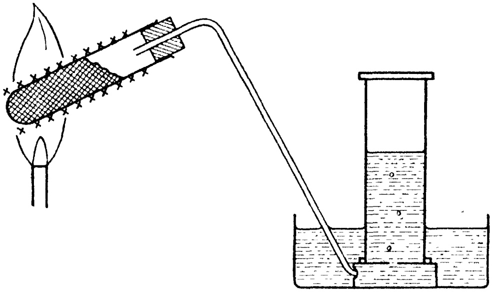


FIG. 53.

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

Perform the following experiments:—

(a) Apply a light to the first jar. Note colour of flame, and test the residual gas for carbon dioxide.

(b) Take the second jar, hold a dry jar mouth downward over it, and allow the methane to pass upward into the dry jar. While still inverted light the gas in the upper jar. Note that moisture is formed. Tests (a) and (b) establish the presence of carbon and hydrogen in the hydrocarbon.

(c) Invert the third jar in a trough of water. Pour a drop or two of bromine into the water and adjust the jar to include the bromine in its mouth. Leave for 24 hours and then note that (i) methane is coloured by bromine, and (ii) the level of the water has not changed. Bromine has no appreciable action on methane (or on any members of the paraffin series).

By substituting the sodium salt of the next higher acid (propionic acid), ethane may be prepared in a similar manner.

Experiment 197. Preparation of the olefine ethylene.

Apparatus: Large flask ($1\frac{1}{2}$ litres) fitted with tap-funnel; delivery tubes; wash-bottle containing strong caustic soda solution and fitted as in Fig. 54. *Material*: Ethyl alcohol (industrial methylated spirits); anhydrous aluminium sulphate; bromine.

30 c.c. of ethyl alcohol are poured into the flask and about a teaspoonful of aluminium sulphate added to prevent frothing and charring during the subsequent heating. (Dry sand may be substi-

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* If fused sodium acetate is not available, the hydrated salt must first be heated in an evaporating basin on a water-bath, with constant stirring, until anhydrous.

tuted but is less efficient.) 80 c.c. of conc. sulphuric acid is slowly run in from the tap-funnel.* If a large yield of ethylene is required a mixture of equal volumes of alcohol and acid is prepared and run

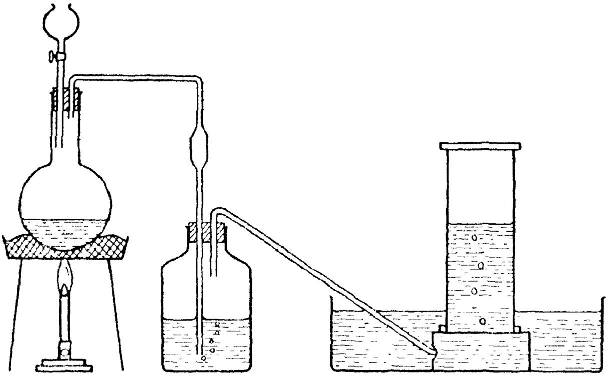

FIG. 54.

in from the tap-funnel as required to maintain the flow of gas. The flask is heated on a sand-tray until action begins, after which the temperature is lowered a little. During the action some alcohol is oxidised at the expense of the acid which is reduced to give a corresponding amount of sulphur dioxide, and it is to remove this that the gas is washed through caustic soda solution.

$$C_2H_5.OH + (H_2SO_4) \rightarrow C_2H_4 + (H_2SO_4.H_2O)$$

Collect four jars of ethylene and carry out tests (a), (b) and (c) as given for methane (Expt. 196). Note points of similarity and of difference and account for them knowing that ethylene is a hydrocarbon but with a higher proportion of carbon than its corresponding paraffin, and that it is unsaturated.

To the fourth jar add a few c.c.s of dilute potassium permanganate solution which has been made alkaline with a few drops of sodium hydroxide solution. On shaking, the purple colour changes to green (potassium manganate) and later a brown suspension of manganese dioxide is formed. The ethylene has been oxidised to ethylene glycol.

$$C_2H_4 + H_2O + O \rightarrow C_2H_4(OH)_2$$

Experiment 198. Preparation of ethylene dibromide.

Apparatus: As in Fig. 55. *Material*: Reagents as in Expt. 197.

Using similar initial quantities as in Expt. 197 and having ready an additional quantity of mixture of alcohol and acid (150 c.c. of

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* See note on p. 146.

each) prepare the gas and pass it through the two bottles containing bromine covered with a little water. Use 25 c.c. of bromine in the first bottle and 10 c.c. in the second (measured in a cylinder).

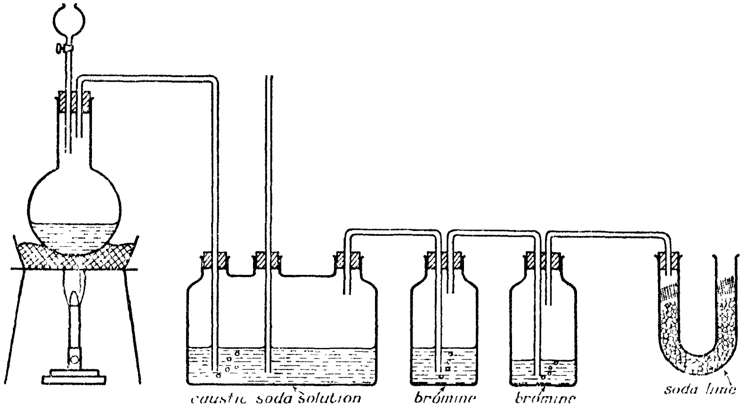

FIG. 55.

The exit of the last bottle is connected to a "U" tube filled with a loosely packed mixture of soda-lime and glass-wool to prevent traces of the irritating bromine vapour from escaping.

Continue to pass the gas, adding more mixture from the tap-funnel as required, until the bromine is decolorised to an oily liquid, ethylene dibromide. (Total time about two hours.)*

$$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br.CH_2Br$$

The product is washed in a separating funnel, first with bench caustic soda diluted with its own volume of water, then with water. It is run off into a flask, left to dry with calcium chloride overnight, and then distilled. The fraction collected at 130° C.—132° C. is retained. Yield 50 gm.

Experiment 199. Preparation of acetylene.

Apparatus: As in Fig. 56. *Material*: Calcium carbide; bromine.

The flask at the start should be quite dry. The bottom of the flask is covered with a thin layer of sand and a few pieces of calcium carbide placed on this. Water is added drop by drop to obtain a steady flow of gas.

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Collect four jars of acetylene and carry out the following tests:—

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* *Note carefully* that the wash-bottle containing caustic soda must be disconnected *before* the bunsen is removed at the end of the experiment.

(a) Ignite the gas in the first jar. Note the smoky flame and the deposit of carbon. Compare with methane and ethylene.

(b) Stand the second jar over bromine in water as was done with methane and ethylene. The gas reacts to form acetylene tetrabromide.

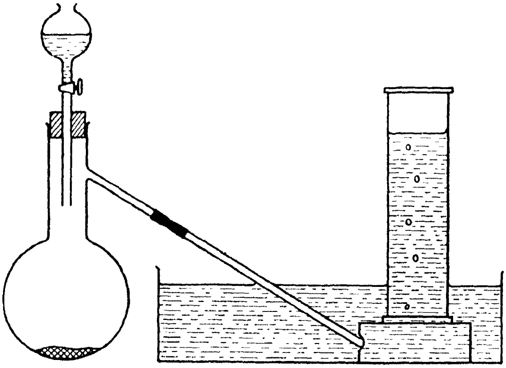


FIG. 56.

$$\underset{}{C_2H_2} + 2Br_2 \rightarrow \underset{\substack{\text{acetylene}\\ \text{tetrabromide}}}{C_2H_2Br_4}$$

(c) Prepare a solution of ammoniacal cuprous chloride by dissolving about a salt-spoonful of copper carbonate in conc. hydrochloric acid in a test-tube, adding a piece of copper and boiling for a few minutes, then pouring into another test-tube half full of water. Decant, and dissolve the white solid, cuprous chloride, in ammonium hydroxide. Now pour this solution into the third gas-jar. The red precipitate is cuprous acetylide.

$$C_2H_2 + Cu_2Cl_2 \rightarrow C_2Cu_2 + 2HCl \text{ (becoming } 2NH_4Cl\text{)}$$

(d) Prepare a solution of ammoniacal silver oxide as described in in Expt. 176(a). Pour it into the fourth gas-jar. A white precipitate of silver acetylide, C_2Ag_2, is obtained. Place a *small* portion on gauze and heat by means of a bunsen burner. (Care!) The silver acetylide suddenly decomposes explosively.

CHAPTER XXXI

AROMATIC COMPOUNDS

THEORY

Compounds derived from benzene or from homologues of benzene are called aromatic compounds. The structure of the benzene molecule is fundamentally different from that of any of the hydrocarbons already mentioned, and, since structure determines the properties of organic compounds, it would be expected that compounds derived from benzene would show marked differences from corresponding compounds derived from ethane or methane. At the same time it would be expected that the properties of an attached group would exert a similar influence on the properties of a compound, regardless of the particular radical to which it was attached. Aromatic compounds do, in fact, show the influence of both the radical and the group in the manner expected. Thus, acetic acid ($CH_3.COOH$) and benzoic acid ($C_6H_5.COOH$) are similar in their acidic properties, but differ in those properties which are functions of the methyl (CH_3) or the phenyl (C_6H_5) radical. Further, the fundamentally different structures of the methyl and phenyl groups influence the characteristics of the attached groups, and in some cases the resulting products are markedly dissimilar; thus, methylamine ($CH_3.NH_2$) is unlike aniline ($C_6H_5.NH_2$) in many respects. It is because of these differences that it is advisable to divide organic compounds into two series, aliphatic and aromatic, and study them separately.

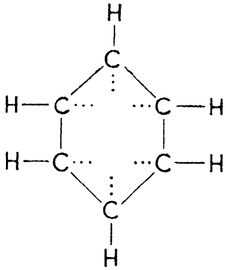


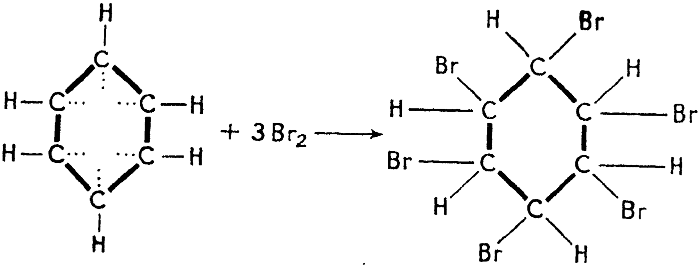
FIG. 57.

Structure of benzene. Reference should be made to a theoretical text-book for a full account of the work of Kekulé and others in elucidating the structure of the benzene molecule; it is sufficient here to state that the six carbon atoms are arranged in the form of a ring, with a hydrogen atom attached to each carbon atom (see Fig. 57). In all attempts to assign a formula to benzene, the chief concern has been to overcome the difficulty arising from the apparent trivalency of carbon. For our present purpose this difficulty is met by accepting the view that in each of the six carbon atoms the fourth valency is usually 'dormant'. One example is given below (Expt. 200) to show that, on rare occasions, the dormant valencies can become active; benzene thus behaving as an unsaturated compound. In the very great majority of cases, however, benzene compounds are made by substituting, either directly or indirectly, a monovalent group for each hydrogen atom displaced; benzene behaves, normally, as a saturated compound.

Experiment 200. Preparation of benzene hexabromide, $C_6H_6Br_6$.

Apparatus: Wide-mouth bottle (about 10 oz.); thistle-funnel. *Material*: Benzene, bromine.

Pour sufficient benzene into the bottle to form a thin layer on the bottom, and stand a crucible on it. By means of a thistle-funnel, run three or four drops of bromine into the crucible. Stopper the bottle and leave it where it will be in sunlight during a few days. The colourless crystals are the addition compound benzene hexabromide.



$$C_6H_6 + 3Br_2 \longrightarrow C_6H_6Br_6$$

SUBSTITUTION

A group may enter the benzene molecule by displacing a hydrogen atom to form a compound of the type, C_6H_5X; this process is known as *direct* substitution. The groups $-NO_2$, $-SO_3H$, $-Cl$, $-Br$, $-CH_3$ (and similar alky groups) and $-COCH_3$ may be introduced directly; of these, the nitro group ($-NO_2$) is the most important because, once introduced, it may be converted, by stages, into other groups to give a large variety of compounds of technical importance. The process of introducing a group into the benzene molecule by converting another group already present is known as *indirect* substitution; examples of this process are given later (see Expt. 213 *et seq.*).

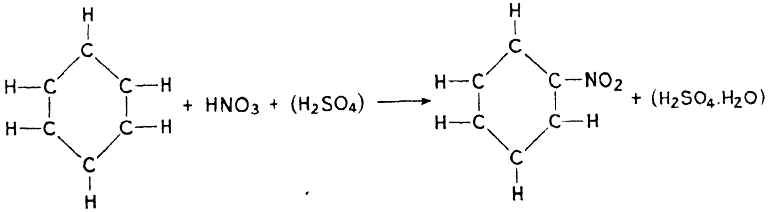
Experiment 201. Preparation of mono-nitrobenzene. Introduction of $-NO_2$.

Formula: $C_6H_5.NO_2$. *Physical properties*: yellow oil. *B.P.* 206·5° C. *Sp.G.* 1·21.

Apparatus: Flask (500 c.c.); thermometer (360° C.); separating funnel; water-bath; distilling flask (150 c.c.); condenser; flask (250 c.c.); measuring cylinder; trough. *Material*: Benzene; calcium chloride.

(a) *Small scale preparation.* Take about 10 c.c. of conc. nitric acid in a boiling-tube and add that volume of conc. sulphuric acid. Cool the mixture under the tap. Add about 5 c.c. benzene in small portions, shaking gently at each addition. Leave the boiling-tube standing in water at a temperature of 50° C. for half an hour. Decant as much as possible of the upper layer (mono-nitrobenzene) into a test-tube and shake gently with sodium carbonate solution to neutralise traces of acids. Decant and then discard the upper (aqueous) layer, and treat again with sodium carbonate solution until there is no further effervescence. Decant as before. Add calcium chloride to the yellow oil and leave until clear, then decant into a dry test-tube. The mono-nitrobenzene is pure enough for later conversion into di-nitrobenzene or into aniline.

(b) *Larger scale preparation.* Measure 55 c.c. of conc. sulphuric acid and add slowly to 50 c.c. of conc. nitric acid in a 250 c.c. flask. Mix well and cool under the tap. When cool transfer to a separating funnel. Take 40 c.c. of benzene in a 500 c.c. flask, stand the flask in a trough of water, and place the stem of the separating funnel in the neck of the flask. Allow the mixture of acids to drip into the benzene at such a rate that the temperature does not exceed 50° C.; a thermometer may be left standing in the flask throughout the experiment for this purpose. (The "nitration" of benzene is exothermic, and a high rise in temperature would cause further nitration to give di-nitrobenzene at the expense of the mono-nitro compound.) Warm on a water-bath for a quarter of an hour, shake well, then heat for a further quarter of an hour. Allow to cool. Transfer to a separating funnel and run off the lower (acid) layer, and discard it. Shake the product in the separating funnel with a dilute solution of sodium carbonate (to neutralise any free acid), then separate, this time retaining the lower layer. (Note that the specific gravity of mono-nitrobenzene (1·21) is less than that of the acid mixture but greater than that of the sodium carbonate solution). Return the product to the funnel and wash with water. Run off the cloudy liquid into a flask and add a few pieces of calcium chloride. Leave until the liquid is clear, then transfer it to a distilling flask. Distil, and collect between 205° C. and 208° C. Yield 35 gm.



$$C_6H_6 + HNO_3 \longrightarrow C_6H_5.NO_2 + H_2O$$

Experiment 202. Preparation of bromo-benzene. Introduction of —Br.

Formula: $C_6H_5.Br$. *Physical properties*: colourless liquid. *B.P.* 157° C. *Sp.G.* 1·5.

Apparatus: Four evaporating basins; measuring cylinder; separating funnel; thermometer (360° C.); distilling flask (150 c.c.); condenser; flask (250 c.c.). See Fig. 58. *Material*: Benzene; bromine; aluminium foil; alcohol (industrial spirit); calcium chloride.

The introduction of bromine by this method requires a catalyst. To prepare the catalyst, weigh 0·5 gm. of aluminium foil and cut it into six pieces. Take four evaporating basins, containing respectively a solution of mercuric chloride, water, alcohol and benzene. Place a piece of aluminium in the mercuric chloride solution for a minute, then wash it in turn in each of the other liquids, leaving it finally to stand in the benzene. Repeat with the other pieces.

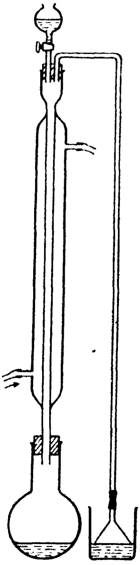
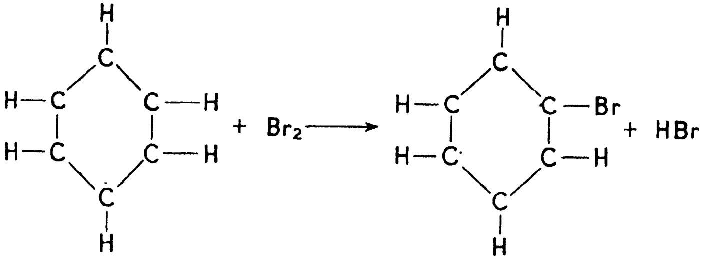


Fig. 58.

Take 55 c.c. of benzene in the flask (Fig. 58), add the prepared catalyst, and attach the flask to the rest of the apparatus. Pour sodium hydroxide solution into the beaker until the rim of the funnel is just submerged. Pour a measured 20 c.c. of bromine into the tap-funnel. (Care when using bromine.) Allow the bromine to drip into the benzene at the rate of one drop a second. (The action is exothermic. Hydrogen bromide is evolved freely and is absorbed by the sodium hydroxide.) When all the bromine has been added, allow the mixture to cool, then transfer it to a separating funnel and shake with dilute sodium hydroxide solution. Run off the lower layer into a flask, add pieces of calcium chloride and leave to dry. When clear, decant into a distilling flask. Distil and collect the fraction between 150° C. and 160° C. Yield 50 gm..



Note. Iron and pyridine will catalyse this reaction. This may be illustrated as follows:—

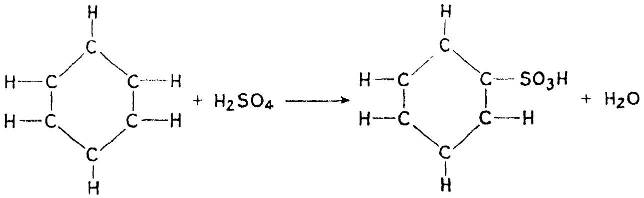
Put 6 drops of benzene into each of three test-tubes followed by three drops of bromine. To one tube add iron filings and to another a few drops of pyridine. Warm if necessary to promote the action. The tube without a "carrier" shows no evidence of reaction whilst hydrogen bromide is evolved in each of the other two.

Experiment 203. Preparation of the sodium salt of benzene sulphonic acid. Introduction of $-SO_3H$.

Formula of the sodium salt: $C_6H_5.SO_3Na$. White crystalline solid.

Apparatus: Flask (250 c.c.) fitted with a reflux condenser; sand-tray; large flask (1·5 litres); Buchner funnel and flask; large evaporating basin; measuring cylinder; water-bath; muslin bag. *Material*: Benzene; slaked lime.

Take 50 c.c. of benzene in the 250 c.c. flask and add 50 c.c. of conc. sulphuric acid. Fit the flask with a reflux condenser* and heat on a sand-tray until the two layers merge into one. (Time about three hours.) Allow to cool, then pour the contents of the flask (chiefly benzene sulphonic acid and excess sulphuric acid) into about a litre of water in the large flask. Heat the solution and add slaked lime as a thick paste until a test drop of the liquid is alkaline to litmus. Filter while hot, first through a muslin bag, and then through a Buchner funnel. (The solution is chiefly the calcium salt of benzene sulphonic acid, and the solid chiefly calcium sulphate.) To obtain the sodium salt, first evaporate the solution to about half its volume and then add a conc. solution of sodium carbonate until a test portion of the filtrate no longer gives a precipitate with sodium carbonate solution. Filter the mixture through a Buchner funnel, several times, until the filtrate is clear. (The solution is sodium benzene sulphonate and the solid is calcium carbonate.) Evaporate the solution on a gauze until crystals begin to deposit, and then continue on a water-bath until general crystallisation occurs. Set the basin aside and when cold filter off the crystals and dry them on a pad of filter papers or on a porous plate. Sodium benzene sulphonate may be used to prepare phenol (see Expt. 211). Yield 60 gm.



$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5.SO_3H + H_2O$$

---

* A wide inner tube without taper at the lower end must be used.

Experiment 204. Preparation of acetophenone. Introduction of —$COCH_3$.

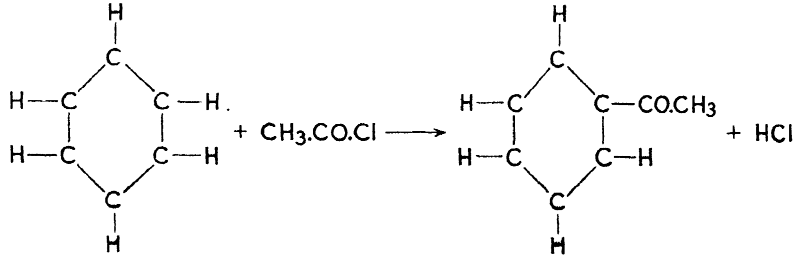
Formula: $C_6H_5.COCH_3$. *Physical properties*: white solid. *M.P.* 20·5° C.

Apparatus: Flask (500 c.c.); reflux condenser; tap-funnel; glass tube (see Fig. 58); **ICE**; thermometer (360° C.); distilling flask; measuring cylinder. *Material*: Benzene; acetyl chloride; fresh anhydrous aluminium chloride.

The preparation is an example of the Friedel and Craft's reaction. Acetophenone is a ketone with the general properties of an aliphatic ketone.

The preparation depends for its success on the quality of the anhydrous aluminium chloride, and although it can be prepared in the laboratory by heating aluminium strongly in a stream of chlorine, the preparation in the quantity required is tedious. It is best to buy the compound as required, preferably in 2 oz. quantities so that the whole bottleful can be used up. Transfer 2 oz. (approximately 56 gm.) to the 500 c.c. flask and cover it immediately with 35 c.c. of benzene. Attach the flask to a reflux condenser, and arrange the apparatus as shown in Fig. 58, but with the flask standing in ice. Take a measured 35 c.c. of acetyl chloride in the tap-funnel and allow it to drip slowly into the flask. When all the acetyl chloride has been added, leave the apparatus in position for an hour and then pour the contents into about 150 c.c. of ice-cold water. Decant the clear liquid from the solid residue into a separating funnel. Add 20 c.c. of benzene, shake well and allow to settle. Run off the lower layer and discard it. Wash the retained solution (of acetophenone in benzene) with water, and again run off the lower layer, then run the acetophenone-benzene solution into a flask, add calcium chloride and leave to dry. Decant the clear liquid into a distilling flask and distil. When the temperature reaches 130° C., empty the condenser and continue with the distillation. Collect the fraction between 195° C. and 200° C. and leave it to solidify. The yield is small.

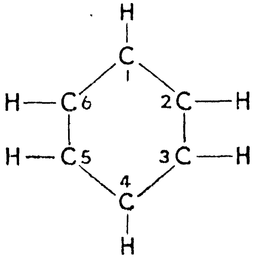
(If ethyl iodide were used in place of acetyl chloride, the ethyl group would be introduced into the benzene molecule to give ethyl-benzene.)

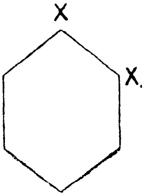


$$C_6H_6 + CH_3.CO.Cl \longrightarrow C_6H_5.CO.CH_3 + HCl$$

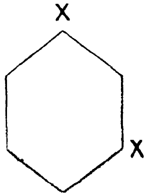
THEORY

Introduction of a second group into the benzene nucleus. When one hydrogen atom of the benzene nucleus has been displaced by a group, a second hydrogen atom may be displaced by a similar or by a different group. There are three possible positions in the benzene nucleus for this second group to occupy, namely, on the next carbon atom, or on the next but one, or on the carbon opposite. If the carbon atoms are numbered for reference, starting with 1 for the position occupied by the group originally present and progressing in a clock-wise direction, the second group may occupy position 2, 3 or 4. Positions 5 and 6 are positionally identical with 3 and 2 respectively. The prefix ortho-, meta-, or para- is given to those substitution compounds which have their groups respectively in positions 1.2, 1.3, or 1.4.

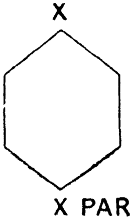




ORTHO



META



PARA

Position occupied by the second group. The group which is first into the benzene nucleus determines the position which the second group will occupy. If the first group is either $-NO_2$, $-SO_3H$, $-CHO$, or $-COOH$, the next incoming group, whatever the group might be, will displace the hydrogen atom which is attached to the carbon atom in the meta position. If the first group is either $-NH_2$, $-OH$, $-Cl$, $-Br$, $-I$, or an alkyl radical, the next incoming group will displace the hydrogen atom attached to the carbon in the ortho position in some of the molecules and the hydrogen atom attached to the carbon in the para position in the remaining molecules. Thus the product will not be a single compound but a mixture of two compounds, and a separation based on their physical differences will be necessary.

Experiment 205. Preparation of meta-dinitrobenzene. Example of further substitution.

Formula: $C_6H_4(NO_2)_2$.

Physical properties: pale yellow solid, *M.P.* 90° C.

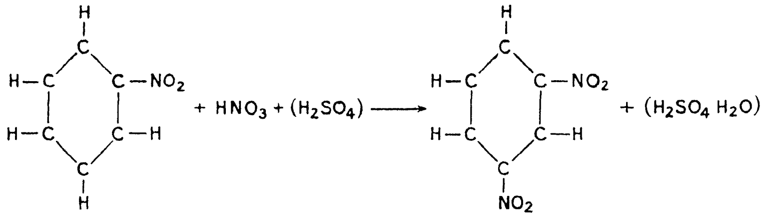
Apparatus: Flask (250 c.c.); large basin; water-bath; filter funnel (preferably a Buchner); crystallising dish; measuring cylinder.

Material: mono-nitrobenzene; fuming nitric acid; industrial spirit.

(a) *Small scale preparation.* Mix five drops each of fuming nitric acid and conc. sulphuric acid in a boiling-tube. Add five drops of mono-nitrobenzene, shake the mixture, and heat almost to boiling for about a minute. Pour into a test-tube half filled with water.

The solid is meta-dinitrobenzene. Filter off the solid, and add it to about 10 c.c. of alcohol. Heat the test-tube and contents in a beaker of boiling water until the solid has dissolved, then pour the solution into a crystallising dish to cool. Filter to obtain pale yellow crystals of meta-dinitrobenzene.

(b) *Larger scale preparation.* Measure 24 c.c. of fuming nitric acid into a 250 c.c. flask. Add 20 c.c. of conc. sulphuric acid and allow the mixture to cool. Add 25 c.c. of mono-nitrobenzene in portions of about 5 c.c., shaking the mixture well between additions. Place the flask on the water-bath and heat for about a quarter of an hour. Test for the completion of the reaction by pouring a few drops of the liquid into a beaker of water to find whether it will solidify; if it does not, continue to heat. Pour the whole of the liquid into about 250 c.c. of water in a basin, and leave until cold. Filter, and recrystallise the yellow solid from alcohol. The product may be used for the preparation of meta-nitraniline (Expt. 209). Yield 25 gm.



$$C_6H_5.NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$$

INDIRECT SUBSTITUTION

Of the groups which are introduced into the benzene ring by an indirect method, —NH_2 is the most important. Not only is aniline ($C_6H_5.NH_2$) of interest, but from aniline other compounds of importance can be produced.

Experiment 206. Preparation of aniline. Introduction of —NH_2 (the amino group).

Formula: $C_6H_5.NH_2$. *Physical properties*: colourless oil. *B.P.* 184° C. *Sp.G.* 1·02.

Apparatus: Large flask (1·5 litres); inner tube of a condenser (about 30 in. long); water-bath; separating funnel; measuring cylinder; distilling flask (250 c.c.); steam distillation apparatus as in Fig. 59. *Material*: Mono-nitrobenzene; tin; caustic soda; ether.

(a) *Small scale preparation.* Take five drops of mono-nitrobenzene in a test-tube and add five times that volume of conc. hydrochloric acid and about 2 gm. of tin. Stand the test-tube in boiling water. Keep the test-tube at this temperature, shaking the tube from time to time, until there are no longer oily drops of nitrobenzene. The action is vigorous at first, and if necessary, the test-tube should be removed until the action moderates. Prepare a solution of caustic soda by dissolving about an eighth of a stick in 10 c.c. of water, and add this solution until the precipitate which first forms is almost dissolved. Cool the test-tube under the tap, then add about 5 c.c. of ether. Shake the mixture gently, allow to stand, and decant the ether layer into a dry test-tube. Stand the test-tube in hot water (no flame) to drive off the ether. The aniline so obtained will be impure, but may be used for the tests described later (Expt. 207).

(b) *Larger scale preparation.* Take a large flask and mix in it 40 c.c. of mono-nitrobenzene and 85 gm. of granulated tin. Fit the flask with a cork and air condenser and heat on a water-bath for a quarter of an hour. From a measured 160 c.c. of conc. hydrochloric acid add 10 c.c. and shake the mixture. Every five minutes add another 10 c.c. of acid and shake. When all the acid has been added, leave the flask warming on the water-bath for half an hour. During this period prepare a solution of 140 gm. (about six sticks) of caustic soda in 200 c.c. of water. (Care should be taken in handling this concentrated solution of caustic alkali.) Add this solution, in portions of about 50 c.c. at a time, until the precipitated stannic hydroxide has almost dissolved and the solution is alkaline. The aniline will then be free and appear as an oil. Distil the mixture in steam, by passing steam from the boiler into the mixture while the latter is being heated on a sand-tray or gauze. Collect the condensed vapours in a receiver (see Fig. 59) until no more oily drops pass down the condenser.

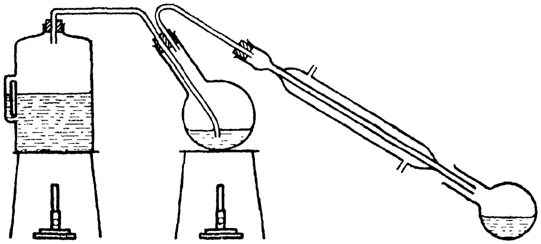


FIG. 59.

Transfer the distillate to a separating funnel and extract the aniline with ether. Use 90 c.c. of ether in three portions of about 30 c.c. each. Shake the first portion of ether with the aqueous aniline, lifting the stopper from time to time to avoid a high pressure in the funnel, then run off the lower (aqueous) layer into a beaker and the upper (ether-aniline) layer into a flask. Return the aqueous layer to the funnel, add the second portion of ether and proceed as before, and so on with the third. To dry the ether-aniline solution, add about half a stick of caustic soda and leave the flask, corked, until the liquid is clear. Decant the liquid into a distilling flask fitted to a sloping condenser, and proceed as described in Expt. 148. Yield 25 gm.

$$C_6H_5.NO_2 + 6H \rightarrow C_6H_5.NH_2 + 2H_2O$$

STEAM DISTILLATION

Aniline boils at 184° C. When steam at 100° C. is passed into aniline a mixture of aniline and water distils over at a temperature below 100° C. The theoretical considerations are as follow:—

(i) Aniline and water are immiscible.

(ii) Mixtures of immiscible liquids have a vapour pressure equal to the sum of the separate pressures of the constituents.

(iii) The boiling point of a liquid (or a mixture of liquids) is the temperature at which the vapour pressure (or total vapour pressure) is equal to the atmospheric pressure.

(iv) During distillation in these circumstances, the vapour contains both constituents, and contains them in the ratio by volume of their separate vapour pressures at the temperature at which the mixture is boiling. Thus if the atmospheric pressure is 760 mm., and if a mixture of aniline and water boils at 98° C., the vapour pressure due to water vapour will be 710 mm. (see Tables, p. 377). By difference, the pressure due to aniline vapour will be 50 mm. The ratio of water vapour to aniline vapour will be given by the expression:—

$$\frac{\text{Volume of water vapour}}{\text{Volume of aniline vapour}} = \frac{\frac{710}{760}}{\frac{50}{760}} = \frac{14{\cdot}2}{1}$$

(v) The mass of each constituent in the distillate will be the product of its volume and its vapour density. Thus,

$$\frac{\text{Mass of water}}{\text{Mass of aniline}} = \frac{\frac{710}{760} \times 9}{\frac{50}{760} \times 46{\cdot}5} = \frac{2{\cdot}75}{1}$$

Experiment 207. Reactions of aniline.

Material: Aniline; bleaching powder; chloroform; **ICE** or solid ammonium chloride; β-naphthol; acetyl chloride.

Two drops of aniline are sufficient for each reaction.

(a) Add three drops of water. Note the immiscibility. To the mixture add five drops of conc. hydrochloric acid. The clear solution contains aniline hydrochloride.

$$C_6H_5.NH_2 + HCl \rightarrow C_6H_5.NH_2.HCl$$

Now add sodium hydroxide solution until the mixture is alkaline. The emulsion is due to the reappearance of free aniline.

(b) Add to a test-tube full of water and shake thoroughly. Add a drop of a prepared solution of bleaching powder in water. The violet coloration serves as a test for aniline. Repeat the test, using a much smaller quantity of aniline and show that the test is a very delicate one.

(c) Repeat the carbylamine (iso-cyanide) test as given in Expt. 169(c).

(d) Add two drops of water and five drops of conc. hydrochloric acid, and to the solution of aniline hydrochloride so made, add bromine water until the solution is just yellow. Shake the solution and leave to stand. The yellow crystals are tribromaniline.

$$C_6H_5.NH_2 + 3Br_2 = C_6H_2.Br_3.NH_2 + 3HBr$$

(e) Prepare aniline hydrochloride solution as above and cool it at least to 4° C. in ice or in a beaker containing water and solid ammonium chloride. Prepare a test-tube a quarter full of a saturated solution of sodium nitrite. Take a third test-tube, add enough β-naphthol to cover the bottom of the tube and add caustic soda solution to dissolve it. Leave the test-tubes to cool for a few minutes, then mix gradually the aniline hydrochloride and sodium nitrite. Finally add the β-naphthol to obtain a red dye.

(f) Add two drops of acetyl chloride. Warm gently, allow to cool and then add water. The solid is acetanilide. (See Expt. 208.)

Experiment 208. Preparation of acetanilide.

Formula: $C_6H_5.NH.CO.CH_3$. *Physical properties*: white crystalline solid. *M.P.* 112° C.

Apparatus: Flask (250 c.c.); inner tube of condenser; thermometer and tubing as shown in the diagram (Fig. 60); Buchner funnel and flask; large basin or trough; large (1 litre) flask. *Material*: Re-distilled aniline; industrial methylated spirits.

In the flask mix 25 c.c. of aniline and 30 c.c. of glacial acetic acid. Attach the air condenser as shown. Heat on a gauze and adjust the flame so that the thermometer in the condenser reads 105° C. Heat for two hours.

Pour the hot liquid into about 500 c.c. of water in a large basin. The crystals are acetanilide. Filter in the Buchner and wash with water. Transfer the crystals to a large flask (1 litre) and fill the flask three-quarters full of water. Add 10 c.c. of alcohol and boil until the solid has dissolved (if some remains undissolved it may be treated later). Pour the solution into a large basin and leave to crystallise. Yield 25 gm.

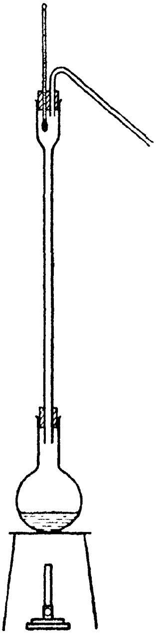
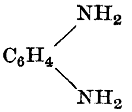


FIG. 60.

$$C_6H_5.NH_2 + CH_3.COOH \rightarrow \underset{\text{(acetanilide)}}{C_6H_5.NH.CO.CH_3} + H_2O$$

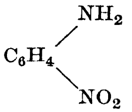
THEORY

Partial Reduction. When meta-dinitrobenzene is reduced with tin and hydrochloric acid, both nitro-groups are reduced to amino- (—NH_2) groups. The product has, therefore, a benzene nucleus with two —NH_2 groups in the meta position to each other; the compound is meta-phenylene diamine,



$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$$

It is, however, possible to reduce one of the —NO_2 groups and leave the other. This resulting compound has the formula,



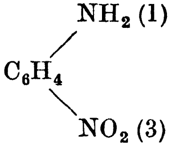
$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NO_2\end{matrix}$$

and is called meta-nitro-aniline or meta-nitraniline.

The reducing agent to effect this partial reduction is hydrogen sulphide in ammoniacal solution.

Experiment 209. Preparation of meta-nitraniline.

Formula:



$$C_6H_4\begin{matrix}\diagup NH_2\,(1)\\ \diagdown NO_2\,(3)\end{matrix}$$

Physical properties: light brown needle crystals. *M.P.* 114° C.

Apparatus: Flask ($\frac{1}{2}$ litre); wash-bottle; water-bath; measuring cylinder; Buchner funnel and flask; crystallising dish. *Material*: Meta-dinitrobenzene; industrial alcohol.

In the flask mix 20 gm. of meta-dinitrobenzene, 75 c.c. of alcohol, and 10 c.c. of conc. (0·880) ammonium hydroxide.

Pass hydrogen sulphide first through water in the wash-bottle and then into the mixture, shaking the flask well from time to time. After half an hour heat the flask on the water-bath for about a quarter of an hour.

Pass hydrogen sulphide in again for a quarter of an hour, then heat again and continue until the gas has been passed in for a full hour (total time including periods of heating is about two hours). Add 200 c.c. of water to precipitate the meta-nitraniline from alcoholic solution, then filter through the Buchner funnel. Discard the filtrate, and return the solid to the flask. Take 200 c.c. of dilute hydrochloric acid, made by adding 150 c.c. of water to 50 c.c. of the conc. acid, and heat almost to boiling. Use the acid in portions of 50 c.c. at a time to dissolve the meta-nitraniline from the solid and decant each time through the Buchner; the undissolved portion consists chiefly of sulphur and unchanged meta-dinitrobenzene.

The solution, which is the hydrochloride of meta-nitraniline, is then made alkaline to set free the base. Add conc. ammonium hydroxide until there is no further precipitation and filter. Test the filtrate with ammonium hydroxide to ensure that the action is complete, then discard the filtrate. Add 200 c.c. of water to the solid and heat to boiling. Decant the solution into a large dish; repeat with any residual solid. When cold, filter off the crystals. Yield 10 gm.

THEORY

Introduction of —OH group into the benzene nucleus. The hydroxyl group may be introduced by two methods:—

1. By 'diazotising' aniline and then heating.
2. By heating sodium benzene sulphonate with caustic soda.

Note (a) the hydroxyl group cannot be introduced directly into the benzene nucleus,

(b) —Cl, —Br and —I cannot be displaced by —OH (compare the hydrolysis of alkyl halides, Expt. 164 (a)). It is important to remember that once a halogen has been introduced into the benzene nucleus it is very difficult to displace it.

Experiment 210. Preparation of phenol from aniline.

Formula of phenol: $C_6H_5.OH$. *Physical properties*: colourless needle crystals. *M.P.* 43° C.

Apparatus: Flask (250 c.c.); steam distillation apparatus as shown in Fig. 59; separating funnel; measuring cylinder; thermometer (360° C.); freezing mixture (**ICE**-salt) in a large basin or trough. *Material*: Re-distilled aniline; sodium nitrite; anhydrous sodium sulphate; ether.

Take 100 c.c. of water in the 250 c.c. flask, add a measured 24 c.c. of conc. sulphuric* acid, and while still hot add 20 c.c. of aniline. Cool the solution to room temperature and then place in the freezing mixture.

Prepare a solution of sodium nitrite by dissolving 16·5 gm. in 40 c.c. of water in the conical flask and transfer it to the tap funnel.

When the aniline hydrogen sulphate solution has cooled to 0° C., allow the sodium nitrite solution to drip in very slowly and then adjust the funnel so that its end is under the surface of the liquid in the flask. Keep the liquid agitated and see that the temperature does not rise above 2° C. during the addition. Shake the mixture and leave in the freezing mixture for a quarter of an hour, then transfer to a water-bath and heat for half an hour. Arrange the apparatus for steam distillation (Fig. 59). Pour the mixture into

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* Sulphuric acid is used in preference to hydrochloric because the intermediate compound benzene diazonium chloride is *slightly* decomposed to give chloro-benzene as an impurity. Benzene diazonium hydrogen sulphate does not decompose in this manner.

the large flask and heat almost to boiling before passing in the steam. When no more phenol distils over, transfer the aqueous distillate to a separating funnel and extract with ether, using 90 c.c. of ether in three fairly equal portions. Dry the ether-phenol solution by adding about 10 gm. of anhydrous sodium sulphate. (To obtain this quantity, heat about 25 gm. of crystalline sodium sulphate in an evaporating basin until there is no further loss of moisture.)

When dry, distil the solution, first over hot water in a water-bath (no bunsen) until the ether has all distilled and then over a gauze. Empty the condenser at 130° C. and continue with the distillation. Collect the fraction between 180° C and 185° C.; this solidifies. Yield 7 gm.

$$C_6H_5.NH_2.H_2SO_4 + HNO_2 \rightarrow C_6H_5N{=}N.HSO_4 + 2H_2O$$
$$C_6H_5.N{=}NHSO_4 + H_2O \rightarrow C_6H_5.OH + N_2 + H_2SO_4$$

THEORY

The action of nitrous acid (sodium nitrite in acid solution) on an amino-group depends (a) on the position of the $-NH_2$ group and (b) on the temperature.

If the $-NH_2$ group is *in the nucleus* and the temperature is in the region of 0° C. the nitrogen of the $-NH_2$ and the nitrogen of the nitrous acid remain in the molecule of the new compound to form a "diazonium compound"

$$\underset{}{C_6H_5.NH_2.HCl} + HNO_2 \rightarrow \underset{\text{benzene diazonium chloride}}{C_6H_5N{=}N.Cl} + 2H_2O$$

If the $-NH_2$ group is in the nucleus and *the temperature is not kept low*, there is an evolution of nitrogen and the $-NH_2$ group is replaced by $-OH$ to give a phenol.

If the $-NH_2$ group is in the side-chain it behaves as it does in an aliphatic compound; *whether hot or cold* it is replaced by an $-OH$ group.

Experiment 211. Preparation of phenol from sodium benzene sulphonate.

Apparatus: Nickel basin (diameter about 3 in.); thermometer (360° C.); flask (250 c.c.); separating funnel; water-bath; distilling flask and condenser. *Material*: Sodium benzene sulphonate; caustic soda; ether; anhydrous sodium sulphate.

Place 1½ sticks (35 gm.) of caustic soda in the basin, add 5 c.c. of water and heat with a small flame until solution is complete. Fit a thermometer with a small test-tube to enclose the bulb (see Fig. 61). Add gradually 20 gm. of crushed sodium benzene sulphonate, using the fitted thermometer as a stirring rod, and keeping the temperature between 240° C. and 250° C. After an hour, the mass is allowed to cool.

Add small quantities of water and heat to dissolve the solid

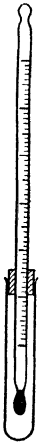


FIG. 61.

and decant the solution into a flask. [The solution contains sodium phenate, $C_6H_5.ONa$, sodium sulphite, and excess caustic soda.] Add conc. hydrochloric acid until the solution is definitely acidic. Note the smell of sulphur dioxide from the sodium sulphite, and the brown oil (phenol).

Extract the phenol with ether, using 45 c.c. in three portions. Dry the ether-phenol solution with anhydrous sodium sulphate and distil as in Expt. 210. The yield is small.

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$
$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$$

Experiment 212. Reactions of phenol.

Apparatus: Thermometer (100° C.). *Material*: Phenol; Millon's reagent; sodium nitrite; zinc powder.

N.B. Phenol is corrosive. When using it take care that solid phenol or a strong solution of it does not remain on the skin.

Make a stock solution of phenol by covering the bottom of a test-tube with the solid and filling almost to the top with water. Use this solution in approximately equal parts for tests (a), (b) and (c).

(a) Add one drop of ferric chloride solution. Note the violet coloration.

(b) Add bromine water and shake. Add sufficient bromine water to leave the solution a definite brown colour. Note the white precipitate of tribromphenol.

$$C_6H_5.OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$$

(c) Add a drop of Millon's reagent (see p. 365). Stand the test-tube in a beaker of water and heat gradually. Note the red coloration.

(d) Take ten drops of conc. sulphuric acid in a test-tube. Add a quantity of sodium nitrite about the size of a match-head and warm gently until dissolved. Add one or two crystals of phenol. Pour the liquid into a beaker one quarter full of water. Note the red coloration. Add caustic soda solution and note the change of colour to blue. This is *Liebermann's Reaction.*

(e) Take enough phenol to cover the bottom of a test-tube and add water to a depth of one inch. Cork the test-tube and shake to obtain an emulsion. Remove the cork, place the test-tube in a beaker of water and warm. Stand a thermometer in the phenol solution and note the temperature when the emulsion clears. Allow to cool and note the reappearance of cloudiness. See Expt. 42.

(f) Take the emulsion from the previous experiment and carefully add caustic soda solution until a clear solution of sodium phenate is obtained. Add a few drops of conc. hydrochloric acid and note the reappearance of phenol.

$$C_6H_5.OH + NaOH \rightarrow C_6H_5.ONa + H_2O$$
$$C_6H_5.ONa + HCl \rightarrow C_6H_5.OH + NaCl$$

(g) Mix in a dry test-tube enough phenol to fill a salt-spoon and about three times that bulk of zinc powder. Heat the mixture and light the benzene vapour at the mouth of the test-tube. The zinc has reduced the phenol and become zinc oxide.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

THEORY

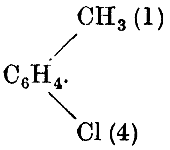
Introduction of groups by diazotisation of aniline. Sandmeyer Reaction. In the preparation of phenol from aniline, the aniline was treated with nitrous acid at 0° C. and gave a diazonium salt.

Diazonium salts are important intermediary compounds for the introduction of —Cl, —Br, —I, —CN. Thus from aniline, chlorobenzene, bromobenzene, iodobenzene and benzonitrile can readily be prepared. Since the —CN group can be reduced to $—CH_2.NH_2$, or hydrolysed to —COOH, benzylamine ($C_6H_5.CH_2.NH_2$) and benzoic acid may be added to the list. Note that —Cl and —Br can also be directly introduced (see Expt. 202) but iodine must be introduced via the diazo compound. The —CN group may be introduced either by a method similar to that used for the preparation of phenol (Expt. 211), namely, by fusing sodium benzene sulphonate with potassium cyanide, or via the diazo compound.

In general the method consists of diazotising the aniline and then mixing the diazonium salt with the cuprous compound containing the group to be introduced. The product is then isolated by steam distillation.

Experiment 213. Preparation of para-chlorotoluene. Sandmeyer Reaction.

Formula:



$$C_6H_4 \begin{cases} CH_3\ (1) \\ Cl\ (4) \end{cases}$$

Physical properties: oily liquid. *B.P.* 163° C.

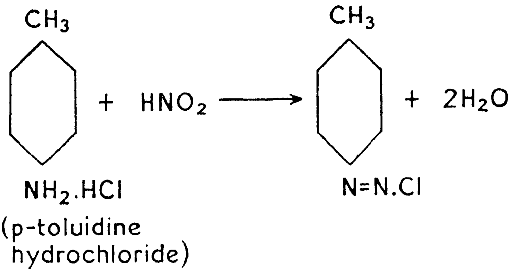
Apparatus: Large flask (1½ litre); flask (250 c.c.); tap funnel; steam distillation apparatus; distilling flask; freezing mixture (**ICE**-salt) in a large basin or trough; measuring cylinder; thermometer (360° C.). *Material*: Para-toluidine; sodium nitrite.

Dissolve 25 gm. of para-toluidine in a solution of 60 c.c. of conc. hydrochloric acid and 40 c.c. of water in a 250 c.c. flask and stand in a freezing mixture.

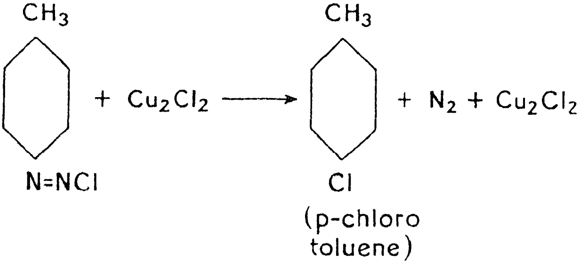
Take 250 c.c. of conc. hydrochloric acid in the 1½ litre flask, add 10 gm. of copper oxide and heat to dissolve. Add 15 gm. of copper foil or turnings to the cupric chloride solution and boil in a fume chamber until the dark colour has disappeared. Cool this solution of cuprous chloride and stand the flask loosely corked in a freezing mixture.

Dissolve 18·5 gm. of sodium nitrite in 40 c.c. of water in the conical flask and transfer it to the tap funnel.

When the para-toluidine hydrochloride solution has cooled to 0° C. allow the sodium nitrite solution to drip slowly into it at such a rate that the temperature does not rise above 8° C. The para-toluidine has then been diazotised.



Add the diazonium compound in portions of about 10 c.c. at a time to the cuprous chloride solution, shaking well between additions, to obtain a golden yellow solid—a loose compound of the diazonium salt and the cuprous chloride.



Arrange the apparatus for steam distillation (Fig. 59) and warm the contents of the flask before passing in the steam. Transfer the aqueous distillate to a separating funnel and shake with dilute caustic soda solution to dissolve any para-cresol. Run off the lower layer into a flask and dry with pieces of calcium chloride.

Distil the dry liquid and collect the fraction distilling between 155° C. and 165° C. Yield 20 gm.

Experiment 214. Preparation of iodobenzene.

Formula: $C_6H_5.I$. *Physical properties*: heavy yellow liquid. *B.P.* 190° C. *Sp.G.* = 1·84.

Apparatus: Flask (250 c.c.); measuring cylinder; separating funnel; water-bath; condenser; distilling flask; apparatus for steam distillation; thermometer (360° C.). *Material*: Re-distilled aniline; sodium nitrite; potassium iodide; ether; calcium chloride.

The method follows the usual course of Sandmeyer Reactions, but in this case the cuprous salt may be replaced by the potassium salt.

Diazotise 20 c.c. of aniline in exactly the same way as in the preparation of phenol from aniline (Expt. 210). To the cold diazonium salt add a solution of 40 gm. of potassium iodide in 100 c.c. of water. Mix well and allow to stand for about a quarter of an hour. Fit the flask with a reflux condenser and heat on a water-bath until effervescence (nitrogen) has almost ceased, then steam distil. See Fig. 59.

Transfer the aqueous distillate to a separating funnel and extract three times with ether, using 30 c.c. of ether for each extraction. Wash the ether-iodobenzene solution first with water, then with dilute caustic soda solution to remove traces of phenol, and then with water again. Run off the ether layer into a flask and dry with calcium chloride.

Distil the dry liquid, first over hot water in a water-bath (no bunsen) and, when the ether has distilled off, over a gauze. When the temperature has reached 130° C., empty the condenser and continue to distil, collecting the fraction between 187° C. and 192° C. Yield 30 gm.

$$C_6H_5NH_2 + HNO_2 + H_2SO_4 \rightarrow C_6H_5N = N.HSO_4 + 2H_2O$$
$$C_6H_5N_2HSO_4 + KI \rightarrow C_6H_5I + N_2 + KHSO_4$$

Experiment 215. Small scale preparation and reactions of benzene diazonium chloride.

Apparatus: Thermometer (100° C.); measuring cylinder. *Material*: Aniline; cuprous chloride in conc. hydrochloric acid; alcohol (industrial spirit); **ICE;** phenol; 20 % potassium iodide solution.

Measure 13 c.c. of conc. hydrochloric acid in a measuring cylinder and add an equal volume of water. Add this to 5 c.c. of aniline in a boiling-tube and stand the test-tube in a beaker containing ice. Make a solution of sodium nitrite containing 4·5 gm. of the solid in about 10 c.c. of water, and add this, a little at a time, stirring with a thermometer and keeping the temperature between 5° and 10° C. (this temperature is low enough to prevent much decomposition without being so low as to retard the action appreciably).

$$C_6H_5.NH_2 + HNO_2 + HCl \rightarrow \underset{\text{(benzene diazonium chloride)}}{C_6H_5.N = N.Cl} + 2H_2O$$

Use about 5 c.c. of this solution for each of the following experiments:—

(a) Boil. Nitrogen is evolved and the smell of phenol observed.

$$C_6H_5.N = N.Cl + H_2O \rightarrow C_6H_5.OH + N_2 + HCl$$

(b) Add about 2 c.c. of potassium iodide solution. On warming, there is an effervescence and a brown liquid, iodo benzene, is formed.

$$C_6H_5N = N.Cl + KI \rightarrow C_6H_5I + N_2 + KCl$$

(c) Add about 2 c.c. of a cuprous chloride solution in hydrochloric acid and warm. Nitrogen is evolved and an oily liquid, chlorobenzene, is formed.

$$C_6H_5N = N.Cl + Cu_2Cl_2 \rightarrow C_6H_5Cl + N_2 + Cu_2Cl_2$$

(d) *Gattermann's reaction.* Prepare a small quantity of finely divided copper by sprinkling zinc dust from a muslin bag into copper sulphate solution. Decant the liquid and wash the copper with dilute sulphuric acid, then with water. Add the copper to the diazonium chloride. Note the effervescence (nitrogen). The main product (chlorobenzene) would be separated, if the experiment were done on a larger scale, by steam distillation.

$$C_6H_5N = NCl \rightarrow C_6H_5Cl + N_2$$

(e) Add a solution of phenol in caustic soda. A light red precipitate of sodium hydroxyazobenzene is formed.

$$C_6H_5N = N.Cl + C_6H_5ONa \rightarrow C_6H_5N = NC_6H_4ONa + HCl$$

(f) Add a few drops of aniline and shake the mixture. The yellow precipitate is diazo-aminobenzene.

$$C_6H_5N = N.Cl + C_6H_5NH_2 \rightarrow C_6H_5N = NNHC_6H_5 + HCl$$

(g) Add 10 c.c. of industrial methylated spirit and warm. Nitrogen is formed, benzene floats on the surface, and a smell of acetaldehyde may sometimes be observed.

$$C_6H_5N = N.Cl + C_2H_5OH \rightarrow C_6H_6 + N_2 + CH_3CHO + HCl$$

Phenetole (phenyl-ethyl-ether) is also formed.

THEORY

Introduction of —Cl group into a side-chain. Toluene consists essentially of the two radicals, phenyl ($-C_6H_5$) and methyl ($-CH_3$) linked together. Actions affecting the methyl group (the side-chain) follow the general course expected with aliphatic compounds. Thus the introduction of the —Cl group into the side-chain requires a different method from either of the two already given for introducing this group into the benzene nucleus. The experiment should be conducted in bright sunlight (a factor which is required for displacing hydrogen by chlorine in methane), and the toluene must be kept at boiling point.

Experiment 216. Preparation of benzyl chloride.

Formula: $C_6H_5.CH_2Cl$. *Physical properties*: colourless fuming, irritating liquid. *B.P.* 176° C.

Apparatus: Retort (250 c.c.); condenser fitted as in Fig. 62; distilling flask; sand-tray; thermometer (360° C.). *Material*: Toluene; steady supply of chlorine; conc. sulphuric acid in a drying bottle; phosphorus trichloride (not essential).

Weigh the retort together with its leading-in tube. Add 50 c.c. of toluene and weigh again. The addition of a little phosphorus trichloride helps the chlorination, but it is not essential. If it is decided to use it, add three or four drops and weigh again. This will be the total weight referred to later.

Connect the retort to the condenser either by a bored cork or by a piece of overlapping rubber tubing. Connect the flask in which the chlorine is to be generated to the drying bottle and that in turn to the tube leading into the retort.

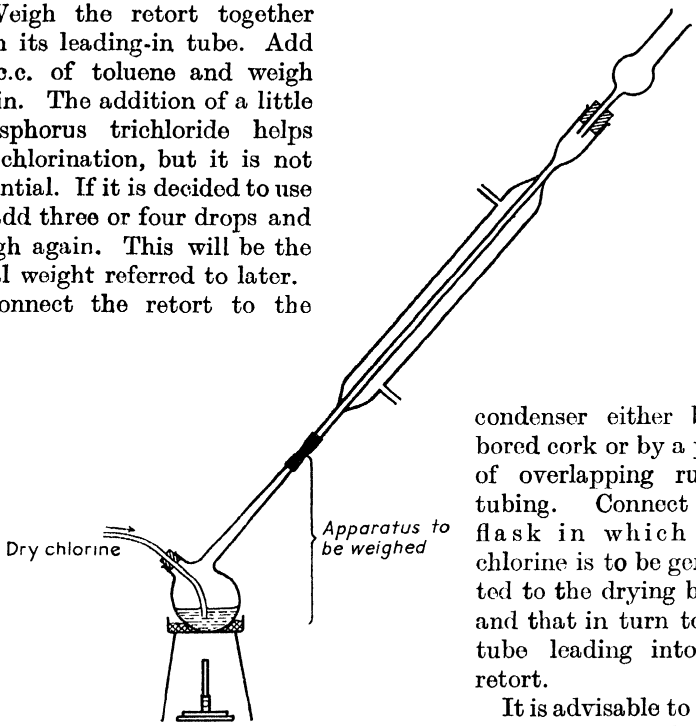
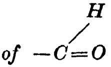
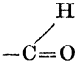


Fig. 62

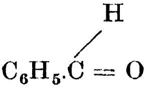
It is advisable to close the calcium chloride tube with a cork and a delivery tube which leads to the window.

Heat the retort on a sand-tray until the toluene boils and then pass in dry chlorine. The liquid becomes progressively darker and hydrogen chloride is evolved. After three hours steady chlorination allow the retort to cool. Since 1 gm. mol. of toluene (92 gm.) is required to lose 1 gm. of hydrogen and gain 35·5 gm. of chlorine, the required gain for the weight of toluene taken can be calculated. Find whether the original total weight has gained by the calculated amount, and if not, reassemble the apparatus and continue to chlorinate as before. When the action is complete, transfer the liquid to a distilling flask and distil. Unchanged toluene distils off at 110° C. and benzyl chloride at 176° C. Collect the fraction distilling between 175° C. and 178° C. Note the irritating smell and compare with its isomer, chlorotoluene. Yield 40 gm.

THEORY

Introduction of  $-\overset{H}{C}=O$ *group into the benzene nucleus.* The usual method of preparing aldehydes in the aliphatic series is to oxidise the corresponding alcohol (see Expt. 173). Groups in the side-chain behave generally as they would in aliphatic compounds and it would be expected that the group $-CH_2.OH$ would oxidise to  $-\overset{H}{C}=O$ and this in fact is the case; benzyl alcohol oxidises to benzaldehyde. Likewise it would be expected that as ethyl chloride hydrolyses to ethyl alcohol, so the group $-CH_2.Cl$ would hydrolyse to $-CH_2.OH$ and this also is true. If then, benzyl chloride were hydrolysed and oxidised benzaldehyde would be the product, and a single agent to effect both of these actions is copper nitrate solution.

Experiment 217. Preparation of benzaldehyde.

Formula:  $C_6H_5.\overset{H}{C}=O$. *Physical properties*: pale yellow liquid with a pleasant smell of almonds. *B.P.* 179·5° C.

Apparatus: Flask (500 c.c.); condenser; separating funnel; Buchner funnel and flask; distilling flask; sand-tray; thermometer (360° C.). *Material*: Benzyl chloride; copper nitrate; supply of carbon dioxide; ether; siphon of sulphur dioxide; calcium chloride.

In the large flask mix 20 c.c. of benzyl chloride, 17 gm. of copper nitrate and 200 c.c. of water. Attach a reflux condenser* and down the inner tube insert a piece of glass tubing long enough to reach into the liquid. Pass carbon dioxide into the liquid to displace air and then, while continuing to pass in carbon dioxide heat the flask on a sand-tray (see Fig. 63). The action takes about eight hours to complete and if the preparation is interrupted the condenser tube should be corked until the action can be resumed. The oil changes slowly to a yellow colour and the copper nitrate solution becomes paler. Transfer the yellow oil to a separating funnel and extract with 90 c.c. of ether taken in

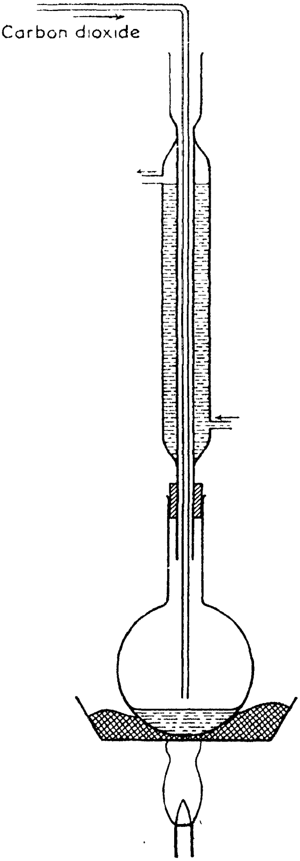


FIG. 63.

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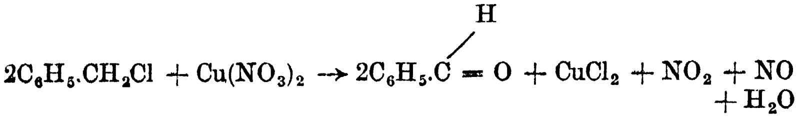
* Avoid using a condenser with a tapered end.

three portions. Distil the ether-benzaldehyde solution on a water-bath to remove the ether.

Prepare a saturated solution of sodium bisulphite in a conical flask by just covering 45 gm. of washing soda with water and then passing in sulphur dioxide until an apple-green solution is formed. Shake the oil with this solution and leave to stand for a quarter of an hour, then filter.

Return the crystals to the large flask and add dilute sulphuric acid in excess (400 c.c.) to decompose the bisulphite compound and steam distil (see Fig. 59).

Extract the aqueous distillate with ether as before and dry the ether solution with pieces of calcium chloride. Distil, first over hot water (to remove the ether) and then on a gauze. Yield 6 gm.



$$2C_6H_5.CH_2Cl + Cu(NO_3)_2 \rightarrow 2C_6H_5.\overset{H}{C} = O + CuCl_2 + NO_2 + NO + H_2O$$

Experiment 218. Reactions of benzaldehyde.

Apparatus: Separating funnel; watch-glass; distilling flask and condenser; stoppered bottle; water-bath. *Material*: Siphon of sulphur dioxide; Fehling's solution; solid caustic potash; ether; phenyl hydrazine hydrochloride.

(a) Take a drop of benzaldehyde on a watch-glass and spread the liquid. Leave to stand in the air. Note crystals of benzoic acid showing the rapid oxidation of benzaldehyde.

(b) Make an ammoniacal solution of silver oxide in a clean test-tube (see Expt. 176(a)). Add a drop of benzaldehyde and note the silver mirror.

(c) Show that benzaldehyde does not reduce Fehling's solution.

(d) Prepare a saturated solution of sodium bisulphite (see Expt. 177}. Add two drops of benzaldehyde to about 5 c.c. of the solution. The crystals are the bisulphite compound of the aldehyde.

(e) Take a small specimen tube with a well-fitted cork. Mix five drops of conc. ammonium hydroxide with one drop of benzaldehyde and set aside. Note the crystals of the condensation compound hydrobenzamide $(C_6H_5.CH)_3N_2$. Contrast with the action of acetaldehyde (*addition* compound, aldehyde-ammonia).

(f) Take enough phenyl hydrazine hydrochloride to cover the bottom of a test-tube. Add one and a half times that bulk of sodium acetate and about 1 c.c. of water to make a solution. Add two drops of benzaldehyde and obtain crystals of the hydrazone, $C_6H_5.CH{=}N.NHC_6H_5$. This reaction is characteristic of all aldehydes and ketones.

(g) Cannizzaro's Reaction. Take a bottle with a well-fitted stopper* (a 4 oz. size is suitable). Mix 20 c.c. of benzaldehyde and a solution of 20 gm. of caustic potash in 10 c.c. of water. Shake to emulsify and leave overnight.

$$2C_6H_5CHO + KOH \rightarrow C_6H_5COOK + C_6H_5.CH_2OH$$

Dissolve the solid product in the least amount of water (about 80 c.c.) and extract with 20 c.c. of ether. Run off the lower layer (potassium benzoate) and acidify with conc. hydrochloric acid to obtain a precipitate of benzoic acid.

Distil the ether-benzyl alcohol solution over hot water to remove the ether, and then heat on a gauze. Collect a few drops of the distillate. Take two drops, add ten drops of water and four drops of conc. nitric acid. Note the smell of benzaldehyde due to oxidation of the alcohol. Boil and obtain benzoic acid on cooling.

Experiment 219. Reactions of benzoic acid. $C_6H_5.COOH$.

Material: Industrial alcohol; lime; phosphorus tri- (or penta-) chloride; zinc powder; benzoic acid.

(a) Take about a salt-spoonful of benzoic acid in a test-tube and fill with water to a depth of two inches. Note the apparent insolubility. Boil to obtain a solution. Cool under the tap to re-precipitate crystals of the acid. Show that the crystals dissolve readily in sodium hydroxide solution to form sodium benzoate, $C_6H_5.COONa$, and are re-precipitated on addition of dilute acid.

(b) In a dry test-tube mix about a salt-spoonful of benzoic acid with four times its bulk of lime. Heat strongly and note the smell of benzene. Light the vapour at the mouth of the test-tube and observe the smoky flame. The lime has removed the elements of carbon dioxide to form chalk and benzene.

$$C_6H_5.COOH + CaO \rightarrow C_6H_6 + CaCO_3$$

(c) Take enough of the acid to cover the bottom of a test-tube. Add five drops of alcohol and two drops of conc. sulphuric acid. Warm gently and recognise the smell of the ester, ethyl benzoate, $C_6H_5.CO.OC_2H_5$.

(d) In a dry test-tube take enough benzoic acid to cover the bottom of the tube with a thin layer. Add an equal portion of phosphorus pentachloride or two drops of the trichloride. The liquid is benzoyl chloride.

$$3C_6H_5.COOH + PCl_3 \rightarrow 3C_6H_5.CO.Cl + H_3PO_3$$

(e) Add five drops of alcohol to the benzoyl chloride prepared in (d). Warm gently and recognise ethyl benzoate.

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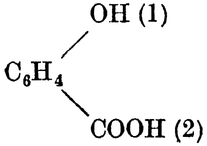
* If a glass stopper is used it should be treated with vaseline.

(f) Prepare benzoyl chloride as in (d). Take another test-tube containing three drops of conc. ammonium hydroxide and add this to the benzoyl chloride. The action is vigorous. The solid formed is benzamide.

$$C_6H_5.CO.Cl + NH_3 \rightarrow C_6H_5.CO.NH_2 + HCl \text{ (becoming } NH_4Cl\text{)}$$

(g) Heat a salt-spoonful of benzoic acid very gently with about three times the bulk of zinc powder. Note a slight smell of benzaldehyde due to partial reduction of the acid.

Experiment 220. Reactions of salicylic acid.

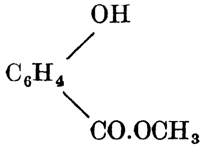


Material: Lime; salicylic acid; aspirin; methyl alcohol.

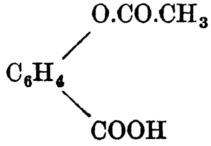
(a) Heat about a salt-spoonful of the acid with four times its bulk of lime. Note the smell of phenol. Compare the action with the similar result when benzoic acid was used.

(b) Shake two or three crystals with 10 c.c. of water in a test-tube. Add a drop of ferric chloride solution. Compare the violet coloration with that obtained with phenol. Salicylic acid is both an acid and a phenol and each group retains its individual properties.

(c) Take enough salicylic acid to cover the bottom of a test-tube. Add five drops of methyl alcohol and two drops of conc. sulphuric acid. Warm gently and recognise the "oil of wintergreen" smell of the ester, methyl salicylate.



(d) Aspirin is acetyl salicylic acid, in which the acetyl group, $-CO.CH_3$, has displaced the hydrogen atom of the $-OH$ group.



Place an aspirin tablet in a test-tube and add water to a depth of about 2 in. Add a drop of ferric chloride solution. Note the slight violet coloration. Add two drops of conc. sulphuric acid and boil. Allow to cool and observe the intense violet coloration due to hydrolysis of aspirin to salicylic acid and the subsequent action of the acid on ferric chloride.

(e) Take a test-tube one quarter full of equal parts of water and conc. sulphuric acid. Add an aspirin tablet and boil. Note the smell of acetic acid due to hydrolysis.

PART IV

THE ESSENTIALS OF VOLUMETRIC ANALYSIS

CHAPTER XXXII

INTRODUCTION

As its name implies, volumetric analysis relies on methods involving accurate measurement of volumes of liquids, though one or more weighings may also be needed. Gravimetric analysis involves only weighings. Of the two methods of analysis, gravimetric analysis is the more accurate but volumetric analysis is much more rapidly carried out. Volumetric analysis is, however, by no means inaccurate and the error involved in an analysis carried out by an experienced worker should not exceed 0·2%.

Standard Solutions. Normality. In general, a volumetric analysis is carried out by preparing a standard solution of the given material (or using a solution supplied) and determining the volume of it needed to react exactly with a known volume of another solution of accurately known strength, in a chemical reaction for which the equation is known. The course of the reaction is traced by some means, usually by an indicator showing change of colour when the reaction is complete. To take a simple case, the strength of a solution of caustic potash could be determined by adding to it the indicator methyl orange, and then causing the alkali to react with a standard solution of hydrochloric acid slowly added until the solution just becomes orange, the acid being then just in excess. This process of adding one standard solution to another to determine equivalent volumes is called *titration.*

A standard solution is one of which the concentration is known. Any kind of unit of weight or volume may be used, e.g., solutions containing, say, two oz. of common salt per gallon or three grains of sodium bicarbonate per fluid ounce, are standard solutions, inconvenient though they are for scientific purposes.

For volumetric analysis, the system of working in *normal* solution (or some multiple or submultiple of this strength) is almost universal. A normal solution is a particular kind of standard solution and is defined in the following way:—

> A normal solution of a substance is one which contains the gram-equivalent weight of the substance in one litre of solution.

For convenience such an expression as "a normal solution of caustic soda" is usually written concisely as "N.NaOH". Double normal ($2N$), semi-normal ($N/2$), decinormal ($N/10$) and centinormal ($N/100$) solutions are also commonly used and have the appropriate multiple or sub-multiple of the concentration of a normal solution.

Some Normal Solutions. One litre of a normal solution must, by definition, contain the weight in grams of the solute which is equivalent to one gram* of replaceable hydrogen. The student should make sure that he understands the following calculations and can apply the principles to similar cases.

(1) *Sulphuric Acid.*

H_2SO_4; molecular weight is 98
↑ ↑
2 gm. replaceable hydrogen in 98 gm. of acid.
∴ $N.H_2SO_4$ contains 49 gm. of the acid per litre.

Thus, for monobasic acids (i.e., acids which contain one atom of displaceable hydrogen per molecule), the equivalent is numerically the same as the molecular weight; for dibasic acids, the equivalent is half the molecular weight:—

	Equivalent
Hydrochloric acid, HCl	36·5
Nitric acid, HNO_3	63
Sulphuric acid, H_2SO_4 (Molecular Weight=98)	49
Oxalic acid, $H_2C_2O_4$ (Molecular Weight=90)	45
Oxalic acid, cryst, $H_2C_2O_4.2H_2O$ (Molecular Weight =126)	63

(2) *Caustic Soda.*

$NaOH + HCl \rightarrow NaCl + H_2O$
↑
40 gm. 1 gm. of replaceable hydrogen.
∴ $N.NaOH$ contains 40 gm. of caustic soda per litre.

The equivalent of an alkali is the weight of it which reacts, as shown in the equation, with the equivalent weight of an acid:—

$$\begin{aligned}
NaOH + HCl &\rightarrow NaCl + H_2O \\
KOH + HCl &\rightarrow KCl + H_2O \\
NaHCO_3 + HCl &\rightarrow NaCl + CO_2 + H_2O \\
Na_2CO_3 + 2HCl &\rightarrow 2NaCl + CO_2 + H_2O \\
K_2CO_3 + 2HCl &\rightarrow 2KCl + CO_2 + H_2O
\end{aligned}$$

	Equivalent
Caustic soda, $NaOH$	40
Caustic potash, KOH	56
Sodium bicarbonate, $NaHCO_3$	84
Sodium carbonate, Na_2CO_3 (Molecular Weight=106)	53
Potassium carbonate, K_2CO_3 (Molecular Weight=138)	69

(3) *Potassium Permanganate.*

This compound, when reacting in acid solution (p. 248), yields oxygen for oxidation purposes according to the basic equation:—

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* Or more accurately 1·008 gm. (O = 16·000).

$$\begin{aligned} 2KMnO_4 + 3H_2SO_4 &\rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ \therefore\ 2KMnO_4 &\equiv 5[O] \\ \therefore\ 2KMnO_4 &\equiv \underset{\uparrow}{10H} \end{aligned}$$

2(39 + 55 + 64) 10 gm. replaceable
316 gm. hydrogen.

∴ N.$KMnO_4$ should contain 31·6 gm. of potassium permanganate per litre. Such a solution cannot be used in practice because of limitations imposed by the low solubility of the compound; $N/10$ $KMnO_4$ solutions, containing 3·16 gm. per litre are usually employed.

(4) *Silver Nitrate*

$$AgNO_3 + \underset{\uparrow}{H}Cl \rightarrow AgCl + HNO_3$$

170 gm. 1 gm. of replaceable
hydrogen.

∴ N.$AgNO_3$ contains 170 gm. of silver nitrate per litre. Usually $N/10$ $AgNO_3$ (17 gm. per litre) is used.

The theoretical justification for the concentration of other normal solutions will be found at appropriate places in the text. It should be noted particularly that the **concentration of a normal solution must be calculated from the equation for the reaction which the compound is to undergo in the analysis to be performed.** This is most important when a compound is capable of reacting in two or more different ways. Consider the following reactions involving acid potassium oxalate:—

(1) Reaction between potassium hydrogen oxalate and caustic potash solution.

$$K\underset{\uparrow}{H}C_2O_4 + KOH \rightarrow K_2C_2O_4 + H_2O$$

1 gm. of hydrogen
to be replaced.

∴ N.KHC_2O_4 contains 128 gm. per litre.

(2) Reaction between acidified potassium hydrogen oxalate and an oxidising agent.

$$\begin{aligned} &2KHC_2O_4 + H_2SO_4 + 2[O] \rightarrow \\ &\quad K_2SO_4 + 2H_2O + 4CO_2 \\ &\therefore\ 2KHC_2O_4 \equiv 2[O] \equiv 4H \end{aligned}$$

∴ N.KHC_2O_4 contains 64 gm. per litre.

Potassium hydrogen oxalate possesses two equivalents each appropriate to a particular reaction; consequently, two solutions of different concentrations may be prepared, each of which is *normal* when considered in relation to its appropriate reaction.

It follows from the definition of normal solutions that they must contain chemically equivalent weights of the compounds per litre of solution and, consequently, that equal volumes of different normal solutions are chemically equivalent to one another, e.g., 25 c.c. of N.HCl react exactly with

25 c.c. of N.NaOH
or 250 c.c. of $N/10$ KOH
or 12·5 c.c. of $2N.Na_2CO_3$
or 50 c.c. $N/2$ NaOH
or 500 c.c. $N/20$ $AgNO_3$
or 2,500 c c. $N/100$ KOH

It is also convenient to note that if V_1 c.c. of a solution of normality N_1 is equivalent to V_2 c.c. of a solution of normality N_2 then

$$V_1N_1 = V_2N_2$$

For example $\quad$ 10 c.c. 1·08 $N \equiv$ 10·8 c.c. N.

INSTRUMENTS OF VOLUMETRIC ANALYSIS

The course of a volumetric analysis is usually the following:—A standard solution of the material to be analysed is made up by weighing in *a weighing bottle* an appropriate quantity of the material, making it up to 250 c.c.* of aqueous solution in a *measuring flask*, transferring 25 c.c.* of this solution to a conical flask by means of a *pipette* and titrating it with a standard (often decinormal) solution of some reagent from a *burette*, using a suitable indicator. Each of these measuring instruments and the manner of its use will now be considered. A measuring cylinder may occasionally be used but it is less accurate.

Weighing Bottle. This consists of a cylindrical glass vessel with an accurately ground stopper (Fig. 64), in which the materials can be weighed out of contact with the open atmosphere. The weighing bottle is usually heated in a steam oven before use to ensure dryness and is then allowed to cool in a desiccator. It should be handled in a dry cloth to avoid contamination with grease from the fingers. It may be used in one of two ways. The first method is to weigh the bottle empty, powder the material given in a clean dry mortar and then weigh out an amount of material exactly against counterpoising weights. This has the disadvantage of being tedious and exposing the material to the atmosphere while adjustments of amount are being made. A spatula of horn or stainless metal is used to transfer the material. The second method is to weigh the bottle containing an amount of the material known to be roughly suitable

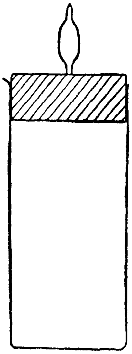

FIG. 64.

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* It is also convenient to make 100 c.c. of solution and to take 20 c.c. portions.

for the purpose in hand, to transfer the material to a measuring flask as described in the next paragraph and weigh the bottle containing a trace of residual material, after which the actual weight transferred to the measuring flask can be obtained by difference. The second method is much quicker and is preferable except where solutions of an exact normality are being prepared directly: the first method is then essential.

Note. To weigh substances not appreciably affected by the atmosphere a watch-glass may be used.

The degree of accuracy necessary in the weighings will be considered later (p. 217).

Measuring Flask. Measuring flasks of 250 c.c. capacity are usually employed (Fig. 65) because the amount of solution used in a single titration is usually 25 c.c. and several such titrations may be carried out by drawing from the 250 c.c. of solution prepared. Measuring flasks of 100 c.c., 200 c.c., 500 c.c., 1,000 c.c., and 2,000 c.c. are also in frequent use.

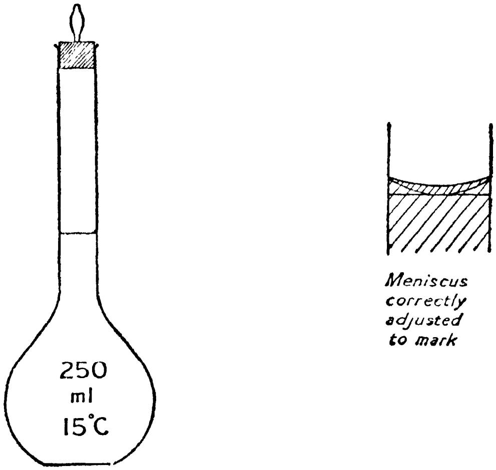

FIG. 65.

It should be noted that a measuring flask is made to *contain* a volume of liquid and will not *deliver* that volume, because some liquid is inevitably retained as a film on the sides of the flask. Measuring flasks are usually graduated at 15° C. and should only be used at temperatures close to this.

When a solution is to be made up the measuring-flask should first be well rinsed with several small quantities of the solvent (usually distilled water) that is to be used. This removes any traces of impurities. A small beaker should be similarly rinsed and the material transferred to it carefully from the weighing bottle. The solvent is then added from a wash-bottle down the sides of the beaker so that there is no splashing. Gentle stirring with a glass rod will hasten the process of solution, but the rod should not be removed from the beaker unless all solution is first washed from its surface into the beaker. (If the solvent is used hot, the solution must finally be cooled to room temperature. The solution must also, of course, remain unchanged by heat.) When the solute is completely dissolved the glass rod should be placed in a funnel which rests in the neck of the measuring flask and the solution poured down it from the beaker into the flask. The entire interior surface of the beaker should then be washed several times with the solvent and the washings transferred to the flask down the rod which will also be washed by them. (If the material is being weighed by difference, the weighing bottle should now be weighed again. If not, the weighing bottle should be washed out with solvent in the same way as the beaker and the washings added to the contents of the flask). The measuring flask is then filled with the solvent from a wash-bottle until the bottom level of the meniscus is at the mark (Fig. 65). A pipette should be used to add the last drop or two. (When deciding whether the level is correctly adjusted, lower the eye until the mark is at your eye-level and so avoid error due to parallax.) The flask should then be stoppered and **shaken vigorously** for some few minutes to make the solution uniform.*

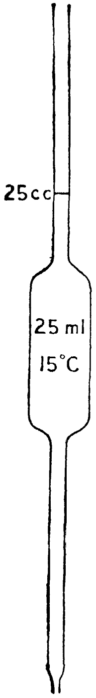

FIG. 66.

If time is an important factor the solution can be made uniform more quickly by pouring it into a large dry flask in which it can easily be swirled round for a short time. **It is essential that the solution should be of uniform concentration throughout.** Whenever the words "shake well" appear in the text they mean this essential process of making the solution uniform.

Pipette. The pipette (Fig. 66) is designed to *deliver* a certain volume of liquid. When filled to the mark it contains more than this volume, a little of the liquid being retained after delivery as a film on the sides of the pipette and in the tip. The actual volume *delivered* from the pipette should be constant, and it is therefore important to observe certain conditions when using the pipette so that the small volume of liquid retained in it is constant.

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* After shaking, the solution will be *below* the mark. This is because some of the solution is retained as a film on the stopper and neck of the flask. The total volume is still, however, 250 c.c. and 25 c.c. taken from it will be accurately one-tenth. Do not be tempted to make the solution up to the mark again. This proceeding makes the volume 250 c.c. plus an unknown added volume.

The pipette is filled above the mark by sucking* solution into it and this liquid is allowed to drain away. This process of filling and allowing the liquid to run away should be repeated to ensure that the pipette contains nothing but the solution which is to be measured. The pipette is then filled above the mark and the liquid is retained by pressing the forefinger on the open end of the stem. The pipette is then raised so that the mark is at eye-level and by controlled release of the finger from the stem, the liquid is allowed to fall slowly until the bottom level of the meniscus is at the mark. The tip of the pipette is then placed inside a conical flask which should be dry or should contain only distilled water. By removing the finger from the stem, the liquid may be delivered from the pipette into the flask. A 25 c.c. pipette should deliver its contents in not less than 20 secs.† and a drainage time of about 15 secs. should be allowed with the point of the pipette touching the side of the vessel. A little liquid will be retained in the tip; no attempt should be made to expel it as the pipette will already have *delivered* 25 c.c. of liquid which is now available for titration with a standard solution from a burette, using a suitable indicator. The greatest difference between deliveries from a 25 c.c. pipette should not exceed 0·025 c.c.

Burette. The burette is illustrated in Fig. 67. Burettes employed in volumetric analysis usually have a capacity of 50 c.c. and are graduated in c.c. and 1/10 c.c. A glass-stoppered‡ burette is to be preferred and the stopper should turn smoothly. (If it sticks, the socket and stopper should be dried and a *very thin* smear of vaseline placed on the stopper. If too much is used, the vaseline may block the hole in the stopper. A rubber band may be used to prevent the stopper from sliding out of the socket.) The burette is first washed out with the solution it is to contain, the washings being allowed to run away *through the jet* so as to wash this part also. A second washing is desirable to ensure complete elimination of impurities. It is then filled up to the region of the zero mark with the solution and *the jet is filled* by opening the tap for a second or two.

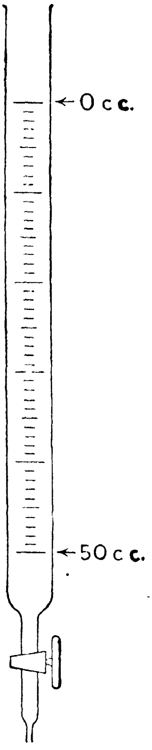

FIG. 67.

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* A vacuum bottle or a burette should always be used for poisonous solutions. If a liquid is taken into the mouth it should be spat out at once and the mouth washed out.

† If delivery is more rapid than this, the volume delivered is not constant. A pipette which delivers too rapidly should have its extreme tip heated very gently in a flame, when the hole will close slightly.

‡ A Mohr burette is quite satisfactory for most purposes, but it should not be used with iodine solutions. The rubber connection is attacked by iodine.

Time is then allowed for drainage down the sides of the burette, after which with the surface of the liquid at eye-level, the reading of the *bottom level* of the meniscus is taken. A white sheet of paper held behind the liquid at an angle of 45 degrees will help to define the meniscus and a good approximation to the second decimal place may be obtained. The titration is then completed and the new reading taken, after which the volume of liquid delivered is found by difference.

As a titration must be accurate to one drop of reagent and the volume of it needed is at first only very approximately known, it is almost always a saving of time to carry out a rough titration first in the following way, after which accurate titration can be quickly performed. To the solution and indicator in the conical flask, add the solution from the burette 1 *c.c. at a time,* until excess is present as shown by the change in the indicator. Suppose that the indicator changes between the 23rd and 24th c.c. added. Then it is clear that in subsequent titrations 23 c.c. of solution can be safely added from the burette, after which adjustment to the accurate end-point must be made drop by drop, but the greatest possible addition at this slow rate can only be 1 c.c. and will probably be much less. It is usually quicker to carry out a deliberately approximate titration first, although with some indicators a fairly accurate first titration is possible because the indicator shows signs of the arrival of the end-point. In the second and subsequent titrations, the flask should be shaken at intervals and the reagent should be added in quantities of not more than about 5 c.c. because the large local excess of reagent which may result is apt to induce undesirable variants of the main reaction.

A burette (including the tap) should always be well washed out after use. If an alkaline solution has been in the burette, about 10 c.c. of dilute acid should be run into the burette after running out the alkali, and the burette then well washed out with water.

SOURCES OF ERROR

The following are the chief sources of error in volumetric analysis.

Solution not Homogeneous. This is a frequent source of error. After the solution has been made up to the mark, it is essential either to shake very well or to pour the solution into a large flask and swirl.

Inaccuracy of Instruments Used. Measuring flasks, burettes and pipettes of reasonable price are necessarily manufactured by mass-production methods and inaccuracies are certain to arise. An experienced analyst can calibrate his apparatus and so practically eliminate errors from this source. Actually the least accurate of the instruments is the burette for the following reasons:—

(1) An error of a drop may arise in the titration because this is the least amount that can be added. The volume of a drop from an ordinary school burette may be about 0·04 c.c., but the error may be reduced by averaging three close titrations.

(2) The burette may drain irregularly. For this reason, burettes should be treated at intervals with a cleaning mixture (such as 10% chromic acid in sulphuric acid) to remove grease.

(3) The second decimal place in the readings can only be obtained approximately.

The probable error in using the burette is about 1 part in 500, and this is usually the greatest error an experienced analyst will encounter. The other instruments are generally more accurate, provided that they are consistently used as previously described in the text.

Errors in Weighing. As the error in using the burette is about 1 part in 500, there is no point in weighing out material extremely accurately. If one gm. or more is being weighed, a mistake of one unit in the third decimal place will introduce an error of one part in 1,000, which is much less than the burette error. Thus a weighing of one gm. or more of material should not be carried beyond the third decimal place.

Impurity of Materials. It is obvious that if analyses are based on solutions made up from impure chemicals, the results will be unreliable. There has, however, been a remarkable improvement in recent years in the quality of analytical reagents, and chemicals of analytical* reagent quality are now so pure that the errors they introduce, compared with those from other sources, are almost always negligible.

Errors may arise from the action of light, atmospheric carbon dioxide, dust particles or oxygen on standard solutions. These may be minimised by the use of coloured glass bottles, tightly fitting stoppers, soda-lime tubes to absorb carbon dioxide and in other ways. If a solution is kept for a long time, it should be standardised at frequent intervals.

Inaccuracy in the End-point Recorded.

If too much indicator is added to the solution to be titrated, a certain amount of the reagent added will be needed to cause the colour change to take place. It is often helpful to perform a "blank" experiment to ascertain the volume of reagent necessary to affect the indicator which has been added to a volume of water approximately

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* These chemicals (A.R. quality) should always be used. Moisture is nearly always present to the extent of 0·2 to 0·5% in any powder not specially dried. This impurity can usually be removed by storing the substance before use for a few hours in a desiccator.

equal to the final volume of solution likely to be obtained in the actual titration. Furthermore, where a change in colour indicates the end-point of a reaction, practice is often necessary before the change can be clearly recognised. It is sometimes useful to have on the bench for comparison a flask containing a few drops of the unchanged indicator added to water, so that any alteration in colour can be easily observed.

CHAPTER XXXIII

INDICATORS

Ionisation. The aqueous solutions of some substances will readily conduct an electric current and decomposition occurs as a result. These substances are termed electrolytes, and acids, alkalis, and the majority of salts belong to this class. Thus a solution of hydrochloric acid in water conducts an electric current and is decomposed into hydrogen (which is evolved at the negative pole or cathode) and chlorine (at the anode or positive pole). This is explained by assuming that ions are present in the liquid before any current is passed through it. These ions are electrically charged atoms or groups of atoms, ions of metals or metallic groups being positively charged and ions of non-metals and non-metallic groups being negatively charged. The amount of charge is directly proportional to the valency of the atom or group. Since the majority of the volumetric processes depend upon the interaction of ions we shall often represent a substance, not by its usual formula, but by its ionic formula. This indicates the ions furnished by that substance when dissolved in water. Thus:—

HCl		$H^+ + Cl^-$
H_2SO_4		$2H^+ + SO_4^{--}$
$NaOH$	may be represented	$Na^+ + OH^-$
$Ca(OH)_2$	as indicated opposite.	$Ca^{++} + 2OH^-$
KNO_3		$K^+ + NO_3^-$
$BaCl_2$		$Ba^{++} + 2Cl^-$

The plus sign between them merely indicates that the ions are present in the same solution in those proportions. It does not imply any chemical bond between the ions. They are free to move anywhere in the solution. When an electric current is passed, however, the negative ions or anions move to the positive pole and the positive ions or cations to the negative pole, and the phenomenon of electrolysis is observed.

Definitions. *An acid* is a substance which contains hydrogen and when dissolved in water furnishes hydrogen ions, as the only cations.

$$\text{e.g., } HCl \rightarrow H^+ + Cl^-$$

A base is a substance which will react with hydrogen ions to give a salt and water only. The alkalis are substances which when dissolved in water furnish hydroxyl ions as the only anions.

$$\text{e.g., } NaOH \rightarrow Na^+ + OH^-$$

Neutralisation is a reaction between an acid and a base producing a salt and water only, e.g.,

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

It will be clearly seen that, since the common salt produced is in the form of ions of sodium and chlorine, neutralisation consists essentially of the action between hydrogen ions and hydroxyl ions to form molecules of water which are undissociated. (See p. 22.)

ionically: $H^+ + OH^- \rightarrow H_2O$

Weak and Strong Electrolytes. According to Arrhenius the ions are furnished by a reversible reaction in which an undissociated molecule splits up into ions to an extent which varies considerably from substance to substance and according to the dilution of the solution. The greater the dilution the greater the dissociation.

Strong electrolytes* are dissociated to a considerable extent even in fairly concentrated solution, whereas weak electrolytes are only slightly dissociated. The following table shows how the dissociation varies for a few weak electrolytes and also how the dilution affects the degree of dissociation.

TEMPERATURE 18° C.	DEGREE OF DISSOCIATION		
	N/10.	*N*/100.	*N*/1000.
Ammonium hydroxide	0·0133	0·0415	0·125
Acetic acid	0·0133	0·0415	0·125
Boric acid	0·00007	0·00024	0·0007

Thus in *N*/10 acetic acid 1·33% of the weight of the acetic acid consists of hydrogen ions and acetate ions.

Dissociation Constant. Consider an electrolyte AB which ionises when in solution.

$$AB \rightleftharpoons A^+ + B^-$$

According to the Law of Mass Action, when equilibrium has been attained,

$$\frac{(\text{Conc. of } A^+)\ (\text{Conc. of } B^-)}{(\text{Conc. of unionised } AB)} = \text{a constant}$$

where the concentrations are expressed in gram-ions and gram-molecules per litre of solution respectively. The equation is often expressed thus:—

$$\frac{[A^+]\ [B^-]}{[AB]} = K \text{ (the equilibrium constant).}$$

---

* Strong electrolytes are now believed to be completely dissociated even in concentrated solution, and it is because their mobility (i.e., the free movement of the ions) is restricted in concentrated solution that they appear to be to some extent undissociated.

The equilibrium constant in this case is termed the dissociation constant of the electrolyte. This can be calculated from the above table thus:—

Dissociation Constant for Acetic Acid.

	CH_3COOH	$\rightleftharpoons$	H^+	$+$	CH_3COO^-
Conc. in *N*/10 sol.:	0·09867 gm.-mol. per l.		0·00133 gm.-ions per l.		0·00133 gm.-ions per l.

$$\therefore K = \frac{(0{\cdot}00133)^2}{0{\cdot}09867} = 1{\cdot}8 \times 10^{-5}$$

Ionic Product of Water. We have seen that neutralisation consists of the formation of molecules of undissociated water by the chemical union of hydrogen ions and hydroxyl ions.

$$H^+ + OH^- = H_2O.$$

Like other ionic reactions this is to some extent reversible.

It is true that pure water is practically a non-conductor of electricity, but from conductivity experiments it can be shown that pure water does contain minute quantities of both hydrogen ions and hydroxyl ions. Then:

$$H_2O \rightleftharpoons H^+ + OH^-$$

represents the equilibrium between the ions and undissociated water, and the dissociation constant K would be represented by

$$\frac{[H^+]\ [OH^-]}{[H_2O]} = K$$

The amount of the ions is so small, however, that $[H_2O]$ can be considered to be constant without serious error and the expression $[H^+]\ [OH^-]$ is therefore also constant and is termed the ionic product of water. The value of this product at 25° C. is very nearly 10^{-14}, and since the ions are present in equal amounts (1 gm.-mol. of water gives 1 gm.-ion of hydrogen and 1 gm.-ion of hydroxyl ion) it follows that pure water contains a concentration of hydrogen ion of 10^{-7} gm. per litre.

$$[H^+]\ [OH^-] = 10^{-14} \text{ (at } 25^\circ \text{ C.)}$$

Concentrations are expressed in gm.-ions per litre thus:—

$[H^+] = 10^{-7}$ gm.-ions per litre or 10^{-7} gm. of hydrogen ions per litre.

$[OH^-] = 10^{-7}$ gm.-ions per litre or 17×10^{-7} gm. of hydroxyl ions per litre.

Although this ionic product is exceptionally small it is of great importance because it is this constant which is used to trace the alteration of the hydrogen ion concentration which takes place during neutralisation.

It is important to note that however strongly acidic an aqueous solution may be, it is never completely free from OH^- because there must be enough OH^- to satisfy the equation:—

$$[H^+]\,[OH^-] = 10^{-14}$$

Similarly, an alkaline solution is never completely free from H^+. When H^+ and OH^- are present in equal proportions, the concentration of each can only be 10^{-7} gm. ions per litre, and this constitutes a neutral solution.

Hydrolysis. The presence in water of hydroxyl ions and hydrogen ions accounts for the phenomenon of hydrolysis. This action can be considered as the reverse of neutralisation and occurs when the ions of water react with the ions derived from a substance in solution. Thus, sodium carbonate in solution furnishes carbonate ions and sodium ions.

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}$$

We have present in sodium carbonate solution the following ions:

$$Na^+,\ CO_3^{--},\ H^+,\ OH^-$$

although the last two are only present to a very small extent. Now carbonic acid is a very weak acid and dissociates only very slightly, hence the following reaction occurs until there is left only that small quantity of hydrogen ions necessary to maintain the very small equilibrium constant for carbonic acid:

$$2H^+ + CO_3^{--} \rightleftharpoons H_2CO_3$$

As hydrogen ions are removed from the sphere of action by the formation of this undissociated acid more hydrogen ions are liberated by the dissociation of water to maintain the value of the ionic product

$$[H^+]\,[OH^-] = 10^{-14}$$

Finally an equilibrium is set up leaving in solution an excess of hydroxyl ions over hydrogen ions which causes the solution to be alkaline.

By a similar type of reasoning it can be shown that a sodium bicarbonate solution (which is a solution of an *acid* salt) is alkaline. Thus:—

$$\begin{array}{l} H_2O \rightleftharpoons H^+ + OH^- \\ HCO_3^- + H^+ \rightleftharpoons \underset{\text{only slightly dissociated.}}{H_2CO_3} \end{array}$$

The removal of the hydrogen ions to form undissociated carbonic acid leaves an excess of OH^-, hence the solution is alkaline.

Similarly ammonium chloride furnishes ammonium and chloride ions in solution.

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Ammonium hydroxide is only slightly dissociated and hence the ammonium ion reacts with the hydroxyl ions present to form undissociated ammonium hydroxide.

$$NH_4^+ + OH^- \rightarrow NH_4OH$$

This removes hydroxyl ions from the solution, leaving an excess of hydrogen ions which cause the solution to be acidic. (See p. 20.)

It follows that the solution of a normal* salt in water is by no means certain to be neutral. Whether such a salt will form an acidic or an alkaline solution can usually be predicted by an examination of the possible reactions of its ions with hydrogen ions or hydroxyl ions.

pH Value. It was suggested by Sørensen that a useful method of denoting the hydrogen ion concentration of a solution would be by using the logarithm of the concentration with the sign reversed.

By this means the concentration of an acidic or an alkaline solution can be expressed in the same terms, since if the pH value is known the concentration of the hydroxyl ion can be at once determined from the equation:—

$$[H^+]\,[OH^-] \doteq 10^{-14}$$

By definition

$$pH = -\log [H^+]$$

e.g., let $[H^+] = 10^{-2}$ gm.-ions per litre, i.e., $\frac{1}{100}$ gm. per litre as would be the case in a solution of a strong† acid of concentration $N/100$,

then $\log [H^+] = -2$

$\therefore$ pH value $= 2$.

pH Value of N/10 Acetic Acid.

In $N/10$ acetic acid, degree of dissociation $= 0{\cdot}0133$.

$$\begin{aligned} \therefore\ [H^+] &= \frac{1}{10} \times 0{\cdot}0133 \text{ gm.-ions per l.} \\ &= 0{\cdot}00133 \text{ gm.-ions per l.} \\ p\text{H value} &= -\log 0{\cdot}00133 \\ &= -[\bar{3}{\cdot}1239] \\ &= -[-2{\cdot}8761] \\ &= 2{\cdot}8761. \end{aligned}$$

(Compare $N/1000$ HCl; *p*H value $= 3{\cdot}000$, assuming complete dissociation.)

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* i.e., a salt formed by replacing all the replaceable hydrogen by a metal.

† It is assumed that the strong acid is completely dissociated.

pH Value of N/100 Sodium Hydroxide.

$$[OH^-] = \frac{1}{100} \text{ or } 10^{-2} \text{ gm.-ions per l.}$$

$$\text{but} \quad [OH^-][H^+] = 10^{-14} \text{ at } 25^\circ \text{ C.}$$

$$\therefore [10^{-2}][H^+] = 10^{-14}$$

$$\therefore [H^+] = 10^{-12}$$

$$\therefore pH = 12.$$

It follows that an exactly neutral solution is one of pH value 7, since this solution will contain equal amounts (expressed as gm. ions) of hydrogen ion and hydroxyl ion. The smaller the pH value the more acidic the solution and the larger the pH value the more alkaline the solution. (See p. 18.)

Another advantage of using the pH system is that changes in concentration too large to be represented graphically can easily be traced by using pH value. As an example, consider the addition of 25 c.c. of *N* HCl to 25 c.c. *N* NaOH. The hydrogen ion concentration of the alkaline solution if completely ionised is $\frac{1}{100,000,000,000,000}$ gm. per litre, whereas that of the *N* acid is 1 gm. per litre and at exact neutrality the hydrogen ion concentration is $\frac{1}{10,000,000}$ gm. per litre (the above figures are approximate).

Using pH value this change can be shown graphically as in Fig. 68. *It can be seen there is a rapid change of pH value as the solution changes from being slightly alkaline to being slightly acidic.

To calculate change of pH value as one drop of excess acid falls into the neutral solution.

If 25 c.c. *N*.HCl have been added to 25 c.c. *N*.NaOH the solution will be exactly neutral and its pH value will be 7. 1 drop $= \frac{1}{20}$ c.c. (approximately), and will contain $\frac{1}{20} \times \frac{1}{1000}$ gm. of hydrogen ions. This is added to 50 c.c. of neutral solution, and hence

$$[H^+] = \frac{1000}{50} \times \frac{1}{20} \times \frac{1}{1000} \text{ gm. per litre}$$

$$= \frac{1}{1000} \text{ gm. per litre} = 10^{-3}.$$

$$\therefore \text{pH value} = 3$$

Neglecting the readjustment due to the existing small amount which is merely $\frac{1}{10,000,000}$ gm. per litre we see that one drop of acid *at this stage* produces an increase in $[H^+]$ of 10,000 times its value.

By a similar argument it can be shown that a further 10 drops ($\frac{1}{2}$ c.c.) would be required to change the pH value to 2.

Theory of Indicators. Most of the indicators used in acidimetry and alkalimetry are weak acids or weak alkalis and their degree of dissociation is greatly affected by alteration of hydrogen ion concentration of the solution, thus producing a change in colour. Consider a very weak organic acid HA. Roughly its dissociation can be regarded as the splitting up of the molecule into a hydrogen ion and an ion negatively charged.

$$\underset{\text{(colourless)}}{HA} \rightleftharpoons H^+ + \underset{\text{(pink)}}{A^-}$$

Now suppose the ion A^- is coloured pink whilst the unionised* molecule is colourless. If dissociation occurs to any marked extent it is clear that a pink colour will be observed whereas if the undissociated acid is mainly present no colour will be observed. Consider the effect of an acidic solution. According to the Law of Mass Action, the hydrogen ion concentration which is high (compared with the concentration of H^+ furnished by the indicator) will suppress the dissociation of the indicator by increasing the speed of the reverse reaction, i.e., right to left. Hence the indicator will be practically unionised and no colour will be observed. In an alkaline solution, however, hydrogen ions from the indicator will react with some of the hydroxyl ions present to form undissociated water, and hence the dissociation of the weak acid will be increased with a corresponding increase in the coloured ions A^- which will make the solution pink. This colour change takes place at different concentrations with different indicators, and below is a list of some of the indicators in common use together with the range of pH value over which the colour change takes place.

pH range.	*Indicator.*	*Colour change.* *Acid-alkali.*
3·0–4·4	Methyl orange.	Red-yellow.
4·4–6·3	Methyl red.	Red-yellow.
6·0–7·6	Bromo-thymol blue.	Yellow-blue.
6·0–8·0	Litmus.	Red-blue.
8·2–10·0	Phenolphthalein.	Colourless-red.

It is quite obvious from Fig. 68 that any of these indicators will give a sharp end point if a strong base is being titrated against a strong acid, because the addition of only one or two drops of acid

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* Recent research has shown that the colour change of an indicator is not due to ionisation alone, but it is also due to a tautomeric change in the unionised portion, e.g., $\underset{\text{colourless}}{HXO} \rightleftharpoons \underset{\text{coloured}}{HOX} \rightleftharpoons H^+ + \underset{\text{coloured}}{OX^-}$.

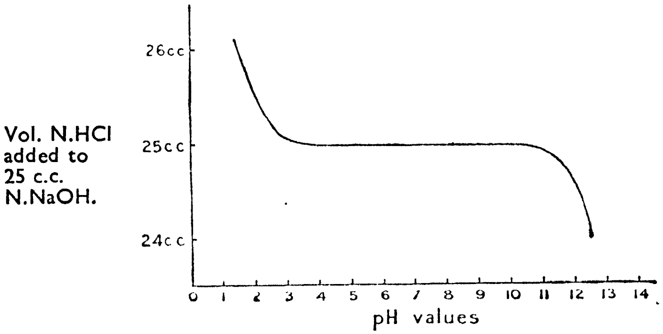

FIG. 68.

causes the pH value to move over the whole of the flat portion of the curve.

Essential Characteristics of a Good Indicator.

(1) The colour change of the indicator must be clear and sharp, i.e., it must be sensitive. Thus it would be useless if 2 or 3 c.c. of the reagent were necessary to bring about the colour change.

(2) The pH range over which the colour change takes place must be such as to indicate when the reaction (as shown by the equation) is complete. See Expt. 16.

CHOICE OF INDICATOR

(*a*) **For Titration of Weak Acids.** We have already seen, p. 223, that a weak acid is only slightly dissociated, and hence its hydrogen ion concentration is low. Now a strong acid in *N*/10 solution will have a pH value of about 1, and we will suppose that our weak acid has in *N*/10 solution a pH value of 4. (It would still be definitely on the acid side of the neutral point.) Now if we titrate this weak acid against *N*/10 alkali (pH value 13) it is clear that no matter how much acid we added we could not, for example, obtain a solution of pH value 3.

In other words the range of pH value of the solutions as the two are mixed cannot be outside the limits pH = 4 to pH = 13. For this reaction it would be useless to choose an indicator which changed at pH value 3. It would show no change. We can go further. We should not think it advisable to choose an indicator which changed at pH value 5 because the pure acid itself would have to be present in a concentration somewhere near *N*/100 to produce this effect. The best indicator to use would be one which changed at about pH value 9. The graph, Fig. 69, shows the pH change as a weak acid is added to a strong alkali. For this titration the best indicator is phenolphthalein.

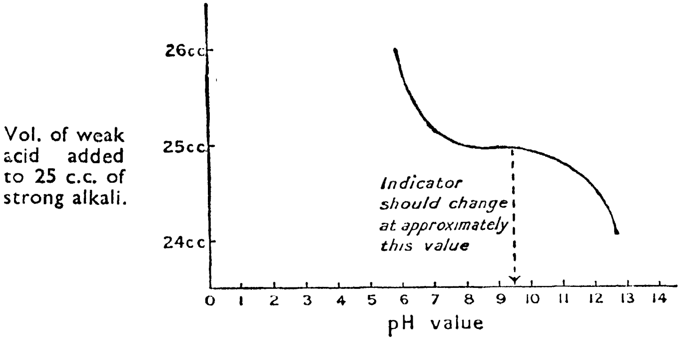

FIG. 69.

Hence, when titrating:—

Oxalic Acetic Succinic Formic Boric Carbonic Sulphurous or any weak acid	against a strong alkali use phenolphthalein as an indicator.

If the alkali is being run into the acid solution the first sign of pink coloration gives the correct end-point. In a short time the carbon dioxide of the air may dissolve sufficiently to cause the pink colour of the phenolphthalein to disappear.

(*b*) **For Titration of a Weak Alkali.** The case is reversed when we are considering the indicator to use if a strong acid and a weak alkali

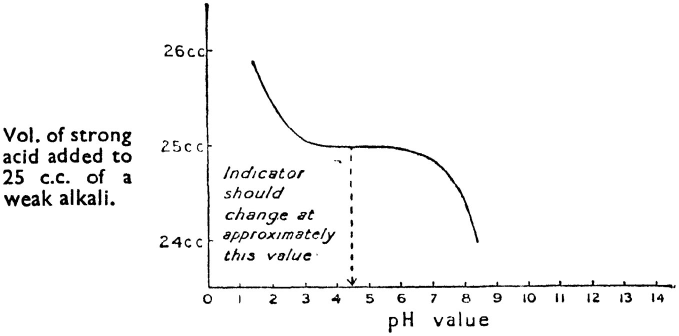

FIG. 70.

are to be titrated. The pH value of the weak alkali in the concentration used may not exceed 10 (i.e., the solution could not have a high concentration of hydroxyl ions). The pH value cannot vary outside the limits 1–10 (for, say, decinormal solutions) and comparatively large concentrations of the alkali might be necessary to obtain a pH value anywhere approaching 10. Fig. 70 shows the pH change during a titration of a strong acid against a weak alkali. Hence for this type of reaction (weak alkali—strong acid) an indicator changing at a pH value of about 4 is essential. That used in practice is methyl orange or methyl red.

Hence when titrating:—

$$\left.\begin{array}{l}\text{Ammonium hydroxide}\\ \text{Sodium carbonate}\\ \text{Borax}\\ \text{or any weak alkali}\end{array}\right\}\begin{array}{l}\text{against a strong acid use}\\ \text{methyl orange or methyl red.}\end{array}$$

It is impossible to follow the neutralisation of a weak acid by a weak alkali as there is no point in the titration at which a rapid change of pH value takes place.

NOTES ON SOME OF THE INDICATORS IN GENERAL USE

Litmus contains several dyes and the colour change is therefore not easy to follow if very accurate work is being done. Furthermore, the solution does not keep well out of contact with air. Litmus contains azolitmin, and this latter is a very sensitive dye, and can with advantage be substituted for litmus.

Litmus Solution. [Colour change red-blue pH 6·0–8·0.]

Digest 10 gm. of commercial litmus with about 500 c.c. of warm water and allow to stand for some time. Filter off and add to the filtrate a few drops of dilute nitric acid until the purple colour is obtained. Keep in a bottle with a loose cork.

Azolitmin. [Colour change red-blue pH 5·0–8·0.]

Dissolve about 5 gm. of azolitmin in 500 c.c. of water to which a little caustic soda solution has been added. Add dilute nitric acid until the purple colour is obtained.

Methyl Orange. [Colour change red-orange pH 3·0 to 4·4.]

This is an excellent indicator for use as described above if the concentration of the solutions is greater than $N/5$. In decinormal solutions the end-point is not too easy to determine.

Methyl Orange. 1 gm. of methyl orange to 500 c.c. water. Use two or three drops for 25 c.c. of solution to be titrated.

Methyl Orange modified with Xylene Cyanol F.F. [Colour change green—neutral grey—magenta.] Hickman and Linstead advocate mixing this dye with xylene cyanol F.F., which has the effect of producing with the methyl orange a neutral grey tint at the pH value 3·8 which corresponds with the end-point given by methyl orange. The colour change (with the addition of xylene cyanol F.F.) is:—

Green —	neutral grey —	magenta
alkaline side of pH 3·8.	pH 3·8	acid side of pH 3·8.

Mix 1 gm. methyl orange with 1·4 gm. cyanol and 500 c.c. of 50% alcohol and water. Use two or three drops for 25 c.c. of solution to be titrated.

Methyl Red [colour change red-yellow pH 4·4 to 6·3] is a sensitive indicator and very useful for titrating weak organic bases and ammonia. Dissolve 1 gm. of the dye in 500 c.c. of 60% alcohol. Use one or two drops only for 25 c.c. of liquid to be titrated.

Phenolphthalein. [Colour change colourless-red pH 8·2 to 10·0.] For use see p. 227.

Dissolve 1 gm. in 500 c.c. of 50% alcohol.

CHAPTER XXXIV

ACIDIMETRY AND ALKALIMETRY

Before estimations involving acids or alkalis can be carried out on given substances or mixtures, it is necessary to obtain accurately standard acidic and alkaline solutions. The common acids and alkalis cannot be employed directly for making standard solutions because they are variable in composition for the reasons given.

Hydrochloric Acid. This is volatile in high concentrations.

Sulphuric Acid. This is hygroscopic.

Nitric Acid. This is volatile and subject to decomposition.

Furthermore, the so-called "pure" mineral acids of the laboratory are not pure substances: they contain varying quantities of water.

Caustic Soda and Potash. These are deliquescent and react with carbon dioxide from the air.

$$\text{e.g., } 2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Slaked Lime. This is insufficiently soluble and also reacts with carbon dioxide from the air.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Ammonia. This is volatile, and is a solution of variable concentration.

Characteristics of a good standardising reagent:—

(*a*) It should be obtainable in a high degree of purity.

(*b*) It should be stable and unaffected by the atmosphere. (It should not be deliquescent or efflorescent, so that it may be weighed easily.)

(*c*) It should be fairly cheap.

For standardisation of acids the materials commonly used are

(1) Pure sodium carbonate prepared by heating sodium bicarbonate (or A.R. anhydrous sodium carbonate).

(2) Pure borax $Na_2B_4O_7.10H_2O$.

(3) Iceland spar, pure calcium carbonate.

Alkaline solutions may be standardised by using solid crystalline organic acids such as oxalic acid or succinic acid, which can be crystallised to a high state of purity.

Experiment 221. To standardise a solution of hydrochloric acid.

Material: Sodium bicarbonate, or A.R. sodium carbonate.

Concentrated hydrochloric acid is roughly 10 *N*. Pour out into a measuring cylinder about 30 c.c. of concentrated hydrochloric acid, transfer to a 250 c.c. flask and make up to the mark with water. Shake well. Put some pure sodium bicarbonate or A.R. anhydrous sodium carbonate into an evaporating dish and heat gently over a low flame for about 15 minutes. Take care not to heat the mass too strongly (or fusion may take place which will seriously retard solution and also cause slight decomposition) and stir continuously. It will be obvious when carbon dioxide is being evolved as the mass appears unusually light as it is being stirred. Allow the dish to cool in a desiccator (because anhydrous sodium carbonate absorbs moisture to form the monohydrate) and weigh. Heat again for five minutes, cool and weigh. Repeat this process until the weight is constant.

$$\begin{array}{l} \mathrm{Na_2CO_3} + \underset{\uparrow}{\mathrm{2HCl}} \rightarrow \mathrm{2NaCl} + \mathrm{H_2O} + \mathrm{CO_2} \\ 106 \text{ gm.} \quad 2 \text{ litres } N. \\ \therefore\ 250 \text{ c.c. } N\ \mathrm{HCl} \equiv 13{\cdot}25 \text{ gm. } \mathrm{Na_2CO_3} \end{array}$$

Weigh a clean dry weighing bottle* and weigh out exactly 13·25 gm. of the pure sodium carbonate into it. Transfer the carbonate to a beaker containing a little hot water (shaking gently as the carbonate comes in contact with the water) and wash the weighing bottle carefully by means of the wash-bottle, allowing the washings to drop into the beaker. Stir gently to dissolve, warming if necessary. Smear an almost imperceptible amount of vaseline on the lip of the beaker and pour the solution down a glass rod into a funnel resting in the neck of a clean (but not necessarily dry) 250 c.c. flask. Wash the beaker out with further small quantities of water, pouring all washings down the rod and funnel into the 250 c.c. flask to ensure that no solution is left on the walls of the beaker. It is well to remember that once you have weighed out the sodium carbonate into the weighing bottle every particle of it, whether as solid or as a solution, must be transferred into the 250 c.c. flask. If you have previously warmed the liquid, the flask and its contents must now be cooled under the tap. Make up to the mark with water from a pipette, shake well or pour into a large dry beaker in order that the solution may become homogeneous. Take 25 c.c. of the *N.* sodium carbonate solution by means of a pipette, run it into a conical flask, add two or three drops of methyl orange solution, make a note of the burette reading and run in the acid from a burette. The first 15 to 18 c.c. of the acid may be run in without fear of overshooting the end-point. Then run in 1 c.c. at a time, shaking after each addition until the colour changes from yellow to pink. This is a trial titration and unless you are convinced of its accuracy† it should not be used in

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* It is convenient to keep a weighing bottle of known approximate weight for volumetric purposes in a desiccator. Its accurate weight can then be quickly found.

† In cases such as this and in many others where the approximate strength of the solution is known it is possible with a little care to obtain an accurate titration at first. The indicators often show signs of the approach of the end-point. If the strength of the solution is only very approximately known, to attempt to obtain an accurate first titration is a waste of time.

the calculation. The titration should now be repeated with further portions of 25 c.c. of the *N*. carbonate solution until two readings are obtained which agree to 0·1 c.c.

Readings.

I.	2nd reading	23·4 c.c.	TRIAL. Therefore not very accurate.
	1st reading	1·2 c.c.	
		22·2 c.c.	
II.	2nd reading	45·4 c.c.	Mean 22·0 c.c.
	1st reading	23·4 c.c.	
		22·0 c.c.	
III.	2nd reading	25·4 c.c.	
	1st reading	3·4 c.c.	
		22·0 c.c.	

∴ 22·0 c.c. of the acid were required to neutralise 25 c.c. of the Normal sodium carbonate solution.

This is analogous to a situation in which a tug-of-war team of 22 men (of equal strength) is just holding another team of 25 men (also of equal strength). Which men individually are the stronger? Obviously the 22.

Similarly, since 22·0 c.c. of the acid neutralise 25 c.c. of the sodium carbonate solution, each c.c. of acid must be more concentrated than each c.c. of sodium carbonate solution, and the acid must be stronger than the sodium carbonate in the ratio $\frac{25}{22}$.

But the sodium carbonate solution was Normal.

$$\therefore \text{ the concentration of the acid is } \frac{25}{22} \times N = 1{\cdot}136N$$

$$Na_2CO_3 + \underset{\substack{73\text{ gm.}\\ \text{contain 2 gm.}\\ \text{replaceable hydrogen.}}}{2HCl} \rightarrow 2NaCl + H_2O + CO_2$$

∴ 1 litre *N* HCl contains 36·5 gm.

Normal hydrochloric acid contains 36·5 gm. per litre.

$$\therefore \text{ concentration of acid is } \frac{25}{22} \times 36{\cdot}5 \text{ gm. per litre}$$

$$= 41{\cdot}5 \text{ gm. per litre.}$$

To make the acid Normal.
22 c.c. of acid neutralised 25 c.c. of *N*. alkali.

If the acid had been exactly *N*., 25 c.c. of it would have neutralised 25 c.c. of the sodium carbonate solution.

∴ 3 c.c. of water must be added to every 22 c.c. of acid left.

On measuring the acid in a large measuring cylinder, 920 c.c. were left.

$$\text{Amount of water to add} = \frac{920}{22} \times 3 \text{ c.c.} = \frac{2760}{22} \text{ c.c.} = 126 \text{ c.c.}$$

Add this volume of water to the acid and stir well. It should then be exactly Normal, but should be checked by titration since the measuring cylinder is not a very accurate instrument.

Experiment 222. *Alternative Method.* **Use of borax to standardise a solution of hydrochloric acid.**

Material: Approx $N/10$ hydrochloric acid; pure borax.

It is best not to rely on one standardisation to determine the normality of a solution. If time is a pressing factor you may estimate the accuracy of your working by titrating your own normal solution against a known normal solution of alkali.*

Borax ($Na_2B_4O_7.10H_2O$) is not very soluble (a saturated solution would be more dilute than $N/2$ at ordinary temperature). Hence, if only normal acid is available it should be diluted to $N/5$ or $N/10$ by running 50 c.c. or 25 c.c. from a pipette into a clean 250 c.c. measuring flask and making up to the mark with distilled water.

$$Na_2B_4O_7.10H_2O + 2HCl \rightarrow \underbrace{2NaCl + 4H_3BO_3 + 5H_2O}_{\text{Too weak an acid to affect the methyl orange.}}$$

From the equation it is evident that the equivalent of borax is half the molecular weight since a molecule of it reacts with 2 atoms of hydrogen from the acid.

Molecular weight = 382. Equivalent = 191

A litre of $N/10$ solution therefore contains 19·1 gm.

To make 250 c.c. of $N/10$ solution, weight of borax required = ¼ of 19·1 gm. = 4·775 gm.

Weigh out 4·775 gm. of pure borax, make up to 250 c.c. Take 25 c.c. of this solution, add a few drops of methyl orange and titrate with the $N/10$ HCl. The boric acid liberated does not affect the end-point if methyl orange is used as an indicator. This method can be used for nitric and hydrochloric acids, but with sulphuric acid the end-point is not satisfactorily defined.

* By diluting normal alkali purchased from your supplier to $N/10$ it is possible to make this check at almost negligible cost.

Experiment 223. To standardise a solution of caustic soda by means of oxalic acid.

Material: Caustic soda; hydrated oxalic acid.

N.B. Oxalic acid is very poisonous.

$$2NaOH + H_2C_2O_4.2H_2O^* \rightarrow Na_2C_2O_4 + 4H_2O$$

80 gm.	126 gm.
Or 2 l. normal.	or 2 l. normal.
∴ *N*/10 is 4 gm. per l.	∴ *N*/10 is 6·3 gm. per l.
∴ 250 c.c. *N*/10 NaOH contain 1 gm.	∴ 250 c.c. *N*/10 oxalic acid crystals contain 1·575 gm.

Quickly weigh out on to a watch-glass about 1·25 gm. of stick caustic soda (the purest form available for purchase). Put it into a beaker, add a few c.c. of water, swill round for a few moments and discard the solution. (This will have removed most of the surface layer of carbonate.) Dissolve the remainder in water and make up to about 250 c.c. in a flask. Weigh out exactly 1·575 gm. of pure oxalic acid crystals in a weighing bottle. (A.R. quality should be used —oxalic acid frequently contains both calcium and potassium oxalates as impurity.) Dissolve the acid in water in a beaker and transfer the solution completely to a 250 c.c. flask and make up to the mark, shake well or pour into a large flask and swirl. Fill a burette with the acid and titrate against 25 c.c. of the caustic soda solution using phenolphthalein as an indicator (one drop should be sufficient to colour the caustic soda solution pink). Run the acid in until the solution becomes colourless. Obtain two consecutive identical readings for the volume of acid necessary to neutralise 25 c.c. of the alkali.

Suppose 25 c.c. of the alkali required 29·0 c.c. of *N*/10 oxalic acid.

$$\text{Then concentration of alkali} = \frac{29}{25} \times \frac{N}{10}$$

$$= \frac{29}{25} \times 4 \text{ gm. per l.}$$

$$= 4{\cdot}64 \text{ gm. per l.}$$

*To obtain a solution exactly N/*10.

If to each 25 c.c. of alkali are added 4 c.c. of water, then 29 c.c. of this solution would neutralise 29 c.c. of *N*/10 oxalic acid since the water would have no effect other than to increase the volume. But these volumes are identical. Hence the solutions are of the same normality, i.e., *N*/10. If the volume of the remaining alkali solution is V c.c., add $\frac{V}{25} \times 4$ c.c. of water and shake well. The solution will then be exactly *N*/10.

---

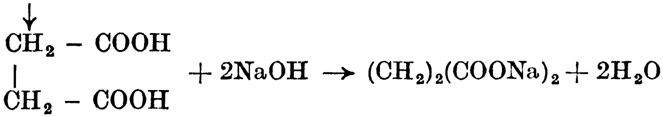
* This water of crystallisation takes no part in the reaction. It is included here because the crystals contain it.

Experiment 224. To standardise a solution of caustic soda by means of succinic acid.

Material: Approx. *N* caustic soda; succinic acid.

Prepare an approximately normal solution of caustic soda as indicated in Expt. 223, using ten times the quantity of caustic soda. Cool the solution to laboratory temperature before using.

This hydrogen
does not ionise.



$$\begin{array}{l} \downarrow \\ CH_2 - COOH \\ | \\ CH_2 - COOH \end{array} + 2NaOH \rightarrow (CH_2)_2(COONa)_2 + 2H_2O$$

Succinic acid
118 gm.   80 gm.
or
2 l. *N*   2 l. *N*.

$$1{\cdot}475 \text{ gm. } \left(\frac{118 \times 25}{2000}\right) \text{ succinic acid} \equiv 25 \text{ c.c. } N.\text{NaOH}.$$

Weigh out accurately from a weighing bottle about $1\frac{1}{2}$ gm. of succinic acid and add to water in a conical flask. Warm in order to dissolve the acid. (Do not be alarmed if it does not all dissolve—the disappearance of the solid will give an early indication of the approach of the end-point.) Add two drops of phenolphthalein and run in *N*.NaOH from the burette, proceeding more cautiously* as you are approaching the end-point (a rough calculation can be made to give the approximate volume of caustic soda necessary). Shake well after each addition and note the reading at the first permanent pink tinge. The whole experiment can be repeated with a further quantity of succinic acid.

Suppose 1·503 gm. of succinic acid required 24·3 c.c. caustic soda.

∴ Concentration of caustic soda solution

$$= \frac{1{\cdot}503}{1{\cdot}475} \times \frac{25}{24{\cdot}3} \times 40 \text{ gm. per l.}$$
$$= 41{\cdot}9 \text{ gm. per l.}$$

N.B. Use a rubber stopper for the bottle in which you are keeping the caustic soda and wash the burette out with water and then with very dilute acid and again with water to prevent the tap of the burette from sticking in its socket. This procedure should be adopted whenever an alkaline solution is placed in the burette.

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* In this case and any other where only one titration is performed with a weighed quantity of material, it is advisable to transfer a small quantity of the solution by means of a pipette into a clean test-tube. It can be added later together with the washings from the pipette and test-tube when the approximate end-point has been found.

Experiment 225. Standardisation of an acid (HNO_3) by the Iceland Spar method.

Material: Conc. nitric acid; Iceland spar.

This method depends on determining the weight of pure calcium carbonate (Iceland spar) dissolved by a known volume of the acid. It is suitable as a check, particularly when the acid solution is fairly concentrated. Note that it cannot be used to standardise sulphuric acid because calcium sulphate is only sparingly soluble.

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$\begin{aligned} &\text{100 gm. of calcium carbonate} &&\equiv \text{2 l. } N.HNO_3 \\ \therefore\ &\text{1·25 gm. of calcium carbonate} &&\equiv \text{25 c.c. } N.HNO_3 \end{aligned}$$

Dilute some concentrated nitric acid with about 10 times its own volume of water. Shake well. Weigh out accurately on a watch-glass a crystal of Iceland spar (2–3 gm.) and introduce it carefully into a conical flask and add about 50 c.c. of water. Run into this water exactly 25 c.c. of the nitric acid solution, place a funnel in the neck and leave in a safe place until the next day (or until effervescence ceases).

Pour away the solution surrounding the crystal and wash it several times with distilled water. Transfer the crystal to a weighed watch-glass, dry it thoroughly in a steam-oven and weigh it.

Suppose loss in weight of crystal is 1·340 gm.

From the equation 25 c.c. $N.HNO_3 \equiv$ 1·25 gm. of $CaCO_3$.

$$\begin{aligned} \therefore\ \text{Concentration of acid is } & \frac{1·340}{1·25} \times N. \\ &= 1·072\ N. \\ &= 67·54 \text{ gm. per l.} \end{aligned}$$

Experiment 226. To determine the equivalent of calcium carbonate by the method of back titration.

Material: Precipitated chalk; *N*. acid; *N*/10 alkali.

The gram-equivalent weight of a compound (which is numerically the same as the equivalent) is that weight of it (in grams) which will combine with or displace 1 gm. of hydrogen. But one l. *N*. acid contains 1 gm. of replaceable hydrogen, and therefore the gm.-equivalent is that weight of the compound which will react with one l. normal acid.

Now calcium carbonate is insoluble in water and difficulties would arise in titrating a standard acid against it. These difficulties can be avoided by dissolving a known quantity of the carbonate in excess acid and determining the amount of excess by titration with alkali. The strength of the latter should be less than that of the acid used, as the amount of acid left will be considerably less than the amount taken up.

Weigh accurately a weighing bottle containing about 1·5 gm. (not more) of pure dry precipitated calcium carbonate. Empty this carefully into a funnel resting in a 250 c.c. flask containing 50 c.c. *N*.HCl and weigh the weighing bottle accurately. Wash the carbonate through into the flask and when effervescence has ceased make up to the mark with water and shake well. Withdraw 25 c.c. and titrate against *N*/10 alkali. Use methyl orange or methyl red as an indicator.

Calculation.

Suppose the weight of calcium carbonate taken = 1·47 gm.; and that 20·6 c.c. *N*/10 alkali neutralised 25 c.c. of residual solution.

∴ 20·6 c.c. *N*. alkali would neutralise 250 c.c. of residual solution.

Volume of *N*. acid originally present = 50 c.c.

∴ (50 − 20·6) c.c., i.e., 29·4 c.c. is the volume of *N*. acid used up.
Hence 29·4 c.c. *N*. acid ≡ 1·47 gm. calcium carbonate.

$$\therefore\ 1{,}000 \text{ c.c. } N. \text{ acid} \equiv \frac{1{\cdot}47}{29{\cdot}4} \times 1{,}000 \text{ gm. of calcium carbonate}$$

$$= 50{\cdot}0 \text{ gm.}$$

∴ The equivalent is 50·0.

In the determination of the equivalent of an unknown compound on these lines it would be necessary, before weighings were made, to assume an equivalent. Then after making up the solution to 250 c.c., it would be necessary to verify that the solution was still acid, and if not, a further 25 c.c. of acid should be added and the solution made up to 500 c.c. If, on back-titrating, an *N*/10 solution of alkali were found to be unsuitable a stronger solution could be used.

Experiment 227. To determine the number of molecules of water of crystallisation in washing soda crystals.

Material: *N*/5 hydrochloric acid.

$$\underset{106\text{ gm.}}{Na_2CO_3} + \underset{2\text{ l. }N.}{2HCl} \rightarrow 2NaCl + H_2O + CO_2$$

∴ 106 gm. of sodium carbonate ≡ 2 l. *N*. acid.

∴ *N*/5 soln. would contain 10·6 gm. of sodium carbonate per l.

Weigh out accurately about 5 gm. of soda crystals (this is assuming about half to be water of crystallisation) being careful to pick translucent crystals. Dissolve these in water in a beaker, transfer the liquid with washings to a 250 c.c. flask, and make up to the mark. Shake well. Take 25 c.c. of this solution in a conical flask, add a few drops of methyl orange and run in *N*/5 hydrochloric acid until the first permanent orange colour is observed. Repeat to obtain two concordant results.

Calculation.

Suppose the weight of soda crystals taken = 5·35 gm.
Suppose 25 c.c. of soda solution required 18·7 c.c. $N/5$ acid.

$\therefore$ Normality of soda solution $= \dfrac{18{\cdot}7}{25} \times \dfrac{N}{5}$

$\therefore$ Conc. in terms of anhydrous sodium carbonate $= \dfrac{18{\cdot}7}{25} \times \dfrac{53}{5}$ gm. per l.

$\therefore$ Weight of anhydrous sodium carbonate in 250 c.c. solution $= \dfrac{18{\cdot}7 \times 53}{25 \times 5 \times 4}$ gm.

$= 1{\cdot}982$ gm.

Let the formula be $Na_2CO_3.xH_2O$

then
$$\frac{Na_2CO_3}{Na_2CO_3.xH_2O} = \frac{1{\cdot}982}{5{\cdot}35} = \frac{106}{106 + 18x}$$

Whence $x = 9{\cdot}9$.

$\therefore$ The number of molecules of water of crystallisation = 10 (since x must be a whole number).

N.B. It is advisable to work with sodium carbonate solution in concentrations not less than $N/5$. In $N/10$ solution the end-point using methyl orange is scarcely sharp enough.

Experiment 228. To determine the amounts of sodium carbonate and sodium hydroxide in a mixture. (*Double indicator method.*)

Material: Mixture of about 5 gm. each, sodium hydroxide and sodium carbonate, in one l. solution; $N/5$ hydrochloric acid.

Principle.

		Indicator to exhibit completion of reaction.
I.	$NaOH + HCl \rightarrow NaCl + H_2O$	Any indicator.
IIa.	$Na_2CO_3 + HCl \rightarrow NaHCO_3 + HCl$	Phenolphthalein.
IIb.	$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$	Methyl orange.

As we have already seen the neutralisation of a strong alkali by means of a strong acid can be followed by the use of any indicator. Sodium bicarbonate solution is slightly acid to phenolphthalein (you should verify this experimentally) whereas sodium carbonate solution is definitely alkaline to it. If acid is added to a mixture of caustic soda and sodium carbonate in solution using phenolphthalein as indicator then the pink colour of the indicator is discharged when reactions I and IIa are complete. If methyl orange is now added and a further quantity of acid added the amount required will be that necessary to complete reaction IIb. But one molecule of sodium bicarbonate has been formed from one molecule of sodium carbonate and hence the amounts of acid required for reactions IIa and IIb will be the same.

Suppose the volume of acid needed to reach the end-point as indicated by the phenolphthalein is *a* c.c. and the *additional* volume of acid to reach the end-point as indicated by the methyl orange is *b* c.c.

Then volume of acid reacting with sodium carbonate is 2 *b* c.c.
" " " " " hydroxide is
$(a + b) - 2b$ c.c. $= (a - b)$ c.c.

Method. Take 25 c.c. of the solution containing the mild and caustic alkali and add 1–2 drops of phenolphthalein solution and run in $N/5$ HCl until the pink colour is just discharged. Note the burette reading and add a few drops of methyl orange (or better methyl yellow) and add a further quantity of acid until the yellow colour of the methyl orange changes to orange.

Calculation. Suppose 25 c.c. of mixture required 21·3 c.c. of $N/5$ HCl (phenolphthalein) and that the same 25 c.c. of mixture required a further 7·9 c.c. of $N/5$ HCl (methyl orange).

Total volume of $N/5$ HCl used = 29·2 c.c.

Half of the Na_2CO_3 required 7·9 c.c. of $N/5$ acid.

∴ All the Na_2CO_3 required 15·8 c.c. of $N/5$ acid.

∴ The NaOH required (29·2 − 15·8) c.c. or 13·4 c.c. of $N/5$ acid.

∴ Concentration of the sodium carbonate solution is $\frac{15 \cdot 8}{25} \times \frac{N}{5}$

$$= \frac{15 \cdot 8}{25} \times \frac{53}{5} \text{ gm. per l.}$$

$$= 6 \cdot 7 \text{ gm. per l.}$$

Concentration of the caustic soda solution is $\frac{13 \cdot 4}{25} \times \frac{N}{5}$

$$= \frac{13 \cdot 4}{25} \times \frac{40}{5} \text{ gm. per l.}$$

$$= 4 \cdot 29 \text{ gm. per l.}$$

Note: The above exercise is a useful one on mixed indicators and one requiring thought. Unless the conditions are carefully controlled, however, and end points correctly determined its accuracy leaves much to be desired. As an aid to the memory the student is reminded (*a*) the reaction between the alkali NaOH and hydrochloric acid cannot take place in two stages as can the reaction $Na_2CO_3 \rightarrow NaHCO_3 \rightarrow NaCl$ (see equation, p. 238);

(*b*) that the phenolphthalein must obviously be the indicator first added since it is colourless in acid solution and will not mask the colour of the methyl orange added later.

Experiment 229. Determination of the amounts of sodium carbonate and sodium hydroxide in a mixture (C. Winkler).

Material: *N*/10 hydrochloric acid; mixture of 2–3 gm. each, sodium hydroxide and sodium carbonate in one l. solution; *N*/5 barium chloride.

Where accuracy is of prime importance the method due to Winkler is more satisfactory. The solutions used may be much more dilute without loss in accuracy.

Principle. The total alkali present (carbonate and hydroxide) is determined by titration with *N*/10 acid using methyl orange as an indicator. To a second portion excess barium chloride solution is added

$$Na_2CO_3 + BaCl_2 \rightarrow 2NaCl + BaCO_3 \downarrow$$

Thus the carbonate is removed as insoluble barium carbonate. The hydroxyl ions from the alkali remain in solution. The strength of these is determined in the usual way, using phenolphthalein as an indicator.

Method. Make up a solution of the mixture of strength about *N*/10. To 25 c.c. of this solution add methyl orange and titrate with *N*/10 hydrochloric acid until the yellow colour changes to orange. To a further 25 c.c. of the original solution add about an equal volume of *N*/5 barium chloride solution and add 1–2 drops of phenolphthalein and titrate with *N*/10 hydrochloric acid, noting the burette reading when the solution is decolorised. Take care to run in the acid slowly otherwise some of the barium carbonate may be acted upon before the end-point is reached.

Calculation. Suppose 25 c.c. of mixed sodium hydroxide and carbonate solution required *a* c.c. *N*/10 HCl (methyl orange).
A further 25 c.c. after treatment with $BaCl_2$ required
b c.c. *N*/10 HCl (phenolphthalein).

∴ Volume of acid required to react with NaOH = *b* c.c.
,, ,, ,, ,, ,, $Na_2CO_3 = (a - b)$ c.c.

$$\therefore \text{ Concentration of NaOH } = \frac{b}{25} \times \frac{N}{10}$$

$$= \frac{b \times 40}{250} \text{ gm. per l.}$$

$$\text{Concentration of } Na_2CO_3 = \frac{(a-b)}{25} \times \frac{N}{10}$$

$$= \frac{(a-b) \times 53}{25 \times 10} \text{ gm. per l.}$$

Experiment 230. Estimation of ammonia in ammonium sulphate by the indirect method.

Apparatus: Condenser tube and cork. *Material*: *N*. alkali; *N*/10 acid; ammonium sulphate.

The ammonium salt (as solid or solution) is boiled with excess alkali and the excess determined by back-titration with acid.

$$\underset{132\text{ gm.}}{(NH_4)_2SO_4} + \underset{2\text{ l. }N.}{2NaOH} \rightarrow Na_2SO_4 + \underset{34\text{ gm.}}{2NH_3} + 2H_2O$$

$\therefore$ equivalent of ammonium sulphate = 66

$$\therefore \text{ 1 gm. pure ammonium sulphate} \equiv \frac{1000}{66} \text{ c.c. } N. \text{ alkali}$$

$$\equiv 15{\cdot}1 \text{ c.c. } N. \text{ alkali.}$$

Weigh accurately a weighing bottle containing about 1·5 gm. of pure ammonium sulphate and transfer this to a conical flask. Weigh the bottle. Run in exactly 50 c.c. of *N*.NaOH into the conical flask and insert in the flask a rubber cork into which a condenser tube is fitted (Fig. 71). (This prevents loss of caustic soda solution.) Boil the contents of the flask for about 15 minutes or until no smell of ammonia is perceptible. Pour a little water down the condenser tube and so wash any caustic soda solution back into the flask. Pour the whole solution into a 250 c.c. flask, adding several washings from the conical flask, cool the solution under the tap, and make up to the mark. Shake well. Titrate portions of 25 c.c. of this solution against *N*/10 acid using methyl orange as an indicator.

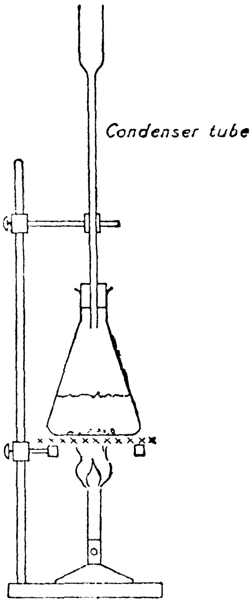

FIG. 71.

Calculation. Suppose *a* gm. of ammonium sulphate were taken and that 25 c.c. of solution (made up to 250 c.c.) required *b* c.c. of *N*/10 acid.

$\therefore$ 250 c.c. would require *b* c.c. *N*. acid.

$\therefore$ $(50 - b)$ c.c. of *N*.NaOH were used up.

But one l. N.NaOH $\equiv$ 17 gm. NH_3.

$$\therefore\ (50 - b)\ \text{c.c.} \equiv \frac{17}{1000} \times (50 - b)\ \text{gm.}\ NH_3$$

$$\therefore\ \%\,NH_3\ \text{in sample} = \frac{17}{1000}\,\frac{(50 - b)}{a} \times 100\%.$$

Experiment 231. Estimation of ammonia in an ammonium salt (e.g., ammonium sulphate) by the direct method.

Apparatus: As in Fig. 72. *Material*: N. acid; $N/10$ alkali; ammonium sulphate.

This experiment can be made to serve as a useful test of the strength of an acid solution you have made. (The strength of the acid should be about normal.) Ammonium sulphate can be obtained in a very pure state, and this method is used in industry to standardise acid solutions.

Principle. A weighed amount of the ammonium sulphate is boiled with excess caustic soda solution. The ammonia which is driven off is absorbed in excess of standard acid and the volume of the latter used up is found by back-titration.

Weigh accurately a weighing bottle containing about 1·5 gm. of ammonium sulphate (see Expt. 230) and empty this carefully into a funnel in a round-bottomed flask which should contain a few pieces of porous pot. Wash the sulphate through with distilled water.

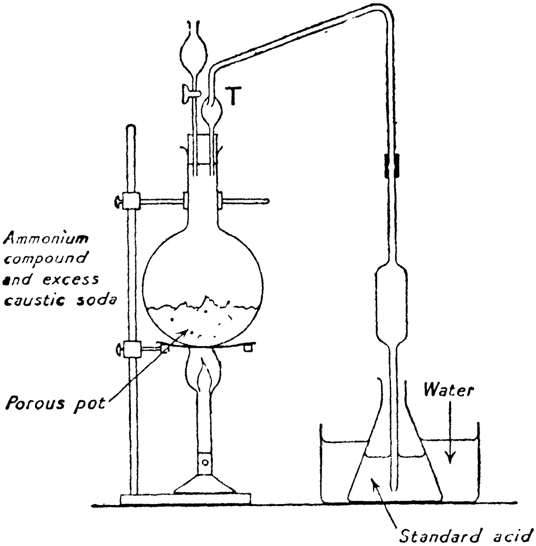

FIG. 72.

Weigh the weighing bottle. Run in exactly 50 c.c. *N*. sulphuric acid (or hydrochloric acid) into a conical flask standing in cold water. Fit up the apparatus shown in Fig. 72. The trap T is to prevent droplets of caustic soda from being mechanically carried over into the standard acid.

Pour about 100 c.c. (a large excess) of bench caustic soda into the flask containing the ammonium sulphate. Warm the contents of the flask gently and finally boil for about ten minutes. At the end of that time remove the cork and smell the vapour. If the ammonia can be detected the boiling must be continued for a few more minutes and the test repeated until no ammonia can be smelled. Remove the burner from underneath the solution, raise the pipette out of the acid solution, wash back into the conical flask any acid solution clinging to it inside or outside. Make up the residual acid to 250 c.c. taking care to include all washings and titrate 25 c.c. of this against *N*/10 caustic soda solution using methyl orange as an indicator. Calculate the percentage of ammonia from the fact that one l. *N*. $H_2SO_4 \equiv$ 17 gm. of ammonia.

Experiment 232. To determine the degree of temporary hardness in water.

Material: *N*/10 hydrochloric acid; temporarily hard water.

Prepare a temporarily hard water (if one is not available) by bubbling a rapid stream of carbon dioxide through lime water (there is no need to wait until the solution is clear—any precipitate can be filtered off). Take 100 c.c. of the solution, add a few drops of methyl orange and run in the standard hydrochloric acid (about *N*/10) until the yellow colour changes to orange.

Suppose *a* c.c. of 0·104 *N*. acid are required for 100 c.c. of the temporarily hard water

$$a \text{ c.c. of } 0{\cdot}104\ N.\text{ acid} \equiv 0{\cdot}104 \times a \text{ c.c. } N.\text{ acid.}$$

Now hardness is conventionally expressed as parts by weight of *calcium oxide** per 100,000 parts by weight of water.

Since 100 c.c. of the water required 0·104 × *a* c.c. *N*. acid.

∴ 100,000 c.c. of the water would require 104 × *a* c.c. *N*. acid.

$$= \frac{104\,a}{1000} \text{ l. } N.\text{ acid.}$$

$$\begin{array}{ll} Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O + 2CO_2 \\ 162 \text{ gm.} \qquad 2 \text{ l. } N. \end{array}$$

∴ One l. *N*. $Ca(HCO_3)_2$ contains 81 gm.

---

* Hardness is also sometimes expressed as parts of calcium carbonate per 100,000 parts of water.

But 81 gm. of calcium bicarbonate would form 28 gm. calcium oxide if heated, and this is the equivalent weight of calcium oxide.

$$\therefore \text{ No. of degrees of hardness} = \frac{104\,a}{1000} \times 28 \text{ degrees.}$$

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1) *Material*: Formaldehyde† solution; *N*. hydrochloric acid; *N*. ammonium chloride; *N*. sodium hydroxide.

Investigate the reaction between ammonia and formaldehyde in aqueous solution. The following experiments are suggested.

(*a*) Mix excess (50 c.c.) of the formaldehyde solution with 20 c.c. of the normal ammonium chloride; add 40 c.c. of the normal sodium hydroxide, and leave the liquid fifteen minutes before titrating with normal hydrochloric acid using phenolphthalein.

(*b*) Mix excess (50 c.c.) of the normal ammonium chloride with 20 c.c. of the formaldehyde solution, add 40 c.c. of the normal sodium hydroxide, and leave for fifteen minutes before titrating with normal hydrochloric acid. Litmus may be used, but brom-thymol-blue will be found more satisfactory. Repeat the experiment but omit the formaldehyde. State briefly the conclusions at which you arrive.

(Cambridge Schol. 1935.)

(2)* *Material*: *N*. ammonium hydroxide; M/10 copper sulphate; *N*/20 sulphuric acid; chloroform.

Determine the composition of the complex cuprammonium ion formed when excess ammonia is added to a copper sulphate solution. Mix 25 c.c. of *N*. ammonia (solution A) with 25 c.c. of M/10 copper sulphate (solution B). Shake the resulting liquid with 75 c.c. of chloroform for ten minutes. Separate off 50 c.c. of the chloroform and determine the amount of ammonia in it by titration in a stoppered bottle with the standard *N*/20 acid provided. Assume that free ammonia distributes itself between the solution and chloroform in the ratio

$$\frac{\text{Concentration in aqueous solution}}{\text{Concentration in chloroform.}} = 26.$$

Note: Use a measuring cylinder and not a pipette for the chloroform.

(Cambridge Schol. 1935.)

(3) *Material*: Impure calcium carbonate; *N*. hydrochloric acid; *N*/10 sodium hydroxide.

The substance A is a mixture of calcium carbonate and silica. You are required to find its percentage composition by weight.

Weigh out accurately about 1 gm. of the mixture and transfer it to a graduated 250 c.c. flask. Add 50 c.c. of normal hydrochloric acid. When the reaction is complete make the liquid up to the mark with distilled water, shake well to

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† A 4 per cent solution will be found to be satisfactory.

ensure thorough mixing and titrate 25 c.c. portions with decinormal sodium hydroxide solution using methyl orange as indicator.

H = 1, C = 12, O = 16, Na = 23, Cl = 33·5, Ca = 40.

(N.U.J.B. 1935.)

(4)* *Material*: Sodium hydrogen sulphate; sodium bicarbonate.

Determine the purity of the laboratory specimen of sodium bisulphate. You are supplied with pure sodium carbonate (or bicarbonate).

(5) *Material*: Sodium hydroxide and ammonium chloride solution; *N*/10 hydrochloric acid.

You are provided with a solution containing ammonium chloride and caustic soda in such proportions that concentration (by weight) of ammonium chloride: concentration (by weight) of caustic soda is $\nless$ 53·5 : 40. Find the concentration of each in gm. per litre. You are provided with *N*/10 HCl.

(6)* *Material*: *N*/10 sodium carbonate.

Estimate the strength of the barium chloride solution in the reagent bottles. You are supplied with *N*/10 Na_2CO_3. Phenolphthalein will show the end point of the reaction:—

$$BaCl_2 + Na_2CO_3 \rightarrow BaCO_3 \downarrow + 2NaCl$$

(7)* *Quantitative Verification of Solubility Product* (*F. G. Mee*). *Material*: Pure sodium hydroxide *N*/10; *N*/10 hydrochloric acid.

Lime should have a smaller solubility in a solution of caustic soda than in water, and it is the object of this experiment to verify that the decrease of solubility that occurs is that which would be expected from the application of the Law of Mass Action to the ionic equilibrium.

$$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$$

If we provide extra OH ions from some other source—NaOH in this case—the concentration of Ca^{++} ions should decrease in such a way that the product of it and the square of the concentration of OH ions remains a constant, if the solution is saturated.

To verify this solutions of lime are made up in (1) water, (2) *N*/40 soda, (3) *N*/20 soda, (4) *N*/10 soda. The soda should be as free as possible from carbonate, and the solutions can be made by adding a quantity of slaked lime to each of the soda solutions and allowing to stand, with shaking at intervals. Each of these solutions is titrated with *N*/10 HCl, which will, in each case, give a measure of the total OH concentration present. The OH concentration due to the soda is known, assuming this to be fully ionised also. Subtraction will yield the concentration of OH due to dissolved lime, and the concentration of Ca^{++} is exactly half of this. This titration will thus give us all we require to calculate the solubility product.

A typical set of results is the following:—

Twenty c.c. of each of the four solutions were titrated with *N*/10 HCl, using phenolphthalein indicator, with results shown in the second column of the table.

Solution in	Titration c.c.	Ionic concentrations in gm.-ions./litre.				$[Ca^{++}] \times [OH]^2$.
		Total OH present.	OH due to soda.	OH due to lime.	Ca^{++}	
Water	9·5	0·0475	—	0·0475	0·0237	$5{\cdot}4 \times 10^{-5}$
N/40 soda	11·6	0·058	0·025	0·033	0·0165	5·6 . . .
N/20 soda	14·2	0·071	0·050	0·021	0·0105	5·3 . . .
N/10 soda	21·8	0·1090	0·100	0·0090	0·0045	5·4 . . .

The constancy of the product is striking. The effect of decreasing the solubility due to the NaOH appears during the experiment, before the detailed calculation is made. Lime in water gave a titration 9·5 c.c.; *N*/20 soda alone would give 10 c.c. Yet lime in *N*/20 soda gives but 14·2 c.c., showing that the solubility has been reduced to about one-half by the presence of soda at this concentration. The result with *N*/10 soda cannot be expected to be very accurate, since at this concentration the lime contributes so very little to the total OH. If more than four results are desired, they should therefore be taken with soda solutions between the above values, and not stronger than *N*/10.

(Taken by kind permission of Messrs. John Murray from the Science Master's Book.)

QUESTIONS AND CALCULATIONS

(*Answers appear on p.* 301).

(1) Explain the term *decinormal* solution.

What weights of caustic potash, sulphuric acid, potassium permanganate are present respectively in a litre of a decinormal solution of each substance?

Describe how you would find the strength of a solution of sodium carbonate if you were provided with a decinormal solution of sulphuric acid.

Atomic weights: K = 39, Na = 23, O = 16, S = 32, Mn = 55, C = 12.

(Durham H.S.C. Subsid. 1934.)

(2) 0·56 gm. of the oxide of a metal was dissolved in 250 c.c. of a solution of hydrochloric acid containing 3·65 gm. per litre. To neutralise the excess of acid 50 c.c. of a solution of caustic soda containing 4·0 gm. per litre were required. Calculate the equivalent of the metal.

(N.U.J.B. Subsid.)

(3) What do you understand by the terms acid, base, salt? 10 c.c. of a solution of caustic potash containing 4 gm. of KOH per litre required for neutralisation 12·5 c.c. of a solution of sulphuric acid.

Calculate the number of grams of sulphuric acid in 1 litre of solution. What is the normality of the solution?

(Atomic weights: K = 39, O = 16, H = 1, S = 32.)

(Durham H.S.C. Subsid. 1936.)

(4) 4·35 gm. of a mixture of sodium chloride and anhydrous sodium carbonate were dissolved in distilled water and the solution made up to 100 c.c. 20 c.c. of this solution required 75·5 c.c. of decinormal sulphuric acid to react completely with the sodium carbonate. Calculate the percentage composition by weight of the original mixture.

Na = 23, Cl = 35·5, C = 12, H = 1, O = 16, S = 32.

(N.U.J.B. Subsid.)

(5) A solution of sodium carbonate and bicarbonate gave the following results when analysed. Explain the two methods adopted, and calculate the weight of each salt present in a litre of the solution.

(*a*) 20 c.c. required 11·1 c.c. of 0·09 *N*.HCl for neutralisation when phenolphthalein was used as the indicator, and a further 33·3 c.c. of acid when methyl orange was added.

(*b*) 20 c.c. of 1·1 *N*.NaOH were added to 100 c.c. of the solution. Excess of barium chloride solution was then added, and the liquid was finally titrated with 0·8 *N*.HCl, the indicator used being phenolphthalein. 15 c.c. were required. (Use also the result of the methyl orange titration given in (*a*).)

[Na = 23, C = 12, O = 16.]

(Oxford H.S.C. 1936.)

CHAPTER XXXV

POTASSIUM PERMANGANATE

Potassium permanganate, $KMnO_4$, is a powerful oxidising agent and is used for the estimation of many reducing agents, especially compounds of iron, and oxalic acid and its salts.

Conditions of Use of Potassium Permanganate. In acid solution two molecules of potassium permanganate yield, for oxidation purposes, 5 atoms of oxygen. The essential part of the reaction is represented by the ionic equation:—

$$2KMnO_4 \rightarrow 2K^+ + 2MnO_4^-$$

$$2MnO_4^- + 6H^+ \rightarrow 2Mn^{++} + 3H_2O + 5[O] \text{ for oxidation.}$$

This equation is more usually written in the form:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \text{ for oxidation.}$$

In alkaline solution, two molecules of potassium permanganate yield three atoms of oxygen for oxidation purposes, together with manganese dioxide as a brown precipitate. Consideration of these facts makes it clear at once that for quantitative work, potassium permanganate must be used in conditions which exclude entirely one of these reactions. In practice, potassium permanganate is almost always used to titrate solutions which are sufficiently acidic to exclude altogether the formation of manganese dioxide.

Of the three mineral acids available, only sulphuric acid is suitable for use with potassium permanganate, for this compound reacts with hydrochloric acid:—

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2,$$

while nitric acid is itself an oxidising agent and might interfere with the oxidising action of the permanganate. The solution which is in process of titration with potassium permanganate must be sufficiently acidic to prevent the formation of any precipitate of manganese dioxide. As bench* sulphuric acid is usually $2N$ and potassium permanganate solution about $N/10$, a bulk of bench acid equal to half that of the solution to be titrated will usually provide a sufficient excess of acid.

Indicator and End-point. In the presence of sulphuric acid, potassium permanganate reacts with reducing agents according to the fundamental equation:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \text{ for oxidation.}$$

---

* Bench sulphuric acid is often more concentrated than $2N$. The smaller volume then required can be calculated.

As the titration proceeds, potassium and manganese sulphates accumulate, but at the dilution used, both give colourless solutions. As soon as potassium permanganate is in excess, the solution becomes pink and therefore potassium permanganate acts as its own indicator, the end-point being the first permanent pink coloration.

Standard Solution of Potassium Permanganate. From the equation given in the preceding paragraph we obtain the equivalency

$$2KMnO_4 \equiv 5[O]$$

i.e., 2(39+55+64) gm. of potassium permanganate

$$\equiv 5\,(16)\text{ gm. of oxygen}$$

i.e., $316\text{ gm. } KMnO_4 \equiv 80\text{ gm. of oxygen}$

and $31{\cdot}6\text{ gm. } KMnO_4 \equiv 8\text{ gm. of oxygen.}$

Since the equivalent is the number of parts by weight of a substance *which combines with or gives* 8 *parts by weight of oxygen,* 31·6 is the equivalent of potassium permanganate.

Hence a litre of *N*/10 $KMnO_4$ solution contains 3·16 gm. of the salt, and will under the stated conditions, give 0·8 gm. of oxygen.

An accurately *N*/10 solution of potassium permanganate cannot be made up directly from the solid because this may be reduced by organic matter from the atmosphere and so rendered impure; further, organic matter present in the water in which the salt is dissolved may reduce it. It is therefore desirable to make up a solution slightly stronger than *N*/10 (say about 3·25 gm. per litre) and allow it to stand several days. It may then be standardised by methods described below, and diluted to *N*/10 by appropriate addition of water. (The added volume of water will be relatively small and organic matter in it negligible.) A potassium permanganate solution slowly decomposes and should be protected from light and standardised again at intervals. It may be standardised by a pure ferrous salt or a pure oxalate.

Experiment 233. Standardisation of potassium permanganate solution by a ferrous salt (ferrous ammonium sulphate).

Material: Approx. *N*/10 $KMnO_4$; ferrous ammonium sulphate.

The oxidation of a ferrous salt by potassium permanganate may be expressed ionically thus:—

$$2Fe^{++} + \underset{\substack{\text{from}\\ H_2SO_4}}{2H^+} + \underset{\substack{\text{from}\\ KMnO_4}}{[O]} \rightarrow 2Fe^{+++} + H_2O$$

or using ferrous sulphate, since $2KMnO_4 \equiv 5[O]$, the oxidation may be written in the more usual form:—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Ferrous sulphate crystals, $FeSO_4.7H_2O$, cannot be used for standardisation because they are rendered impure by efflorescence and by atmospheric oxidation to form a brown basic sulphate as a result of a reaction of the type:—

$$12FeSO_4 + 3O_2 + 6H_2O \rightarrow 4[Fe(OH)_3.Fe_2(SO_4)_3]$$

The salt, ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is free from these disadvantages and can be obtained in a high state of purity. (See Expt. 142.) In solution, it breaks up into ferrous ions, sulphate ions and ammonium ions. Only the former react with the permanganate.

From the equation given above, we have

$$\begin{aligned} 2KMnO_4 &\equiv 10FeSO_4 \\ \therefore \quad 2KMnO_4 &\equiv 10[FeSO_4.(NH_4)_2SO_4.6H_2O] \\ 316 &\equiv 10 \times 392 \\ 31{\cdot}6 &\equiv 392 \end{aligned}$$

Since 31·6 is the equivalent of potassium permanganate, 392 is the equivalent of ferrous ammonium sulphate.

A litre of $N/10$ ferrous ammonium sulphate solution will contain 39·2 gm. of the salt, and 250 c.c. will contain 9·8 gm.

This amount should be weighed out in a weighing bottle. To prevent oxidation, the ferrous ammonium sulphate should now be dissolved in diluted sulphuric acid, which has been boiled to remove air and then cooled. Make up the 9·8 gm. of ferrous ammonium sulphate to 250 c.c. of solution in this way. It is then accurately $N/10$.

Titration. Measure out 25 c.c. of the solution into a conical flask. Add a few c.c. of bench sulphuric acid and titrate with the potassium permanganate solution from a burette until the first permanent pink coloration is observed. (No brown precipitate should appear—add more acid if it does.) Repeat the titration twice.

Suppose the following results are obtained:—

Titrations.

$N/10$ Ferrous ammonium sulphate solution.	$KMnO_4$ *solution.*
25 c.c.	23·45 c.c.
25 c.c.	23·35 c.c.
25 c.c.	23·40 c.c.

Calculation. The average volume of potassium permanganate solution is 23·4 c.c. for each 25 c.c. of the ferrous ammonium sulphate. Then, since the ferrous salt solution is exactly $N/10$ the permanganate solution must be $\frac{25}{23{\cdot}4} \cdot \frac{N}{10}$ or $0{\cdot}1068N$, and since $N/10$ $KMnO_4$

contains 3·16 gm. per litre this permanganate solution contains 0·1068 × 3·16 gm. per litre.

$$= 3{\cdot}375 \text{ gm. per l.}$$

To make it exactly *N*/10, 68 c.c. of water must be added to each litre of the potassium permanganate solution (see p. 233), shaking or stirring to produce uniformity.

Experiment 234. Standardisation of potassium permanganate solution by sodium oxalate $Na_2C_2O_4$.

Material: Approx. *N*/10 potassium permanganate; sodium oxalate.

An acidified solution of an oxalate is for purposes of titration with potassium permanganate solution equivalent to a solution of oxalic acid itself:—

$$\begin{aligned} Na_2C_2O_4 &\rightleftharpoons 2Na^+ + C_2O_4^{--} \\ C_2O_4^{--} + \underset{\text{from acid}}{2H^+} &\rightleftharpoons H_2C_2O_4 \end{aligned}$$

Sodium oxalate is used for standardisation because it can be obtained in a pure state more easily than can oxalic acid.

The oxidation of oxalic acid is represented essentially by the equation:—

$$H_2C_2O_4 + \underset{\substack{\text{from} \\ KMnO_4}}{[O]} \rightarrow 2CO_2 + H_2O$$

The complete equation is:—

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

$$\begin{aligned} \text{From this} \quad 2KMnO_4 &\equiv 5H_2C_2O_4 \\ \text{i.e.,} \quad 2KMnO_4 &\equiv 5Na_2C_2O_4 \\ 316 &\equiv 5 \times 134 \\ 31{\cdot}6 &\equiv 67 \end{aligned}$$

The equivalent of sodium oxalate is therefore 67, and a litre of *N*/10 solution will contain 6·7 gm. of the salt.

∴ 250 c.c. of *N*/10 solution contains 1·675 gm.

Weigh out this amount and make up to 250 c.c. of *N*/10 solution with distilled water. When measuring this solution in a pipette be careful not to allow it to enter your mouth. Oxalates are poisonous.

Titration. Potassium permanganate does not oxidise oxalates in cold solution; a temperature of 60° C. is necessary to cause the reaction to begin.

To 25 c.c. of the *N*/10 $Na_2C_2O_4$ solution in a conical flask add about 15 c.c. of bench sulphuric acid and heat the mixture to 60° C. (This temperature can be estimated accurately enough by testing with the palm of the hand. When the bottom of the flask is just too hot to hold, the temperature of the liquid is approximately correct.) Titrate with potassium permanganate, heating again as the liquid cools,* till a permanent pink coloration is observed. Repeat the titration twice with further portions of 25 c.c.

Calculate the concentration of the permanganate solution as described under the heading of standardisation with ferrous ammonium sulphate (p. 250).

The standard potassium permanganate solution so obtained may be used for a variety of estimations, of which the following are typical:—

Experiment 235. Determination of the number of molecules of water of crystallisation in a molecule of ferrous sulphate crystals ($FeSO_4.xH_2O$).

Material: $N/10$ potassium permanganate.

$$\begin{aligned} 10(FeSO_4.xH_2O) + 2KMnO_4 + 8H_2SO_4 &\rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 \\ &\quad + 2MnSO_4 + (10x + 8)H_2O. \end{aligned}$$

$$\begin{aligned} 2KMnO_4 &\equiv 10(FeSO_4.xH_2O) \\ 316 &\equiv 10 \times (152 + 18x) \\ 31{\cdot}6 &\equiv 152 + 18x \end{aligned}$$

Therefore, $(152 + 18x)$ is the equivalent of ferrous sulphate crystals, and

a litre of $N/10$ solution contains $\dfrac{152 + 18x}{10}$ gm. of the salt.

$\therefore$ 250 c.c. of $N/10$ solution contains $\dfrac{152 + 18x}{40}$ gm.

x will probably be between 1 and 10, i.e., the weight of crystals should be between 4·3 gm. and 8·3 gm. Weigh out about 7 gm. of crystals and make up to 250 c.c. of acidified solution, as described for ferrous ammonium sulphate (p. 250). Titrate against $N/10$ $KMnO_4$ solution.

Calculation. Suppose *a* gm. of crystals were made up to 250 c.c. of solution and 25 c.c. of this solution required *b* c.c. $N/10$ $KMnO_4$ solution for oxidation.

$$10(FeSO_4.xH_2O) \equiv 2KMnO_4$$

Suppose *a* gm. of crystals were made up to 250 c.c. This is a concentration of 4*a* gm. per litre.

If 25 c.c. of this solution required *b* c.c. of $N/10$ $KMnO_4$ solution

---

* Manganese sulphate formed during the reaction has a catalytic effect, but side reactions are prevented if the temperature is still maintained at about 60° C.

for oxidation, the solution would be $\frac{b}{25} \times N/10$ and would contain

$$\frac{b}{25} \times \frac{(152 + 18x)}{10} \text{ gm. of the salt per l.}$$

But this is $4a$ gm. by preparation,

$$\therefore \quad \frac{b}{25} \times \frac{(152 + 18x)}{10} = 4a$$

$$\text{or,} \quad 152 + 18x = \frac{1000a}{b}$$

Solve for x.

Experiment 236. Estimation of the percentage by weight of iron in iron wire.

Apparatus: Bunsen valve. *Material*: $N/10$ potassium permanganate; iron wire.

A suitable weight of iron is converted to ferrous sulphate solution, which is then titrated with $N/10$ $KMnO_4$.

From the equation on p. 249.

$$\begin{aligned} 2KMnO_4 &\equiv 10Fe \\ 316 &\equiv 10 \times 56 \\ 31{\cdot}6 &\equiv 56 \end{aligned}$$

$\therefore$ the equivalent of iron in this reaction is 56.

56 gm. of iron when dissolved and made up to a litre would be a normal solution.

$\therefore$ To make 250 c.c. of $N/10$ solution required weight of pure iron is $\frac{5{\cdot}6}{4}$ gm. $= 1{\cdot}4$ gm.

Weigh accurately 1·3 to 1·5 gm. of the wire.

Preparation of the Ferrous Sulphate Solution. The iron is treated with dilute sulphuric acid, heat being necessary to secure a sufficiently rapid reaction. Conditions must be such that ferric compounds are not formed. While the reaction is actually proceeding, the hydrogen generated acts as a reducing agent, but when solution is complete and the liquid is still hot, entry of air might bring about oxidation. To prevent this, the "Bunsen valve" is used. It consists of a piece of rubber tubing, carrying a longitudinal slit for part of its length, closed at the upper end by glass rod and connected by a stopper and glass tubing to the reaction flask (Fig. 73). The slit opens outwards only; it allows the escape of

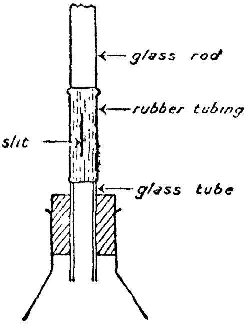

FIG. 73.

hydrogen, but when the flask is cooling air cannot be drawn in because the valve closes. When the solution is cool, the risk of oxidation is negligible.

Fit a "Bunsen valve" to a small flask and in it warm the weighed iron wire with dilute sulphuric acid till all the iron is dissolved.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

The solution will probably be cloudy. This effect is caused by precipitation of fine particles of carbon, an impurity in the iron. They will not interfere. When the reaction is complete and the flask has cooled, transfer the solution to a 250 c.c. flask, wash out the reaction flask several times with air-free distilled water and add the washings to the 250 c.c. flask. Make up to the mark with air-free distilled water and shake well. Titrate against $N/10$ $KMnO_4$.

Calculation. Suppose *a* gm. iron wire are converted into 250 c.c. of ferrous sulphate solution and 25 c.c. of this require *b* c.c. $N/10$ $KMnO_4$ for oxidation

$$\begin{aligned} 2KMnO_4 &\equiv 10Fe \\ 316 &\equiv 10 \times 56 \\ 31{\cdot}6 &\equiv 56 \end{aligned}$$

a gm. of iron in 250 c.c. of solution is 4*a* gm. of iron per litre.
From the titration,
25 c.c. of this solution is oxidised by *b* c.c. of $N/10$ $KMnO_4$

$$\therefore \text{ the solution is } \frac{b}{25} \times \frac{N}{10}$$

$$\text{and contains } \frac{b}{25} \times \frac{56}{10} \text{ gm. of iron per l.}$$

$$\therefore \text{ \% of iron in the wire } = \frac{\frac{b \times 56}{250}}{4a} \times 100$$

Experiment 237. Estimation of ferric iron in ferric ammonium alum.

Material: $N/10$ potassium permanganate; ferric ammonium alum.

Estimation of iron in the ferric state is carried out by first reducing it quantitatively to the ferrous state and then titrating the resulting ferrous solution by $N/10$ $KMnO_4$.

$$\begin{aligned} 2KMnO_4 &\equiv 10Fe \\ \therefore\ 2KMnO_4 &\equiv 5[Fe_2(SO_4)_3{\cdot}(NH_4)_2SO_4{\cdot}24H_2O] \\ 316 &\equiv 5 \times 964 \\ 31{\cdot}6 &\equiv 482 \end{aligned}$$

482 is therefore the equivalent of ferric ammonium alum under the conditions stated.

A litre of $N/10$ solution will contain 48·2 gm. of the salt.
∴ to make 250 c.c. of solution, 12·05 gm. will be required.

Weigh out accurately about 12 gm. of the alum and make up this weight to 250 c.c. of solution, acidifying with dilute sulphuric acid to prevent hydrolysis.

Reduction of the Ferric Salt to the Ferrous State by "Nascent" Hydrogen. Measure out 25 c.c. of the iron alum solution in a conical flask, add dilute sulphuric acid and several pieces of zinc. (The zinc must be free from iron.) Allow effervescence to proceed for twenty minutes (set up two more similar reduction flasks in the meantime). The mixture may then be tested for completion of the reduction.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + [2H]$$
$$[2H] + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4$$

Test. Place on a white tile a drop of a solution of potassium thiocyanate, KCNS. Dip a glass rod into the reduction flask and allow a drop of liquid from it to mix with the drop of solution on the tile. If a reddish brown tinge appears, ferric thiocyanate has been formed, i.e., ferric salt still remains and reduction is not complete.

ionically: $$\underset{\text{ferric ion.}}{Fe^{+++}} + 3CNS^- \rightarrow \underset{\text{red ferric thiocyanate.}}{Fe(CNS)_3}$$

Continue the reduction until the test is negative, i.e., the mixture remains colourless or is only very faintly coloured.

Cool the contents of the flask, filter through glass-wool (for speed), wash the zinc and flask well with air-free distilled water. Add the washings to the main solution and titrate against $N/10$ $KMnO_4$. (Acidify further if necessary.) Repeat with the other two flasks, but delay the test for completion until reduction has proceeded for at least as long as was necessary before. This prevents loss of solution in repeated testing.

Calculation. Suppose *a* gm. of iron alum were made up to 250 c.c. of solution and 25 c.c. of this, after reduction, required *b* c.c. $N/10$ $KMnO_4$ for oxidation.

$$2KMnO_4 \equiv 10Fe$$
$$316 \equiv 560$$
$$31{\cdot}6 \equiv 56$$

Since 25 c.c. of ferric alum solution, after reduction, required *b* c.c. $N/10$ $KMnO_4$.

$$\text{the solution is } \frac{b}{25} \times \frac{N}{10}$$

$$\text{and contains } \frac{b}{25} \times \frac{56}{10} \text{ gm. of iron per l.}$$

The solution was made by dissolving *a* gm. of ferric alum in 250 c.c., i.e., contains 4*a* gm. of salt per litre.

$$\therefore \quad \frac{\frac{b}{25} \times \frac{56}{10}}{4a} \times 100 = \% \text{ iron in the alum.}$$

Experiment 238. Other methods of reducing the ferric salt. Use of zinc amalgam.

Material: Mercury; zinc foil.

The method of reduction given above is rather slow. A more rapid result is achieved by using zinc amalgam. To prepare it, weigh out 200 gm. of mercury and 5 gm. of zinc foil. Put the mercury into a dish and heat it on the steam bath. Add a few drops of dilute sulphuric acid and stir into the mercury a thin strip of the zinc foil until all the zinc is dissolved. If the amalgam solidifies when cold, warm it and add a little more mercury. Add a small quantity of dilute sulphuric acid to the amalgam in a stoppered conical flask. Run in 25 c.c. of the ferric alum solution, insert the stopper and shake gently for a few minutes. (No gas is evolved.) The reduction should be complete in about five minutes. Decant the reduced solution (test as described in Expt. 237) into a flask, wash the amalgam several times with small quantities of distilled water, adding the washings to the reduced solution. Titrate against *N*/10 $KMnO_4$. The amalgam may now be used to reduce a further portion of 25 c.c. of the ferric alum solution.

ionically: $Zn + 2Fe^{+++} \rightarrow Zn^{++} + 2Fe^{++}$

Experiment 239. Estimation of oxalic acid and one of its soluble salts in a mixture of the two, e.g., oxalic acid and sodium oxalate.

Material: *N*/10 potassium permanganate; *N*/10 sodium hydroxide; mixture of oxalic acid and sodium oxalate.

The oxalic acid is determined separately by titration with *N*/10 NaOH; the total oxalate is determined by titration with *N*/10 $KMnO_4$.

$$H_2C_2O_4 + 2NaOH \rightarrow 2H_2O + Na_2C_2O_4$$

From the equation it is evident that oxalic acid contains two atoms of displaceable hydrogen per molecule.

Molecular Weight of $H_2C_2O_4$ = 90
Equivalent = 45

A litre of *N*/10 solution of oxalic acid contains 4·5 gm. of the acid.
For 250 c.c. of *N*/10 solution 1·125 gm. of anhydrous oxalic acid are needed.

Allowing for the fact that the given mixture will probably contain hydrated crystals of the acid ($H_2C_2O_4.2H_2O$) and for the higher molecular weight of sodium oxalate ($Na_2C_2O_4 = 134$), about 2 gm. of the mixture will probably provide 250 c.c. of a suitable solution. Weigh out accurately about 2 gm. of the mixture and make up to 250 c.c. of solution.

Titrations. (*a*) Titrate 25 c.c. of the solution with *N*/10 NaOH using phenolphthalein as indicator.

(*b*) Titrate 25 c.c. of the solution, acidified with dilute sulphuric acid and heated to 60° C. with $N/10$ $KMnO_4$.

The caustic soda solution reacted with the free oxalic acid only; the potassium permanganate solution reacted with the oxalic acid and sodium oxalate.

But, since both solutions are $N/10$, the volume of potassium permanganate solution needed to oxidise the oxalic acid must be equal to the volume of caustic soda solution needed to neutralise it (the equivalent of oxalic acid is the same in an acid-alkali and oxidising reaction). Thus we may separate the volume of permanganate into the portions reacting with oxalic acid and sodium oxalate.

Calculation. Suppose a gm. of the mixture were made up to 250 c.c. solution and 25 c.c. of this needed b c.c. $N/10$ NaOH and d c.c. $N/10$ $KMnO_4$ for titration.

Then since b c.c. $N/10$ NaOH $\equiv$ b c.c. $N/10$ $KMnO_4$, volume of $N/10$ $KMnO_4$ needed to titrate sodium oxalate in 25 c.c. solution $=$ $(d - b)$ c.c.

$$\underset{90}{H_2C_2O_4} \equiv 2NaOH$$

$\therefore$ Equivalent of anhydrous oxalic acid $= 45$.

From the titration,

25 c.c. of solution neutralised b c.c. of $N/10$ alkali.

$\therefore$ Oxalic acid solution is $\frac{b}{25} \times \frac{N}{10}$

and contains $\frac{b}{25} \times \frac{45}{10}$ gm. oxalic acid per l.

Weight of mixture in a litre $= 4a$

$$\% \text{ Weight of oxalic acid in mixture} = \frac{\frac{b}{25} \times \frac{45}{10}}{4a} \times 100\%$$

$$\begin{aligned} 2KMnO_4 &\equiv 5Na_2C_2O_4 \\ 316 &\equiv 5 \times 134 \\ 31{\cdot}6 &\equiv 67 \end{aligned}$$

$\therefore$ the equivalent of sodium oxalate is 67.

From the titration,

25 c.c. of solution required $(d - b)$ c.c. of $N/10$ $KMnO_4$ for oxidation of sodium oxalate.

$\therefore$ The sodium oxalate solution is $\frac{(d-b)}{25} \times \frac{N}{10}$

and contains $\frac{(d-b)}{25} \times \frac{67}{10}$ gm. sodium oxalate per l.

$$\therefore \quad \% \text{ Wt. of oxalate in mixture} = \frac{\frac{(d-b)}{25} \times \frac{67}{10}}{4a} \times 100\%$$

Experiment 240. Estimation of hydrogen peroxide.

Apparatus: Graduated pipette. *Material*: "10- or 20-vol." hydrogen peroxide; $N/10$ potassium permanganate.

An acidified solution of hydrogen peroxide reacts with potassium permanganate,* liberating oxygen, and can be estimated by this reaction.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

The "10-volume" and "20-volume" solutions of hydrogen peroxide are both much stronger than $N/10$, but, as hydrogen peroxide decomposes slowly at ordinary temperature, the appropriate ratio of dilution for a given sample must be found by trial.

Estimation of Dilution Ratio. By means of a 5 c.c. graduated pipette measure out 1 c.c. of the given solution of hydrogen peroxide into a conical flask, acidify it with dilute sulphuric acid and run in $N/10$ $KMnO_4$ (from a burette) 0·5 c.c. at a time till the mixture is pink. (No attempt should be made to obtain an accurate end-point.) If d c.c. of potassium permanganate solution are needed, the hydrogen peroxide solution must be diluted with distilled water so that the original and diluted volumes are in the ratio of $1 : d$ approximately.

Titration. Repeat the titration with 25 c.c. of the diluted hydrogen peroxide solution, acidified with dilute acid and obtain an accurate end-point.

Calculation. Suppose a c.c. of the original hydrogen peroxide solution were diluted to b c.c. and 25 c.c. of the diluted solution were titrated by p c.c. $N/10$ $KMnO_4$.

$$\begin{aligned} 2KMnO_4 &\equiv 5H_2O_2 \text{ (see equation above)} \\ 316 &\equiv 5 \times 34 \\ 31{\cdot}6 &\equiv 17 \end{aligned}$$

$\therefore$ the equivalent of hydrogen peroxide is 17.

From the titration,

25 c.c. of diluted solution required p c.c. of $N/10$ $KMnO_4$

$$\text{The diluted solution is } \frac{p}{25} \times \frac{N}{10}$$

$$\text{and contains } \frac{p}{25} \times \frac{17}{10} \text{ gm. of } H_2O_2 \text{ per l.}$$

$$\text{The original solution contains } \frac{b}{a} \times \frac{p}{25} \times \frac{17}{10} \text{ gm. of } H_2O_2 \text{ per l.}$$

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* Mannitol and other carbohydrates are often present in H_2O_2 solution to retard its decomposition. They will react with $KMnO_4$ giving a high reading.

Experiment 241. Estimation of percentage purity of commercial sodium nitrite.

Material: Sodium nitrite; $N/10$ potassium permanganate.

An acidified solution of sodium nitrite is oxidised by potassium permanganate to nitrate.

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

The nitrite solution cannot be titrated with permanganate solution from a burette in the usual way, because, as soon as it is acidified, the nitrous acid formed begins to decompose.

$$\begin{aligned} 2NaNO_2 + H_2SO_4 &\rightarrow Na_2SO_4 + 2HNO_2 \\ 3HNO_2 &\rightarrow HNO_3 + H_2O + 2NO \end{aligned}$$

The nitrite solution is placed in the burette and is added, *slowly* and with constant stirring, to an acidified solution of $N/10$ $KMnO_4$.

$$\begin{aligned} 5NaNO_2 &\equiv 2KMnO_4 \\ 5 \times 69 &\equiv 316 \\ 34{\cdot}5 &\equiv 31{\cdot}6 \end{aligned}$$

The equivalent of sodium nitrite is 34·5.

A litre of $N/10$ sodium nitrite solution contains 3·45 gm. of the salt.

For 250 c.c. $N/10$ solution 0·86 gm. of sodium nitrite would be required.

To allow for impurity make up a solution containing about 1 gm. of sodium nitrite in 250 c.c.

Titration. Pipette 25 c.c. $N/10$ $KMnO_4$ solution into a porcelain dish, acidify with 10–15 c.c. of bench dilute sulphuric acid and, from a burette with the jet dipping into the solution, add the sodium nitrite solution slowly and with continual stirring till the permanganate colour is just discharged. Repeat the titration to obtain two concordant results.

Calculation. Suppose a gm. of sodium nitrite were made up to 250 c.c. of solution and 25 c.c. of $N/10$ $KMnO_4$ were titrated by b c.c. of this solution.

From the titration,

b c.c. of sodium nitrite solution required 25 c.c. $N/10$ $KMnO_4$ for oxidation.

$$\therefore \text{ Sodium nitrite solution is } \frac{25}{b} \times \frac{N}{10}$$

and contains $\frac{25}{b} \times \frac{34\cdot5}{10}$ gm. of sodium nitrite per litre.

Weight of impure sodium nitrite used per litre = $4a$ gm.

$$\therefore \quad \% \text{ purity of sodium nitrite} = \frac{\frac{25}{b} \times \frac{34\cdot5}{10}}{4a} \times 100$$

Experiment 242. Given that ferrous ammonium sulphate has the formula $FeSO_4 . (NH_4)_2SO_4 . xH_2O$ determine x.

Material: Ferrous ammonium sulphate; $N/10$ potassium permanganate.

$$\begin{aligned} 10[FeSO_4.(NH_4)_2SO_4.xH_2O] &\equiv 2KMnO_4 \text{ (M. wt. 316)} \\ FeSO_4.(NH_4)_2SO_4.xH_2O &\equiv 31\cdot6 \end{aligned}$$

The molecular weight of the salt is ∴ its equivalent. 1/10 of the molecular weight will be required to make a litre of $N/10$ solution.

Making a reasonable assumption for a value of x calculate the approximate weight of ferrous ammonium sulphate solution needed for 250 c.c. $N/10$ solution. Make up this solution in dilute sulphuric acid (p. 250) and titrate with $N/10$ $KMnO_4$.

Experiment 243. Analyse a given mixture of potassium sulphate and potassium permanganate.

Material: Mixture of potassium sulphate and potassium permanganate; $N/10$ ferrous ammonium sulphate.

Make up an accurately $N/10$ solution of ferrous ammonium sulphate (p. 250) in dilute sulphuric acid. Assuming that the proportion of potassium permanganate in the given mixture is about 50%, make up a solution of accurately known concentration and about $N/10$. Titrate the ferrous ammonium sulphate solution with it.

$$\begin{aligned} 10[FeSO_4.(NH_4)_2SO_4.6H_2O] &\equiv 2KMnO_4 \\ FeSO_4.(NH_4)_2SO_4.6H_2O &\equiv 31\cdot6 \end{aligned}$$

The molecular weight of ferrous ammonium sulphate being its equivalent, use 1/10 of this weight in gm. to make a litre of $N/10$ solution.

Experiment 244. Determine the solubility of ammonium oxalate in water at room temperature in gm. of anhydrous salt per litre of solution.

Apparatus: Graduated pipette. *Material*: Ammonium oxalate, $N/10$ $KMnO_4$.

Prepare about 100 c.c. of a saturated solution of ammonium oxalate at room temperature by heating the salt with distilled water at about 50° C., adding so much of the salt that a small sample cooled in a test-tube yields crystals. Cool the whole solution under the tap, determine its temperature and filter through dry glass-wool into a dry flask. Titrate 1 c.c. of this filtrate, using the method of Expt. 240, with $N/10$ $KMnO_4$. On this evidence, dilute a known volume of the saturated solution to 250 c.c. in a measuring flask to give approximately a $N/10$ solution.

Titrate portions of 25 c.c. with $N/10$ $KMnO_4$ solution.

$$5(NH_4)_2C_2O_4 \equiv 2KMnO_4 \text{ (see p. 257)}$$
$$5 \times 124 \equiv 316$$
$$62 \equiv 31{\cdot}6$$

the equivalent of ammonium oxalate is 62 gm. and 6·2 gm. will be required to make a litre of $N/10$ solution of the salt.

Experiment 245. Determine accurately the equivalent weight in grams of the given organic acid (which is oxidised by potassium permanganate).

Material: Organic acid;* $N/10$ potassium permanganate.

Assume the equivalent of the acid to be between 40 and 60 and prepare accurately a solution of the acid which is roughly $N/10$. Titrate it with $N/10$ $KMnO_4$. Find the equivalent weight in grams given the following relationship:—

$$2KMnO_4 \equiv 100 \text{ l. } N/10 \equiv 10 \times \text{(gm. equivalent weight of the acid.)}$$

Experiment 246. Determine the percentage of manganese dioxide in a given sample of pyrolusite.

Material: Pyrolusite; $N/2$ oxalic acid; $N/10$ potassium permanganate. (See Expt. 249 for alternative method.)

Assume that manganese dioxide reacts with oxalic acid in sulphuric acid solution according to the equation:—

$$MnO_2 + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2$$

Make up 250 c.c. of a solution of oxalic acid which is about $N/2$, i.e., 31·5 gm. of crystals per litre.

Transfer 100 c.c. of it (accurately measured by pipette, taking care not to suck any solution into the mouth) to a flask and add 20–30 c.c. bench sulphuric acid. Weigh a weighing-bottle containing about 1·1 gm. of the powdered pyrolusite, add the powder to the acidified oxalic acid solution and obtain the weight of the powder by difference. Boil the mixture gently (with a funnel in the neck of the flask) until the remaining solid particles (silica) are white. Transfer the liquid after cooling to a 250 c.c. flask, wash the flask and funnel and add

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* Use oxalic acid, potassium tetroxalate, etc.

the washings to the bulk of the solution. Make up to the mark. Titrate with $N/10$ $KMnO_4$.

Dilute 100 c.c. of the original oxalic acid to 250 c.c. and titrate 25 c.c. portions with $N/10$ $KMnO_4$.

(The smaller volume of $N/10$ $KMnO_4$ solution needed in the first case is due to oxidation of some of the oxalic acid by the MnO_2. Since both solutions were diluted in the same ratio of 100 : 250 the difference between the *total* volumes of $N/10$ $KMnO_4$ needed for titration measures the oxidising action of the MnO_2).

$$\begin{aligned} 5MnO_2 &\equiv 2KMnO_4 \\ 5\,(55 + 32) &\equiv 316 \\ \frac{87}{2} &\equiv 31{\cdot}6 \end{aligned}$$

∴ the equivalent of manganese dioxide is 43·5, and in this reaction 4·35 gm. oxidises a litre of $N/10$ oxalic acid.

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1)* *Material*: Soln. of formic acid 1–2 gm. per l.; $N/10$ potassium permanganate; $N/10$ sodium hydroxide.

1. Titrate the solution of formic acid (HCOOH) with the standard sodium hydroxide solution, and thereby determine its concentration in gram molecules per litre.

2. Add to 25 c.c. of the formic acid solution an excess of sodium carbonate solution, heat almost to boiling and titrate while hot with the standard potassium permanganate solution until the clear liquid above the precipitate is coloured pink.

3. Titrate 25 c.c. of the solution of formic acid, heated to boiling but without neutralisation with the sodium carbonate, with the potassium permanganate solution.

4. Interpret your results as far as you can.

(Oxford Schol. 1935).

(2)* The following solutions are provided:—

Potassium permanganate . . .	$N/20$
Potassium iodide	$N/5$
Potassium bromide	$N/5$
Hydrochloric acid	2 N

†Sodium thiosulphate.
†Sodium arsenite.

Perform the following titrations:—

1. Mix 25 c.c. of the potassium iodide solution with 10 c.c. of the hydrochloric acid solution and 25 c.c. of the potassium permanganate solution.

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† $N/20$ solutions will be found of suitable concentration.

Titrate (without using starch solution) with the sodium thiosulphate solution.

2. Carry out a titration similar to (1) using potassium bromide instead of potassium iodide solution.

3. Proceed as in (2), but before performing the titration add 25 c.c. of the potassium iodide solution.

4. Take 25 c.c. of sodium arsenite solution (*from a burette*), add 10 c.c. of hydrochloric acid and titrate with potassium permanganate solution.

5. Make up a mixture as in (1), add 2 or 3 gm. of solid sodium bicarbonate and titrate with sodium arsenite solution.

6. Carry out a titration similar to (5), using potassium bromide instead of potassium iodide solution.

7. Tabulate your results, and attempt to interpret them.

(Oxford Schol. 1933.)

(3)* *Material*: Unknown solid; *N*/10 sodium hydroxide; potassium permanganate 4 gm. per l.

The substance A possesses one of the following formulæ:—

(*a*) $H_2C_2O_4xH_2O$. (*b*) $KHC_2O_4yH_2O$. (*c*) $KHC_2O_4.H_2C_2O_4zH_2O$

(i) Determine the percentage by weight of acidic hydrogen in A.

(ii) Determine the percentage by weight of the oxalate radical C_2O_4.

(iii) State, giving reasons, which formula the substance A possesses.

(You are not asked to determine the number of molecules of water of crystallisation.)

You are provided with a solution of sodium hydroxide containing 4 gm. of NaOH per litre, and also one of potassium permanganate containing 4 gm. of $KMnO_4$ per litre.

A solution of about 8 gm. of A per litre will be found to be of convenient strength for titration.

(Oxford Schol. 1934.)

(4)* *Material*: Pyrolusite; *N*/5 potassium permanganate; oxalic acid about 20/25 gm. per l.

(*a*) You are provided with a *N*/5 solution of potassium permanganate. Determine the number of grams per litre of anhydrous oxalic acid in the solution AA.

(*b*) Weigh portions of about 0·3–0·4 gm. of the pyrolusite BB, and add to each portion a suitable quantity (40–50 c.c.) of the oxalic acid solution AA, and about 50 c.c. of 10 per cent sulphuric acid. Warm the mixture to about 80°–90° C. until a clear solution is obtained, and titrate with the potassium permanganate solution. Calculate the percentage of MnO_2 in the pyrolusite BB.

$$[H = 1, C = 12, O = 16, Mn = 55.]$$

(O. & C., H.S.C., 1936.)

(5) *Material*: Unknown potassium permanganate; unknown oxalic acid; ferrous ammonium sulphate.

By means of the given pure ferrous ammonium sulphate

$$[FeSO_4.(NH_4)_2SO_4.6H_2O]$$

determine the normality of the solution of potassium permanganate D and use this solution to determine the amount of oxalic acid ($H_2C_2O_4$) in 1 litre of solution E.

(The solution of ferrous ammonium sulphate should contain between 9·6 and 10·0 gm. in 250 c.c. and 25 c.c. portions should be used for titration.)

(London H.S.C. 1936.)

QUESTIONS AND CALCULATIONS

(*Answers on p.* 301.)

(1) Starting with manganese dioxide, how would you prepare in the laboratory a crystalline specimen of potassium permanganate?

Why are 3·16 gm. of potassium permanganate required to make a litre of $N/10$ $KMnO_4$?

State very briefly how a standard solution of permanganate can be used to determine the strength of solutions of

(*a*) a ferrous salt;
(*b*) oxalic acid;
(*c*) hydrogen peroxide.

Atomic weights: K = 39, Mn = 55, O = 16.

(Durham H.S.C. 1934.)

(2) Give an account of the chemistry underlying the use of iodine and potassium iodide in volumetric analysis. Illustrate your answer by reference to *three* examples in addition to the reactions mentioned below.

25 c.c. of a solution of potassium permanganate on mixing with excess of potassium iodide in the presence of dilute sulphuric acid liberated iodine which reacted with exactly 40 c.c. of decinormal sodium thiosulphate.

What was the concentration of the potassium permanganate solution in grams per litre?

(C.W.B., H.S.C. 1934.)

(3) Calculate the volume of a decinormal solution of potassium permanganate required for the complete oxidation of 1 gm. of ferrous oxalate (FeC_2O_4).

(C = 12, O = 16, Fe = 56.)

(London H.S.C. 1934.)

(4) A neutral solution of potassium permanganate is said to react with a hot solution of potassium iodide according to the equation—

$$2KMnO_4 + KI + H_2O \rightarrow 2MnO_2 + KIO_3 + 2KOH.$$

Describe the experiments which you would undertake in order to verify this statement.

(Oxford H.S.C. 1934.)

(5) 50 c.c. of a solution of hydrogen peroxide were diluted to 1 litre with water, 25 c.c. of this solution, when acidified, reacted with 23·9 c.c. of $N/10$ $KMnO_4$. Calculate the strength of the original hydrogen peroxide solution in grams per litre.

(6) Calculate x in the formula, $FeSO_4.xH_2O$, from the following data: 12·20 gm. of ferrous sulphate crystals were made up to 500 c.c. of acidulated solution. 25 c.c. of this solution required 21·9 c.c. $N/10$ $KMnO_4$.

(7) 1·500 gm. of iron were converted to 250 c.c. of acidulated ferrous sulphate solution, 25 c.c. of which were found to require 24·4 c.c. of 0·1088 $N.KMnO_4$. Calculate the percentage by weight of iron in the wire.

(8) Calculate the weights of anhydrous sodium oxalate and crystalline oxalic acid, $H_2C_2O_4.2H_2O$, per litre of a solution from the following data: 25 c.c. of the solution required 19·8 c.c. of $N/10$ NaOH for neutralisation, using phenolphthalein as indicator; 25 c.c. of the solution required 34·2 c.c. of 0·106 $N.KMnO_4$ for oxidation.

(9) Calculate the percentage of manganese dioxide in a sample from the following data: 25 c.c. of a certain oxalic acid solution was titrated with 0·107 *N*/10 $KMnO_4$. After prolonged boiling of the same volume of the oxalic acid solution with 0·142 gm. of the manganese dioxide and dilute sulphuric acid, the volume of the same $KMnO_4$ solution required was reduced by 24·4 c.c.

(10) Calculate the weights of anhydrous ferrous and ferric sulphate per litre of a solution given that 25 c.c. of it needed 21·6 c.c. of 0·105 *N*.$KMnO_4$ for oxidation while, after reduction of the same volume of the solution by zinc amalgam, 22·8 c.c. more of the $KMnO_4$ solution were needed for oxidation.

CHAPTER XXXVI

POTASSIUM DICHROMATE

Potassium dichromate is used as an oxidising agent in reactions very similar to those described in the last chapter in which potassium permanganate was employed, especially for titration of ferrous salts.

It will be remembered that potassium permanganate is not used with chlorides because (especially in the presence of ferric salts) it may be used up in oxidising hydrochloric acid. Potassium dichromate is free from this disadvantage and may be used in the presence of hydrochloric acid or its salts. Until recently, the great disadvantage of potassium dichromate has been that one of its reduction products is a chromium salt. This chromium salt is deep green in colour and effectively masks the colour of any excess of potassium dichromate, which cannot act (like potassium permanganate) as its own indicator. Further, until recently, no suitable internal indicator was known and it was necessary to undertake the very tedious business of titrating with an indicator outside the reaction mixture. Lately, a satisfactory internal indicator has been introduced (see below) and titrations with potassium dichromate may now be expeditiously performed.

Decinormal Potassium Dichromate Solution. In acid solution potassium dichromate will yield three atoms of oxygen, for oxidation purposes, from its molecule. Expressed in ionic terms, the reaction is:—

$$Cr_2O_7^{--} + 8H^+ \rightarrow 2\,Cr^{+++} + 4H_2O + 3[O]$$

or, in the more usual molecular form,

$$K_2Cr_2O_7 + 8HCl \rightarrow 2KCl + 2CrCl_3 + 4H_2O + 3[O]$$

From this equation.

$$\begin{aligned} K_2Cr_2O_7 &\equiv 3[O] \\ (78 + 104 + 112) &\equiv 3 \times 16 \\ \frac{294}{6} &\equiv 8 \end{aligned}$$

As in the case of potassium permanganate (p. 249) the equivalent is the weight of a substance *which combines with or gives* 8 *units of oxygen.* The equivalent of potassium dichromate is $\frac{294}{6} = 49$

A litre of $N/10$ $K_2Cr_2O_7$ will contain 4·9 gm. of the salt.

The solution may be made up directly from the pure salt if it is first melted in a porcelain dish, so that no water remains in it, and ground to powder after cooling.

Indicator.* The internal indicator is diphenylamine, and this compound, which is used in concentrated sulphuric acid solution, has no influence on the colour of the mixture, but, when oxidised by a slight excess of potassium dichromate, it produces an intensely coloured blue compound. It is necessary, however, to prevent ferric ions, which are formed in the course of titration of a ferrous salt, from oxidising the diphenylamine prematurely, i.e., before potassium dichromate is in excess, and for this purpose phosphoric acid is used. The ferric ions are then taken up, as fast as they are produced by oxidation, into a ferric phosphate complex which is almost undissociated and the ferric ions are prevented from oxidising the diphenylamine.

The titration is carried out in the following way: Make a solution of 1 gm. of diphenylamine in 50 c.c. of concentrated sulphuric acid. Dilute some syrupy phosphoric acid with twice its bulk of water. To 25 c.c. of the solution to be titrated add one drop of the diphenylamine solution and 5 c.c. of the diluted phosphoric acid. Titrate with potassium dichromate solution till the mixture (which is deep green in colour) just turns blue.

Potassium dichromate solution may be used for the estimation of ferrous and ferric iron by any of the methods previously described employing potassium permanganate. The following estimation is instructive. Potassium permanganate could not be used because of the presence of chlorides.

Experiment 247. Estimation of the percentage purity of a sample of metallic tin.

Apparatus: Measuring cylinder. *Material*: Tin; ferric chloride; *N*/10 potassium dichromate; diphenylamine; phosphoric acid.

Method. The tin is converted to stannous chloride solution, which is then used to reduce a portion of a ferric solution to the ferrous state. The ferrous solution is then oxidised back to the ferric condition by *N*/10 potassium dichromate solution.

The reducing action of stannous chloride solution on a ferric salt may be expressed ionically in the form:

$$Sn^{++} + 2\,Fe^{+++} \rightarrow Sn^{++++} + 2\,Fe^{++}$$

or in a general way, in the form:

$$Sn^{++} + 2\,H^{+} + [O] \rightarrow Sn^{++++} + H_2O$$

From this

$$Sn \equiv 2\,H$$

$$119 \text{ gm.} \equiv 2 \text{ gm.}$$

59·5 is the equivalent of tin under the given conditions. When

---

* The external indicator used was potassium ferricyanide solution which gave a blue colouration so long as ferrous ions were present.

5·95 gm. of tin are dissolved and made up to a litre, the solution will be $N/10$.

To make 250 c.c. of $SnCl_2$ solution, $\frac{5{\cdot}95}{4}$ gm., i.e., 1·49 gm. are required.

Weigh out accurately about 1·5 gm. of tin, place in a conical flask and add about 50 c.c. of conc. hydrochloric acid preferably in a fume chamber. Put a funnel into the neck of the flask to prevent loss by splashing and when the tin is completely dissolved transfer the stannous chloride solution to a 250 c.c. flask. Wash the funnel and beaker well with acid of the strength previously used* and add the washings to the main solution, finally making up to the mark with distilled water.

Make up a solution containing about 9 gm. of ferric chloride in 250 c.c. bench hydrochloric acid. (This solution is about 0·13 N.) Measure out 25 c.c. of it by a pipette into a conical flask and add 25·0 c.c. of the stannous chloride solution. Since the ferric solution is stronger than $N/10$, all the stannous ions are converted into stannic ions. Titrate the mixture with $N/10$ potassium dichromate solution, using indicator and conditions as described on p. 267. Repeat to obtain concordant results.

Calculation. Suppose *a* gm. of tin were converted into 250 c.c. of stannous chloride solution and 25 c.c. of this reduced the ferric chloride solution so that *b* c.c. of $N/10$ $K_2Cr_2O_7$ were required for its oxidation.

$$\begin{aligned} Sn + 2HCl &\rightarrow SnCl_2 + H_2 \\ SnCl_2 + 2FeCl_3 &\rightarrow SnCl_4 + 2FeCl_2 \end{aligned}$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O$$

From these equations:

$$\begin{aligned} K_2Cr_2O_7 &\equiv 3Sn \\ 294 \text{ gm.} &\equiv 3 \times 119 \text{ gm.} \end{aligned}$$

The equivalent of potassium dichromate is 1/6 of its molecular weight (p. 266), therefore 59·5 is the equivalent of tin (a fact already deduced on p. 267).

From the titration,

25 c.c. of stannous chloride solution is of equal value to *b* c.c. of $N/10$ $K_2Cr_2O_7$

$\therefore$ the stannous chloride solution is $\frac{b}{25} \times \frac{N}{10}$

and will contain $\frac{b}{25} \times \frac{59{\cdot}5}{10}$ gm. of tin per l.

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* Excess hydrochloric acid is necessary to prevent precipitation of basic tin salts.

To make the solution, 4*a* gm. of impure tin were used per litre,

$$\text{Percentage purity of tin} = \frac{\frac{b}{25} \times \frac{59\cdot5}{10}}{4a} \times 100$$

Experiment 248. To determine the percentage purity of a sample of potassium chromate.

Apparatus: Measuring cylinder. *Material*: Potassium chromate; $N/10$ ferrous ammonium sulphate; diphenylamine; phosphoric acid.

Potassium chromate is converted by acids into potassium dichromate.

$$2\,CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O$$

or $$2K_2CrO_4 + H_2SO_4 \rightarrow K_2SO_4 + K_2Cr_2O_7 + H_2O$$

Calculate the weight of potassium chromate needed to produce 250 c.c. $N/10$ $K_2Cr_2O_7$ when in acidified solution (p. 266). Weigh out this amount of potassium chromate (by difference) and including in the solution 50 c.c. of bench sulphuric acid, make up to 250 c.c. with distilled water.

Titrate this, from a burette, against $N/10$ ferrous ammonium sulphate solution (p. 250), using diphenylamine as internal indicator. Calculate the percentage purity from the equations given above.

Experiment 249. To determine the percentage of potassium chlorate in a given sample.

Apparatus: Measuring cylinder. *Material*: Potassium chlorate; $N/5$ ferrous ammonium sulphate; $N/10$ potassium dichromate; diphenylamine; phosphoric acid.

In hot acid solution, potassium chlorate* oxidises ferrous salts.

$$6Fe^{++} + 6H^+ + ClO_3^- \rightarrow 6Fe^{+++} + Cl^- + 3H_2O$$

i.e., $$KClO_3 \equiv 6\,H \equiv K_2Cr_2O_7$$

$$\text{Gm. Mol. Wt.} \equiv 6\text{ gm.} \equiv 294\text{ gm.}$$

$$\frac{\text{Gm. Mol. Wt.}}{6} \equiv 1\text{ gm.} \equiv 49\text{ gm.}$$

The equivalent of potassium chlorate is, therefore, 1/6 of its molecular weight.

Calculate the weight of potassium chlorate which is required for 250 c.c. $N/10$ solution and weigh out this amount. Make it up to 250 c.c. of solution with distilled water.

Prepare 250 c.c. of $N/5$ ferrous ammonium sulphate solution (p. 250). To 25 c.c. of this solution, add 25 c.c. of the $KClO_3$ solution,

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* The percentage purity of manganese dioxide, red lead and many other oxidising agents can be obtained by using these substances in the place of potassium chlorate in Expt. 249.

about 15 c.c. of dilute sulphuric acid, and boil the mixture, with a funnel in the mouth of the flask, for about twenty minutes. Repeat this twice to obtain three results.

Then wash the funnels, cool the mixture and titrate with *N*/10 $K_2Cr_2O_7$. Calculate the percentage purity from the equations given above.

Experiment 250. To determine the percentage of iron in a sample of iron alum, reducing the iron by stannous chloride.

Apparatus: Measuring cylinder. *Material*: Iron alum; *N*/10 potassium dichromate; stannous chloride; diphenylamine; phosphoric acid.

Prepare a solution of iron alum of accurately known concentration and roughly *N*/10.

Prepare a solution of stannous chloride by dissolving about 3 gm. of the salt ($SnCl_2.2H_2O$) in 50 c.c. of concentrated hydrochloric acid and diluting to 250 c.c.

Add 5 c.c. of concentrated hydrochloric acid to 25 c.c. of the alum solution in a conical flask and boil the liquid. Run in the stannous chloride solution drop by drop from a burette until the yellow colour of the ferric ions is discharged. Add two or three more drops of the stannous chloride solution to make certain that the reduction is completed. (Care should be taken not to add too great an excess of stannous chloride.) Now add 1 or 2 c.c. of a saturated solution of mercuric chloride. A small white precipitate should be observed showing that sufficient stannous chloride had been added. Titrate this solution with *N*/10 dichromate using diphenylamine as internal indicator.

Experiment 251. Determine the percentage of iron in a sample of spathic iron ore (ferrous carbonate).

Apparatus: Measuring cylinder. *Material*: Iron ore; zinc amalgam; *N*/10 potassium dichromate; diphenylamine; phosphoric acid.

Most of the iron in this ore is in the ferrous but some is in the ferric condition.

$$\begin{array}{lrcl} & 2\,Fe^{++} + 2H^{+} + [O] & \rightarrow & 2Fe^{+++} + H_2O \\ \text{i.e.,} & Fe^{++} & \equiv & H^{+} \\ \text{or} & FeCO_3 & \equiv & H \\ & 56 + 12 + 48 & & \\ & 116\text{ gm.} & \equiv & 1\text{ gm.} \end{array}$$

The equivalent of ferrous carbonate is 116, and 11·6 gm. will, after solution and making up to a litre, be *N*/10 ferrous salt solution.

To make 250 c.c. of *N*/10 ferrous solution, 3 gm. of the ore will be required.

Weighing by difference, put the ore into a conical flask and add about 50 c.c of bench hydrochloric acid. Cover the mouth of the flask with a small watch-glass and warming the mixture and adding more acid if necessary, allow the action to continue till no brown particles remain. (Silica will remain undissolved.)

Wash the watch-glass and reduce all the iron to the ferrous state by zinc-amalgam (p. 256). Make up the reduced solution to 250 c.c. in a measuring flask. Titrate with $N/10$ $K_2Cr_2O_7$ solution, using diphenylamine as internal indicator. Calculate the percentage of iron in the ore from the above equations.

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1)* Oxidising power of $KMnO_4$ and $K_2Cr_2O_7$. *Apparatus*: Measuring cylinder. *Material*: Tenth molar solution of each; ferrous ammonium sulphate; diphenylamine; phosphoric acid.

You are supplied with tenth molar solutions of potassium permanganate and potassium dichromate and ferrous ammonium sulphate. Compare the oxidising powers of the two solutions in acid solutions by oxidation of a solution of ferrous ammonium sulphate (this need not be made up accurately). Explain your result by means of equations.

(2) Estimation of potassium sulphate and potassium dichromate in a mixture of the two. *Apparatus*: Measuring cylinder. *Material*: Mixture containing potassium dichromate and potassium sulphate. Ferrous ammonium sulphate; diphenylamine; phosphoric acid.

Make a solution of the mixture to be approximately $N/10$ with respect to the dichromate (assume the solid to contain 50% of the dichromate). Make up a standard solution of ferrous ammonium sulphate and titrate with the unknown solution using diphenylamine as an indicator.

(3)* Estimation of purity of sodium arsenite. *Apparatus*: Measuring cylinder. *Material*: Sodium arsenite; potassium dichromate; $N/20$ ferrous ammonium sulphate; diphenylamine; phosphoric acid.

$$3Na_3AsO_3 + \underset{\text{from } K_2Cr_2O_7}{3[O]} \rightarrow 3Na_3AsO_4$$

This equation represents the action, in acid solution, of potassium dichromate on sodium arsenite.

Weigh out accurately about 1·25 gm. of potassium dichromate and dissolve in distilled water in a 250 c.c. flask, also adding some dilute hydrochloric acid. Weigh out accurately about 1·25 gm. of the arsenite (sufficient to react with about half the dichromate) and add this carefully to the acidified dichromate solution. Shake until all the arsenite has dissolved, make up to 250 c.c. and shake well. Put some of this solution into the burette and titrate against the $N/20$ ferrous ammonium sulphate solution. Calculate the purity of the arsenite from your readings.

N.B. Arsenite solutions are very poisonous.

(4) *Material*: $N/10$ potassium dichromate; $N/10$ ferric sulphate; $N/10$ titanous sulphate; solution of hydroxylamine in sulphuric acid.†

Hydroxylamine (NH_2OH) can be reduced to NH_3 or oxidised to definite stages such as N_2, N_2O, HNO_2 or HNO_3. You are given decinormal solutions of potassium dichromate, ferric sulphate and titanous sulphate and a solution of hydroxylamine in sulphuric acid. Given that titanous sulphate reduces hydroxylamine quantitatively to ammonia determine the nitrogen compound to which it is oxidised by (*a*) ferric sulphate, (*b*) potassium dichromate.

(Oxford Schol., Dec., 1936.)

CALCULATIONS

(*Answers on p.* 301.)

(1) 2 gm. of a specimen of hydrated ferric oxide were dissolved in hydrochloric acid and the solution was made up to 250 c.c. 25 c.c. of this solution after reduction to the ferrous state required 13·7 c.c. $N/10$ $K_2Cr_2O_7$ for oxidation. Calculate the percentage of Fe_2O_3 in the specimen.

(2) 8·3 gm. of pure tin were dissolved in hydrochloric acid and the solution was made up to 1 litre. 25 c.c. of this solution required 26·7 c.c. of a solution of potassium dichromate for complete oxidation. Calculate the strength of the dichromate solution in gm. per litre.

(3) 1 gm. of pure potassium permanganate and 1 gm. of pure potassium dichromate were dissolved in water and excess acidified potassium iodide solution was added. What volume of double normal sodium thiosulphate would be required to react with the iodine so produced?

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† A solution of hydroxylamine containing about 1·5 gm. per litre will be suitable.

CHAPTER XXXVII

IODINE AND SODIUM THIOSULPHATE

Sodium thiosulphate reacts with iodine, producing sodium iodide and sodium tetrathionate

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

or *ionically*: $$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--}$$

This reaction may be used for the estimation of iodine or, indirectly, for the estimation of a substance which participates in a reaction in which iodine is liberated.

Standard Sodium Thiosulphate Solution. The sodium thiosulphate purchased for laboratory purposes is the hydrated salt $Na_2S_2O_3.5H_2O$.

From the above equation:—

$$\begin{array}{lccccc} & 2Na_2S_2O_3 & \equiv & I_2 & & \\ \text{i.e.,} & Na_2S_2O_3.5H_2O & \equiv & I & \equiv & HI \\ & & & & & \uparrow \\ & 248\ \text{gm.} & & & & 1\ \text{l.}\ N. \end{array}$$

From this relation 1 litre of $N/10$ sodium thiosulphate solution contains 24·8 gm. of the pure hydrated salt. An accurately standard solution of the salt cannot be made up directly from the salt as usually purchased because it is not sufficiently pure. Make up a roughly $N/10$ solution by dissolving 25 gm. of sodium thiosulphate crystals in warm distilled water and diluting to one litre in a measuring flask. This solution must now be standardised. This is usually carried out by the use of either accurately $N/10$ $KMnO_4$ or pure potassium iodate KIO_3.

Indicator and End-point. The indicator used in titrating iodine solutions with sodium thiosulphate is starch solution. With free iodine it produces a deep blue coloration, the blue colour disappearing as soon as sufficient sodium thiosulphate has been added to react with all the iodine.

The procedure is as follows: Sodium thiosulphate solution is run from a burette into the iodine solution until its original brown colour is changed to pale yellow. Then a few drops of starch solution are added producing a blue coloration. Further drop-by-drop addition of thiosulphate solution is continued until the blue coloration disappears.

Preparation of the Starch Indicator. Mix 1 gm. of starch to a thin paste with water in an evaporating dish, then pour the paste into about 350 c.c. of boiling water. Boil the mixture for two to three minutes then cool it for use. (This solution will not keep; moulds will grow on it. The addition of about $\frac{1}{2}$ gm. of salicylic acid to the 350 c.c. of water before boiling will prevent such growth and the starch indicator will then keep for a long time.)

Experiment 252. Standardisation of sodium thiosulphate solution by N/10.$KMnO_4$.

Material: $N/10$ potassium permanganate; approx. $N/10$ sodium thiosulphate; potassium iodide.

The $N/10$ $KMnO_4$ is added to acidified potassium iodide solution. Iodine is liberated and is titrated with the thiosulphate solution.

$$2KMnO_4 + 10KI + 16HCl \rightarrow 12KCl + 2MnCl_2 + 8H_2O + 5I_2$$

ionically: $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 8H_2O + 5I_2$.

Dissolve about 1·5 gm.* of potassium iodide in about 20 c.c. distilled water in a conical flask and acidify with an equal volume of bench hydrochloric acid.

Add 25 c.c. $N/10$ $KMnO_4$ and dilute the brown solution to about 100 c.c. From a burette, add the sodium thiosulphate solution until the mixture is pale yellow; add the starch indicator and continue titration till the blue colour is discharged. Repeat the titration two or three times.

Calculation. Suppose 25 c.c. $N/10$ $KMnO_4$ liberate iodine requiring 24·7 c.c. of the sodium thiosulphate solution.

Then the sodium thiosulphate solution is $\frac{25}{24{\cdot}7} \times \frac{N}{10}$ or $0{\cdot}1012\,N$.

Its concentration in grams of hydrated salt per litre is 248 × 0·1012 gm. per litre (p. 273).

The solution could be made $N/10$ by adding 12·15 c.c. of water per 1,000 c.c. of the solution and shaking to produce uniformity.

$N/10$ potassium dichromate solution may be substituted for $N/10$ permanganate, the estimation being otherwise identical.

Experiment 253. Standardisation of sodium thiosulphate solution by pure potassium iodate KIO_3.

Material: Approximately $N/10$ sodium thiosulphate; A.R. potassium iodate; potassium iodide.

Standard potassium iodate solution reacts with excess potassium iodide in acidified solution and the liberated iodine is titrated with the sodium thiosulphate solution,

ionically: $IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$

or $KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3I_2$

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* KI ≡ 1 litre N.
166 gm.

The equivalent of potassium iodide is 166, and to make a litre of $N/10$ solution 16·6 gm. of the salt is required. To make 25 c.c. of solution 1/40 of this wt. will be required, i.e., 0·415 gm. 1·5 gm. of potassium iodide provides an excess for solution of the liberated iodine.

From the equation,

$$\begin{aligned} KIO_3 &\equiv 3\,I_2 \\ 214\text{ gm.} &\equiv 6\,I \equiv 6\,H \end{aligned}$$

The equivalent of potassium iodate is $\frac{214}{6}$. To make a litre of $N/10$ solution $\frac{214}{60} = 3{\cdot}57$ gm. will be required.

For 250 c.c. of $N/10$ KIO_3 0·892 gm. are needed.

Make up a solution of potassium iodate to contain 0·892 gm. in 250 c.c. Pipette 25 c.c. of it into a conical flask and add about 1·5 gm.* of potassium iodide. Acidify the solution with about 10 c.c. of bench sulphuric acid and titrate the liberated iodine with the sodium thiosulphate solution as described before. Repeat the titration two or three times. The calculation is similar to that given in Expt. 252.

Experiment 254. To prepare a standard iodine solution.

Material: Iodine; potassium iodide; $N/10$ sodium thiosulphate.

Iodine is only very slightly soluble in water. It is, however, readily soluble in potassium iodide solution forming a brown liquid which contains the compound KI_3. This compound liberates iodine so readily that the solution behaves as if the dissolved iodine were all free iodine.

$$\begin{array}{cc} I \equiv HI \\ 127\text{ gm.} \quad 1\text{ l. } N. \end{array}$$

A litre of $N/10$ iodine solution contains 12·7 gm.† Weigh out 13 gm. of iodine in a weighing bottle. Transfer it to a litre flask. Dissolve about 25 gm. of potassium iodide in 100 c.c. of water and add about 80 c.c. of it to the iodine, using the remaining 20 c.c. for washing out the weighing bottle. When the iodine is dissolved, dilute the solution to 1 litre and shake well.

Titrate 25 c.c. of this solution with standard ($N/10$) sodium thiosulphate solution. Calculate the normality of the iodine solution.

Experiment 255. Estimation of available chlorine in bleaching powder.

Material: Bleaching powder; potassium iodide; acetic acid; $N/10$ sodium thiosulphate.

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* See footnote, p. 274.

† Iodine can be purchased sufficiently pure to justify direct preparation of a standard solution, but it is volatile enough to make it almost impossible to avoid loss while the solution is being prepared. Hence, standardisation is necessary.

Note: It is suggested that the active constituent of bleaching powder possesses the formula $CaOCl_2.H_2O$ (alternatively it may be considered as a mixture of calcium hypochlorite and basic calcium chloride) and liberates chlorine when reacting with a dilute acid. This chlorine is available for bleaching and is known as "available" chlorine.

$$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2.$$

Bleaching powder may deteriorate for two reasons:—

(i) Because it is attacked by carbon dioxide of the air

$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2.$$

(ii) Because of an internal change in which one molecule of $CaOCl_2$ is oxidised to calcium chlorate $Ca(ClO_3)_2$ at the expense of five molecules of $CaOCl_2$ which are reduced.

Both these changes reduce the "available" chlorine content and an old sample of bleaching powder may be almost worthless for bleaching. The following method estimates "available" chlorine.

Method. Bleaching powder is mixed with potassium iodide solution and the mixture is acidified. The liberated iodine is titrated by $N/10$ sodium thiosulphate solution. Acetic acid is used to liberate the chlorine.

$$\underset{145\text{ gm.}}{CaOCl_2.H_2O} + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + 2H_2O + Cl_2$$

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

From these equations,

$$\begin{array}{ll} CaOCl_2.H_2O & \equiv I_2 \\ \quad 145\text{ gm.} & \quad 2 \times 127\text{ gm.} \\ \quad 72{\cdot}5\text{ gm.} & \quad 127\text{ gm. (the gm.-equivalent of iodine)} \end{array}$$

∴ the equivalent of bleaching powder is 72·5, and to make a litre of $N/10$ solution 7·25 gm. will be required. To make 250 c.c. of $N/10$ bleaching powder solution, 1·81 gm. will be required.

To allow for impurity in the bleaching powder and for deterioration in "available" chlorine content, about 2·5 gm. should be used. Weigh accurately a weighing bottle containing about 2·5 gm. of bleaching powder which has been powdered as finely as possible. Prepare in a 250 c.c. measuring flask a solution of 4 to 5 gm. of potassium iodide in 20 c.c. of water. Transfer the bleaching powder to a clean mortar and weigh the bottle again. Rub the bleaching powder into a paste with a little water at a time, transferring the paste to the 250 c.c. flask, until all the bleaching powder is in the flask. Acidify the mixture with acetic acid* and make up the clear brown solution to 250 c.c. Shake the flask well and titrate 25 c.c. of the solution against $N/10$ sodium thiosulphate solution as described previously, using starch indicator. Repeat the titration two or three times.

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* A mineral acid, such as hydrochloric, would allow calcium chlorate in the bleaching powder to liberate iodine from the potassium iodide, giving a result which is too high.

Calculation. Suppose *a* gm. of bleaching powder were used and 25 c.c. of the resulting iodine solution required *b* c.c. $N/10$ $Na_2S_2O_3$.

$$CaOCl_2.H_2O + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + 2H_2O + Cl_2$$

145 gm. of bleaching powder ≡ 71 gm. of chlorine.
72·5 gm. ,, ,, ,, ≡ 35·5 gm. ,, ,,

The equivalent of chlorine is 35·5, being the weight which combines with 1 unit of hydrogen.

From the titration data,

25 c.c. of bleaching powder solution finally required *b* c.c. of $N/10$ $Na_2S_2O_3$.

The bleaching powder solution is $\frac{b}{25} \times \frac{N}{10}$ and will contain $\frac{b}{25} \times \frac{35{\cdot}5}{10}$ gm. chlorine per l.

Since the solution was made by using 4*a* gm. of bleaching powder per litre, % of available chlorine in bleaching powder is

$$\frac{\frac{b}{25} \times \frac{35{\cdot}5}{10}}{4a} \times 100$$

Experiment 256. Estimation of copper, e.g., determination of the percentage of copper sulphate in a sample of copper sulphate crystals.

Material: Copper sulphate; potassium iodide; $N/10$ sodium thiosulphate.

The copper solution must be free from anything but a trace of mineral acid, otherwise the end-point is not accurate. This solution then liberates iodine from potassium iodide solution in accordance with the equation:—

$$\underset{\substack{\text{from the}\\ \text{solution of}\\ \text{the copper}\\ \text{salt.}}}{2Cu^{++}} + \underset{\substack{\text{from the}\\ \text{potassium}\\ \text{iodide.}}}{4I^{-}} \rightarrow \underset{\substack{\text{ppt. of}\\ \text{cuprous}\\ \text{iodide.}}}{Cu_2I_2} + I_2$$

The iodine is titrated by $N/10$ $Na_2S_2O_3$.

From the equation

$$2Cu \equiv I_2 \equiv 2Na_2S_2O_3,$$

i.e.,

$$\underset{499\text{ gm.}}{2CuSO_4.5H_2O} \equiv I_2 \equiv 2Na_2S_2O_3$$

Since 499 gm. liberate 2 gm. equivalents of iodine, 249·5 gm. is the gm. equivalent of hydrated copper sulphate. To make a litre of $N/10$ solution 24·95 gm. of the salt will be required, and for 250 c.c. of $N/10$ solution, 6·24 gm. will be required.

Weigh accurately from a weighing bottle about 6 gm. of copper sulphate crystals into a beaker. Dissolve the crystals in water in the beaker and transfer the solution completely to a 250 c.c. graduated flask. Add sodium carbonate solution till a *slight* permanent bluish precipitate of copper carbonate has formed. Acidify the mixture with a little dilute acetic acid when a clear blue solution is obtained. Make the solution up to 250 c.c. with distilled water and shake well. Pipette 25 c.c. of the solution into a conical flask containing about 1·5 gm. potassium iodide dissolved in a little water. Titrate the liberated iodine against $N/10$ sodium thiosulphate solution as previously described. Calculate the percentage of copper sulphate present.

$$\underset{159\cdot5\text{ gm.}}{CuSO_4} \equiv I \equiv 1\text{ l. }N.\text{ sodium thiosulphate.}$$

(theoretical result = 63·9%).

Experiment 257. Estimation of a sulphite, e.g., determination of the percentage of anhydrous sodium sulphite in a sample of the crystals.

Material: $N/10$ iodine; $N/10$ sodium thiosulphate; potassium iodide; sodium sulphite crystals.

Standard sodium sulphite solution is added to an excess of standard iodine solution and the excess of iodine is estimated by $N/10$ $Na_2S_2O_3$.

In the presence of sodium bicarbonate (sodium hydroxide is not used because of its reaction with iodine), sodium sulphite is oxidised quantitatively by iodine to sodium sulphate.

$$Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2HI$$
$$2HI + 2NaHCO_3 \rightarrow 2NaI + 2H_2O + 2CO_2.$$

From this equation:

$$Na_2SO_3.7H_2O \equiv I_2$$
$$252\text{ gm.} \equiv 2\text{ gm.-equivalents}$$

∴ The equivalent of crystalline sodium sulphite is 126, and to make a litre of $N/10$ solution, 12·6 gm. of crystals will be required or 3·15 gm. for 250 c.c. of solution.

Make up a solution containing 3·3 to 3·4 gm. of the impure crystals.

Pipette 50 c.c. of $N/10$ iodine solution into a conical flask and from a pipette run into it, slowly and with constant shaking, 25 c.c. of the sodium sulphite solution. Add about 2 gm. of sodium bicarbonate, shake the flask and titrate the excess iodine with $N/10$ sodium thiosulphate solution, using starch indicator as previously described. Repeat the estimation two or three times.

Calculation. Suppose a gm. of sodium sulphite crystals were made up to 250 c.c. of solution and, after 25 c.c. of this solution had been added to 50 c.c. $N/10$ iodine solution, b c.c. $N/10$ sodium thiosulphate solution were needed to titrate excess iodine, i.e., b c.c. $N/10$ iodine solution were left in excess.

$$\begin{aligned} Na_2SO_3 &\equiv I_2 \\ 126 \text{ gm.} &\equiv 2 \text{ gm.-equivalents} \end{aligned}$$

$\therefore$ The equivalent of anhydrous sodium sulphite is 63. To make a litre of $N/10$ solution 6·3 gm. will be required.

25 c.c. of sodium sulphite solution reacted with (50–b) c.c. $N/10$ iodine solution.

the sodium sulphite solution is $\frac{(50-b)}{25} \times \frac{N}{10}$

and contains $\frac{(50-b)}{25} \times \frac{63}{10}$ gm. of anhydrous sodium sulphite per l.

The solution was made by using $4a$ gm. of sodium sulphite crystals per litre.

Percentage of anhydrous sodium sulphite in the crystals

$$= \frac{\frac{(50-b)}{25} \times \frac{63}{10}}{4a} \times 100\%$$

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1)* *Material*: Malachite; $N/10$ sodium thiosulphate. The substance A is an impure specimen of copper carbonate. Estimate by the following method the percentage weight of copper which the substance contains.

Weigh out accurately about 3 gm. of the specimen A, dissolve it with caution in the minimum amount of dilute hydrochloric acid, add sodium carbonate solution drop by drop until a faint precipitate appears and then add dilute acetic acid until this precipitate just dissolves. Make up the solution to 250 c.c. with distilled water. To aliquot portions of this solution add a few crystals (not less than 1 gm.) of potassium iodide, and when these have dissolved titrate the liberated iodine with the decinormal sodium thiosulphate solution provided.

Equation:

$$2CuCl_2 + 4KI \rightarrow Cu_2I_2 + 4KCl + I_2.$$

(N.U.J.B., 1934.)

(2) *Material*: Unknown potassium sulphate solution; barium chromate in dilute hydrochloric acid†; potassium iodide; $N/10$ sodium thiosulphate.

Estimate the weight of potassium sulphate (K_2SO_4) per litre of the given solution A by the following method:

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† A solution containing 5 gm. per l. will be suitable.

You are provided with a solution of barium chromate in dilute hydrochloric acid. To 100 c.c. of this solution at the boiling temperature add 20 c.c. of the sulphate solution A. Subsequently, cool and then add ammonia cautiously to the liquid until the colour changes from orange to yellow. Filter, and treat the filtrate with hydrochloric acid and potassium iodide. Titrate the iodine as produced with the standard solution of sodium thiosulphate provided.

(Cambridge Schol., 1933.)

(3) *Material*: Unknown mixture of copper sulphate and sodium chloride; 1·02 *N*/10 iodine; sodium thiosulphate approximately *N*/10; potassium iodide 10%.

By means of the given solution of iodine which is 1·02 *N*/10 determine the normality of the solution of sodium thiosulphate C and use this solution to determine the amount of copper sulphate ($CuSO_4$) in the mixture D which contains copper sulphate and sodium chloride. [The solution D should contain between 8·6 and 9·0 gm. in 250 c.c. and 25 c.c. portions should be used for titration. A 10% solution of potassium iodide is provided.]

(London H.S.C., 1933.)

(4)* Estimation of purity of a specimen of arsenious oxide. *Material*: Arsenious oxide; *N*/10 iodine; *N* hydrochloric acid. *N.B.* Arsenious oxide is very poisonous.

Weigh out accurately about 1·25 gm. of the oxide and place it in a beaker. Dissolve it in a solution of sodium carbonate (about 4 gm. Na_2CO_3 in 50 c.c. of water). Add two drops of phenolphthalein, run in *N*.HCl until red colour disappears, pour the solution into a 250 c.c. flask and make up to the mark. Shake well. Fill the burette with the arsenite solution. Take 25 c.c. of the *N*/10 iodine solution, add about 2 gm. of sodium bicarbonate and shake until the solid has dissolved. Run in the arsenite solution until the colour of the iodine has almost disappeared, add starch solution and run in the arsenite until the blue colour just disappears.

Equation:

$$As_2O_3 + 2I_2 + 2H_2O \rightarrow 4HI + As_2O_5,$$

or *ionically*:

$$AsO_3^{---} + I_2 + H_2O \rightarrow 2H^+ + 2I^- + AsO_4^{---}$$

QUESTIONS AND CALCULATIONS

(*Answers on p.* 301.)

(1) Describe the chief properties of manganese dioxide (which occurs in nature as the mineral pyrolusite). What elements did Scheele discover during his investigation of the reactions of this substance?

0·200 gm. of the mineral pyrolusite was heated with excess of concentrated hydrochloric acid, and the gas evolved passed into excess of potassium iodide solution. The iodine released required 35·0 c.c. of a decinormal solution of sodium thiosulphate for complete reaction. Calculate the percentage of manganese dioxide in the pyrolusite.

(C.W.B., H.S.C., 1935.)

(2) 500 c.c. of a mixture of oxygen and ozone at N.T.P. are allowed to react with an acidified solution of potassium iodide. The iodine liberated reacts

with 37·6 c.c. of decinormal sodium thiosulphate solution. Calculate the percentage by weight of ozone in the gas.

(One gram-molecule of a gas occupies 22·4 litres at N.T.P.)

(London H.S.C., 1933.)

(3) You are provided with a pure sample of potassium tetroxalate ($KH_3(C_2O_4)_2 \cdot 2H_2O$; Mol. Wt. = 254·15) as reference substance and approximately $N/10$ solutions of potassium permanganate and sodium thiosulphate. Explain how you would prepare and standardise a solution of iodine of the order of decinormal. An accuracy of 0·1% is required.

Sulphur dioxide reacts with iodine and water as follows:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI.$$

10·0 c.c. of a saturated solution of sulphur dioxide in water at 20°C. are diluted to a litre with air free water. 25·0 c.c. of this diluted solution are treated with 25·0 c.c. of 0·1000 N. solution of iodine (excess) and back-titrated with 0·1000 N of thiosulphate, requiring 16·70 c.c. Calculate the strength of the saturated solution of sulphur dioxide in grams per litre.

Why is this method of back-titration employed?

(C.W.B., H.S.C., 1936.)

CHAPTER XXXVIII

SILVER NITRATE

Silver nitrate is a non-hygroscopic solid capable of being prepared in a high degree of purity, and hence very satisfactory for use in volumetric analysis. Its use depends upon the insolubility of its halogen salts and it is commonly used to estimate chlorides.

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl$$

or *ionically*: $Ag^+ + Cl^- \rightarrow AgCl.$

It can be used as its own indicator, for example, by running a solution of the nitrate into a solution of common salt until on allowing the precipitate of silver chloride to settle, a further drop produces no precipitate. This is the end-point. It is clear that this method would be tedious and difficult for a beginner. Hence it is usual to employ as indicator potassium chromate solution. If silver nitrate solution is added to a sodium chloride solution containing potassium chromate solution the silver chloride is selectively precipitated before the silver chromate. The reason is that the solubility product of silver chloride is much smaller than that of silver chromate, and hence the concentration of silver ions is not sufficiently great to bring about the precipitation of the silver chromate until all the chloride has been removed as silver chloride. Silver nitrate solution in excess will produce sufficient silver ions to exceed the solubility product of the silver chromate, and hence that is precipitated as a brick-red substance, and the end-point is the first appearance in the mixture of a reddish tinge

ionically: $2Ag^+ + CrO_4^{--} \rightleftharpoons Ag_2CrO_4.$

Limitations of Use of Potassium Chromate. Potassium chromate can only be used in neutral solutions. This is because

(*a*) Silver chromate is soluble in acids;

(*b*) An alkaline solution would react with the silver nitrate to form silver oxide.

ionically: $2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O.$

If an acidic solution of a chloride is to be estimated there are available the following alternatives:—

(*a*) Neutralise the acid with excess of calcium carbonate (free from chloride) and use potassium chromate as an indicator. (See p. 284.)

(*b*) Use an adsorption indicator.

(*c*) Add excess silver nitrate and estimate the excess by potassium thiocyanate. (See p. 293.)

These titrations are very accurate and therefore solutions of silver nitrate are usually used in concentrations approximately decinormal or weaker than decinormal.

N.B. Solutions of silver nitrate must be made up with distilled water because tap water usually contains dissolved chloride.

Experiment 258. Standardisation of silver nitrate solution.

Material: Silver nitrate; pure sodium chloride.

An accurate solution of silver nitrate can be made up by weighing the silver nitrate directly. It may be necessary, however, to standardise a solution of silver nitrate of unknown strength.

$AgNO_3 + HCl \rightarrow AgCl + HNO_3$
170 gm. 1 l. *N*.
1 l. *N*. $AgNO_3$ contains 170 gm. of the solid.

$$\therefore \ 250 \text{ c.c. } N/10 \ AgNO_3 \text{ contains } \frac{170}{10} \times \frac{250}{1{,}000} = 4{\cdot}25 \text{ gm.}$$

Weigh accurately a weighing bottle containing about 4·25 gm. of small crystals of silver nitrate. Transfer these to a 250 c.c. flask and weigh the bottle accurately. Add distilled water to the flask and shake after each addition. When all the silver nitrate has dissolved, add distilled water up to the mark by means of a pipette and shake well.

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
1 l. *N*. 58·5 gm.

∴ 250 c.c. *N*/10 NaCl solution should contain 1·4625 gm. NaCl.

Proceed in exactly the same way as the above to make an approximately *N*/10 solution of sodium chloride, weighing out accurately about 1·5 gm. of pure dry sodium chloride.

Take 25 c.c. of the sodium chloride solution, add 1 c.c. of a 5% solution of potassium chromate and run in the silver nitrate from the burette. Proceed slowly towards the end-point and take the reading when the first permanent reddish tinge is apparent.* Repeat the experiment two or three times until concordant results are obtained.

Calculation. Suppose weight of NaCl taken = 1·52 gm. in 250 c.c.
Suppose 25 c.c. of NaCl solution required 26·2 c.c. of the silver nitrate solution.
Concentration of NaCl = 1·52 × 4 gm. per litre = 6·08 gm. per l.

$$\therefore \ \text{Normality of NaCl solution is } \frac{6{\cdot}08}{5{\cdot}85}.\frac{N}{10}.$$

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* An allowance may be made for the nitrate used to affect the indicator by performing a "blank" experiment, using 1 c.c. potassium chromate solution in 50 c.c. of water.

∴ Normality of $AgNO_3$ solution is

$$\frac{25}{26{\cdot}2} \times \frac{6{\cdot}08}{5{\cdot}85} \times \frac{N}{10} = 0{\cdot}0992\,N.$$

(This factor should be written on a label and attached to the bottle.)

$$\text{Concentration of } AgNO_3 = \frac{25}{26{\cdot}2} \times \frac{6{\cdot}08}{5{\cdot}85} \times \frac{170}{10} \text{ gm. per l.}$$

$$= 16{\cdot}86 \text{ gm. per l.}$$

Experiment 259. Standardisation of hydrochloric acid by means of silver nitrate.

Material. Approx. $N/10$ hydrochloric acid; $N/10$ silver nitrate; chloride-free calcium carbonate.

You will probably have prepared a solution of hydrochloric acid approximately $N/10$. This may be standardised by means of the silver nitrate solution.

Use of Calcium Carbonate. This will react with the acid (any unused carbonate remaining undissolved) producing an equivalent amount of chloride in neutral solution. The carbonate removes the free hydrogen ions which would affect the indicator and leaves the chloride ions undisturbed.

$$CaCO_3 + 2H^+ \rightarrow Ca^{++} + H_2O + CO_2.$$

From this equation

100 gm. of $CaCO_3$ would neutralise 2 l. N.HCl.
25 c.c. $N/10$ HCl require 0·125 gm. of $CaCO_3$.

This need not be weighed out—use a liberal excess—say about 1 gm.

Method. Run 25 c.c. of the hydrochloric acid from a pipette into a conical flask and add about 1 gm. of precipitated chalk. Add 1 c.c. of 5% potassium chromate solution and run in the silver nitrate from the burette until the first permanent reddish tinge is observed. Repeat twice or until two concordant results are obtained.

Calculation. Suppose 25 c.c. of the acid required 24·3 c.c. of 0·0993 $N.AgNO_3$.

$$\begin{aligned} \therefore \text{ Normality of HCl solution} &= \frac{24{\cdot}3}{25} \times 0{\cdot}0993\,N. \\ &= 0{\cdot}0965\,N. \\ \therefore \text{ Conc. of HCl solution} &= 0{\cdot}0965 \times 36{\cdot}5 \text{ gm. per l.} \\ &= 3{\cdot}52 \text{ gm. per l.} \end{aligned}$$

Equations.

$$\begin{aligned} CaCO_3 + 2HCl &= CaCl_2 + H_2O + CO_2 \\ CaCl_2 + 2AgNO_3 &= 2AgCl + Ca(NO_3)_2 \\ \therefore\ 2HCl &\equiv 2AgNO_3. \end{aligned}$$

Experiment 260. Determination of amounts of sodium and potassium chloride in a mixture.

Material: Mixture* of potassium and sodium chlorides (about 3 gm. of each to make 1 litre of solution); *N*/10 silver nitrate.

$$\begin{array}{ll} KCl + AgNO_3 \rightarrow AgCl + KNO_3 \\ 74{\cdot}5 \text{ gm.} \quad 1 \text{ l. } N. \\ NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \\ 58{\cdot}5 \text{ gm.} \quad 1 \text{ l. } N. \end{array}$$

Assuming the mixture to consist of approximately equal proportions of sodium and potassium chloride one l. *N*. solution would contain about 65 gm. Hence amount to be dissolved in 250 c.c. to make solution $N/10 = 65 \times \frac{250}{10{,}000}$ gm. (approx.) $= 1{\cdot}625$ gm.

Weigh accurately a weighing bottle containing about 1·6 gm. of the mixture. Transfer the solid to a 250 c.c. flask and again weigh the bottle. Make up the solution to 250 c.c. in the distilled water and shake well. Titrate 25 c.c. with *N*/10 $AgNO_3$ using 1 c.c. of 5% potassium chromate solution as an indicator.

Take the burette reading at the first permanent reddish tinge and repeat the experiment two or three times.

Calculation. Suppose weight of mixed chlorides is 1·55 gm. in 250 c.c. Then the concentration is 6·20 gm. of mixture per litre.

Suppose 25 c.c. of solution required 23·1 c.c. *N*/10 $AgNO_3$.

Then the solution is $\frac{23{\cdot}1}{25} \times \frac{N}{10}$

and contains $\frac{23{\cdot}1}{25} \times \frac{1}{10}$ gm.-equivalents of chloride ion per l.

$= \frac{23{\cdot}1}{250}$ gm.-equivalents of chloride ion.

Let the 6·2 gm. of mixture contain x gm. of sodium chloride and $(6{\cdot}2 - x)$ gm. of potassium chloride.

In the litre of solution there will be

$\frac{x}{58{\cdot}5}$ gm.-equivalents of sodium chloride giving $\frac{x}{58{\cdot}5}$ gm.-equivalents of chloride ion, and similarly,

$\frac{6{\cdot}2 - x}{74{\cdot}5}$ gm.-equivalents of potassium chloride giving $\frac{6{\cdot}2-x}{74{\cdot}5}$ gm.-equivalents of chloride ion.

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* After making up the mixture it is advisable to heat it gently for some time and allow to cool in a desiccator.

Total chloride ion per litre =

$$\frac{x}{58{\cdot}5} + \frac{6{\cdot}2-x}{74{\cdot}5} \text{ gm.-equivalents.}$$

This expression equates with $\frac{23{\cdot}1}{250}$ gm.-equivalents (above)

$$\therefore \quad \frac{x}{58{\cdot}5} + \frac{6{\cdot}2-x}{74{\cdot}5} = \frac{23{\cdot}1}{250}$$

Solving: $x = 2{\cdot}5$ gm. of sodium chloride
$6{\cdot}2-x = 3{\cdot}7$ gm. of potassium chloride.

$$\% \text{ of NaCl by weight} = \frac{2{\cdot}5}{6{\cdot}2} \times 100 = 40{\cdot}3\%$$

$$\text{and of KCl} = 59{\cdot}7\%$$

N.B. The results from this experiment cannot be expected to show the same accuracy as an ordinary estimation, for example, of the amount of sodium chloride in a solution. An error of 0·1 c.c. in a titration requiring about 25 c.c. of $N/10$ $AgNO_3$ would produce an error of about 5% in the above estimation of the amount of sodium chloride in a mixture, but less than ½% in the estimation of the amount of sodium chloride in a solution.

Experiment 261. To determine the number of molecules of water of crystallisation in barium chloride crystals.

Material: $N/10$ silver nitrate; barium chloride crystals; sodium sulphate.

If this experiment is to be performed using potassium chromate solution as indicator then the barium ions must first be removed from the solution, since the reaction

ionically: $Ba^{++} + CrO_4^{--} \rightarrow \underset{\text{Insoluble}}{BaCrO_4 \downarrow}$

would remove the indicator from the solution. The barium ions can be removed by adding excess sodium sulphate, which removes the barium as insoluble barium sulphate.

ionically: $Ba^{++} + SO_4^{--} \rightarrow BaSO_4 . \downarrow$

The result is, in effect, that an equivalent solution of sodium chloride is titrated instead of the barium chloride solution.

Quantities. $\underset{208\text{ gm.}}{BaCl_2} + \underset{142\text{ gm.}}{Na_2SO_4} \rightarrow BaSO_4 + 2NaCl$

$2NaCl + \underset{2\text{ l. }N.}{2AgNO_3} \rightarrow 2AgCl + 2NaNO_3$

From these equations it is evident that

$$208 \text{ gm. } BaCl_2 \text{ require} \begin{cases} 142 \text{ gm. } Na_2SO_4 \text{ to precipitate the barium.} \\ 2 \text{ l. } N.AgNO_3 \text{ to precipitate the chloride.} \end{cases}$$

Hence weight of *anhydrous* barium chloride in 250 c.c. of $N/10$ solution

$$= \frac{208}{20{,}000} \times 250 \text{ gm.}$$
$$= 2{\cdot}60 \text{ gm.}$$

and 25 c.c. of this solution would require

$$142 \times \frac{25}{20{,}000} \text{ gm. sodium sulphate.}$$
$$= 0{\cdot}18 \text{ gm. of sodium sulphate.}$$

(Hence about 1 gm. of the anhydrous solid (or 2 gm. of the crystals $Na_2SO_4.10H_2O$) would provide ample excess.)

Allowing for the presence of water of crystallisation a suitable weight of barium chloride to use would be about 3 gm.

Method. Weigh out accurately (by means of a weighing bottle) about 3 gm. of barium chloride crystals and make up to 250 c.c. with distilled water. Shake well. Take 25 c.c. of this solution by means of a pipette, transfer to a conical flask, add about 1 gm. of anhydrous sodium sulphate and shake. Add about 1 c.c. of 5% potassium chromate solution and run in $N/10$ $AgNO_3$ from a burette until a permanent reddish tinge is observed.

Repeat the experiment two or three times.

Calculation. Suppose weight of barium chloride crystals made up to 250 c.c. = a gm. and 25 c.c. of this solution required b c.c. of silver nitrate solution of strength c N. (where c is the factor, e.g., 0·0104).

$$\text{Conc. of } BaCl_2 \text{ solution} = \frac{b \times c}{25} N.$$

$$\therefore \quad \text{Weight of } BaCl_2 \text{ in 1 litre solution} = \frac{b.c.}{25} \times \frac{208}{2} \text{ gm.}$$

$$\text{Hence} \qquad \frac{BaCl_2}{BaCl_2.xH_2O} = \frac{b.c.}{25} \times \frac{208}{2} \times \frac{1}{4a}$$

$$\therefore \quad 208 \times a = (208 + 18x)\,\frac{b.c.}{25} \times \frac{208}{8} \text{ from which } x \text{ can be}$$

obtained.

Experiment 262. Estimation of chloride and alkali in a solution containing them both.

Material: $N/10$ hydrochloric acid; $N/10$ silver nitrate. Alkaline sodium chloride solution.*

Principle. Silver nitrate cannot be used in alkaline solution with potassium chromate as an indicator. Hence the alkali is neutralised with standard hydrochloric acid and the total chloride present is estimated with standard silver nitrate solution.

Method. Take 25 c.c. of the alkaline sodium chloride solution and add a few drops of phenolphthalein solution. It will turn red. Run $N/10$ HCl into this solution until the pink colour is just discharged. Note the reading. Add 1 c.c. of 5% solution of potassium chromate to this neutral solution and run in $N/10$ $AgNO_3$ solution until the first reddish tinge is observed. Note the reading and repeat the process twice.

Calculation. Suppose 25 c.c. of alkaline sodium chloride solution required *a* c.c. $N/10$ HCl.

Suppose the same neutral solution required *b* c.c. $N/10$ $AgNO_3$.

Concentration of caustic soda

$$= \frac{a}{25} \times \frac{N}{10}$$

$$= \frac{a}{25} \times \frac{40}{10} \text{ gm. per l. NaOH.}$$

Concentration of sodium chloride

$$= \frac{b - a}{25} \times \frac{N}{10}$$

$$= \frac{b - a}{25} \times \frac{58{\cdot}5}{10} \text{ gm. per l. NaCl.}$$

Equations.

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$$

Experiment 263. Alternative method for Expt. 262.

Material: Alkaline sodium chloride solution; $N/10$ hydrochloric acid; $N/10$ silver nitrate; precipitated chalk.

(*a*) *Alkalinity.* If the strength of the solution with respect to alkali is required, titrate with $N/10$ HCl as indicated above.

(*b*) *Chloride Content.* To a separate 25 c.c. of the solution add a few c.c. of bench nitric acid (about 5 c.c. should be ample) and then precipitated chalk until some is in excess. If no effervescence is

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* A solution of suitable strength can be quickly made by putting a known weight (about 3 gm.) of sodium chloride in water in a 1000 c.c. flask. Add 500 c.c. of $N/10$ NaOH solution and make up to the mark.

observed on adding a little chalk, then more nitric acid is added. The solution is now neutral and can be titrated with $N/10$ $AgNO_3$, using potassium chromate as an indicator. In this case the silver nitrate reading gives the chloride content directly because no hydrochloric acid has been added.

Experiment 264. Estimation of chloride and acid in a solution containing both.

Material: Acidified chloride solution,* $N/10NaOH$; $N/10AgNO_3$.

Silver nitrate cannot be used to titrate an acid solution of a chloride using potassium chromate as an indicator. The strength of the acid is first determined by means of standard alkali and a further quantity of solution is made neutral with calcium carbonate and the chloride content determined from this. Titrate 25 c.c. of the original solution against $N/10$ NaOH, using phenolphthalein as an indicator. To a further 25 c.c. add excess of precipitated chalk (see p. 284) and 1 c.c. of 5% potassium chromate solution as an indicator and titrate with $N/10$ $AgNO_3$. The strengths of the acid and chloride are calculated from the volumes of alkali and silver nitrate respectively.

Experiment 265. Estimation of percentage of potassium chlorate in a mixture of potassium chlorate and potassium sulphate.

Material: Mixture of pure potassium chlorate and potassium sulphate; $N/10$ silver nitrate.

Principle. Potassium chlorate will react with concentrated hydrochloric acid liberating chlorine and is reduced to the chloride which is estimated in the usual way with $N/10$ $AgNO_3$.

$$\begin{array}{llll} KClO_3 + 6HCl \rightarrow & KCl & + 3H_2O + 3Cl_2 \\ 122{\cdot}5 \text{ gm.} & 74{\cdot}5 \text{ gm. or } 1 \text{ l. } N. & \end{array}$$

Method. Weigh out accurately about 3 gm. of the mixture and place the solid in a large evaporating dish. Add about 20 to 30 c.c. of concentrated hydrochloric acid, cover the dish with a clock glass and heat gently in a fume chamber for twenty to thirty minutes. There should now be no smell of chlorine. Wash any splashed liquid from the clock glass into the dish, place on a water bath and evaporate carefully down to dryness. Make up the solid left to 250 c.c. and titrate with $N/10$ $AgNO_3$.

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* This solution can be conveniently prepared by putting about 3 gm. of pure sodium chloride in a 1,000 c.c. flask, adding 500 c.c. $N/10$ HCl and making up to the mark.

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1) *Material*: Solution of sodium carbonate and sodium chloride; $N/10$ hydrochloric acid; $N/10$ silver nitrate.

The solution A contains only sodium carbonate and sodium chloride. Estimate the separate amounts of each salt in grams per litre. You are provided with standard solutions of hydrochloric acid and silver nitrate.

(2) *Material*: Solution containing sodium chloride, sodium hydroxide and sodium carbonate; $N/10$ hydrochloric acid; $N/10$ silver nitrate.

The solution A contains sodium chloride, sodium hydroxide and sodium carbonate. Estimate the weight of each compound in 1 litre of the solution. Standard solutions of silver nitrate and of hydrochloric acid are provided.

(In the estimation of sodium hydroxide the sodium carbonate should first be precipitated by an excess of barium chloride and advantage taken of the fact that the concentration of hydrogen ion required to decompose barium carbonate is greater than that to decolorise phenolphthalein.)

(Cambridge Schol., 1934.)

3) *Material*: Solutions A and B, $N/10$ silver nitrate; $N/10$ potassium permanganate.

You are required to determine the percentage proportion of potassium chlorate and potassium chloride in a mixture X of these two compounds.

You are provided with two solutions labelled A and B and with exactly decinormal solutions of silver nitrate and potassium permanganate. Solution A contains in each litre the residue left on ignition (to constant weight) of 13·57 gm. of X.

Solution B contains in each litre the product of boiling 13·57 gm. of X dissolved in sulphuric acid with 60 gm. $FeSO_4$, the ferrous sulphate being in excess of that required for the reaction:

$$ClO_3^- + 6Fe^{++} + 6H^+ \rightarrow Cl^- + 6Fe^{+++} + 3H_2O$$

$$(Cl = 35{\cdot}5. \quad Fe = 56. \quad O = 16. \quad K = 39)$$

(Oxford Schol., 1936.)

(4)* To determine the solubility of barium chloride at the temperature of the laboratory. *Material*: Barium chloride crystals; $N/10$ silver nitrate.

Crush some crystals of barium chloride and add to water in a boiling-tube. Shake vigorously, add more crystals if necessary, and allow to stand with intermittent shakings for about twenty minutes. Work out the weight of solution required to dilute to 250 c.c. in order to be roughly $N/10$. You are told the solubility will be of the order of 40 gm. per 100 gm. water at the temperature of the laboratory. Weigh a weighing bottle empty, filter off about the calculated weight into the weighing bottle and weigh again. (If you use a pipette it must be washed out with the saturated solution.) Transfer completely the contents of the weighing bottle to a 250 c.c. flask, empty all washings from the bottle into the flask and make up to 250 c.c. Proceed as in Experiment 261 and calculate the result in gm. solute per 100 gm. solvent.

(5)* To determine the percentage purity of a sample of potassium bromide.
Material: Potassium bromide; *N*/10 silver nitrate.

$$\begin{array}{ll} AgNO_3 + KBr \rightarrow AgBr + KNO_3. \\ 1\ l.\ N. \qquad 119\ gm. \end{array}$$

Hence decinormal KBr will contain 11·9 gm. per litre. Weigh out accurately about 3 gm. of potassium bromide. Make up to 250 c.c. with distilled water. Titrate against *N*/10 $AgNO_3$ using potassium chromate solution as an indicator. Calculate the percentage purity from the equation.

CALCULATIONS

(*Answers on p.* 302.)

(1) 2·5 gm. of a mixture of potassium chloride and sodium chloride were made up to 250 c.c. 20 c.c. of this solution required 32 c.c. of *N*/10 $AgNO_3$ for complete precipitation of the chloride. Calculate the percentage by weight of the two salts in the original mixture.

(2) A solution contained a mixture of sodium carbonate and sodium chloride. 25 c.c. of the solution required 20·4 c.c. of 0·095 *N*.HCl to convert the carbonate into the chloride. The same 25 c.c. containing also the chloride converted from the carbonate required 38·7 c.c. *N*/10 $AgNO_3$ to precipitate the chloride completely. Calculate the strength of sodium carbonate and sodium chloride in 1 litre of the original solution.

(3) A solution of strontium chloride in water was made by dissolving 3·01 gm. of the crystalline salt in distilled water and the solution was made up to 250 c.c. 20 c.c. of this solution required 17·7 c.c. *N*/10 $AgNO_3$ for complete precipitation of the chloride. Calculate the number of molecules of water of crystallisation per molecule of $SrCl_2$ (Sr = 88).

(4) 20 c.c. of a solution of sodium cyanide required 29·8 c.c. of 0·0104 *N*. $AgNO_3$ for the formation of the double salt $NaAg(CN)_2$. Calculate the strength of the sodium cyanide solution in grams per litre.

CHAPTER XXXIX

POTASSIUM THIOCYANATE

Volhard's method.

By the use of a solution of either potassium or ammonium thiocyanate the strength of a silver nitrate solution can be estimated. This estimation can be carried out in acid solution which is sometimes very advantageous (see p. 282). If the solution is neutral it is necessary to add nitric acid to prevent hydrolysis of the ferric salt used as indicator. The reaction depends upon the insolubility of silver thiocyanate.

ionically: $CNS^- + Ag^+ \rightarrow AgCNS \downarrow$

A solution of ferric salt (usually iron alum) is the indicator. If a thiocyanate solution is added to an acidic silver nitrate solution containing ferric sulphate the silver thiocyanate is selectively precipitated before the production of any ferric thiocyanate. This is because of the very small solubility product of the silver thiocyanate.

As soon as the thiocyanate ions are in excess they react with the ferric ions present to produce the blood red coloration due to ferric thiocyanate.

ionically: $Fe^{+++} + 3CNS^- \rightarrow \underset{\text{blood red}}{Fe(CNS)_3}$

Volhard's method can be applied to chlorides in acid solution by precipitating all the chloride by the addition of excess silver nitrate solution and determining the excess silver nitrate by titration with potassium thiocyanate.

Note that in this method it is not necessary for the silver nitrate to be in the burette. The thiocyanate solution is run into the silver nitrate solution. The reason for this is that the precipitated silver thiocyanate can adsorb thiocyanate ions, and this would take place to some extent if the potassium or ammonium thiocyanate were in the conical flask and silver nitrate solution were added from the burette.

Experiment 266. Standardisation of potassium thiocyanate solution.

Material: Potassium thiocyanate; $N/10$ silver nitrate; ferric alum.

Potassium thiocyanate (also ammonium thiocyanate) is a very deliquescent solid and it is impossible to weigh out exactly the amount required for any particular solution.

$$\underset{\substack{97\text{ gm.}\\ \text{or } 1\text{ l. } N.}}{KCNS} + \underset{\substack{170\text{ gm.}\\ \text{or } 1\text{ l. } N.}}{AgNO_3} \rightarrow AgCNS + KNO_3$$

Hence one l. *N*/10 KCNS will contain 9·7 gm. of anhydrous potassium thiocyanate.

Weigh out about 12 gm. of the crystals on a watch-glass and transfer the crystals to a litre measuring flask, add distilled water to make up about 1 litre and shake well. Measure out 25 c.c. of *N*/10 $AgNO_3$ (its strength must be accurately known) into a conical flask, add 2 or 3 c.c. of a 10% solution of ferric alum and a few c.c. of dilute nitric acid. The acid prevents the hydrolysis of the ferric sulphate, which would otherwise cause the solution to be brownish in colour and so prevent a clear indication of the end-point. Put the thiocyanate solution into a burette and run in the thiocyanate until the first permanent reddish tinge is observed. Repeat the process two or three times.

Calculation. Suppose 25 c.c. of 0·104 *N*. $AgNO_3$ required 23·7 c.c of KCNS solution.

$$\begin{aligned} \text{Normality of KCNS solution} &= \frac{25}{23{\cdot}7} \times 0{\cdot}104\ N. \\ &= 0{\cdot}1097\ N. \\ \text{Conc. of KCNS solution} &= 0{\cdot}1097 \times 97 \text{ gm. per l.} \\ &= 10{\cdot}64 \text{ gm. per l.} \end{aligned}$$

To make the solution exactly *N*/10 1 litre of the solution must be made up to 1097 c.c. Hence add 97 c.c. of distilled water to 1 litre of solution.

$$\begin{aligned} \text{The strength would then be } &\frac{1000}{1097} \times 0{\cdot}1097\ N. \\ &= 0{\cdot}1000\ N. \end{aligned}$$

Experiment 267. Estimation of purity of sodium chloride by Volhard's method.

Material: Sodium chloride; *N*/10 silver nitrate; *N*/20 potassium thiocyanate; ferric alum.

Principle. The sodium chloride is dissolved in water, excess silver nitrate added; the precipitated silver chloride is removed and the excess of silver nitrate is determined by back titration.

Method. Weigh accurately a weighing bottle containing not more than 0·4 gm. of sodium chloride. Transfer this to a 250 c.c. flask, adding a little distilled water to dissolve the sodium chloride. Reweigh the weighing bottle. Run in 150 c.c. *N*/10 $AgNO_3$ solution, add 2 to 3 c.c. of concentrated nitric acid, replace the stopper and shake until the precipitated silver chloride settles, leaving a clear supernatant liquid. Add distilled water up to the mark and shake thoroughly. Filter* the solution through a dry filter paper. Measure

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* The reason for filtering is that the silver chloride is more soluble than the silver thiocyanate and tends to react with the ferric thiocyanate.

out 50 c.c. of the filtrate by means of a pipette, add 2 or 3 c.c. of ferric alum solution and run in the $N/20$ KCNS solution until the first permanent reddish tinge is observed. Repeat the titration two or three times.

Results. Suppose weight of sodium chloride = 0·376 gm.

To this 150 c.c. $N/10$ $AgNO_3$ were added and the solution was made up to 250 c.c.

Suppose 50 c.c. of this solution required 34·8 c.c. $N/20$ KCNS

$$\underset{58\cdot5\text{ gm.}}{NaCl} + \underset{10\text{ l. }N/10}{AgNO_3} \rightarrow AgCl + NaNO_3$$

$$\therefore\quad 50\text{ c.c. of the solution} \equiv 17\cdot4\text{ c.c. }N/10\text{ KCNS}$$

$$\therefore\quad 250\text{ c.c. of the solution} \equiv 87\text{ c.c. }N/10\text{ KCNS}$$

(150 − 87) c.c. of $N/10$ $AgNO_3$ were used up by the chloride, i.e., 63·0 c.c. $N/10$ $AgNO_3$ ≡ 0·376 gm. of the impure sodium chloride.

$$\text{But }10\text{ l. }N/10\ AgNO_3 \equiv 58\cdot5\text{ gm. NaCl}$$

$$\therefore\quad 63\cdot0\text{ c.c. }N/10\ AgNO_3 \equiv \frac{58\cdot5}{10{,}000} \times 63\text{ gm. NaCl}$$

$$= 0\cdot3686\text{ gm.}$$

$$\text{Purity} = \frac{0\cdot3686}{0\cdot376} \times 100\%$$

$$= 98\cdot0\%$$

Experiment 268. To determine the percentage of silver in an alloy, e.g., a coin.

Material: Silver alloy; $N/10$ potassium thiocyanate.

For this purpose the alloy should not contain too high a proportion of copper. If too much copper is present the colour of the copper ions interferes. The pre-1914 war silver coinage is excellent for this purpose as it contains 92·5% of silver. The present day coin is not suitable (1947 "silver" coinage is not silver but Cu—Ni alloy).

Weigh accurately a piece of silver of weight about 2 gm. and introduce the metal carefully into a conical flask. Add about 5 c.c. of distilled water followed by 5 c.c. of concentrated nitric acid. Place a funnel in the neck of the flask, and put the flask in a fume chamber and allow the metal to dissolve. When the metal has dissolved boil the solution to expel nitrous acid and add distilled water down the funnel, washing the sides of the neck of the flask so that no silver nitrate solution is lost. Transfer the solution completely to a 250 c.c. graduated flask. Make up to the mark and shake well. Measure out 25 c.c. of this solution with a pipette, add 2 or 3 c.c. of ferric alum solution and titrate with $N/10$ thiocyanate solution. Note the burette reading at the first permanent reddish tinge, and repeat the titration two or three times.

$$Ag + 2HNO_3 \rightarrow AgNO_3 + H_2O + NO_2$$
$$AgNO_3 + KCNS \rightarrow AgCNS + KNO_3$$

Hence $Ag \equiv KCNS$

i.e., $108 \text{ gm.} \equiv 10 \text{ l. } N/10$

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

1) Solution A contains 5 gm. of a mixture of potassium nitrate and silver nitrate made up to 250 c.c. of solution. Given $N/10$ KCNS determine the strengths of the two salts in gm. per litre.

(2) Determination of the strength of a solution of sodium arsenate. *Material*: Sodium arsenate solution about $N/10$; $N/10$ silver nitrate; $N/10$ potassium thiocyanate.

Method. Add excess silver nitrate to precipitate the arsenate from the sodium arsenate solution and determine the excess silver nitrate by titration with $N/10$ KCNS.

N.B. Use a vacuum bottle to take 25 c.c. of the arsenate solution.

(3)* Estimation of percentage purity of potassium bromide. *Material*: Potassium bromide; $N/10$ silver nitrate; $N/20$ potassium thiocyanate.

Repeat Experiment 267, using potassium bromide instead of sodium chloride. Weigh out about 0·7 gm. of the bromide. As silver bromide is less soluble than silver thiocyanate there is no need to filter off the precipitated silver bromide.

(4)* Estimation of the strength of mercuric nitrate solution. *Material*: Mercuric nitrate; $N/10$ potassium thiocyanate; sodium nitroprusside.

Sodium nitroprusside gives a permanent precipitate with mercuric nitrate but not with potassium thiocyanate. Make up a solution of mercuric nitrate to be about $N/10$. Run this from a burette into 20 c.c. of potassium thiocyanate solution to which a few drops of a 10% solution of sodium nitroprusside have been added. Take as the end-point the first permanent turbidity.

$$Hg(NO_3)_2 + 2KCNS \rightarrow Hg(CNS)_2 + 2KNO_3.$$

(5) *Material*: Sodium chloride; arbitrary silver nitrate; unknown ammonium thiocyanate.

By means of the given pure sodium chloride (NaCl) determine the normality of the solution of silver nitrate E, and use this solution to determine the amount of ammonium thiocyanate (NH_4CNS) in 1 litre of solution F. (the solution of sodium chloride should contain between 1·3 and 1·5 gm. in 250 c.c. and 25 c.c. portions should be used for titration).

(London H.S.C., 1932.)

CALCULATIONS

(*Answers on p.* 302.)

(1) Determine the strengths in gm. per litre of potassium cyanide and potassium chloride in a solution containing both from the following data:—

(*a*) 25 c.c. of the solution required 22·4 c.c. $N/10$ $AgNO_3$ for the appearance of the first permanent precipitate. This indicates the end-point of the reaction.

$$AgNO_3 + 2KCN \rightarrow KAg(CN)_2 + KNO_3.$$

(*b*) To 25 c.c. of the original solution 100 c.c. $N/10$ $AgNO_3$ were added and the solution was acidified with nitric acid, filtered and the filtrate required 32·0 c.c. $N/10$ KCNS to precipitate the residual silver.

(2) 6 gm. of pure copper sulphate crystals were dissolved in water and the solution was made up to 250 c.c. 25 c.c. of this solution were treated with a reducing agent and 50 c.c. $N/10$ KCNS, and the precipitate of cuprous thiocyanate was filtered off. The filtrate was equivalent to 25 c.c. of a silver nitrate solution. Calculate the strength of the silver nitrate solution in gm. per litre.

(3) One gram of an alloy containing silver was dissolved in nitric acid and the solution was made up to 100 c.c. 20 c.c. of this solution required 16·8 c.c. of $N/10$ KCNS to precipitate the silver. Calculate the percentage of silver in the alloy.

CHAPTER XL

ADSORPTION INDICATORS

Adsorption indicators are playing a most important part in the development of volumetric analysis. It was only recently shown that certain dyes could act as indicators for many types of reaction. These adsorption indicators are very sensitive, enabling dilute solutions to be employed. New methods of using these indicators are being found almost daily and they are being used for an increasingly large number of reactions. The following example gives an idea of the mechanism of an adsorption indicator.

Charge on Colloidal Particle alters as Reaction is Complete. Many precipitates are colloidal in nature and the colloidal particles can adsorb ions from solution. Ions are not adsorbed by the colloidal particles indiscriminately, for the latter show preference for certain ions over others. The colloidal particles of a silver bromide precipitate will adsorb either bromide or silver ions from solutions containing either of these. Thus silver bromide in potassium bromide solution will adsorb bromide ions but not potassium ions, and silver bromide in silver nitrate solution will adsorb silver ions but not nitrate ions.

Consider the action which takes place when silver nitrate is run into a solution of potassium bromide. So long as the latter is in excess (i.e., before the reaction is complete) we shall have present potassium ions, bromide ions, nitrate ions and silver bromide particles, i.e., assuming excess KBr

$$2K^+ + 2Br^- + Ag^+ + NO_3^- \rightarrow AgBr\downarrow + 2K^+ + NO_3^- + Br^-$$

The colloidal silver bromide adsorbs the bromide ions forming a *negatively* charged complex which we may regard as $[AgBr].Br^-$, i.e., a negatively charged particle. As soon as the reaction is complete there will be no bromide ions in excess and a further drop of silver nitrate will produce a solution containing potassium ions, nitrate ions, *silver ions* and silver bromide particles.

I.e., assuming excess $AgNO_3$

$$K^+ + Br^- + 2Ag^+ + 2NO_3^- \rightarrow K^+ + 2NO_3^- + Ag^+ + AgBr\downarrow$$

The conditions are now altered. The $[AgBr]Br^-$ complex is decomposed and the silver bromide will now adsorb silver ions to form a complex such as $[AgBr]Ag^+$ which will be *positively* charged. The important point to note is that as the reaction is completed and a further quantity of the reagent (in this case silver nitrate) is added, the colloidal particle changes in sign from negative to positive.

Mechanism of the Indicator. We will consider eosin to have the formula NaEo to indicate that the solution in water contains sodium cations and eosinate anions. These latter impart a pink colour to the solution. (Red ink is a solution of sodium eosinate in water.)

$$\underset{}{\text{NaEo}} \rightleftharpoons \underset{\text{colourless}}{\text{Na}^+} + \underset{\text{pink.}}{\text{Eo}^-}$$

Whilst the bromide adsorbed complex $[AgBr]Br^-$ is present there is no tendency for the colloidal particle to attract to itself the coloured eosinate ions, which therefore *colour the solution but not the precipitate.* When the silver adsorbed complex $[AgBr]Ag^+$ is formed some of the eosinate ions are at once attracted to it by reason of their opposite charge and the precipitate becomes coloured by the eosinate ions. Furthermore, the colour of the eosinate ions when adsorbed by the colloidal particle is not exactly the same as the colour observed when the eosinate ion is in solution (the eosinate ion may combine with the silver ion to form silver eosinate). Hence quite a definite change in colour is observed, and it is the precipitate which becomes coloured. This is an important point in the use of adsorption indicators. It is the precipitate which must be observed and not the solution.

It is also often noticed that the precipitate coagulates as the end-point is reached.*

If difficulty is experienced in noticing the end-point, the following method will help. To two conical flasks add some of the reagent, e.g., hydrochloric acid and sufficient calcium carbonate to render the solution neutral, and a few drops of fluorescein. Into flask A run an amount of silver nitrate obviously insufficient to cause any alteration of colour and into flask B sufficient to give a definite change, i.e., an amount greater than that necessary to attain the end-point.

Now place the solution to be titrated by the side of these and run the silver nitrate into it. The first permanent change will be then quite obvious.

The following examples are simple and the indicators used are either eosin (red ink will do) or fluorescein.

Experiment 269. To standardise a solution of hydrochloric acid using fluorescein as indicator.

Material: Approximately *N*/10 hydrochloric acid; *N*/10 silver nitrate; calcium carbonate; fluorescein.

Although many adsorption indicators can be used in acid solution fluorescein can only be used in neutral solution.

Measure out from a pipette 25 c.c. of the hydrochloric acid solution to be standardised and add about 1 gm. of precipitated calcium carbonate (see Expt. 259 for theoretical consideration) or until there remains a little calcium carbonate undissolved.

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* This is also the isoelectric point where there is no charge on the colloid particles. Hence they coagulate.

Add 2 or 3 drops of fluorescein (which will colour the solution green) and run in the silver nitrate solution from the burette until the precipitate (which is yellowish at first) turns pink. Repeat the experiment two or three times. Calculate the normality of the acid from the equation

$$\begin{array}{llll} \text{HCl} & + \ \text{AgNO}_3 & \rightarrow \text{AgCl} & + \ \text{HNO}_3 \\ 36{\cdot}5 \text{ gm.} & & & \\ \text{or} & & & \\ 10 \text{ l. } N/10 & 10 \text{ l. } N/10 & & \end{array}$$

Note 1. This equation does not represent the actual reaction which took place. The silver nitrate was titrated against an equivalent solution of calcium chloride.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$
$$CaCl_2 + 2AgNO_3 \rightarrow Ca(NO_3)_2 + 2AgCl$$

Note 2. The effect of light upon the silver chloride may interfere with observation of the colour change. To minimise this effect a paper jacket covering the conical flask may be used.

Experiment 270. To find the equivalent weight of potassium bromide.

Material: $N/100$ silver nitrate; potassium bromide; eosin.

Weigh accurately a weighing bottle containing about 0·3 gm. of pure potassium bromide and transfer this to a 250 c.c. flask and reweigh the bottle. The weighing must be accurate, for a small actual error in weighing this small amount would create a large percentage error. Dissolve the bromide in distilled water, make the solution up to the mark, and shake well. Measure out 25 c.c. of this solution from a pipette, add two or three drops of eosin and titrate with $N/100$ $AgNO_3$ from a burette. Note the reading when the precipitate becomes salmon-pink in colour. Repeat two or three times.

Calculation. Suppose a gm. of KBr were made up to 250 c.c. of solution and 25 c.c. of this solution required b c.c. of $N/100$ $AgNO_3$

$$\begin{aligned} b \text{ c.c. of } N/100\ AgNO_3 &\equiv 25 \text{ c.c. of KBr solution.} \\ \therefore\ 10\,b \text{ c.c. } N/100\ AgNO_3 &\equiv 250 \text{ c.c. of KBr solution} \\ &\equiv a \text{ gm. of KBr} \\ 1 \text{ c.c. } N/100\ AgNO_3 &\equiv \frac{a}{10b} \text{ gm. KBr} \end{aligned}$$

$$100{,}000 \text{ c.c. } N/100\ AgNO_3, \text{ i.e., } 1 \text{ l. } N$$
$$\equiv \frac{a}{10b} \times 100{,}000 \text{ gm. KBr}$$
$$= \frac{10{,}000 \times a}{b} \text{ gm. KBr}$$

which is the equivalent weight of potassium bromide.

Equation. $KBr + AgNO_3 \rightarrow AgBr + KNO_3$

Experiment 271. To estimate the purity of lead nitrate crystals by titration against sodium hydroxide.

Material: $N/10$ sodium hydroxide; lead nitrate; fluorescein.

$$\underset{331\text{ gm.}}{Pb(NO_3)_2} + \underset{2\text{ l. }N/10}{2NaOH} \rightarrow Pb(OH)_2 + 2NaNO_3$$

Weigh accurately a weighing bottle containing about 4 gm. of pure lead nitrate crystals and transfer it to a 250 c.c. flask. Reweigh the weighing bottle. Add distilled water to the crystals, shake, and when dissolved make up to the mark, shake and allow to stand. Fill the burette with the lead nitrate solution. Measure out 25 c.c. of $N/10$ NaOH into a conical flask and add two to three drops of a solution of fluorescein. This will colour the solution green. As the lead nitrate solution is run in, the precipitate becomes yellowish in colour. Run in the lead nitrate solution until there is the first permanent pink coloration on the precipitate. Repeat the experiment two or three times.

Experiment 272. To determine the strength of a potassium thiocyanate solution.

Material: $N/10$ silver nitrate; approximately $N/10$ potassium thiocyanate; fluorescein.

The solution of potassium thiocyanate should be approximately $N/10$ because it is necessary in silver nitrate titrations with adsorption indicators to proceed rapidly. Otherwise the action of light upon the precipitate may obscure the change. Measure out 25 c.c. of the potassium thiocyanate solution, add a few drops of fluorescein and rapidly run in silver nitrate solution until the precipitate coagulates and turns pink. Make two or three more accurate determinations, proceeding more slowly towards the end of the titration.

$$AgNO_3 + KCNS \rightarrow AgCNS + KNO_3.$$

From the equation

$$1\text{ l. }N/10\ AgNO_3 \equiv 9{\cdot}7\text{ gm. }KCNS$$

calculate the strength of the potassium thiocyanate in gm. per litre.

EXERCISES

An asterisk indicates that the particular problem can be attacked without previous preparation of solutions, the strengths of which have not to be divulged to the student.

(1)* *Material*: Lead acetate; sodium hydroxide; dichlorofluorescein. Investigate the possibility of using dichlorofluorescein to indicate the end-point of the reaction:—

$$Pb(CH_3COO)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2CH_3COONa.$$

Use solutions of approximately decinormal strength and allow the acetate to run into the caustic soda solution.

(2) Strength of sodium oxalate solution. *Material*: Unknown sodium oxalate; fluorescein.

The lead acetate solution prepared above may be used to estimate the strength of a solution of sodium oxalate (or any normal oxalate) using fluorescein as adsorption indicator. The precipitate becomes permanently pink in colour at the end-point.

(3) Estimation of bromide and iodide in a mixture. *Material*: Mixture of potassium bromide and iodide; di-iodofluorescein, eosin; $N/50$ silver nitrate.

Weigh out accurately about 1 gm. of the mixture and dissolve in distilled water and make up to 250 c.c. Titrate 25 c.c. of the solution

(*a*) with silver nitrate using di-iodofluorescein (yellow to pink) which indicates the end-point when the iodide only has been precipitated;
(*b*) with silver nitrate using eosin which indicates the end-point when the whole of the halide has been precipitated.

Estimate the strengths of the iodide and bromide in gm. per litre.

ANSWERS TO CALCULATIONS

Chapter XXXIV. Page 246.

(1) 5·6 gm. 4·9 gm. 3·16 gm.
(2) 20.
(3) 2·8 gm. 0·057 N.
(4) 45·98% Na_2CO_3; 54·02% NaCl.
(5) 5·295 gm. Na_2CO_3; 8·392 gm. $NaHCO_3$.

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(2) 5·056 gm.
(3) 208·3 c.c.
(5) 32·5.
(6) 7.
(7) 99·1%.
(8) 4·99 gm. 4·409 gm.
(9) 80%.
(10) 13·79 gm. $FeSO_4$. 19·15 gm. $Fe_2(SO_4)_3$.

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(1) 54·8%.
(2) 6·40 gm.
(3) 26·03 c.c.

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(1) 76·125%.
(2) 12·12%.
(3) 106·2 gm.

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(1) 29·8% KCl; 70·2% NaCl.
(2) 4·109 gm. Na_2CO_3; 4·521 gm. NaCl.
(3) 6.
(4) 1·519 gm.

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(1) 11·65 gm. KCN; 6·914 gm. KCl.
(2) 17·65 gm. per litre.
(3) 90·72 %.

PART V

A SYSTEM OF QUALITATIVE ANALYSIS

CHAPTER XLI

PRELIMINARY TESTS AND MAKING A SOLUTION

Action of Heat in Dry Tube.

Change.	*Indication of presence of*
Sublimation	Ammonium halides, mercurous or mercuric halides, arsenious oxide and other less common substances, mirror-mercury.
Melting	Sodium, potassium or ammonium nitrate, potassium chlorate, or many less common substances.
Decrepitation	Sodium chloride, lead nitrate, potassium chlorate.
Loss of gas or vapour.	
Water vapour	Water of crystallisation, some basic hydroxides, basic carbonates, acid salts. Water absorbed from the atmosphere.
Oxygen	Oxides of silver and mercury, peroxides, sodium or potassium nitrate, permanganates and chlorates.
Carbon dioxide	Carbonate or bicarbonate.
Ammonia	An ammonium compound.
Nitrogen peroxide	Nitrates of heavy metals.
Sulphur trioxide	Some sulphates.
Halogens	By oxidation of halide.

Flame Coloration.

Metal.	*Colour of the flame.*
copper	bluish green
calcium	red
strontium	crimson
barium	light green
sodium	intense golden yellow (nil, through blue glass)
potassium	lilac (crimson through blue glass)
lead arsenic antimony	light blue

Borax Bead Reactions.

Metal.	*Colour of bead in outer oxidising flame.*
copper	light blue or green
iron	brown while hot, yellow when cold
chromium	emerald green
manganese	amethyst
cobalt	deep blue
nickel	brown

Heat on Charcoal with Fusion Mixture.

Metal.	*Appearance.*	*Incrustation.*
silver	shining metal particles	—
bismuth	pinkish globules; brittle	yellowish
copper	red scales	—
lead	greyish-white soft globules	red—hot; yellow—cold
tin	hard white beads	—
zinc		yellow—hot; white—cold
cadmium		brown
arsenic	fumes, smelling of garlic	white, at some distance from flame

If residue after heat on charcoal block is white, moisten with cobalt nitrate solution and heat again.

Appearance of residue.	*Indication.*
Blue mass	Aluminium (also caused by fusible phosphates, arsenates, borates and silicates).
Green mass	zinc
Pink mass	magnesium

Action with Dilute Hydrochloric Acid (heat if necessary).

Gas evolved.	*Indication.*
Carbon dioxide	carbonate or bicarbonate
Hydrogen	some free metals
Sulphur dioxide	sulphite or bisulphite
Sulphur dioxide and sulphur	thiosulphate
Hydrogen sulphide	sulphide
Nitrogen dioxide	nitrite
Chlorine	hypochlorite or oxidising agent

Heat with Concentrated Sulphuric Acid.

Gas evolved.	*Indication.*
Hydrogen chloride	chloride
Nitric acid	nitrate
Oxygen	peroxide, permanganate, chromate, dichromate
Chlorine peroxide (yellowish-green gas. Violent action)	chlorate
Sulphur dioxide	sulphite, thiosulphate or reducing agent
Hydrogen bromide, bromine and sulphur dioxide	bromide
Hydrogen iodide, iodine and hydrogen sulphide	iodide
Carbon monoxide and carbon dioxide	oxalate
Carbon monoxide only	formate
Acetic acid	acetate

If organic acid present, substance should be ignited, extracted with dilute hydrochloric acid and filtered before proceeding with main group separation.

Action with Caustic Soda Solution.

Warm. If ammonia gas is evolved, indicates presence of **ammonium** compound.

To make the Solution for the Group Analysis.

Test small portions of the substance to see whether it can be brought into solution by reagents 1–6 below. (See p. 334.)

A. Dissolve about 1 gm. of the substance in the first reagent on the list capable of doing so:

(1) Water.
(2) Dilute hydrochloric acid.
(3) Concentrated hydrochloric acid, 2·0 to 5·0 c.c. When all is dissolved, dilute the solution to about five times its bulk. Cool. Dilution may again yield a precipitate, due to hydrolysis of chlorides of bismuth, arsenic, antimony or tin. Add a few drops of conc. hydrochloric acid to reverse the effects of hydrolysis.
(4) Dilute nitric acid. This may dissolve compounds of the metals of Group I. In general nitric acid should be avoided if possible

because it may oxidise hydrogen sulphide, the group reagent of Group II, to sulphur. With dilute nitric acid this action is negligible. (See 6 below.)

(5) *Aqua regia.* Heat with concentrated hydrochloric acid. Add a few drops of conc. nitric acid. Dilute as in (3).

(6) Concentrated nitric acid. Warm with 2·0 to 5·0 c.c.

N.B. If nitric acid is used, the solution must be evaporated to dryness and the residue dissolved in water or hydrochloric acid.

B. If any insoluble residue remains, filter it off, wash it, and fuse it in a crucible with four times its bulk of fusion mixture. Cool, boil with water, filter. Test filtrate for acid radicals. Dissolve precipitate of metal carbonates in hydrochloric acid, and analyse separately. (If the solution so obtained gives no precipitate with that obtained by A. above, they may be analysed together.)

CHAPTER XLII

TESTS FOR ACID RADICALS IN SOLUTION

Some of the acidic radicals have already been detected in the preliminary tests. A further examination for acidic radicals is carried out by reactions in solution.

It is essential, before testing a solution for acidic radicals, to remove any heavy metals, because they would interfere with the tests. To take a simple case, the test for a sulphate radical in solution is to add dilute hydrochloric acid and barium chloride solution, when a white precipitate of barium sulphate indicates the presence of a sulphate.

ionically: $Ba^{++} + SO_4^{--} \rightarrow BaSO_4 \downarrow$

But if the solution already contains the silver ion, then, on the addition of hydrochloric acid, there would be observed a white precipitate of silver chloride, and any further test for a sulphate would be worthless.

ionically: $Ag^{+} + Cl^{-} \rightarrow AgCl \downarrow$

Possibilities such as this make it necessary to eliminate all heavy metal radicals before testing for acidic radicals, leaving only sodium, potassium or ammonium in solution.

This is done by boiling the finely divided solid (or a solution of it) with sodium carbonate solution. Heavy metals are then precipitated as carbonates, or by hydrolysis, as the hydroxides. The precipitates are filtered off. Occasionally, as with copper, a soluble double carbonate may be formed, but such cases are rare. The acidic radicals, originally combined with the heavy metals, are now in the filtrate as the sodium salts, double decomposition usually having taken place, e.g., if a mixture contained barium chloride and calcium nitrate, the reactions would be:—

$$BaCl_2 + Na_2CO_3 \rightarrow \underset{\text{in ppt.}}{BaCO_3} + \underset{\text{in solution.}}{2NaCl}$$

$$Ca(NO_3)_2 + Na_2CO_3 \rightarrow \underset{\text{in ppt.}}{CaCO_3} + \underset{\text{in solution.}}{2NaNO_3}$$

The filtrate can now be tested, without interference, for these acidic radicals. It is certain to be alkaline with the excess of sodium carbonate used, and for the tests it must be made acidic with the acid appropriate for each test as given below. The acid to use is that which contains as acid radical the same as that of the testing reagent which you are adding, e.g., with barium chloride use hydrochloric acid, with silver nitrate nitric acid, and so on. In this way you are certain not to add the radical you are testing for, a mistake often made by beginners. If the solutions were not made acid, the sodium carbonate present would again precipitate, as heavy metal carbonate, the metal of the testing reagent.

The procedure is as follows: Take about 1 gram of the original powder, finely ground, put it into a small flask or dish (if soluble, dissolve it in a little water), add sodium carbonate solution and boil for a few minutes. Filter. The filtrate should be alkaline, showing excess of sodium carbonate. Use a *portion* of the filtrate for each of the following tests:—

(1) **Sulphate Radical.**

Add excess dilute hydrochloric acid, and then barium chloride solution. A white precipitate of barium sulphate proves sulphate radical present.

ionically: $Ba^{++} + SO_4^{--} \rightarrow BaSO_4 \downarrow$

This test is specific for sulphates, but confirmation may be obtained by heating the original mixture with fusion mixture on a charcoal block and testing the residue on a wet silver coin. A black stain of silver sulphide indicates a sulphide formed by partial reduction of the sulphate. This test is not applicable if sulphide was known to be present in the original mixture.

(2) (*a*) **Chloride Radical.**

Add excess dilute nitric acid, followed by silver nitrate solution. A white curdy precipitate of silver chloride, readily soluble in ammonia, proves the presence of chloride radical.

ionically:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$
$$AgCl + 2NH_3 \rightarrow \underset{\text{soluble silver ammine}}{Ag(NH_3)_2Cl.}$$

To confirm chloride prepare chromyl chloride. See Expt. 118(c).

(*b*) **Bromide Radical.**

Test as for (*a*). A pale yellow precipitate (often only seen to be yellow by comparison with the chloride) of silver bromide, sparingly soluble in ammonia proves the presence of bromide radical.

ionically: $Ag^+ + Br^- \rightarrow AgBr \downarrow$

(*c*) **Iodide Radical.**

Test as for (*a*). A yellow precipitate of silver iodide, insoluble in ammonia, proves the presence of iodide.

$$Ag^+ + I^- \rightarrow AgI \downarrow$$

To confirm bromide or iodide, heat the *solid* with a little manganese dioxide and concentrated sulphuric acid. The element bromine (dark red vapour) or iodine (violet) will be seen.

(d) Other radicals may conveniently be detected at this stage as follows: Filter off the ppt. obtained above and to the solution add ammonia drop by drop. (This test depends on the presence of excess silver nitrate in the filtrate.)

Precipitate.	*Indication.*
yellow	phosphate (arsenite)
brick red	arsenate
crimson red	chromate
white	antimonate, borate, oxalate

(3) Nitrate Radical.

Place some of the filtrate in a test-tube and add a slight excess of dilute sulphuric acid. The solution must be quite cold. Add to it excess freshly prepared ferrous sulphate solution. The depth of solution in the boiling tube should now be adjusted to about 1 inch. Hold the tube firmly in a slanting position and pour concentrated sulphuric acid (Care!) down the side of the tube to form a separate layer underneath the solution, and to be about ½ inch deep. The acid must not mix with the solution or heat will be generated and the test spoiled. A brown ring will presently be seen at the junction of acid and solution, proving the presence of a nitrate.

Explanation: The nitrate and the concentrated sulphuric acid first generate nitric acid, which is then reduced by some of the ferrous sulphate to nitric oxide. This reacts with more ferrous sulphate to form the brown compound seen at the junction of the two liquids as a ring.

$$6FeSO_4+2NaNO_3+5H_2SO_4 \rightarrow 2NaHSO_4+3Fe_2(SO_4)_3+4H_2O+2NO$$
$$NO + 2FeSO_4 \rightarrow NO.2FeSO_4.$$

On shaking, the brown colour spreads, but as acid and water mix, the solution becomes warm, and the unstable brown compound decomposes and the colour disappears.

$$NO.2FeSO_4 \rightarrow NO + 2FeSO_4.$$

Nitrate in presence of bromide or iodide. If a bromide or iodide is also present a ring due either to free bromine or to free iodine will be formed. (The presence of ferrous sulphate has no part in this reaction.) If the ions of either of these halogens have been shown to be present, first add a solution of silver *sulphate* to precipitate the halogen as its silver salt and test the filtrate for the nitrate ion.

Nitrate in presence of nitrite. If a nitrite has been shown to be present by the action of dilute hydrochloric acid in the preliminary tests, a brown ring (more diffused than that for a nitrate) will be formed on performing the nitrate test. To find whether a nitrite and a nitrate are present together, add a concentrated solution of urea, then dilute sulphuric acid and warm until there is no further effervescence of nitrogen. (See Expt. 297(c).) The nitrite ion having been eliminated test the solution for nitrate ion.

Confirm the presence of the nitrate radical by warming a mixture of the original *solid* with a little copper and a few drops of conc. sulphuric acid. A yellow or brown gas indicates nitrate. The nitrate with conc. sulphuric acid forms nitric acid which, with copper, gives nitrogen dioxide.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2\uparrow$$

(4) Borate Radical.

Put a little of the unknown substance into a test-tube, add a few c.c.s of concentrated sulphuric acid, and shake well to mix the two. Put some methylated spirit into an evaporating dish until it is about one-quarter filled, stir with a glass rod and, whilst stirring, add the mixture from the test-tube. Warm the dish over a Bunsen burner and light the vapour rising from the dish. The presence of a green colour in the flame shows a borate to be present. The green colour is produced by the volatile compound, ethyl borate,

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$
$$H_3BO_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 + 3H_2O.$$

(This test is not given by a few minerals containing boron, e.g., borosilicates.)

To confirm borate acidify the solution and test with turmeric paper. Dry the paper over a small flame. The change of colour from yellow to brown, which becomes blue or bluish-black in caustic soda solution indicates a borate.

(5) Phosphate Radical.

Although provision is made later for the test for a phosphate, it may quite conveniently be done at this stage.

To a little of the solution of the unknown substance in a test-tube add dilute nitric acid and ammonium molybdate solution, so that the latter is in a large excess. *Warm gently* but *do not boil.* A yellow coloration, with probably a precipitate on standing, indicates a phosphate. The precipitate is ammonium phosphomolybdate

$$(NH_4)_3PO_4.12MoO_3$$

(6) Arsenate Radical.

This is conducted as for a phosphate but a yellow precipitate is obtained only on boiling. The precipitate is ammonium arseno-molybdate

$$(NH_4)_3AsO_4.12MoO_3$$

(7) **Acetate Radical.**

To a little of the solid add an equal bulk of alcohol and then a few drops of conc. sulphuric acid. Warm gently and smell the vapour. The fruity smell of ethyl acetate indicates the presence of an acetate in the original substance, e.g.,

$$\underset{\text{sodium acetate}}{CH_3COONa} + C_2H_5OH + H_2SO_4 \rightarrow CH_3COOC_2H_5 + NaHSO_4 + H_2O$$

(8) **Oxalate Radical.**

The presence of an oxalate will have been shown in the preliminary tests by the action of conc. sulphuric acid. To confirm, make a solution of the substance with water, add excess calcium chloride solution and boil. Wash the precipitate of calcium oxalate by decantation and warm it with dilute sulphuric acid. While still warm add a few drops of potassium permanganate solution which is decolorised.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

(9) **Chromate Radical.**

Acidify with dilute nitric acid, add ammonium hydroxide until *just* alkaline, then boil. Divide the solution into two parts. To one part add silver nitrate solution. A crimson red precipitate, soluble in dilute nitric acid indicates chromate.

ionically: $2Ag^+ + CrO_4^{--} \rightarrow Ag_2CrO_4 \downarrow$

To the other part add barium chloride solution. A yellow precipitate soluble in hydrochloric acid confirms chromate.

ionically: $Ba^{++} + CrO_4^{--} \rightarrow BaCrO_4 \downarrow$

CHAPTER XLIII

EXAMINATION FOR METALLIC RADICALS

Chemistry of Group Separations.

The system of qualitative analysis is based on specific differences between the properties of one metallic radical and those of another. The table used for elementary work contains 23 metals and a first separation is made into groups by selecting a reagent which precipitates a few of the metals but leaves the remainder to be precipitated by a different reagent or reagents. A precipitate obtained in a given group may contain one or more of the metals of that group and it is then that use is made of specific differences of properties of the metals likely to be present. Properties of metals and their compounds are given in Part II and it may be considered advisable to study them in conjunction with the system of analysis, e.g., the properties of silver, mercury and lead might be studied prior to precipitating them as their chlorides in Group I.

It is certainly advantageous to precede group separations by showing how each metal in the group behaves towards the various reagents used, and to illustrate the procedure the following experiments are given for Group I; the student will be able to suggest similar experimental work for the subsequent groups.

Experiment 273. Preliminary experiments before the separation of Group I metals, silver, mercurous mercury, and lead.

Material: mercurous nitrate.

(*a*) To a test-tube one-quarter full of solutions of silver nitrate, mercurous nitrate (in dilute nitric acid because of hydrolysis) and lead acetate respectively, add an equal volume of dilute hydrochloric acid. The white precipitate in each case is the insoluble metal chloride.

ionically:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$
$$Hg_2^{++} + 2Cl^- \rightarrow Hg_2Cl_2 \downarrow$$
$$Pb^{++} + 2Cl^- \rightarrow PbCl_2 \downarrow$$

(*b*) Decant the liquid from each tube, retaining as much as possible of the solids. Fill each tube half-full with distilled water. Show that lead chloride is easily soluble in boiling water, but that mercurous chloride and silver chloride are both apparently insoluble. Add a few drops of potassium chromate to the clear solution of lead chloride; the precipitate is lead chromate.

ionically: $Pb^{++} + CrO_4^{--} \rightarrow \underset{\text{(yellow ppt.)}}{PbCrO_4}$

(*c*) Decant the liquid from the precipitates of silver chloride and mercurous chloride, then to each add dilute ammonium hydroxide and shake. Silver chloride dissolves because of the formation of a complex ion, a soluble silver ammine.

$$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2Cl + 2H_2O$$

$$\text{or} \quad AgCl + 2NH_4^+ + 2OH^- \rightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$$

Mercurous chloride turns black due to the formation of mercury; mercuric chloro-amine (white) is also formed, but its colour is masked by the mercury.

$$Hg_2Cl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl + NH_4Cl + 2H_2O + Hg$$

SEPARATION INTO GROUPS.

Add to the material (in solution if possible) **dilute hydrochloric acid.** (If there is effervescence, pass the gas into lime water. A turbidity shows **carbonate** or **bicarbonate** present.) **Filter cold.**

<table>
<tr><td rowspan="5"><i>Precipitate</i>
may contain $AgCl$, $PbCl_2$ or Hg_2Cl_2 as white ppt. Examine by table for GROUP I.</td><td colspan="5"><i>Filtrate</i>
should give no ppt. on adding a drop of HCl. Heat. Pass* hydrogen sulphide until there is no further ppt. Filter. Dilute a portion of the filtrate about five times with water, pass* more hydrogen sulphide. If more ppt. appears, dilute the whole and pass the gas until no more ppt. is given. Filter through same filter paper. (If no ppt. occurs on dilution, discard the diluted portion.)</td></tr>
<tr><td rowspan="4"><i>Precipitate</i>
may contain HgS, PbS, Bi_2S_3, CuS, CdS. Also As_2S_3, Sb_2S_3, SnS, SnS_2. Examine by table for GROUP II.</td><td colspan="4"><i>Filtrate</i>
Put into evaporating dish and boil off H_2S for several minutes. Allow solution to concentrate if bulky. To a little of the solution add dilute nitric acid and excess ammonium molybdate solution. Warm (but do not boil), and allow to stand. Yellow ppt. shows phosphate. Reject this. To the rest of the main solution add 1–2 c.c. of conc. nitric acid† and boil to oxidise ferrous iron to ferric. Transfer to boiling tube, add ammonium chloride solution and ammonium hydroxide in excess.‡ Boil and filter.</td></tr>
<tr><td rowspan="3"><i>Precipitate</i>
may contain $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Examine by table for GROUP III.</td><td colspan="3"><i>Filtrate</i>
should contain excess ammonia. To test shake vigorously and smell. Pass* hydrogen sulphide. Boil, filter. If the filtrate is brown, nickel is present in the solution. Boil the filtrate until no more ammonia is evolved. Filter. The filtrate should not now be brown.</td></tr>
<tr><td rowspan="2"><i>Precipitate</i>
may contain ZnS, MnS, NiS, CoS. Examine by table for GROUP IV.</td><td colspan="2"><i>Filtrate</i>
Add ammonium carbonate solution. Warm. Filter.</td></tr>
<tr><td><i>Precipitate</i>
may contain $CaCO_3$, $BaCO_3$, $SrCO_3$. Examine by table for GROUP V.</td><td><i>Filtrate</i>
Examine by table for GROUP VI.</td></tr>
</table>

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* If a test portion gives no ppt. on passing hydrogen sulphide, discard and treat remainder for later groups.

† If original solution gives negative tests for iron addition of conc. nitric acid may be omitted.

‡ If the solution is not boiled, some chromium may come through in solution as ammine, $Cr(NH_3)_6(OH)_3$, giving a pale purple solution. This ammine is decomposed to chromium hydroxide on boiling.

Group I.

THE INSOLUBLE CHLORIDES.

$$PbCl_2,\ AgCl,\ Hg_2Cl_2.$$

Precipitate may contain lead, silver and mercurous chlorides. Wash two or three times with a little cold water. Discard washings. Make a hole in the filter paper with a pointed glass rod, and wash ppt. through into a beaker. Boil with water. Filter **hot.**

<table>
<tr><td colspan="2"><i>Residue</i>
Wash well with hot water. Pour warm ammonium hydroxide solution through the filter paper.</td><td rowspan="2"><i>Filtrate</i>
contains $PbCl_2$ (white crystals may separate on cooling). Add potassium chromate solution. Yellow ppt. of lead chromate proves presence of lead.</td></tr>
<tr><td><i>Residue</i>
If black, due to presence of finely divided metallic mercury. This proves mercurous mercury present.</td><td><i>Filtrate</i>
contains the silver. Acidify with nitric acid. White ppt. of silver chloride turning violet on exposure to light proves silver present.</td></tr>
</table>

Equations (the first four are ionic).

Precipitation by hydrochloric acid.

$$Pb^{++} + 2Cl^- \rightarrow PbCl_2 \downarrow \qquad Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

$$Hg_2^{++} + 2Cl^- \rightarrow Hg_2Cl_2 \downarrow$$

Action of potassium chromate on lead chloride.

$$Pb^{++} + CrO_4^{--} \rightarrow PbCrO_4 \downarrow$$

Action of ammonia on silver and mercurous chlorides.

$$AgCl + 2NH_4OH \rightarrow \underset{\text{soluble ammine}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Hg_2Cl_2 + 2NH_4OH \rightarrow \underset{\text{mercuric chloramine.}}{Hg(NH_2)Cl \downarrow} + NH_4Cl + 2H_2O + Hg \downarrow$$

Precipitation of silver chloride by nitric acid.

$$Ag(NH_3)_2Cl + 2HNO_3 \rightarrow 2NH_4NO_3 + AgCl \downarrow$$

CONFIRMATORY TESTS WITH ORIGINAL SOLUTION OR SOLID.

Silver	Add potassium chromate solution to neutral solution of silver salt, brick red ppt. obtained.
Mercury	Heat solid mixed with anhydrous sodium carbonate in tube. Grey metallic mirror obtained which can be scraped together to form bead of metallic mercury.
Lead	With potassium iodide solution, solutions of lead salts give yellow ppt. soluble in boiling water.

Also see Chapter XLV for confirmatory tests.

Equations(mainly ionic).

Precipitation of the sulphides.

$$Pb^{++} + S^{--} \rightarrow PbS \downarrow \quad \text{(Similarly } Hg^{++}, Cu^{++}, Cd^{++}\text{)}$$
$$2Bi^{+++}\ 3S^{--} \rightarrow Bi_2S_3 \downarrow$$

The red ppt. produced at first from a lead salt on passing H_2S is $PbS.PbCl_2$. It is decomposed by more of the gas to black lead sulphide. The ppt. from mercuric chloride may first be white ($HgCl_2.2HgS$). It changes to yellow, brown and black by gradual decomposition of this compound into black mercuric sulphide by more hydrogen sulphide.

Action of dilute nitric acid.

$$CuS + 2H^+ \rightarrow Cu^{++} + H_2S \uparrow \quad \text{(Similarly CdS, PbS)}$$
$$Bi_2S_3 + 6H^+ \rightarrow 2Bi^{+++} + 3H_2S \uparrow$$

together with some oxidation to sulphate in each case,

e.g., $$CuS + 8HNO_3 \rightarrow CuSO_4 + 8NO_2 + 4H_2O$$

Mercuric sulphide is unchanged.

Action of ammonia on bismuth, copper and cadmium nitrate solutions.

$$Bi^{+++} + 3OH^- \rightarrow Bi(OH)_3 \downarrow$$
$$Cu^{++} + 4NH_4OH \rightarrow \underset{\text{deep blue ion}}{[Cu(NH_3)_4]^{++}} + 4H_2O$$
$$Cd^{++} + 4NH_4OH \rightarrow [Cd(NH_3)_4]^{++} + 4H_2O$$

Confirmatory test for bismuth.

$$Bi(OH)_3 + 3H^+ \rightarrow Bi^{+++} + 3H_2O$$
$$Bi^{+++} + H_2O + Cl^- \rightarrow BiOCl \downarrow + 2H^+$$

Confirmatory test for copper.

$$[Cu(NH_3)_4]^{++} + 4H^+ \rightarrow Cu^{++} + 4NH_4^+$$
$$2Cu^{++} + \underset{\text{ferrocyanide ion}}{Fe(CN)_6^{----}} \rightarrow \underset{\text{copper ferrocyanide}}{Cu_2Fe(CN)_6 \downarrow}$$

Confirmatory test for cadmium.

The copper ion is converted by potassium cyanide into a complex cyanide ion (see Expt. 55(d)) which yields insufficient copper ions to exceed the solubility product of copper sulphide on passing hydrogen sulphide. The complex cadmium-cyanide ion $[Cd(CN)_4]^{--}$ is unstable and furnishes sufficient cadmium ions to exceed the solubility product of cadmium sulphide on passing hydrogen sulphide.

$$Cd^{++} + S^{--} \rightarrow CdS \downarrow$$

Confirmatory test for lead.

$$Pb^{++} + CrO_4^{--} \rightarrow PbCrO_4 \downarrow$$

Confirmatory test for mercuric mercury.

The concentrated hydrochloric acid and potassium chlorate mixture oxidises the mercuric sulphide by a complex reaction into soluble mercuric chloride. Then, on adding stannous chloride solution,

$$2HgCl_2 + SnCl_2 \rightarrow \underset{\substack{\text{mercurous}\\ \text{chloride, white}\\ \text{ppt.}}}{Hg_2Cl_2} + \underset{\substack{\text{stannic}\\ \text{chloride}\\ \text{soluble.}}}{SnCl_4.}$$

Group II.

SULPHIDES INSOLUBLE IN DILUTE HYDROCHLORIC ACID.

HgS, PbS, Bi_2S_3, CuS, CdS. GROUP IIa.
As_2S_3, Sb_2S_3, SnS, SnS_2. GROUP IIb.

Keep ppt. covered by a watch-glass over the funnel to minimise oxidation of copper sulphide to copper sulphate which would be washed out.

Wash ppt. well with hot water. Make a hole in the filter paper with a glass rod, and wash ppt. through into evaporating dish. Add **caustic soda solution** and a few drops of yellow **ammonium sulphide**. Digest for a few minutes. Filter.

Residue.	*Filtrate.*
GROUP IIA.	GROUP IIB.

Group IIa.

Wash ppt. well with hot water. Make a hole in the filter paper with a glass rod, and wash the ppt. into a dish. Add **dilute nitric acid** and boil for a few minutes. (Sulphur will usually remain here.) Transfer the whole to a boiling-tube, add dilute sulphuric acid and a little alcohol to complete the precipitation of lead sulphate. (Omit this if lead not found present in GROUP I.) Allow to stand for a few minutes. Filter.

<table>
<tr><td colspan="2"><i>Residue</i>
may contain lead sulphate, mercuric sulphide and sulphur. Wash with hot water. Wash ppt. into a boiling-tube and boil with ammonium acetate solution. Filter.</td><td colspan="2"><i>Filtrate</i>
may contain bismuth, copper and cadmium as nitrates. Add ammonia in excess. Warm and filter.</td></tr>
<tr><td><i>Residue</i>
is mercuric sulphide, usually with sulphur. Wash, warm in a dish in fume chamber with conc. HCl and potassium chlorate until dissolved. Dilute, add stannous chloride soln. White silky ppt. of mercurous chloride proves mercuric mercury present.</td><td><i>Filtrate</i>
contains lead. Add potassium chromate soln. Yellow ppt. of lead chromate proves presence of lead.</td><td><i>Residue</i>
is white bismuth hydroxide. Wash; dissolve by pouring a little warm dil. HCl through the filter paper, Pour filtrate into beaker nearly full of water. Turbidity (perhaps delayed) due to bismuth oxychloride proves presence of bismuth.</td><td><i>Filtrate</i>
Divide into two parts.
PART I. (If liquid is colourless omit this.) Acidify with dilute acetic acid, add potassium ferrocyanide solution. Brown colour or ppt. due to copper ferrocyanide proves presence of copper.
PART II. If coloured, add potassium cyanide solution until colourless. Pass H_2S. Yellow ppt. of cadmium sulphide proves presence of cadmium.</td></tr>
</table>

CONFIRMATORY TESTS WITH ORIGINAL SOLID OR SOLUTION.

Copper	Ammonia gives a pale blue ppt. which dissolves in excess to give a deep blue solution.
Cadmium	Ammonia gives white ppt. easily soluble in excess.
Bismuth	As given on page 306.

Also see Chapter XLV for confirmatory tests.

Equations (mainly ionic).

Precipitation of sulphides.

$$\begin{array}{llll} 2As^{+++} & + 3S^{--} & \rightarrow & As_2S_3 \downarrow \\ 2Sb^{+++} & + 3S^{--} & \rightarrow & Sb_2S_3 \downarrow \\ Sn^{++} & + S^{--} & \rightarrow & SnS \downarrow \\ Sn^{++++} & + 2S^{--} & \rightarrow & SnS_2 \downarrow. \end{array}$$

Action of caustic soda and ammonium sulphide.

The sulphur of the polysulphide ammonium sulphide oxidises the lower sulphide and forms a thio-salt, e.g.,

$$As_2S_3 + 3S^{--} + \underset{\text{from polysulphide}}{2S} \rightarrow \underset{\text{thio-arsenate ion}}{2AsS_4^{---}}$$

The addition of acid precipitates the higher sulphide:

$$2AsS_4^{---} + 6H^+ \rightarrow \underset{\text{arsenic sulphide.}}{As_2S_5} + 3H_2S \uparrow$$

Action of ammonium carbonate.

$$As_2S_5 + 5(NH_4)_2CO_3 + 3H_2O \rightarrow \underset{\text{arsenic acid.}}{2H_3AsO_4} + 5(NH_4)_2S + 5CO_2,$$

with subsequent passage of H_2S:—

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_5 + 8H_2O$$

Action of conc. hydrochloric acid on boiling with antimony and tin sulphides.

$$Sb_2S_3 + 6H^+ \rightarrow 2Sb^{+++} + 3H_2S \uparrow$$
$$SnS + 2H^+ \rightarrow Sn^{++} + H_2S \uparrow$$

Confirmatory test for antimony.

$$2Sb^{+++} + 3S^{--} \rightarrow Sb_2S_3 \downarrow$$

Confirmatory test for tin.

$$\underset{\text{stannous ion}}{Sn^{++}} + 2Hg^{++} + 2Cl^- \rightarrow \underset{\text{stannic ion}}{Sn^{++++}} + \underset{\text{mercurous chloride}}{Hg_2Cl_2} \downarrow$$

Group IIb.

ARSENIC, ANTIMONY AND TIN.

May contain antimony, arsenic, stannous and stannic sulphides.

Acidify with dilute **hydrochloric acid** the filtrate from GROUP II after treatment with caustic soda and ammonium sulphide. If GROUP IIB present it will precipitate now, and **if absent white sulphur only will be seen.** If a ppt. appears, pass H_2S to complete the precipitation, warm and filter (discarding the filtrate). Wash the ppt. with hot water, make a hole in the filter paper, and wash the ppt. through into a dish. Add a piece of **solid ammonium carbonate,** digest for a few minutes, and filter.

Residue		*Filtrate*
may contain antimony and tin as sulphides. Wash. Make a hole in the filter paper and wash through with **conc. hydrochloric acid** into a dish. Boil for a few moments. Divide the solution into two parts. Cool.		may contain arsenic. Add **dilute HCl** carefully in a dish until effervescence ceases. **Pass H_2S and boil.** Yellow ppt. of arsenic sulphide, which will settle, proves presence of **arsenic.**
PART I. Dilute with its own volume of water. **Pass H_2S.** Orange-red ppt. of antimonious sulphide proves **antimony.**	PART II. Add **zinc foil** in a dish until no further effervescence. If **tin** present, it will be as a grey ppt. round TOP of dish. Collect with rod and **dissolve** in a test-tube **with conc. HCl.** Pour this solution **into** a solution of **mercuric chloride.** White silky ppt. at once or on standing is mercurous chloride, proving presence of **tin.**	

CONFIRMATORY TESTS WITH ORIGINAL SOLUTION OR SOLID

Antimony	As above.
Arsenic	Heat original solid on charcoal with fusion mixture. Fumes smelling of garlic obtained.
Tin	Obtain a borax bead containing a little copper sulphate. Add a little of original solid and heat again. Red bead obtained.

Also see Chapter XLV for confirmatory tests.

Group III.

Equations (*all ionic*).

Precipitation of hydroxides.

$$\begin{aligned} Fe^{+++} + 3OH^- &\rightarrow Fe(OH)_3 \downarrow \\ Cr^{+++} + 3OH^- &\rightarrow Cr(OH)_3 \downarrow \\ Al^{+++} + 3OH^- &\rightarrow Al(OH)_3 \downarrow \end{aligned}$$

Action of caustic soda and hydrogen peroxide. Ferric hydroxide unchanged.

ionically: $$2Cr(OH)_3 + \underset{\substack{\text{from}\\\text{oxidising}\\\text{agent}}}{3O} + 4OH^- \rightarrow \underset{\substack{\text{chromate}\\\text{ion}}}{2CrO_4^{--}} + 5H_2O$$

$$Al(OH)_3 + OH^- \rightarrow \underset{\substack{\text{meta-aluminate}\\\text{ion}}}{AlO_2^-} + 2H_2O$$

Confirmatory test for iron:

ionically: $$Fe^{+++} + 3CNS^- \rightarrow \underset{\text{ferric thiocyanate}}{Fe(CNS)_3}$$

Confirmatory test for chromium.

ionically: $$Pb^{++} + CrO_4^{--} \rightarrow \underset{\substack{\text{lead chromate}\\\text{(yellow)}}}{PbCrO_4 \downarrow}$$

Confirmatory test for aluminium.

$$\begin{aligned} AlO_2^- + 4H^+ &\rightarrow Al^{+++} + 2H_2O \\ Al^{+++} + 3OH^- &\rightarrow Al(OH)_3 \downarrow \end{aligned}$$

Recent work has left the reactions involving ferrocyanides and ferricyanides of iron still obscure. They cannot be precisely represented by simple equations.

Group III.

THE GROUP OF INSOLUBLE HYDROXIDES.

$Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$.

The precipitate may contain ferric, chromic and aluminium hydroxides. Wash well with hot water. Make a hole in the filter paper with a glass rod, and wash the ppt. through into a wide-mouthed boiling-tube. Add **caustic soda solution** and **hydrogen peroxide** solution and **boil** for a few minutes (oxygen). Filter.

Residue	*Filtrate*	
is brown ferric hydroxide. Dissolve in **dil. HCl**, add **potassium ferrocyanide** solution. Blue ppt. proves presence of **iron**. To the original solution add (1) **potassium ferricyanide** solution. Blue ppt. proves **ferrous** iron present. (2) **potassium thiocyanate** (KCNS) solution. Red coloration proves **ferric** iron present. A little manganese hydroxide may occur here, but may be neglected. It will appear in bulk in GROUP IV.	may contain chromium and aluminium as sodium chromate and sodium aluminate. **If yellow,** chromium is present. Divide into two parts.	
	PART I. If soln. not yellow, omit this. Add **acetic acid** in excess, and then **lead acetate** soln. Yellow ppt. of lead chromate proves **chromium** present.	PART II. Add **litmus.** Add **dil. HCl** in excess, then **ammonia just** in excess. Shake. Allow to stand. **Blue lake** of aluminium hydroxide and litmus proves **aluminium** present.

CONFIRMATORY TESTS WITH ORIGINAL SOLUTION OR SOLID

Iron	As above.
Aluminium	Heat solid on charcoal with fusion mixture, add a few drops of cobalt nitrate solution and heat again. Blue mass obtained.
Chromium	Fuse with sodium carbonate and a little potassium nitrate in a porcelain crucible. Dissolve in water, add acetic acid and lead acetate solution. Yellow ppt. obtained.

Also see Chapter XLV for confirmatory tests.

Group IV.

Equations (all ionic except formation of manganese sesquioxide).

Precipitation of sulphides.

$$\begin{aligned} Zn^{++} + S^{--} &\rightarrow ZnS\downarrow \\ Mn^{++} + S^{--} &\rightarrow MnS\downarrow \\ Co^{++} + S^{--} &\rightarrow CoS\downarrow \\ Ni^{++} + S^{--} &\rightarrow NiS\downarrow \end{aligned}$$

If ammonium sulphide is used, some sulphur may also occur because ammonium sulphide has not really the simple formula NH_4HS, but contains also polysulphides of the type NH_4HS_x. A typical reaction would be:—

$$Zn^{++} + S_2^{--} \rightarrow ZnS\downarrow + S\downarrow$$

Action of very dilute hydrochloric acid.

Cobalt and nickel sulphides are unchanged.

$$\begin{aligned} ZnS + 2H^+ &\rightarrow Zn^{++} + H_2S\uparrow \\ MnS + 2H^+ &\rightarrow Mn^{++} + H_2S\uparrow \end{aligned}$$

Action of excess sodium hydroxide solution on zinc and manganese chlorides.

$$\begin{aligned} Zn^{++} + 2OH^- &\rightarrow Zn(OH)_2\downarrow \\ Zn(OH)_2 + 2OH^- &\rightarrow \underset{\text{zincate ion (soluble)}}{ZnO_2^{--}} + 2H_2O \\ Mn^{++} + 2OH^- &\rightarrow Mn(OH)_2\downarrow \end{aligned}$$

On exposure to air the manganese hydroxide turns into brown manganic hydroxide.

$$4Mn(OH)_2 + O_2 \rightarrow \underset{\substack{\text{hydrated} \\ \text{manganese sesquioxide.}}}{4MnO\,.\,OH} + 2H_2O$$

Confirmatory test for zinc.

$$2ZnO_2^{--} + 8H^+ + 2S^{--} \rightarrow 2ZnS\downarrow + 4H_2O$$

Confirmatory test for manganese.

$$2Mn(OH)_2 + \underset{\substack{\text{from oxiding} \\ \text{agents}}}{5O} \rightarrow \underset{\substack{\text{purple} \\ \text{permanganate} \\ \text{ion}}}{2MnO_4^-} + 2H^+ + H_2O$$

Group IV.

GROUP OF INSOLUBLE SULPHIDES PRECIPITATED BY HYDROGEN SULPHIDE IN ALKALINE SOLUTION.

$ZnS, MnS, CoS, NiS.$

Precipitate may contain zinc, manganese, cobalt and nickel sulphides and sulphur. If it is not black, cobalt and nickel are both absent. Wash the ppt. Dilute the bench dil. hydrochloric acid with about five times its own volume of water and pour this through the filter paper.

<table>
<tr>
<td rowspan="2"><i>Residue</i>
may contain cobalt or nickel as sulphides. Transfer residue to a dish, add conc. hydrochloric acid and a crystal of potassium chlorate. Heat until dissolved and then evaporate nearly to dryness.
Nickel. Add alkaline solution of dimethyl glyoxime: red coloration or ppt. shows Nickel.
Cobalt. Solution will be pink and deposit of crystals blue.
To confirm, apply borax bead test.
Blue bead cobalt.
Brown bead nickel.</td>
<td colspan="2"><i>Filtrate</i>
may contain zinc and manganese chlorides. Boil in a dish for several minutes to remove hydrogen sulphide. (If the liquid is still turbid, finely divided sulphur is suspended in it. Add a little potassium chlorate and boil until clear.) Cool. Add excess sodium hydroxide solution. Filter.</td>
</tr>
<tr>
<td><i>Residue</i>
is manganese hydroxide. Turns brown on filter paper. Wash through into a boiling-tube, allow to settle, pour off as much water as possible. Add conc. nitric acid and lead dioxide and boil. Dilute and allow to settle. Crimson coloration, due to permanganic acid proves presence of manganese.</td>
<td><i>Filtrate</i>
contains zinc as sodium zincate. Pass hydrogen sulphide. White ppt. (often discoloured) of zinc sulphide proves zinc present.
For confirmatory test, filter and dissolve ppt. in a little conc. nitric acid. Add a little cobalt nitrate solution, evaporate to concentrate, and soak a filter paper in the mixture. Ignite. A green ash (Rinmann's green) confirms zinc.
(The green substance is a compound of zinc and cobaltous oxides.)</td>
</tr>
</table>

Confirmatory tests with original solution or solid.

Zinc, Cobalt, Nickel. As above.

Manganese	Fuse with sodium carbonate and a little potassium nitrate in porcelain crucible. Bluish green mass obtained.

Also see Chapter XLV for confirmatory tests.

Group V.

Equations (*all ionic*).

Precipitation of carbonates.

$$\begin{aligned}
&Ba^{++} + CO_3^{--} \rightarrow BaCO_3 \downarrow\\
&Sr^{++} + CO_3^{--} \rightarrow SrCO_3 \downarrow\\
&Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \downarrow
\end{aligned}$$

Action of dilute acetic acid.

$$\begin{aligned}
&BaCO_3 + 2H^+ \rightarrow Ba^{++} + H_2O + CO_2 \uparrow\\
&SrCO_3 + 2H^+ \rightarrow Sr^{++} + H_2O + CO_2 \uparrow\\
&CaCO_3 + 2H^+ \rightarrow Ca^{++} + H_2O + CO_2 \uparrow
\end{aligned}$$

Action of potassium chromate.

$$Ba^{++} + CrO_4^{--} \rightarrow \underset{\text{barium chromate.}}{BaCrO_4} \downarrow$$

Calcium and strontium chromates are soluble in acetic acid, and so do not precipitate.

Test for strontium, and elimination of strontium.

$$Sr^{++} + SO_4^{--} \rightarrow SrSO_4 \downarrow$$

Test for calcium.

$$Ca^{++} + \underset{\text{oxalate ion}}{C_2O_4^{--}} \rightarrow \underset{\text{calcium oxalate}}{CaC_2O_4} \downarrow$$

Group V.

GROUP OF INSOLUBLE CARBONATES.

$CaCO_3$, $BaCO_3$, $SrCO_3$.

Precipitate may contain calcium, strontium and barium carbonates. Wash well with hot water. Pour through the filter paper some warm dilute **acetic acid.** To a small portion of the filtrate add **potassium chromate** solution and boil. If there is a ppt. add potassium chromate solution to the whole and boil. If there is no ppt. discard sample and treat whole as filtrate. Filter.

<table>
<tr><th rowspan="2"><i>Residue</i></th><th colspan="2"><i>Filtrate</i>
may contain calcium and strontium as acetates. Divide into two parts.</th></tr>
<tr><th>PART I.</th><th>PART II.</th></tr>
<tr><td>is pale yellow barium chromate. This ppt. proves presence of barium.
Confirm by flame test.</td><td>Add calcium sulphate solution and boil. Faint white ppt. of strontium sulphate proves presence of strontium.</td><td>If strontium present, add dilute sulphuric acid, boil, filter, and reject the ppt. of strontium sulphate. To filtrate add excess ammonia and ammonium oxalate solution. White ppt. of calcium oxalate proves presence of calcium.
If strontium absent, add excess ammonia and ammonium oxalate solution. White ppt. of calcium oxalate proves presence of calcium.</td></tr>
</table>

CONFIRMATORY TESTS IN ORIGINAL SOLUTION

Barium	Flame test	Light green
Strontium	Flame test	Crimson
Calcium	Flame test	Brick red (green through blue glass)

Also see Chapter XLV for confirmatory tests.

Group VI.

Magnesium, Sodium and Potassium.

If calcium was found in group v, add to the filtrate a little ammonium oxalate solution and boil. Filter, and reject the ppt. of calcium oxalate. If calcium was absent from group v, omit this. Divide the filtrate into two parts.

PART I.	PART II.
Add ammonia and sodium phosphate solution. Shake well and put away to stand. A white crystalline ppt. of magnesium ammonium phosphate proves the presence of **magnesium.**	Evaporate to dryness in a dish (better on platinum foil). Heat until no more fumes from dissociating ammonium compounds are seen. **Examine residue by flame test.** Persistent golden-yellow flame proves presence of **sodium.** Lilac flame proves presence of **potassium.** If sodium present, examine the flame through blue glass for potassium.

CONFIRMATORY TEST WITH ORIGINAL SUBSTANCE

Magnesium	Heat on charcoal with sodium carbonate. Add a few drops of cobalt nitrate solution and heat again. Pink residue obtained.

Also see Chapter XLV for confirmatory tests.

Equation.

Test for magnesium.

ionically: $Mg^{++} + HPO_4^{--} + NH_4^{+} + OH^{-} \rightarrow \underset{\text{magnesium ammonium phosphate.}}{MgNH_4PO_4} \downarrow + H_2O$

CHAPTER XLIV

GROUP ANALYSIS AND THE IONIC THEORY

Certain aspects of the theory have been considered in Chapter II. It is necessary at this stage to apply the theory to precipitation.

A saturated solution is a solution capable of remaining in equilibrium with undissolved molecules of the solute. There will thus be two equilibria, one between the undissolved solute and dissolved molecules, and the other between dissolved molecules and ions formed by dissociation:—

$$\underset{\substack{\text{(undissolved}\\\text{molecules)}}}{XY} \rightleftharpoons \underset{\substack{\text{(dissolved but}\\\text{un-ionised}\\\text{molecules)}}}{XY} \rightleftharpoons \underset{\text{(ions)}}{X^+ + Y^-}$$

However little solid remains undissolved, its tendency to pass into solution is governed by its active mass (i.e., its solution pressure) and, provided the temperature remains constant, the active mass will be constant.

Since, by the Law of Mass Action,

$$\frac{\text{Conc. of Dissolved molecules}}{\text{Conc. of Undissolved molecules}} = K$$

the concentration of dissolved molecules must likewise be a constant. Also, by the same law, if

$$\frac{[\text{Conc. of } X^+]\ [\text{Conc. of } Y^-]}{\text{Conc. of Dissolved mols.}} = \text{constant,}$$

it follows that, in a saturated solution, the product of the concentrations of the ions is a constant mathematical value. Consequently, if relatively large concentrations of the ions are brought together into the same solution, ions of X^+ and Y^- will be precipitated as solid molecules until the concentrations of the remaining ions have such values that the product of their concentrations equals the specific constant (solubility product).

Group I. In this group lead, silver and mercury (mercurous) are precipitated as their chlorides by introducing chloride ions from the fully ionised hydrochloric acid. In terms of the ionic theory, the concentrations of, say, silver and chloride ions which can remain in solution are small, and, in consequence, when a solution of a silver salt (containing an appreciable concentration of silver ions) is mixed with hydrochloric acid, the bulk of the silver and chloride ions unite to form molecular silver chloride and leaves the solution as a solid phase until the remaining ions attain the equilibrium:—

$$(\text{Conc. of silver ions}) \times (\text{conc. of chloride ions}) = \underset{\substack{\text{(solubility}\\\text{product)}}}{1 \times 10^{-10}}$$

It should also be realised that the *product* has the constant value, so that by adding a reasonable excess of chloride ions the concentration of the silver ions may be reduced to a negligible quantity.

Of all the metal chlorides only those of silver, lead and mercurous mercury have low solubility products and consequently the ions of other metals remain in solution, under the given conditions, in the presence of reasonably high concentrations of chloride ions.

Group II.

We may consider hydrogen sulphide to be ionised:—

$$H_2S \rightleftharpoons 2H^+ + S^{--}$$

By the Law of Mass Action,

$$\frac{(\text{conc. of } H+)^2(\text{conc. of } S^{--})}{(\text{conc. of un-ionised } H_2S)} = \text{a constant } (1{\cdot}1 \times 10^{-22})$$

In neutral solution the concentration of sulphide ion is low because hydrogen sulphide is a weak electrolyte. The concentration of hydrogen ion is also low. In acid solution, as used for Group II, the concentration of hydrogen ion is very greatly increased by the presence of the strong acid. Therefore, to maintain the value of the constant, the concentration of the sulphide ion is reduced much below its already small value in neutral solution. The amount of sulphide ion is, however, still great enough to allow the solubility products of the sulphides of mercuric mercury, lead, copper and bismuth momentarily to be exceeded. The same is true for cadmium sulphide if the acid is not too concentrated. Therefore all the sulphides of these metals precipitate.

Compound.	*Solubility product.*
lead sulphide	4×10^{-28}
copper sulphide	8×10^{-45}
mercuric sulphide	4×10^{-54}
cadmium sulphide	$3{\cdot}6 \times 10^{-29}$
manganese sulphide	$1{\cdot}4 \times 10^{-15}$
zinc sulphide	$1{\cdot}2 \times 10^{-24}$

The concentration of sulphide ion in acid solution is not great enough to allow the higher (though still low comparatively) solubility products of the sulphides of manganese, zinc, cobalt or nickel to be reached with any possible concentration of metal ion, so that these sulphides do not precipitate. They come down later in Group IV, where the precipitating agent is the highly ionised salt, ammonium sulphide, and the concentration of the sulphide ion from it is correspondingly high.

Group III.

The precipitating agent in Group III is ammonium hydroxide.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

By the Law of Mass Action $\dfrac{(\text{conc. of } NH_4^+)\ (\text{conc. of } OH^-)}{(\text{conc. of un-ionised } NH_4OH)} =$ a constant.

Ammonia is a weak base, and therefore does not ionise to a very great extent, and the value of the above constant will be small, since most of the ammonium hydroxide will be dissolved but un-ionised. The value of this constant is about 2×10^{-5}. Suppose ammonia is added to the solutions of soluble salts of zinc, manganese, cobalt and nickel to make the solutions $N/2$ with respect to ammonia. The degree of ionisation of ammonia at this dilution is 0·006, so that the concentration of the hydroxyl ion is $0{\cdot}5 \times 0{\cdot}006$ gram-ions per litre or 3×10^{-3} gram-ions per litre. This concentration, together with the concentration of the metal ion, is great enough to exceed momentarily the low solubility products of these hydroxides, and they precipitate. Supposing that ammonium hydroxide alone were the precipitating agent for Group III, then, together with the hydroxides of iron, aluminium and chromium, we should find those of zinc, manganese, cobalt and nickel. Suppose now that ammonium chloride solution and ammonia are added to soluble salts of these metals to make the solutions $N/2$ with respect to both ammonia and ammonium chloride. Ammonium chloride is a salt and is highly ionised, its degree of ionisation being about 0·8. Then

conc. of NH_4 ions from ammonium chloride $= 0{\cdot}5 \times 0{\cdot}8$ gm.-ions per litre
$= 0{\cdot}4$ gm.-ions per litre

As above, $\dfrac{(\text{conc. of } NH_4^+)\ (\text{conc. of } OH^-)}{(\text{conc. of un-ionised } NH_4OH)} = 2 \times 10^{-5}.$

Neglecting the NH_4 from the ammonia in comparison with that from the ammonium chloride,

$$\frac{(0{\cdot}4)\ (\text{conc. of } OH^-)}{0{\cdot}5} = 2 \times 10^{-5}.$$

whence $(\text{conc. of } OH^-) = 2{\cdot}5 \times 10^{-5}$ gm.-ions per litre.

Thus the concentration of hydroxyl ions in $N/2$ ammonia is 3×10^{3} gm.-ions per litre, and in ammonia which is also $N/2$ with respect to ammonium chloride it is reduced to $2{\cdot}5 \times 10^{-5}$. The addition of ammonium chloride has reduced the concentration of the hydroxyl ion to less than one-hundredth of its former value. In general, therefore, the effect of the addition of ammonium chloride is to depress greatly the ionisation of ammonia, and so reduce the hydroxyl ion concentration in the solution.

The small hydroxyl ion concentration in a solution of ammonia which is also fairly concentrated with respect to ammonium chloride is still large enough to cause a precipitation of the hydroxides of ferric iron, chromium and aluminium, but not great enough to precipitate those of zinc, manganese, cobalt and nickel. Manganese hydroxide may precipitate slightly if the concentration of ammonium chloride is not sufficiently great.

In this way the ionic hypothesis explains the experimental facts discovered in the previous chapter.

Group IV.

In the explanation of precipitation of metallic sulphides in Group II it was shown that the presence of hydrogen ions from the added acid reduced the concentration of sulphide ion, but that even this reduced value was still great enough to allow the solubility products of the metallic sulphides in the group to be exceeded. In Group IV, hydrogen sulphide is added to a solution which has been made alkaline with ammonium hydroxide, and which therefore contains excess of hydroxyl ion.

$$\frac{(\text{conc. of } H^+)^2 \ (\text{conc. of } S^{--})}{(\text{conc. of un-ionised } H_2S)} = \text{a constant.}$$

Since the ionic product of water, $[H^+] \times [OH^-]$ has a very small value (10^{-14}), the hydroxyl ions from ammonium hydroxide lower the concentration of hydrogen ion in the above expression causing an increased value for the concentration of S^{--} ion. In Group IV those metal sulphides which were not precipitated in Group II because of their relatively high solubility products, are here precipitated. This is a good example of the control which may be exercised on ionic concentration (here of the sulphide ion) by variation of the concentration of the ion with which it is associated (here the hydrogen ion).

Group V.

The metals still remaining in solution include barium, strontium, calcium, magnesium, sodium and potassium. Of these, the first three are precipitated as their carbonates by the addition of CO_3^{--} ions in alkaline solution because of the low values of the solubility products, $[X^{++}]\ [CO_3^{--})= K$. The values of K for the carbonates of barium, strontium and calcium all lie between 10^{-8} and 10^{-9}. The solubility product of magnesium carbonate is low (10^{-5}) and in neutral solution would be precipitated, but its precipitation is avoided in this group by the presence of ammonium ions, chiefly from the ammonium chloride added prior to Group III. In the presence of the large NH_4^+ ion concentration from this source, the concentration of CO_3^{--} ions in the expression

$$\frac{[NH_4^+]^2\,[CO_3^{--}]}{[(NH_4)_2\,CO_3]} = K,$$

is reduced below the required concentration to precipitate magnesium as its carbonate.

A Few Points of General Application for the performing and writing up of an Analysis.

Learn your tables thoroughly, letting them rest upon first principles as much as possible. Make yourself familiar with any new properties of compounds of which you were previously unaware.

Be Methodical. Do not empty the filtrate from GROUP IV down the sink in mistake for an unwanted solution. You are not likely to have time to go through the main group separation more than once. Label any tube or precipitate which you must leave temporarily. Keep your bench clean and tidy.

Record Your Observations Honestly. Do not be biased by a preliminary test, for interference is often possible. Put down exactly what you see. It may seem wrong at the moment, but it may be most illuminating in the light of further knowledge.

Make yourself familiar with precipitates which are not absolutely convincing, e.g.,

Sulphate does not always come down as a copious white precipitate.

Chloride can usually be shown to be present in tap water, due to impurity.

Iron often comes from a frothing over of the Kipps Apparatus, if a trap is not used.

Aluminium hydroxide, zinc sulphide and magnesium ammonium phosphate are often missed because of lack of care in observation.

Sodium is often present on the platinum wire or porcelain rod because you have just used it for a borax bead test.

Remember an examiner has only what you have written by which to judge the success of your experiments. Do not leave the writing up until the very last minute. Do it as you go along, whilst waiting for a solution to filter, etc.

Interpret your Result in the Light of Reason. Do not return barium and a sulphate if the original powder was soluble in water. Do not return copper or chromium if the original substance dissolved in water to form a colourless solution.

THE COURSE OF AN ANALYSIS

Note. The following suggested allocation of time and procedure is given as a guide, until the student has worked out the scheme which best suits his individual requirements.

It is assumed (a) that the total available time is $1\frac{1}{2}$ hours.
(b) that the given mixture contains not more than four radicals.
(c) that the account is written as the work is being done.

Proceed as follows:—

(1) Examine the mixture and report on its appearance. As quickly as possible make a solution (see p. 307). The concentration of the solution should be approximately 3% and about 50 c.c. will be needed for all purposes. [Average time 5 mins.]

(2) Test a small portion of the solution with a solution of sodium carbonate. *If a precipitate is obtained,* pour a test-tube full of the solution into a beaker, add about 100 c.c. of sodium carbonate solution and leave to boil. The filtrate from this reaction will be examined later for acid radicals (see p. 310). *If a precipitate is not obtained,* discard the test portion and use the original solution for identifying acid radicals. [Average time 3 mins.]

(3) Carry out preliminary tests (see p. 305), and at a convenient time during the tests allow the boiling solution (previously mentioned) to cool. Care in making observations is essential while each of the tests is being done, but much time can be wasted in passing from operation to operation. An orderly arrangement of the necessary apparatus on the bench saves a great deal of time. [Average time 15 mins.]

(4) Fill a boiling-tube to a depth of about 2 ins. with the solution of the given mixture (prepared as in 1) and proceed to separate the metallic radicals into groups (see p. 316). Label each precipitate with the number of the group in which it was obtained. Do not attempt to identify a metal in a particular group at this stage. (Traces of impurity may give a precipitate which in the light of subsequent knowledge may be disregarded.) During the filtration of the first precipitate, use the available time to filter the solution you are preparing for testing for acid radicals, and at other convenient times continue with these tests in the order as printed on p. 310 *et seq.* The test-tubes used for acid radical tests should be kept apart from those used for the group analysis and should be washed as soon as the tests have been satisfactorily completed. At this stage you should have obtained the precipitates from the groups and you should also know the acid radicals. Test-tubes may now be cleaned ready for the next stage. (Average time 45 mins.]

(5) Examine the group precipitates in numerical order as described on p. 317 *et seq.* [Average time 15 mins.]

(6) Confirm the presence of the radicals suspected present by suitable tests. In some cases confirmatory tests will have been done during the analysis. [Average time 7 mins.]

Give your final report clearly showing the radicals found, e.g.:

Found:— NH_4^+ SO_4^{--}
Al^{+++} Cl^-
[Na^+ traces only]

CHAPTER XLV

ORGANIC REAGENTS IN ANALYSIS

General. The development of the use of organic reagents for spot tests and as precipitants for metals has proceeded rapidly in recent years. Their use in the accompanying tables is confined to confirmatory tests, and even for this purpose many of them are superfluous. For example, the presence of iron in the group precipitate and in the original mixture is seldom in doubt after the usual confirmatory tests. On the contrary, some confirmatory tests take a considerable time and may be masked by the presence of other materials present in a mixture. Aluminium, the Group V metals and magnesium are sometimes missed and sodium is returned when traces only are present. It is suggested that in cases of doubtful identity organic reagents may be used.

The use of organic reagents presents certain drawbacks. They may be costly, or unstable in solution, or not specific in action. Their use should, therefore, be accompanied by a certain amount of "research" to determine the conditions of use and the extent to which other metals interfere.

The table of confirmatory tests included in this chapter contains many tests using organic reagents. In using it, the following points are relevant:—

(*a*) An asterisk indicates a test which has been found to be satisfactory in elementary analysis.

(*b*) The quantities given are those which have usually been selected for accurate quantitative analysis. They serve as a very useful guide when the solution made up is to be used for detection only.

Suppose:—

Weight of aluminium sulphate $= a$ gm.
Weight of aluminium oxide $= b$ gm.

$\therefore$ Weight of aluminium in oxide $= \frac{54}{102} \times b$ gm.

Percentage weight of aluminium in aluminium sulphate $= \dfrac{\frac{54 \times b}{102}}{a} \times 100\%$

Experiment 276. Estimation of sulphate radical in sodium sulphate.

Material: Sodium sulphate crystals.

Weigh accurately about 3 gm. of sodium sulphate crystals, dissolve in about 50 c.c. of distilled water, add about 5 c.c. each of dilute hydrochloric acid and ammonium chloride solution and boil. The object of these additions is to assist the precipitation of barium sulphate. Add excess barium chloride solution and bring to the boil. Leave to settle and then carefully decant *the liquid* into the filter. Finally wash the precipitate into the filter. Dry in an oven. Add a few drops of conc. nitric acid and heat the crucible to redness. Cool and weigh.

Calculation.

$$\text{Mol. Wt. of } BaSO_4 = 137 + (32 + 64) = 233$$

Suppose:—

Weight of sodium sulphate crystals $= a$ gm.
Weight of barium sulphate $= b$ gm.

$\therefore$ Weight of sulphate in barium sulphate $= \frac{96}{233} \times b$ gm.

Percentage weight of sulphate in sodium sulphate $= \dfrac{\frac{96\,b}{233}}{a} \times 100\%$

Experiment 277. Estimation of magnesium in magnesium sulphate.

Material: Magnesium sulphate crystals.

Weigh accurately about 2 gm. of magnesium sulphate and dissolve in about 50 c.c. of distilled water. Add about 10 c.c. of ammonium chloride solution and then ammonium hydroxide until alkaline after stirring. *Magnesium hydroxide should not be precipitated; if it is, more ammonium chloride should be added.* Heat and add sodium phosphate solution in excess, stir, and allow to settle. Filter, wash the precipitate with ammonium hydroxide (about N/2) until all chloride has been removed (test with silver nitrate solution acidified with nitric acid). Heat the solid very gradually, finally strongly, then cool and weigh.

$$MgSO_4 + NH_4OH + Na_2HPO_4 \rightarrow \underset{\text{magnesium ammonium phosphate}}{Mg(NH_4)PO_4} + Na_2SO_4 + H_2O$$

$$2Mg(NH_4)PO_4 \rightarrow \underset{\text{magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Calculation.

$$\text{Mol. Wt. of } Mg_2P_2O_7 = 48 + 62 + 112 = 222$$

Suppose:—

Weight of magnesium sulphate = a gm.
Weight of magnesium pyrophosphate = b gm.

$$\therefore \text{ Weight of magnesium in the pyrophosphate} = \frac{48}{222} \times b$$

$$\text{Percentage magnesium in magnesium sulphate} = \frac{\frac{48b}{222}}{a} \times 100\%$$

Experiment 278. Estimation of calcium in calcium carbonate.

Material: Marble.

Weigh about 1·5 gm. of marble accurately. Place it in a beaker with about 10 c.c. of distilled water and add about 5 c.c. of conc. hydrochloric acid. Warm to dissolve and dilute to about 50 c.c. Add ammonium hydroxide until the solution is alkaline and then bring to boiling point. Add 3 gm. of crushed ammonium oxalate, stir, and again heat to boiling. Allow to settle and carefully decant the liquid into the filter, then wash the precipitate into the filter. Wash the precipitate with water until the filtrate, when tested with silver nitrate solution, is shown to be clear of chloride ions. Dry the precipitate of calcium oxalate, ignite in a muffle furnace, cool and weigh. The final residue is calcium oxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$
$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + NH_4Cl$$
$$CaC_2O_4 + \underset{\text{(from air)}}{O} \rightarrow CaO + 2CO_2$$

Calculation.

$$\text{Mol. Wt. of CaO} = 40 + 16 = 56$$

Suppose:—

Weight of calcium carbonate = a gm.
Weight of calcium oxide = b gm.

$\therefore$ Weight of calcium in oxide $= \frac{40}{56} \times b$ gm.

Percentage weight of calcium in marble $= \frac{40b}{56a} \times 100\%$

Experiment 279. Estimation of tin in solder.

Material: Solder.

Use a rough file to obtain fairly finely divided solder and weigh about 1 gm. Transfer to an evaporating basin and add about 10 c.c. of conc. nitric acid. Heat gently (preferably in a fume chamber) and when action has apparently ceased, add a drop or two of nitric acid and warm again, repeating until there is no further evolution of nitrogen dioxide. Dilute the contents to about 50 c.c. and filter. Wash the precipitate with dilute nitric acid. Dry, ignite, cool and weigh.

The tin was first oxidised to meta-stannic acid. The formula of this is doubtful, probably $H_2Sn_5O_{11}$ or better, $SnO_2.xH_2O$.

$$5Sn + 20HNO_3 \rightarrow H_2Sn_5O_{11} + 20NO_2 + 9H_2O$$
$$H_2Sn_5O_{11} \rightarrow 5SnO_2 + H_2O$$

Calculation.

$$\text{Mol. Wt. of } SnO_2 = 119 + 32 = 151$$

Suppose:—

Weight of solder $= a$ gm.
Weight of stannic oxide $= b$ gm.
$\therefore$ Weight of tin in stannic oxide $= \frac{119\,b}{151}$

Percentage of tin in solder $= \frac{119\,b}{151\,a} \times 100\%$