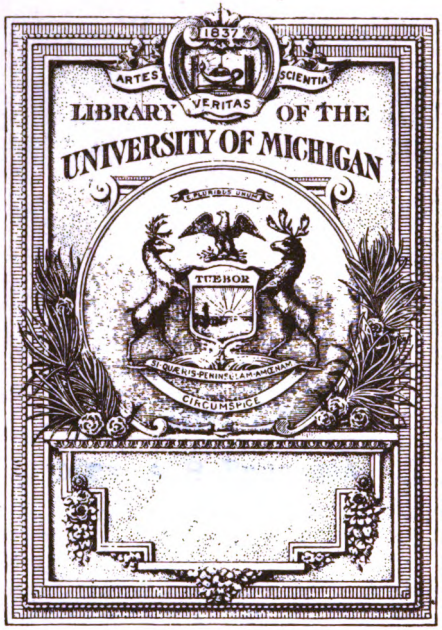
Practical work in organic chemistry

Frederick William Streatfeild



Finsbury Technical Manuals.

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Finsbury Technical Manuals.

A. B. Prescott.

PRACTICAL WORK

IN

ORGANIC CHEMISTRY.

BY

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With a Prefatory Notice by

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PREFATORY NOTICE.

In modern schemes of Technical Education two distinct classes of students have to be catered for. The day student who has completed his school education, and who is about to qualify himself for some branch of industry in which a knowledge of scientific principles is essential, is enabled to distribute the whole of his time among the various subjects which are likely to be of importance in his subsequent career. There is in addition a large and growing class of students whose daily occupations prevent their attendance at college day-courses, but whose commendable desire for self-advancement leads them to seek instruction at evening classes. For both kinds of students provision has been made at the Finsbury Technical College, and the scheme there carried out was originally framed so as to carry on both kinds of instruction. During the six years that it has been my privilege to be responsible for the teaching carried on in the chemical department of that College, the steady increase in the number of evening students, and the zeal with which men who are engaged all day, often in very arduous occupations, will carry on supplementary work in these evening

classes, has convinced me that such instruction supplies a distinct want. That the training which the City and Guilds of London Institute has enabled us to impart is of real value, can be amply shown by the numerous records of promotion or of improved positions which the evening students have been enabled to take. Another favourable sign is the fact that a considerable number of day students who have completed their studies, and who have obtained appointments in the London district, re-enter the College as evening students. Of equal or greater significance is the fact that the competition produced by the spread of the Polytechnic movement has had no appreciable effect upon the evening attendances, and this in spite of the fact that we cater for no examination, and that we profess to qualify students in Chemical Technology only. The importance of such a statement will appear when it is remembered that London is not a first-class centre of chemical manufacture, and that in so well-worn a subject as Chemistry there are already in existence numerous evening schools. The general spread of evening instruction appears rather to have had the effect of raising the standard among those attending the College classes.

The main point in which the chemical training given at a technical college should differ from the ordinary examinational treatment of the subject is in the greater importance which should be attached to practical work in the laboratory. For this reason the

preparation of various inorganic and organic compounds has been made a special feature at Finsbury as soon as the student has acquired sufficient preliminary skill in qualitative and quantitative analysis. Greater value is attached to the knowledge acquired in this way than to attendance at formal lectures, although a certain number of these are also delivered throughout the session. No student is considered qualified to carry on work in organic chemistry until he has previously been through a course on inorganic chemistry, including the general elementary principles of the science. Supposing such preliminary qualification to have been acquired, either by attendance throughout one session at the evening inorganic course at the Finsbury College or elsewhere, the student may pass on to organic work, and the various programmes of instruction which are contained in the present little volume will, it is contemplated, be found of use to those who are following up this branch of the subject. The chief practical difficulty which must be experienced by all teachers of chemical technology is due to the very diverse fields of labour in which evening students pursue their daily occupations.* With reference to organic chemistry, for example, the training which is required by a soap-maker is quite different from that required by a brewer or a tar-distiller. After the

* With day students no such difficulty presents itself, because these come to us while still young, and for the most part with no definite line of future chemical work in view.

general elementary foundation has been laid it is impossible, therefore, to provide a single scheme sufficiently wide to embrace all the chemical industries. For this reason the laboratory work has been subdivided in such a manner as to meet the wants of the various industries. The programmes which the author has drawn up cover very fairly the elementary principles concerned in all the branches of manufacture in which organic chemistry plays a part. If the student wishes to limit himself entirely to his own subject, he can do so after he has shown sufficient evidence of knowledge and skill in the general preliminaries. If he requires to obtain a wider range of knowledge (and this is in all cases recommended), he can work through all the programmes. This recommendation applies especially to day students, who can give more time to, and who are enabled to work more continuously at, the subject. All the experiments described are thoroughly practical, and have been performed by successive classes of students under Mr. Streatfeild's supervision throughout a period of many years. The success with which this method of instruction has been attended in our own College has warranted the belief that the little laboratory companion now offered may be of use in other technical schools, and I have great pleasure in commending it to the notice of teachers of Chemistry.

R. MELDOLA.

AUTHOR'S PREFACE.

THE object of this little book is to meet a want which the author has experienced in teaching the rudiments of Practical Organic Chemistry to students who can devote but little time to the subject.

The subject matter of the following "Programmes of Work" has been chosen partly on account of its technical utility, and partly as affording practice in the application of the more important reagents employed in the investigation of the compounds of carbon.

The writer wishes it to be expressly understood that the book is only intended to be a laboratory guide, and its use should be supplemented by reference to standard works, or still better by personal instruction from the teacher.

For elementary students the author would recommend Professor Ira Remsen's 'Organic Chemistry,' or the excellent little book of Professor Emerson Reynolds, 'Organic Chemistry,' pt. iv.* For more advanced

* Professor Reynolds little books have been translated into German by G. Seibert, under the title of 'Leitfaden zur Einführung in die Experimental-Chemie.' They form a series of excellent German Readers for chemical students.

students, Bernthsen's 'Text Book of Organic Chemistry,' translated by Dr. M'Gowan, will be found very serviceable.

In preparing a work, however elementary, an author feels how much he is indebted, either directly or indirectly, to the labours of previous writers, and to those from whom, as teachers or colleagues, he has derived assistance. In the latter category the thanks of the writer are due to Professor H. E. Armstrong and to Mr. J. Castell-Evans.

The author wishes to acknowledge the help he has received from many scientific and technical journals, and to certain works dealing with organic analysis, especially to Allen's 'Commercial Organic Analysis.'

Thanks are likewise due to Mr. F. C. Robinson, senior chemical student at the Finsbury Technical College, for the great care and attention he has devoted to the drawings, which for the most part were sketched from apparatus *in situ*.

The author also most gratefully acknowledges the encouragement which he has received from Professor R. Meldola, the present head of the chemical department, who has kindly read all the proof sheets, and has made numerous corrections and suggestions.

TO THE STUDENT.

BEFORE commencing work, ascertain fully the object in view. Recollect that the *mere* preparation of chemical compounds, however beautiful in themselves, is not the sole end and aim of your work. Having clearly understood the purpose of the experiment, then set about its execution in a methodical manner. First, find out as far as possible the properties of the proposed preparation. You will then be in a position to fit up the necessary apparatus in an intelligent manner. Great attention must be paid to neatness in fitting up apparatus; corks must be carefully bored, glass tubes must be neatly bent and not unnecessarily long, and all sharp edges must be taken off. Exercise judgment in the selection of flasks, funnels, beakers, dishes, &c.

During the progress of an experiment keep your eyes open, and record in your note-book all changes taking place. Weigh or measure, as the case may be, the quantities prescribed. Note the yield of the product in each case, and compare it with the quantity theoretically obtainable. Examine all crystalline

compounds under the microscope, and see how their appearance tallies with that given in the books. Be careful in your determinations of melting and boiling points; in short, keep steadily in view the fact that you are qualifying yourself to become an original investigator in Chemical Technology.

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PRACTICAL WORK

IN

ORGANIC CHEMISTRY.

OPERATIONS AND ANALYSIS.

Operations.

Purification of Organic Compounds.—Before proceeding to the investigation of the properties of chemical compounds, it is essential that they should be of definite composition; that is, they must be obtained in a state of purity. For the isolation and purification of the carbon compounds a number of processes are employed, varying according to the nature of the substance to be dealt with.

Crystallisation.—This process is more frequently made use of than any other, and is effected by dissolving the substance in some suitable solvent, sometimes digesting with *recently* ignited charcoal to remove colouring matter, filtering if necessary, and allowing the solution to crystallise, concentrating by evaporation if too dilute. The crystals are collected, well drained from mother-liquor, and if still impure recrystallised.

Fractional Crystallisation.—When two or more sub-

stances occur together, they may often be separated by taking advantage of the different degrees of solubility which they possess in a certain menstruum. The substance is dissolved and allowed to crystallise, care being taken not to form a too concentrated solution. The first deposit of crystals will consist of the less soluble portion. It is filtered off and the filtrate (mother-liquor) concentrated by evaporation, when the more soluble compound will separate out. The successive deposits are then recrystallised each in turn until finally the deposits are found to be homogeneous. This operation is called *fractional crystallisation.*

Selection and Application of Solvents.—The selection of a suitable solvent for purposes of purification requires some consideration. The process generally followed in the first instance is to submit a small portion of the material contained in a test-tube to the action of several solvents in succession, until one is found out of which the compound readily crystallises.

The following is a useful list of solvents:—

Water.—Dissolves sugars, gums, starch, and other highly organised bodies which are nearly insoluble in ether or alcohol. It also dissolves most organic acids and salts.

Alcohol.—This substance is largely used as a solvent. Purified methylated spirit may generally replace the more expensive ethyl-alcohol as a solvent. Many organic compounds crystallise well from a more or less dilute spirit.

Benzene.—This is a very useful solvent. Substituted haloid and many nitro-compounds crystallise well from benzene. A peculiar characteristic of this solvent, in which it differs from alcohol and ether, is that many amorphous substances are insoluble in it.

"*Coal Oil.*"—The fraction of coal oil after separation of benzene, containing toluene, xylene, &c., is occasionally useful when a solvent of a somewhat higher boiling-point is required. *Aniline, dimethylaniline,* and *phenol* are sometimes useful solvents.

Light Petroleum Oil, consisting principally of the lower boiling paraffins, is also useful. Compounds which are exceedingly soluble in benzene and ether often crystallise well from petroleum.

Glacial Acetic Acid.—A valuable solvent, and the fact that it dissolves such substances as chromic acid, nitric acid, and bromine, while it is not attacked by them, renders it a particularly useful medium for the moderate application of these reagents to organic compounds.

Ether.—From its low boiling-point, and from its having no chemical action on most organic compounds ether is especially valuable as a solvent. It has the advantage of dissolving a very large number of substances which are indifferently soluble in other liquids.

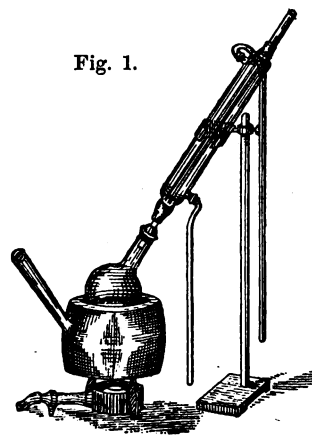
Chloroform, Carbon disulphide, and Carbon tetrachloride are occasionally used, but are not often resorted to until the commoner solvents have been tried.

In particular cases the mineral acids and alkalies are

made use of, but their employment requires great care and judgment, as they often bring about decomposition of the substance.

When a suitable solvent has been found, care must be taken in the case of volatile inflammable liquids that the solution of the substance is effected in an appropriate vessel. In the case of alcohol, benzene, ether, &c., it is a good plan to employ a flask attached to a condenser, and the flask had better be heated by means of a water-bath. (A saucepan answers very well; it should have a piece of cloth at the bottom to prevent the flask touching the metal.) See Fig. 1.

Fig. 1.



Should it be found necessary to use animal charcoal to remove colouring matter, care must be taken not to add it too suddenly to the hot solution. The solution

is cooled down and the purified charcoal added in small portions at a time.*

Very serious accidents may happen through carelessness in this matter; the hot liquid may suddenly froth up, and, if inflammable and in proximity to a flame, take fire.

Should an inflammable liquid be employed in effecting a fractional crystallisation, the mother-liquor had better be distilled off to the desired extent; it is safer than evaporating down in a beaker. Of course, in particular cases these operations have to be modified.

Note.—Recovery of Solvents.—Most chemical laboratories where much organic work is done, keep bottles or jars for residues, such as alcohol, ether, benzene, &c. When these residues have accumulated, they may be "worked up" in an appropriate manner. Their recovery offers good practice to a beginner.

Determination of Melting-point.—The melting-point is a very characteristic property of many solid bodies. If a substance begins to melt at a certain temperature, and does not melt completely at that temperature, experience has shown that it is very probably impure.

In working with compounds of carbon, determinations of melting-points are frequently made. In general, a

* This is prepared by boiling about 1 lb. of freshly ground animal charcoal in half a gallon of common hydrochloric acid diluted with one gallon of water, for about two hours. The liquid is filtered through a linen bag, and the residue washed with hot water till free from acid, dried, and ignited to full redness in a closed crucible. It is bottled while still warm and kept carefully dry.

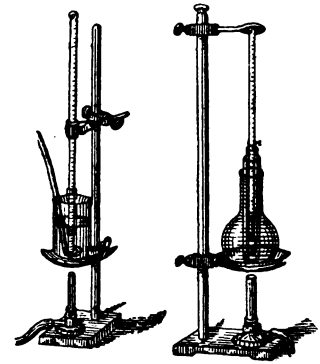
sharp and constant melting-point is regarded as evidence of "individualism" and purity in a compound.

The determination is made as follows :—Small tubes are prepared by heating a piece of scrap combustion tube and drawing it out while hot to a narrow tube. This can be cut up into a number of small tubes about 3 or 4 inches long, and one end of each tube is to be neatly sealed up. These small tubes have thin walls, and must be of such internal diameter that an ordinary thick pin can easily be introduced into them. A small quantity of the substance to be examined (*it must be quite dry*), is placed on a watch-glass and scooped up by the wide open part of the tube, when, by gently tapping the tube, the substance slips down to the bottom, where it forms a little column of about $\frac{1}{8}$ inch in height. The tube is fastened to a thermometer by means of a little indiarubber band cut from a piece of tubing. The band is placed round the upper part of the tube, and the lower part of the tube containing the substance is placed in contact with the bulb of the thermometer. If the capillary tube is very slender it will adhere to the side of the thermometer by virtue of the capillarity of the liquid in the beaker, and the indiarubber ring may then be dispensed with.

A reference to Fig. 2 will show how the thermometer and tube are to be arranged. They are suspended in a beaker containing either water, paraffin-wax, or sulphuric acid. A piece of glass rod bent into a ring at one end is also provided; this is to act as

stirrer during the process of heating, which is to be very gradually conducted. The instant the substance melts the temperature indicated by the thermometer is noted. This is the melting-point required.

Fig. 2. Fig. 3.



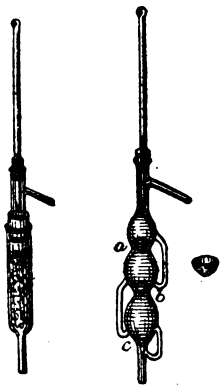
For substances melting above 250° an "air-bath" is very convenient. This can be formed out of a small wide-necked flask and two test-tubes passing one within the other (see Fig. 3). The melting-point tube is fastened to the thermometer by means of a piece of thin wire.

Distillation.—For the purification of volatile liquids the process of distillation is used. For this purpose we may effect our object by (*a*) *simple distillation*, (*b*) *fractional distillation*, (*c*) *steam distillation*. As an illustration of simple distillation we will take the recovery of a solvent, say, benzene. The impure benzene would be placed in a retort or flask connected to a condenser, and the benzene distilled off by the aid of a water-bath.

Fractional Distillation.—It is often possible to separate almost completely by a simple distillation two liquids occurring together in a mixture, when their boiling-points lie widely apart. The more volatile liquid first passes over, the temperature suddenly rises, and the

higher-boiling liquid distils. It is otherwise when we have a liquid consisting of a mixture of bodies boiling very near each other. One distillation only effects a very imperfect separation ; a portion of the *less* volatile liquid is carried over by the vapour of the more volatile substance, the temperature rising throughout the distillation. In order to carry out the separation of volatile liquids recourse must be had to the process of *fractional distillation*. It will be evident that if the vapours which rise from a mixture of boiling liquids are somewhat cooled before reaching the condenser, the *less volatile portion* carried upwards by the vapour of the more volatile liquid will be partially condensed. If this is allowed to flow back to the retort, a greater proportion of the *lower*-boiling liquid will be obtained in the receiver. In order to carry out this partial condensation during the process of distillation several forms of apparatus have been devised.

Fig. 4. Fig. 5.



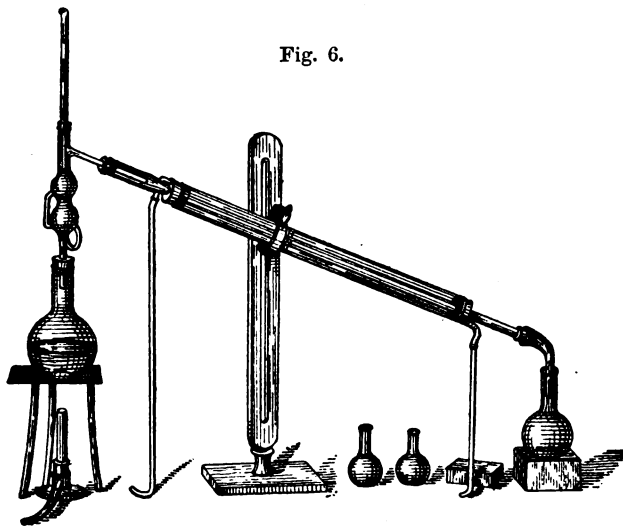
A very effective, and at the same time inexpensive, piece of apparatus is that of Hempel, which consists of a long glass tube containing glass beads or pieces of broken glass. (See Fig. 4.)

Fig. 5 is the apparatus of Le Bel & Henninger ; it has

side tubes, down which the condensed liquid flows. At the narrow parts of the tube *a*, *b*, *c*, are fixed small cups of wire gauze. Little pools of condensed liquid form in these cups, and this liquid washes, so to speak, the vapour passing upwards; in fact, a process of fractionating is carried on in these cups by the ascending vapours.

In carrying out a fractional distillation, the apparatus is to be arranged as in Fig. 6.

Fig. 6.



The flask is heated over wire gauze, or, in the case of a very volatile liquid, in a water-bath. If wire gauze is employed, the burner should be placed in a deep tin basin containing sand, in order to absorb the liquid in the event of the flask or retort cracking.

The fractionating bulb or tube is fitted with a thermometer, the bulb of which is well below the exit-tube (see Fig. 6). A number of clean dry flasks or bottles, fitted with corks and having blank labels attached, are provided for recording the B.P. of the fraction.

In order to indicate the working of this apparatus we will take the rectification of a sample of benzene.

Example.—200 ccm. of the sample of benzene are introduced into an 8 oz. flask, a spiral of platinum wire or two or three pieces of broken pipe-clay are added in order that the liquid may boil quietly. The flask is connected to the condenser by means of the fractionating apparatus and heat so applied to the retort that the distillate *drops* from the condenser; it must not be allowed to come over in a continuous stream. The indications of the thermometer must be carefully noted and the distillate between every five or ten degrees is to be collected in a separate vessel. Each of these fractions is to be redistilled in proper order. Thus, suppose we have the fractions A, B, C, D, E, F. A would first be redistilled, all that comes over within a range of 5° being collected; B would then be added to the residue of A in the flask, distillation continued as before, C would be added to residue of A and B, and so on until we have principally two large fractions, one boiling 79-82° and the other above 105°.

The fraction 79-82°, which is nearly pure benzene, can be further purified by freezing, pressing, and redistilling.

Note.—In carrying out the process of distillation care should be taken not to employ *too great a heating medium*, as the vapour in the flask gets superheated and so causes erroneous thermometric readings. The distillation should be conducted in a place as much sheltered from currents of air as possible.

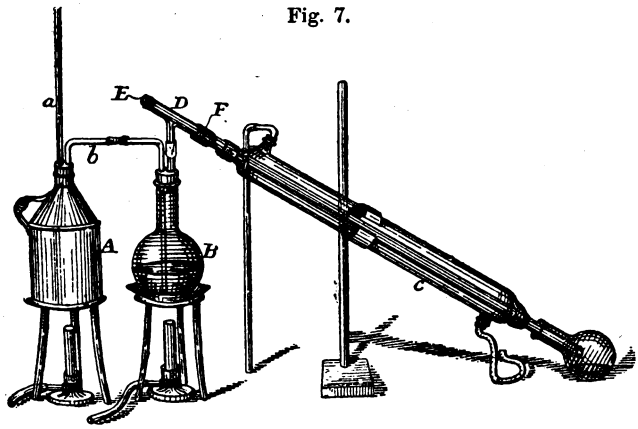
Determination of Boiling-point.—Just as the melting point is characteristic of many solid compounds, so the boiling-point is a very important physical property of many liquids. It is determined with sufficient exactness for ordinary purposes by employing the apparatus used for fractional distillation. The temperature noted on the themometer when the liquid is boiling is the boiling-point. In exact determinations of boiling-points, corrections have to be made for the cooling of that part of the column of mercury which is not in the vapour of the substance. The barometric pressure must also be noted.

Steam Distillation.—It occasionally happens that a substance is volatile in a current of steam, and by taking advantage of this property a compound can often be very readily isolated and obtained in a pure condition. In the following programmes it will often be adopted, and therefore a description of the apparatus employed may be here given. (See Fig. 7.)

A is a tin or copper can; it is fitted with a cork and two tubes *a*, *b*, one (*b*) conveying steam to the flask B and the other (*a*) passing nearly to the bottom of the can, and extending about a yard above the cork. It acts as

a kind of safety tube. The flask is connected to the condenser by the bent glass T-piece D, which in its turn is connected to the condenser by the india-

Fig. 7.



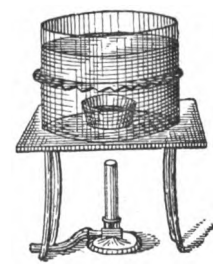
rubber tube F. The T-piece is closed at one end by the cork E; this cork can be removed when necessary and a glass rod inserted to remove any obstruction in the condenser. The T-piece and condensing-tube can be made of one piece if desired, but is more liable to fracture than if connected as at F by indiarubber tube. When operating the flask B with its contents is heated on a sand-bath and a gentle current of steam passed in, when the volatile substance passes over with the steam and is condensed in the usual way.

Sublimation.—Fig. 8 represents a convenient form of apparatus for the sublimation of an organic compound. A sheet of asbestos cardboard supported on a

tripod and having a circular hole cut out for the reception of a small porcelain crucible, is covered with an inverted, thin, shallow, flat glass basin, on the top of which a precisely similar glass dish is placed containing a little cold water.

The substance to be sublimed is placed in the crucible, which is covered with a circular piece of filter paper pierced with pin-holes. (This is to prevent the sublimate from dropping back into the crucible; it is not shown in the sketch.) One of the flat glass dishes is then inverted over the whole, and this again surmounted by its fellow, containing a little cold water, which is renewed from time to time as occasion may require. A piece of moist bibulous paper placed between the two glass dishes greatly facilitates condensation. Matters being thus arranged the crucible is cautiously heated by means of a small burner.

Fig. 8.



Small quantities of substance can often be readily sublimed between two watch-glasses; a circular piece of filter paper pierced with holes being interposed to prevent the sublimate falling back into the lower vessel.

A very moderate temperature suffices for the sublimation of the majority of organic compounds.

Subliming-point.—The temperature at which a sub-

stance sublimes, called the subliming-point, is sometimes an important characteristic, but its value depends very much on the manner in which the operation is carried out.

Determination of Specific Gravity.—The determination of the specific gravity of an organic body, liquid or solid, is often a most valuable indication of its purity and identity.

The specific gravity of a solid or liquid is generally referred to water taken as unity.

For determining the specific gravity of liquids, we may employ either a specific gravity bottle or what is known as a Sprengel tube. A gravity bottle may easily be constructed as follows:—A small glass flask with a long neck, constructed from a piece of glass tube by means of the blow-pipe, is fitted with a cork (Fig. 9). The neck of the flask just above the bulb is narrowed by drawing it out in the flame, and a horizontal mark *m* etched or scratched on it with a file. The bottle, which should have a capacity of about 20–30 ccm., is thoroughly cleaned and dried; when quite cold it should be very carefully weighed plus the stopper. It is then filled up to the mark with the liquid under examination; this can be done by means of a funnel, the stem of which is drawn out so as to allow it to pass through the constricted neck. The bottle with its contents is placed in water and brought to a temperature of 15°·5 C.

Note.—Should the water of the laboratory be higher

than this temperature it can be readily cooled down to the desired extent, by dissolving in the water a few crystals of sodium thiosulphate or ammonium nitrate. After standing in the water for about a quarter to half an hour, the liquid in the flask is so adjusted that the meniscus coincides with the mark on the neck of the flask. The addition of more liquid is made from a small pipette with a capillary tube; if some of the

Fig. 9.

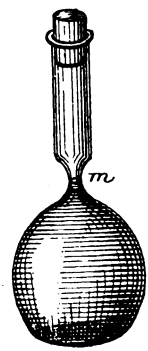
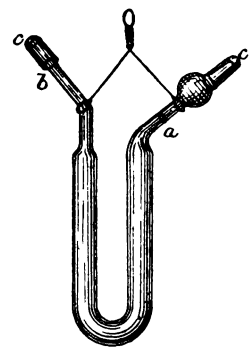


Fig. 10.



liquid has to be removed a small squill of filter paper may be used to absorb it. When the adjustment has been effected the bottle is removed from the water, dried, and allowed to remain a quarter of an hour in the balance case and weighed. The bottle is emptied, cleaned and dried, and filled as before with cold, recently boiled, distilled water. After adjustment at a temperature of 15°·5 C. it is again weighed. Neglecting certain minor corrections, the specific gravity is

found by dividing the weight of substance by the weight of water.

A very useful and delicate piece of apparatus is Perkin's modification of Sprengel's specific gravity tube. This modification is very readily constructed with the blow-pipe out of glass tube. It consists (Fig. 10) of a U-tube drawn out at each end into a fine capillary. The ends are bent over as shown, one arm having a small bulb blown on it. On this limb just below the bulb a mark is scratched. The tube is dried and weighed, and the liquid drawn in through the limb *b* until it half fills the bulb on the limb *a*. The apparatus is cooled down in water at 15°, and the meniscus adjusted to the mark *a* by tilting the tube until the limb *b* has a horizontal position. From the limb *b*, the liquid may be absorbed by cautiously applying a piece of bibulous paper until it sinks to the desired position in the limb *a*. The tube is then dried and weighed, and the operation is repeated with distilled water. In the case of volatile liquids little caps of glass are placed over the ends of the tube.

The apparatus is adapted for small quantities of liquid as it can be made to hold from 1–10 ccm. or more. It is very useful for determining the densities of many fixed oils which are solid or semi-solid at the ordinary temperature. The determination of the density of such substances at the boiling-point of water is very convenient for many reasons. The weight of the Sprengel tube and that of the water contained in it

at 15°·5 C. being known, the tube should be filled with the oil or fat, previously melted if necessary, and suspended in a beaker of boiling water, and the adjustment made in the usual way. When the expansion ceases the tube is removed, cooled, wiped, and weighed. The weight of the contents divided by the weight of water at 15°·5 C., previously known to be contained by the tube, will give the density of the oil at the temperature of boiling water, water at 15°·5 C. being taken as unity. There is no necessity to make any correction for the expansion of glass as all the determinations are comparative.

Collection and Drying of Organic Preparations.—Some judgment has to be exercised as to the mode of collecting organic preparations from the solutions from which they have separated. Certain well crystalline products can be very conveniently collected in the ordinary crystal drainers, or the substance may be collected in a funnel, having a glass stopper or marble placed loosely in the apex (made still more effective by the addition of a little asbestos fibre).

It more frequently happens, however, that the compound to be collected is in a finely divided condition, not capable of being retained by a loose stopper. A more general method for small preparations is to filter on paper aided by a "filter pump."

To carry out this method properly we require some good filter-paper and a supply of parchment paper. The filter-paper is folded in the usual way, but

before placing in the funnel it is fitted with a small parchment cone. The mode of fitting this cone is as follows:—A small circular piece of parchment paper, rendered pliable by just moistening with warm water, is pierced with a few holes, and then folded up with the filter-paper in the same way as we should fold a "double filter." The paper is now dropped into a selected funnel (the sides should be inclined at an angle of 60°), pressed evenly against the sides, and moistened with water or alcohol as the case may be. The stem of the funnel is now pushed through the caoutchouc cork of the filter-flask, or bottle, the substance brought on the funnel, and the pump gently started.

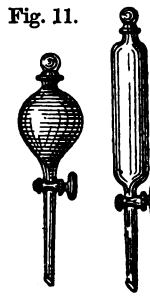
When the parchment cone is properly fitted, it will support a filter filled with liquid under a pressure of an atmosphere without the paper breaking. After the substance has been well drained on the funnel, it may be removed with the filter-paper bodily from the funnel and opened out on some bibulous paper spread on a porous tile, where it may be left to dry spontaneously, or placed in the water or air-oven.

The collection and drying of liquid or oily products requires some consideration. For separating two liquids of different specific gravities we may employ a pipette or a separating funnel. A suitable pipette may easily be constructed by the student. A more convenient apparatus, however, for this purpose is the separating funnel, which consists of a pear-shaped

(Fig. 11) or cylindrical (Fig. 12) glass vessel, furnished with a tap below and a stopper at the top. The funnel should be cleaned immediately after use, and the tap and stopper slightly greased to prevent them sticking. The application of the funnel for the mere separation of two liquids requires no explanation. The funnel is, however, often applied to other purposes. Suppose that it is desired to effect the separation of a substance from an aqueous liquid by agitation with ether: the former is introduced into the funnel, of which it should not occupy more than one-third, acid or alkali added as may be desired, and then a volume of ether about equal to that of the aqueous liquid. The stopper is then inserted, the funnel grasped in such a manner as to prevent the tap and stopper from falling out, and the whole thoroughly shaken together for a minute or two, and then set aside. As a rule, the contents will readily separate into two well-defined layers, the lower of which is aqueous, and the upper ethereal. Sometimes separation into layers does not readily occur, the liquid remaining apparently homogeneous, forming an emulsion. In such a case the addition of a little more ether and reagitation generally bring about separation. The addition of a few drops of alcohol, or, when admissible, strong hydrochloric acid, followed by a gentle rotatory motion of the

Fig. 12.

Fig. 11.



liquid, will almost invariably cause prompt separation.

Separation having taken place, the aqueous layer should, if necessary, be run off by the tap into another separator, where it can again be agitated with ether. The ethereal liquid remaining in the separator can be shaken with a fresh quantity of water, made acid or alkaline, which is then tapped off as before, and the ether further washed by treating it with a little pure water. This having in turn been run off to the last drop, the ethereal solution can next be removed by the tap, but a better plan is to pour it out of the top of the funnel, by which means any contamination by traces of water, &c., adhering to the sides of the glass will be avoided.

The separated ether may be dried by standing over fused chloride of calcium or other drying agent.

Refrigerating Funnel.—It occasionally happens that we have to collect a substance melting at a very low temperature (see Purification of Benzene, p. 114). A very useful piece of apparatus for this purpose is described by J. W. Brühl.*

Fig. 13 shows how the apparatus is put together. B is the funnel made by drawing out a piece of wide glass tube, the narrow part being drawn out to a jet; it is fastened to the tube D carrying the glass tap *h*, by fusing before the blow-pipe at *f*. The tube D passes through a cork into the filter-flask E. A is the vessel containing the freezing mixture; an ordinary bottle

* Ber. Deut. Chem. Gesell., 1889, vol. xxi. p. 236.

with the bottom cut off serves for this purpose. The tube *a*, which can be closed by a clip, is useful for running off melted ice, &c. The glass cover C, furnished with a calcium chloride tube, and fastened to the funnel B by an india-rubber band *c*, is a needful adjunct, where it is necessary to freeze a substance out of contact with air or moisture. The funnel is improved and simplified by employing a narrower piece of tube, which can be closed by an india-rubber stopper carrying the calcium chloride tube. The capacity of the funnel tube is increased to the desired extent by softening and blowing out before the blow-pipe (see Fig. 14) B'.

Fig. 13.

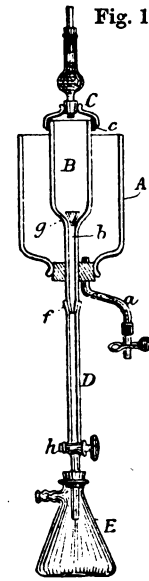
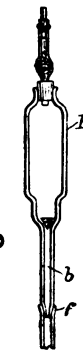


Fig. 14.



To use the apparatus the tap *h* is closed, the cone *g* of platinum or asbestos placed in position, and the liquid which is to be frozen carefully introduced. The funnel is closed, and the freezing mixture placed in the outer vessel.

When properly frozen, the tap *h* is cautiously opened, when any unfrozen liquid drains into the flask E, previously rendered vacuous by means of the pump.

ANALYSIS.

Having briefly described some of the more important operations involved in the isolation and purification of organic compounds, we will now proceed to consider the ultimate analysis of such bodies. Notwithstanding the vast array of the carbon compounds, the number of elements entering into their composition is usually very small. The great majority consist of carbon, hydrogen, and oxygen only. The members of another very large class contain four elements—carbon, hydrogen, oxygen, and nitrogen; others contain chlorine, bromine, iodine, or sulphur, whilst a smaller proportion contain phosphorus, silicon, or the metals; but these are comparatively rare.

Qualitative Analysis.

Detection of Carbon and Hydrogen.—The presence of these bodies may be demonstrated by mixing the substance with *recently ignited* copper oxide and heating to redness in a hard glass tube. The products of combustion are passed first through a cold, dry tube, and then into lime-water. If hydrogen be present it is oxidised to water, which condenses in the tube, while if carbon be present it is burnt to carbon dioxide, of which the presence is shown by the production of turbidity in the lime-water.

Liquid or volatile substances are conveniently absorbed for the purpose of the above experiment by a little recently ignited asbestos.

Detection of Nitrogen.—Many nitrogenous compounds, when heated with caustic soda or potash, evolve the whole of their nitrogen in the form of ammonia. In certain cases, viz. where the nitrogen is contained as an oxide, ammonia is not generated by heating with an alkali. A general test for nitrogen in an organic compound is as follows:—A small quantity of the substance under examination (if liquid, a small piece of asbestos fibre is added to absorb it) is heated with a small pellet of sodium contained in a narrow test-tube. A violent action usually takes place, accompanied by deposition of carbon, whilst the nitrogen and a portion of the carbon combine with the sodium, forming sodium cyanide. On dissolving the product in water, filtering, and adding a few drops of a mixed solution of ferric chloride and ferrous sulphate, potassium ferrocyanide is formed. The whole is now acidulated with an excess of hydrochloric acid; this dissolves the precipitated oxide of iron, which now forms Prussian blue with the ferrocyanide. The presence of very small quantities of nitrogen can be ascertained by this method.

Detection of the Halogens.—These elements may be detected by heating the substance in a small hard glass tube with a little *pure* quicklime; the tube is broken by plunging while hot into water, slight excess of dilute nitric acid is added to dissolve the lime, the

solution is filtered from carbonaceous matter, and the filtrate tested with silver nitrate in the usual way.

Detection of Sulphur and Phosphorus.—Sulphur may be recognised by heating the substance with a small piece of sodium. Sodium sulphide is formed, which on treatment with a dilute mineral acid will generate sulphuretted hydrogen. Another method is to heat the compound under examination with a mixture of pure nitre and dry sodium carbonate. If sulphur is present, a sulphate is formed which, after acidulation with hydrochloric acid, may be precipitated as barium sulphate.

Phosphorus, when fused with the foregoing mixture, is oxidised to phosphoric acid, which can be recognised by the ordinary reagents.

Quantitative Analysis.

Determination of Carbon and Hydrogen.—The principle employed in the detection of carbon and hydrogen in organic compounds, that is, the oxidation of the carbon to carbon dioxide, and the hydrogen to water by ignition with copper oxide or some other body which easily parts with its oxygen, is also adopted in the quantitative determination of these constituents. In order to obtain accurate results, *strict attention must be paid to details of manipulation.* These details can only be obtained from actual practice in the laboratory. The following suggestions are offered as a guide to the student in this branch of analysis. Before proceeding to the deter-

mination of the carbon and hydrogen, we must ascertain what other constituents are present, as the method employed will vary according to the nature and composition of the substance to be examined.

In the modern process of combustion the substance is burnt in a glass tube with cupric oxide or chromate of lead by the aid of a current of air or oxygen.

We will consider by way of example the combustion of a substance containing carbon, hydrogen, and oxygen, such as sugar or oxalic acid.

A combustion furnace is too well known to need description. Various kinds will be found figured in the catalogues of the instrument maker. A good form is that of Erlenmeyer; it is sold with special fire-clay tiles and trough, but as these are somewhat expensive, a commoner tile may be had and the fire-clay trough may with advantage be replaced by one of iron. A thin layer of asbestos fibre is evenly distributed along its entire length to prevent the combustion-tube coming in contact with the heated metal.

Having selected a furnace fitted with a trough, we shall require the following additional articles to make a combustion by means of this apparatus.

1. *A Piece of Combustion-tube.*—This must be of hard glass, 4 inches longer than the trough of the furnace, and of such internal diameter as to readily admit the passage of the little piece of apparatus termed a boat. The sharp edges of the tube should be fused in the blow-pipe flame, so that two caoutchouc stoppers pierced

with holes, may be introduced without being cut or torn.

2. *Copper Oxide and Asbestos.*—Sufficient granulated copper oxide must be provided to fill three-quarters of the combustion-tube. Loose plugs of asbestos are added to keep the oxide in position.

3. *A Platinum or Porcelain Boat,* to contain the substance. This should be of such size as to readily pass into the combustion-tube.

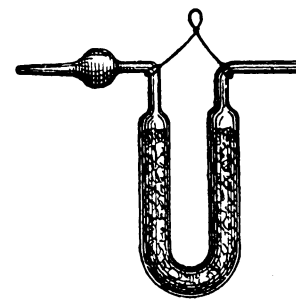
4. *A "Boat-house."*—Two tubes sliding one within the other to contain the boat whilst being carried backwards and forwards from the laboratory to the balance room.

5. *A Glass Bulb* formed by drawing out a piece of hard glass tube before the blow-pipe; it must be of such external diameter as to readily pass into the combustion-tube. It is placed behind the boat in the combustion-tube, and while permitting the passage of the current of air or oxygen, tends by constricting the channel to prevent the vapour of the substance undergoing combustion from subliming back in the tube.

6. *An Apparatus for absorbing the Water formed during Combustion.*—This is an important piece of apparatus, and one of the best forms is that shown in Fig. 15. It is readily made by bending up, and drawing out before the blow-pipe a piece of ½-inch glass tube. The arm containing the bulb is drawn out so as to be slightly tapering; in this form it is readily introduced and withdrawn from the caoutchouc stopper of the combustion-

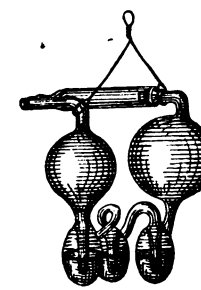
tube, and at the same time a well-fitting connection may be secured. Before the other arm is drawn out the U-tube is filled to the extent indicated with small pieces of *prepared* pumice.*

Fig. 15.



In order to prepare the tube for use, strong sulphuric acid is sucked in through one arm; it is allowed to stand for some time and then the excess of acid drained off through the same arm; the outside of the tube is wiped and the adhering acid expelled from the limb by gently warming in the Bunsen flame. Sufficient acid remains in the tube in contact with the pumice to serve for half a dozen experiments. Most of the water resulting from the combustion condenses in the little bulb, from which it may be expelled after weighing, by tilting the tube, aided by a few gentle jerks, or by cautiously warming and aspirating.

Fig. 16.



7. *An Apparatus to absorb Carbon Dioxide.*—Of the various forms sold for this purpose the one shown in

* To prepare the pumice for this purpose pieces are selected of about the size of large peas. They are digested for some time in a small porcelain basin with strong sulphuric acid, drained from excess of acid, and then ignited. This treatment destroys carbonates, &c.

Fig. 16, and known as Geissler's, is preferred. It has a small additional tube containing broken pieces of potassium hydroxide, attached at one end.

The bulbs are filled to the extent indicated in the figure with a strong solution of potassium hydroxide (1 part by weight of potash to 2 parts of water).

The sulphuric acid tube and potash bulbs are stoppered when not in use, by short lengths of narrow caoutchouc tube closed at one end by small pieces of glass rod.

8. *An Apparatus for drying and removing Moisture and Carbon Dioxide from the Air and from Oxygen.*— This may be arranged as in Fig. 17, which represents a convenient form of apparatus for this purpose, and also indicates the manner in which it is connected to the combustion-tube, &c. A is a vessel containing water supported at about 24 inches above the operation table. On opening the screw-clip *a* water flows into the bottle B, containing oxygen, which is conveyed by means of the bent tube to the U or rather Y tubes, C, C′, packed to the extent indicated with broken pumice. The shanks of these tubes pass through caoutchouc stoppers and dip, C into a strong solution of potash (1 part potash 2 parts water) and C′ into concentrated sulphuric acid. Before connecting the apparatus to the combustion-tube the stoppers at *c c′* and *d d′* (short lengths of caoutchouc tube stoppered with glass rod) are removed, when on applying a gentle pressure from the lips at *d d′* the liquids are forced up into the tubes containing the

pumice. On removing the pressure the liquids flow back into their receptacles. The stoppers are securely replaced and the connection completed.

The small conical flask D, containing a little of the potash solution, serves to regulate the supply of air or oxygen by indicating the speed with which the gas travels through the apparatus, this being controlled by the screw-clip *b*.

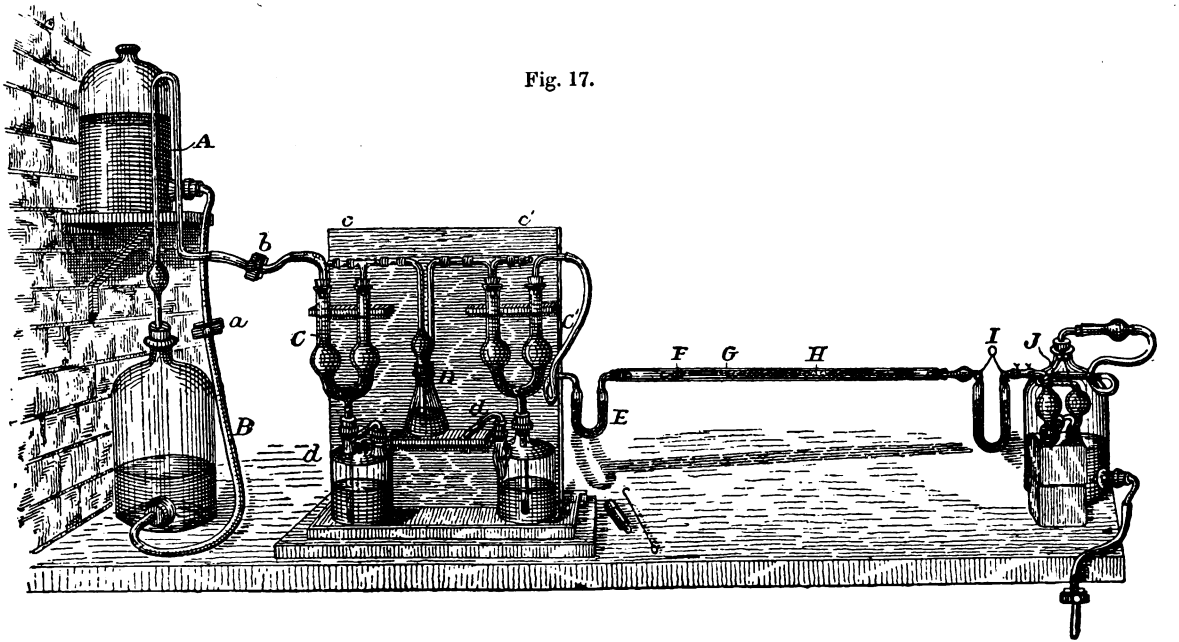
The little tube E contains a few fragments of pumice saturated with concentrated sulphuric acid; one arm of this tube passes *directly* through the caoutchouc stopper of the combustion-tube. Its adoption ensures a most perfect desiccation of the air or oxygen. The arrangement of the rest of the combustion apparatus requires little or no explanation. F is the little glass bulb to prevent backward sublimation, G is the "boat," H represents the cupric oxide kept in position by loose plugs of asbestos, I shows the attachment of the apparatus for absorbing the water resulting from the combustion of the substance. This apparatus is connected with the potash bulbs J by means of a piece of narrow bore thick-walled caoutchouc tube.

The Process.—When everything is arranged, heat the combustion-tube to low redness, having previously removed the boat and glass bulb; detach the caoutchouc tube at *b*, and connect the aspirator to the other end of the combustion-tube, when a slow current of dry air may be drawn over the copper oxide to expel hygro-

scopic moisture, and burn any organic impurity. While the tube is being heated, weigh the potash bulbs and sulphuric acid tube *without their caoutchouc stoppers.*

When you have determined their weight, replace the stoppers. In about thirty minutes turn out the flames underneath that part of the combustion-tube not containing the copper oxide, and allow to cool down in the current of dry air. Now adapt the weighed sulphuric acid tube to the combustion-tube by means of the caoutchouc stopper (having previously removed the aspirator), and connect the potash bulbs by a piece of well-fitting caoutchouc tube in the manner represented in Fig. 17. In the diagram this caoutchouc tube is seen fastened on to the glass arms of the absorption-tubes by means of thin wire, but this is not necessary if an aspirator is employed, since the reduced pressure within the apparatus caused by the column of water effectually prevents leakage. Remove the stopper and small U-tube at further end of the combustion-tube, insert the boat containing the weighed amount of substance (about 0·2 gram), and then the glass bulb. Again fit in the stopper and connect the caoutchouc tube *b* with the bottle containing the oxygen. Attach the aspirator to the end of the potash bulbs, and *cautiously* open the stopcock. Now relight the last two or three burners at the other end of the tube, immediately under the glass bulb, so as to heat it gently, and turn on a slow stream of oxygen (about a bubble every two seconds suffices at the commence-

Fig. 17.



ment of the process); continue to ignite successive burners until the boat is approached. Carefully observe the movements of the liquid in the potash bulbs, and regulate the heat so as to preserve a uniform passage of the gas into the bulbs.

As soon as the substance in the boat appears to be completely charred, increase the heat beneath the boat (by this time the whole of the burners should be lighted), and send a slightly brisker current of oxygen (about one bubble per second) through the apparatus. The carbonaceous matter within the boat gradually burns away; as soon as it has disappeared gradually diminish the flames underneath the glass bulb and boat; turn on a little more oxygen. After a few minutes, disconnect at *b*, and by means of the aspirator send a slow current of air through the tube, &c., to displace the oxygen. In a few minutes detach the potash bulbs and sulphuric acid tube (taking care that in withdrawing the latter from the caoutchouc stopper the water which has condensed in the small bulb does not flow out), fit in their respective stoppers, wipe them, and after standing in the balance room for an hour to cool down, reweigh them (without the stoppers). Allow the combustion-tube to cool gradually; if proper care be exercised in this matter, it will serve a great number of times. The heat must not be so high as to distort the tube. The great majority of organic compounds, especially if they contain oxygen, burn with comparative ease with copper oxide and free oxygen.

The entry of the combustion should thus appear in the note-book :—

ANALYSIS OF OXALIC ACID (for example).

Determination of Carbon and Hydrogen.

Weight of boat + substance		
Weight of boat empty		
Substance .. .. =		
Weight of H_2SO_4 tube (after)		
„ „ (before)		
Water .. .. .. =		
Weight of KOH bulbs (after)		
„ „ (before)		
Carbon dioxide .. =		

From the knowledge that 44 parts of carbon dioxide contain 12 parts of carbon, and that 18 parts of water contain 2 parts of hydrogen, the student can readily calculate the amount of carbon and hydrogen in the substance analysed. If the sum of the amounts of carbon and hydrogen is equal to the weight of the body taken, the substance contains only these elements; if the body contains oxygen in addition, the difference indicates the amount of this constituent.

Analysis of Organic Substances containing Nitrogen.—Nitrogenous organic substances when burnt with copper oxide, particularly if free oxygen be present, are apt to evolve oxides of nitrogen, which condense in the sulphuric acid tube and potash bulbs and vitiate

the results of the carbon and hydrogen determinations. In the combustion of organic substances containing nitrogen, it is necessary therefore to introduce some substance in the front part of the tube capable of decomposing nitroxy-compounds. Metallic copper cannot well be employed, as this would quickly become oxidised in the current of air or oxygen. The most effective agent is metallic silver: a cylinder of silver gauze,* about six inches long, rolled on a thin glass rod or piece of tobacco pipe, is placed in the anterior part of the combustion-tube and kept at a bright red heat during the operation. The carbon and hydrogen may then be determined in the ordinary way.

Analysis of Organic Substances containing Sulphur, Phosphorus, and the Halogens.—When an organic compound containing a halogen (chlorine for example), is burnt with cupric oxide, cuprous chloride is formed, which, being volatile, is carried forward in the stream of gas and condenses in the sulphuric acid tube, and thus renders the determination of the hydrogen inexact. By inserting a roll of silver gauze or a layer of silvered pumice in the anterior portion of the tube any chlorine would be arrested.

* In the absence of silver gauze, which is somewhat expensive, "silvered pumice" may be employed. Boil some pumice (broken into pieces about the size of an ordinary pea) in strong hydrochloric acid, collect in a funnel and wash thoroughly with hot water till free from acid; transfer to a crucible and strongly ignite. Now digest with a pasty solution of silver acetate, dry and ignite strongly. Metallic silver in a finely divided state is left behind on the pumice, which is very effective in breaking up any nitroxy-compound.

The determination of carbon and hydrogen in compounds containing chlorine or bromine is best effected by heating with lead chromate. This substance is readily made by precipitating a solution of lead acetate with potassium chromate, thoroughly washing the dense yellow precipitate, drying, heating to redness in a covered clay crucible, and coarsely powdering it. The combustion is made in the manner already described in the case of copper oxide.

The combustion of organic compounds containing sulphur is most accurately made with lead chromate, care being taken to maintain the anterior portion of the tube, to the extent of 6 or 7 inches, at a very low red heat. Under these circumstances no sulphur dioxide passes into the absorption apparatus.

Should the organic substance contain nitrogen in addition to sulphur or the halogens, it is only necessary to introduce a layer of silvered pumice in the front part of the tube; the carbon and hydrogen may then be accurately determined in the usual way.

Determination of Nitrogen.—Many organic substances containing nitrogen, when heated with a caustic alkali, give up the whole of their nitrogen in the form of ammonia. This reaction constitutes the principle of a convenient method for estimating nitrogen in a number of organic compounds.

The following articles are required for this method:—

(*a*) *Combustion-tube.*—This should have the form

seen in Fig. 18; it is about 24 inches long, and ½ inch in internal diameter.

(*b*) *Soda-Lime.*—Heat a sufficient quantity of the coarsely powdered substance in a porcelain basin just before it is wanted, and allow it to cool.

(*c*) *A substance to evolve Carbon Dioxide.*—This is conveniently prepared by mixing recently ignited sodium carbonate with potassium bichromate in molecular proportions.

(*d*) *Asbestos.* — Ignite a small quantity in the Bunsen flame before use.

(*e*) *A bulbed* U*-tube, fitted with caoutchouc stopper and bent tube.*—On the end of the bent tube is a cork, which fits tightly into the combustion-tube.

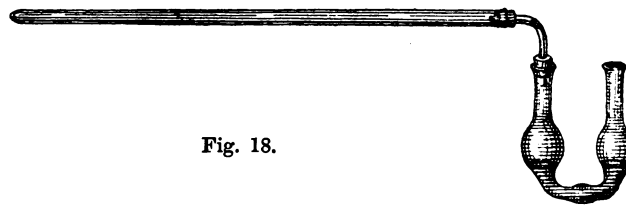


Fig. 18.

The Process.—Introduce a layer of about 4 inches in length of the CO_2-mixture into the posterior end of the tube, and afterwards an equal bulk of soda-lime. Weigh out about 0·2 gram of the substance to be analysed into a small dry porcelain mortar, and mix it with a small quantity of soda-lime. Bring the mixture without loss of time into the tube, and rinse out the mortar with a fresh portion of soda-lime. Fill up the tube to

within two inches of its length with the same, and insert a loosely fitting plug of recently ignited asbestos. Fit in the cork of the U-tube, transfer a known volume of standard acid to the U-tube, and add sufficient water (if necessary) to fill the bulbs to the extent indicated in the figure. Gently tap the combustion-tube on the table so as to form a channel for the evolved gases. Place the tube in the furnace and gradually heat it along its entire length, beginning at the end nearest the U-tube. The heat must be sufficient to cause a steady evolution of gas; towards the end of the operation it should be increased, to break up any cyanides which may have been formed. Do not heat the extreme end of the tube where the CO_2-mixture is situated until the evolution of the gas has almost ceased. When the combustion is at an end and no more gas bubbles through the bulbs, cautiously heat the CO_2-mixture. This occasions a brisk current of carbon dioxide, which sweeps out all the ammonia remaining in the tube. Remove the U-tube when the evolution of the gas has nearly finished. Transfer the liquid to a beaker, wash out the bulbs, and titrate with standard alkali, employing methyl orange as indicator. If much empyreumatic matter be present in the liquid of the bulbs, pour the solution through a moistened filter and evaporate the filtrate nearly to dryness with excess of platinum tetrachloride. Pour over the pasty mass about 25 ccm. of rectified methylated spirit, impart a gentle rotatory motion to the contents of the

dish in order to facilitate the solution of the excess of platinum tetrachloride in the alcohol, pour the clear liquid through a filter, and repeat the digestion with spirit a third and fourth time. Bring the precipitate on to the filter paper and wash the paper carefully until the filtrate is absolutely colourless. Transfer the double chloride to a weighed platinum crucible and dry it slowly; heat the crucible gently to bright redness, and weigh the residual platinum. 197·2 parts of platinum are equivalent in round numbers to 28 of nitrogen. The amount of the nitrogen cannot be calculated from the weight of the double salt, since it is apt to contain considerable quantities of compounds of platinum with organic bases. These bases, however, contain the same proportion of nitrogen and platinum as the ammonio-platinic chloride. By weighing the amount of platinum left on ignition, the proportion of the nitrogen is therefore readily calculated.

Estimation of Nitrogen by Volume.—This process is applicable to all nitrogenous bodies. The substance is burnt by cupric oxide in a tube from which the air has previously been removed by a current of carbon dioxide or by the aid of a mercury pump. The mixed gases resulting from the combustion are passed over strongly heated metallic copper, which serves to break up any oxides of nitrogen; the remaining gases are collected in a measuring tube containing a strong solution of caustic potash, which absorbs the carbon dioxide: the residual nitrogen is accurately measured,

corrected for temperature, barometric pressure, and tension of aqueous vapour, and from the known weight of a litre of nitrogen under the standard conditions its weight is readily calculated.

To carry out the determination, we require the fol lowing apparatus and materials :—

(*a*) *A piece of strong Combustion Tube, carefully cleaned and dry*, about 24 inches long, sealed and rounded at one end like a test-tube. Sharp edges to be rounded in the blow-pipe, so that a caoutchouc stopper, pierced with one hole, may be introduced without being cut or torn.

(*b*) *Cupric Oxide.*—Strongly heat some clean copper scales in a muffle, and when cold coarsely powder in an iron mortar; pass the powder through a sieve of wire gauze, to separate the fine portions. When a good supply of coarse and fine oxide has accumulated, it is reignited (of course separately) and preserved in *stoppered* bottles.

(*c*) *Metallic Copper;* prepared by reducing some of the coarse granular cupric oxide in a stream of hydrogen.

(*d*) *A substance to evolve Carbon Dioxide.*—The mixture of sodium carbonate and potassium bichromate may be employed for this purpose.

(*e*) *Ignited Asbestos.*—This must be kept in a stoppered bottle.

(*f*) *A Mortar and Pestle.*—An agate mortar is preferred, but one of the usual kind sold for organic

analysis will answer; it should be about 3½ inches in diameter, not too deep, and free from scratches.

(*g*) *A small Glass or Copper Funnel.*—This is for introducing the substance, mixed with fine copper oxide, into the combustion-tube.

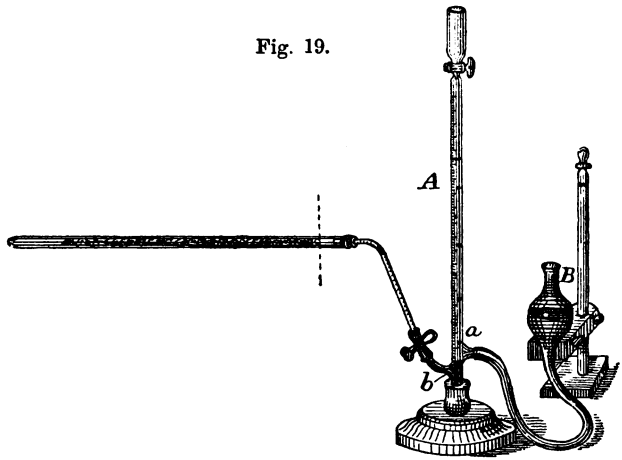
(*h*) *A small Feather.*—This is for brushing out the final particles of copper oxide from the mortar, &c.; the feather is cut down so as to form a moderately stiff brush.

(*i*) *A measuring Tube.*—Various kinds of measuring tubes will be found described in the catalogues of the apparatus dealers. A very useful piece of apparatus for collecting and measuring nitrogen is that of Hugo Schiff, represented in Fig. 19.

The burette A, which is fitted with a glass stop-cock, contains about 100 ccm. down to the side tube *a*, and stands in a wooden foot, which may be rendered more stable by being weighted with lead. At about 1½ inches beneath the side tube *a* is a second tubulus *b*, inclined upwards in the manner seen in the figure. Through this tube mercury is poured to a height of ¼ inch above the lower opening. The vessel B, holding about 150 ccm., is supported by the clamp, and may thus be placed at any desired height; B is connected by strong caoutchouc tubing, previously soaked in melted paraffin, with the side tube *a*. B is filled with a strong solution of caustic potash of sp. gr. 1·5, prepared by dissolving potash in an equal weight of water; its neck is closed by a cork pierced with a small hole.

On closing the tubulus *b* with a piece of thick-walled caoutchouc tube pinched by a brass clip, and on opening the stopcock and raising B, the potash solution

Fig. 19.



flows over into the burette and completely fills it. The stopcock is now closed, and the vessel B is lowered nearly to the foot of the burette; the brass clip may then be removed from *b* without the mercury being forced out.

The Process.—Introduce a layer, about 5 inches long, of the sodium carbonate and bichromate of potash mixture into the combustion-tube. Insert a plug of recently ignited asbestos, pushing it down to within ¼ inch from the mixture, and afterwards add 2 inches of the coarse copper oxide, and then ½ inch of the fine oxide. Weigh out about 0·2 to 0·3 gram of the

nitrogenous substance on to a thin layer of fine copper oxide, contained in the small mortar provided for this purpose, and mix it carefully with an additional quantity of the oxide. Transfer the mixture to the tube, by means of the funnel, without loss, and rinse the mortar and funnel with fresh portions of the fine oxide, adding the rinsings to the tube, employing the feather to brush out final particles. Push down a second plug of asbestos, and then a layer, about 8 inches in length, of coarse copper oxide, and lastly a layer, not less than 4 inches long, of granular metallic copper. Insert another plug of asbestos to keep the copper in position, and introduce the caoutchouc stopper provided with the bent delivery tube.

Heat a portion, say the posterior half, of the carbon-dioxide mixture, and drive out the air within the tube by a brisk current of the gas. At the same time commence to heat the portion of the tube occupied by the metallic copper, including two or three inches of the pure cupric oxide. As soon as the escaping gas is free from air (which is readily ascertained by allowing a quantity to pass into a test-tube filled with potash solution, when no bubble should be left), and the anterior portion of the tube is well heated, the delivery tube of the combustion-tube is then pushed through *b*, and successive portions of the combustion-tube occupied by the mixture of cupric oxide and nitrogenous substance are gradually heated, beginning with the part nearest to the pure copper oxide. As soon as no further

evolution of gas is observed, and the whole length of the tube (with the exception of the part occupied by the undecomposed carbon dioxide mixture) is at a low red heat, heat the remainder, so as to cause an evolution of carbon dioxide, by which the nitrogen still existing in the tube is expelled. Withdraw the delivery tube from the tubulus and close the latter by means of the caoutchouc tube and clip. After allowing the gas to remain over the caustic potash solution for about an hour to absorb the last traces of carbon dioxide, the volume of nitrogen is directly measured, the vessel B being raised until the levels of the potash solution in both pieces of apparatus are coincident. The nitrogen may without sensible error be assumed to be dry. After correcting for temperature and pressure its weight may be calculated: a litre of nitrogen under the standard conditions of temperature and pressure weighs 1·255 gram.

Determination of the Halogens in Organic Compounds.—A narrow piece of combustion-tube about 12 inches long is sealed and rounded at one end like a test-tube. A small quantity of coarsely powdered and recently burnt lime (previously ascertained to be pure) is introduced into it, so as to occupy a length of $2\frac{1}{2}$ inches. The compound to be analysed, if solid, is weighed out into a thin layer of moderately powdered lime contained in a small porcelain mortar. The substance is covered with a little more lime, carefully mixed by means of the pestle, and transferred without loss to the tube; the

mortar and pestle are then rinsed with fresh portions of lime, and the tube is filled with coarsely powdered lime to within two inches from the open end. Before placing the tube in the furnace tap it gently on the table in order to leave a channel for the escaping gases. The tube is placed in a clean trough, and one end of the furnace is so raised that the open end of the combustion-tube is about three inches higher than the closed end: this allows of the ready escape of moisture, &c.

Commence the operation by heating the anterior portion of the tube, and gradually approach the part containing the substance as the lime becomes red hot. Having lighted all the burners beneath it, continue to heat the tube until the whole length is red hot, then push the tube slightly forward so that three or four inches of the open end may cool down. Turn out all the burners, and after a few minutes take the tube from the furnace and plunge it gently, while hot, into a little cold water contained in a moderately thick beaker. The tube cracks and breaks up into small pieces and with ordinary care no loss takes place, nor need any danger be apprehended. Cool down the contents of the beaker and acidify with dilute nitric acid (one part acid, sp. gr. 1·4, to 2 parts water).*

* In the estimation of iodine in organic compounds by the foregoing process, it is necessary to add an excess of sodium or potassium sulphite to the contents of the beaker *before* acidifying with nitric acid. This reduces any *iodate* which would escape precipitation by silver nitrate.

An excess of nitric acid is indicated by the change of colour of the suspended carbonaceous matter. When all the lime is dissolved the precipitate becomes quite black. The liquid is filtered, the residue well washed, and the filtrate treated with silver nitrate solution and the precipitated silver salt, washed, dried, and weighed.

Liquids containing chlorine, &c., are weighed out in bulbs: after the introduction of a layer of lime about 2½ inches long, the bulb is allowed to slide down the tube, which is then filled up with lime. When about half the anterior part of the tube has been heated, expel the liquid from the bulb by gently heating the tube where the bulb is situated, and conduct the remainder of the operation as described.

The combustion of volatile liquids demands great care and attention; the operation must not be hurried, or portions will escape unburnt.

Determination of Sulphur.—Solid substances containing sulphur may be decomposed by fusion with potassium hydroxide and pure potassium nitrate. Place a moderate quantity of pure potassium hydroxide in a silver dish, add about one-fifth of its weight of potassium nitrate, and fuse the mixture. Allow it to cool and add to it the weighed quantity of the sulphur compound. Heat gently, and stir continually with a silver spatula, adding from time to time a small quantity of nitre in order to complete the combustion of the carbon. When the mass is cold, dissolve it in water, acidify with hydrochloric acid, heat to boiling, and precipitate

sulphuric acid with barium chloride in the usual way.

Carius's Method. Applicable to the estimation of Sulphur and Phosphorus in solid and liquid compounds. —From 0·2 gram to 0·3 gram of the substance is weighed out into a thin glass bulb or small test-tube according to the nature of the body dealt with. The bulb or small tube is brought into a tube of hard glass of about $\frac{5}{8}$ of an inch in internal diameter, sealed and rounded at one end like a test-tube, together with from 30 to 60 times its weight of nitric acid of sp. gr. 1·2.

Note.—The tube must not be more than half filled with the liquid. The open end of the tube is now cautiously warmed to expel adhering acid, and then softened in the blow-pipe flame at about an inch from the end; when the softened glass has sufficiently thickened it is drawn out into a thick-walled capillary tube, which is carefully sealed. If the substance is contained in a bulb this may be broken by shaking it smartly against the ends of the tube. Heat the tube to 120–150° for some hours in the air-bath. Allow the bath to cool before withdrawing the tube, wrap it in a towel, and cautiously warm the point so as to expel the liquid which collects in the capillary tube. Soften the end in the blow-pipe flame, the enclosed gases will force their way through the softened glass. Carefully examine the tube, and if you have reason to believe that the oxidation is incomplete, reseal the tube and heat it to 180° for an hour or so. Allow it to

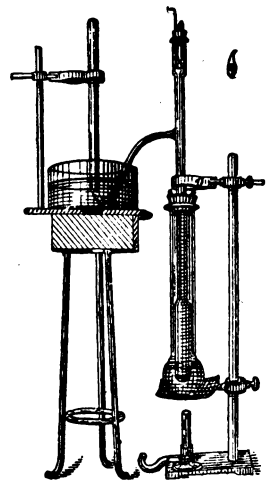
cool, and open with the same precautions as before. If no more gas escapes the operation is finished. Cut off the end of the tube, rinse its contents into a beaker, dilute with water, and, in the case of sulphur, add barium chloride. In the case of phosphorus, add ammonia, ammonium chloride, and magnesia mixture, and convert the precipitate by ignition into magnesium pyrophosphate.

Determination of Molecular Weight.—The most satisfactory determinations are those in which the compound is volatilised at a temperature well above its boiling-point and the specific gravity of its vapour, i. e. its *vapour density* referred to hydrogen as unity. The vapour density when doubled gives the molecular weight in accordance with Avogadro's law.

The various methods for determining the specific gravity of vapours are assumed to have been described in the course on inorganic chemistry, which the student should have followed before beginning the study of organic chemistry. It may, however, here be stated that the method of Victor Meyer, being simpler and more rapid in practice, is now almost universally employed. It involves the use of the apparatus shown in the sketch (Fig. 20). The long glass bulb-tube is corked at the top, near to which point a side tube is sealed, which serves to deliver gas to the measuring tube full of water and standing in the little trough. The bulb-tube is full of air, which is heated to a constant temperature well above the boiling-point of the

substances whose vapour density is to be determined. This is accomplished, in the case of a liquid which boils below 100°, by immersing the bulb-tube in a steam bath obtained by boiling water or other suitable liquid in the large outer vessel. As the air expands on heating, it is allowed to escape without passing into the measuring tube. As soon as the temperature becomes constant, as indicated by no further expansion of the air taking place, the cork is removed from the bulb-tube, a weighed quantity of the substance (0·1 to 0·2 gram) contained in a small bulb or tube is dropped in,* the cork quickly replaced—the time occupied in doing this is so short that no serious error from diffusion arises—and the graduated cylinder filled with water is placed over the orifice of the gas delivery tube. The substance is quickly converted into vapour, which latter expels its *own volume of air* into the measuring vessel. When no more bubbles collect in the graduated cylinder it is removed to a larger

Fig. 20.



* In practice the glass bulb or tube containing the substance is allowed to drop on to a cushion of asbestos or glass wool, arranged at the bottom of the bulb-flask; this avoids risk of fracture.

cylinder filled with water, the internal and external liquids brought to the same level, and after a time the volume of the air (V) read off. The temperature (t), indicated by a thermometer whose bulb is placed about half way up and close to the measuring cylinder, and the height of the barometer (B), are at the same time observed; then if S = weight of substance employed, and w the tension of water vapour at the temperature t, the vapour density of the substance may be found from the following equation:—

$$\text{Vapour density} = \frac{S\ (1 + 0{\cdot}003665\,t) \times 587780}{(B - w)\ V}.$$

This value, when multiplied by 14·47, is the vapour density of the compound in terms of hydrogen.

When the compound is an *acid* and its basicity is known, its silver salt is prepared and the percentage of silver determined in it. If the acid be monobasic, then whatever weight of the compound is united with 108 parts of silver is the molecular weight *less* one atom of hydrogen replaced by silver.

In a similar manner the potassium, sodium, barium, lead, or other salts may be employed.

In the case of basic compounds, such as ethylamine, aniline, &c., either the amount of substance combined with one or more molecules of an acid is determined by analysis, e. g. the hydrochloric acid in the hydrochloride of the base, or the amount of platinum contained in the double salt which many of the hydrochlorides of bases form with platinic chloride.

Determination of Molecular Weight by observation of the depression of Freezing-point. — The method of fixing the molecular formula of a substance by determining its vapour density is only applicable to a comparatively limited extent, as many substances cannot be volatilised without undergoing decomposition. The method of determining this value by the analysis of salts or double salts, as previously explained, is also inapplicable in the case of compounds which have neither acid nor basic properties. In such cases the *probable* molecular formula can only be ascertained by a careful study of the chemical and physical properties of the compound, and a careful investigation of a number of its derivatives. This naturally is not very satisfactory, but till recently no other means was at the disposal of the chemist.

The following method is due to Raoult, and is the outcome of some elaborate investigations on the "Law of the sodification of solvents." *

Raoult has shown that the depression of the freezing point of a solvent, caused by the presence of a liquid or solid in solution, is directly proportional to the amount of substance dissolved, and inversely proportional to its molecular weight.

Thus, let d = depression in degrees C, a = amount in grams of substance of molecular weight M, dissolved in 100 grams of solvent, and R = a constant called the

* 'Annales de Chim'e et de Physique,' 1884-86.

"molecular reduction" (to be determined for each solvent). Then

$$d = \mathrm{R}\frac{a}{\mathrm{M}}.$$

Consequently

$$\mathrm{M} = \frac{\mathrm{R}a}{d}.$$

R may also be calculated from Van't Hoff's equation—

$$d = \frac{0{\cdot}02\,\mathrm{T}}{\mathrm{L}}$$

(where T = freezing-point of solvent on the absolute scale, and L = latent heat of fusion).

In carrying out the operation, any liquid may be used as a solvent provided that it is capable of solidifying at a definite temperature and exerts no chemical action on the substance. It suffices merely to know the value of R for that particular solvent and for certain groups of bodies analogous to the one under experiment.

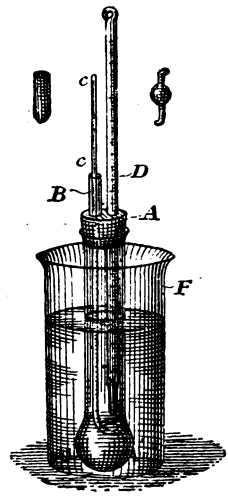
The solvents recommended by Raoult are water, acetic acid, and benzene. The respective values of R for these solvents with organic compounds (with few exceptions) are as follows:—

	R
Water	19
Acetic acid	39
Benzene	49

The accompanying diagram shows a convenient form of apparatus for this operation (Fig. 21).

A large test-tube, widened out at the lower end, is closed by a caoutchouc stopper, A, perforated with two holes. Through one of these a piece of wide glass tubing, B, passes, in which a stirrer, C C, moves freely up and down. The thermometer, D, graduated to $\frac{1}{10}$th of a degree C. and observed through a telescope, serves to show the temperature of the liquid, while, by surrounding the tube with a beaker, F, with ice-water, &c., as required, the temperature may be raised a few degrees above, or depressed a few degrees below, the freezing-point of the solvent.

Fig. 21.



The Process.—A quantity of the solvent sufficient to fill the tube to the extent indicated by the dotted line is weighed out—it suffices to weigh to a tenth of a gram—the caoutchouc stopper, carrying the thermometer and stirrer inserted, and the tube immersed in the outer vessel containing the freezing medium. Near the solidifying point, the column of mercury first sinks slightly, then subsequently a sensible rise takes place; the mercury remains stationary for at least one minute, and then slowly sinks. This highest point of the thermometer Raoult regards as the true solidifying or freezing-point of the solution. During the whole

operation the solution must be kept well agitated by means of the stirrer. After the highest point has been noted, the test-tube is removed from the beaker and the contents completely melted by the aid of the water bath. The tube is again submitted to the freezing medium and the solidification point of the solvent re-determined. The two readings should agree; if not, the operation must be repeated. The contents of the tube are now melted, the caoutchouc stopper momentarily withdrawn, and a weighed quantity of the substance contained in a small tube or bulb introduced (thin glass bulbs of the form shown are readily broken by means of the stirrer). When completely dissolved the freezing point of the solution is determined as before. (It is sometimes necessary to induce solidification by introducing a small crystal of the pure solvent, previously frozen in a separate vessel.)

It will be found that the introduction of the substance has lowered or depressed the freezing-point of the solvent. From this depression we calculate the molecular weight in accordance with the foregoing equation.

Example.—The following results were obtained with naphthalene $C_{10}H_8$, dissolved in glacial acetic acid (R = 39).

Weight of solvent = 101·0 grams. Weight of substance = 1·7865 grams.

Freezing-point of solvent (3 exps.) ..	16°·100
„ „ „ + substance	15°·595
Depres ion =	0°·505

The depression so obtained, calculated for 1 gram substance and 100 grams of solvent, becomes,—

$$\frac{0°\cdot505 \times 1 \times 101}{1\cdot7865 \times 100} = 0°\cdot286,$$

and

$$M = \frac{39\ (= R)}{0°\cdot286} = 136.$$

The true molecular weight of naphthalene is 128. This experiment serves to show the degree of accuracy that may be expected by this method. The results are sufficiently close when the object is merely to control the molecular weight of a substance.

PROGRAMME I.

A STUDY OF OXALIC ACID AND ITS REACTIONS.

Preparation of Oxalic Acid.—Into a 30–40 oz. flask put 100 grams of lump sugar broken into coarse fragments; now introduce half a litre of nitric acid, sp. gr. 1·30; place the flask on wire gauze, and apply a gentle heat until the reaction begins. A small funnel is placed in the neck of the flask to prevent projection of the acid by spirting. As soon as the reaction commences withdraw the flame, when the oxidation will proceed with some violence, accompanied by a copious evolution of red fumes. It is occasionally necessary to plunge the flask into cold water to moderate the reaction. The operation must be conducted under a hood, or in some situation where the fumes can cause no inconvenience. After the reaction has somewhat slackened, apply a small flame and continue to heat gently for an hour or so, then set aside in a cool place to crystallise. After standing some time, crystals will separate out. These are to be collected on a funnel plugged with a small glass stopper, allowed to drain, and washed once or twice with a *small* quantity of cold water, to remove most of the adhering nitric acid.

The acid mother-liquor will furnish another crop of

crystals on careful evaporation. Recrystallise from water the acid thus obtained. After draining well in the funnel, transfer to a pad of filter paper. When the greater portion of the moisture has been removed, the acid is wrapped in a fresh sheet of dry paper, and placed under a moderately heavy weight for a few hours.

With the pure substance the following experiments have to be performed :—(*a*) Dissolve a few crystals in water, and test the solution with red and blue litmus paper. (*b*) Add a crystal or two of sodium carbonate. (*c*) Heat some in a small test tube with strong sulphuric acid, and prove that both oxides of carbon are formed. (*d*) Add a few drops of ammonia, and then a solution of calcium chloride.

The foregoing tests will suffice to show the identity of the substance produced by the oxidation of sugar, with the oxalic acid of commerce. Oxalic acid can be obtained by the action of nitric acid on many organic substances, such as starch, cellulose, &c. On the commercial scale it is manufactured by heating wood shavings or sawdust with potassium or sodium hydroxide to about 250°. The resulting mass is extracted with water, which on evaporation to crystallisation gives the potassium or sodium salt of the acid.

Sublimation of Oxalic Acid.—Commercial oxalic acid very often contains mineral matter; this results from its mode of preparation. Now the acid, when heated to a sufficiently high temperature, sublimes, and ad-

vantage is often taken of this fact to obtain a sample of the pure substance. The method of carrying out this operation on a small scale will readily appear from p. 13 (Operations). The acid must be previously dried by heating in the water-oven for some time. Oxalic acid sublimes without decomposition at 150–160° C.

Determination of Water of Crystallisation.—Crystallised oxalic acid contains water of crystallisation, which it loses when maintained at 100° C. for some time. Procure two medium sized watch-glasses with ground edges; they must be of the same diameter, and when placed one over the other should fit perfectly; they are kept in position by a brass clip. Carefully clean the glasses and clip and weigh them, then, keeping the clip on the balance pan, weigh into one of the glasses about 1·0 gram of oxalic acid, transfer to the water-oven, and so arrange matters that the watch-glass containing the acid is loosely covered with its fellow. (The brass clip is kept in the desiccator.) After heating for an hour or so, remove from the oven, clamp together by means of the clip, and allow to cool down in the desiccator; when cold, weigh. The foregoing operation must be repeated until the acid no longer loses weight, or until the weighings do not differ more than half a milligram. Calculate the percentage of loss.

Preparation of Potassium Salt.—To about 30 grams of oxalic acid dissolved in water add a solution of potassium carbonate until the acid is neutralised; filter

if necessary, and evaporate to crystallisation; drain off mother-liquor and recrystallise. Collect the crystals in a stoppered funnel, drain, and dry between folds of filter paper. With the resulting salt determine water of crystallisation and potassium.

To determine the Potassium:—Weigh off about 1·0 gram of the crystallised salt into a platinum crucible. Place the crucible on a triangle in a slanting position, and add a *few* drops of strong sulphuric acid; cautiously decompose by the *gradual* application of heat, great care being taken that no loss takes place by spirting. The crucible is finally ignited over a Bunsen burner to low redness, and the resulting potassium sulphate weighed. The crucible is again ignited, and so on until a constant weight is obtained. Calculate the percentage of potassium in the crystallised salt. Calculate also the equivalent of acid (carbon and oxygen) in the anhydrous salt.

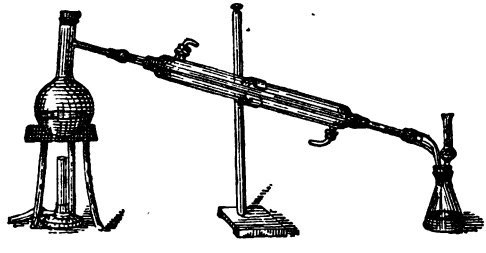
Preparation of the Calcium Salt.—Dissolve about 10 grams of oxalic acid in water, neutralise with a little ammonia, and then add a solution of calcium chloride, collect the precipitate on a filter and wash with cold water until the washings are free from chlorine. Dry at 110°, and determine the calcium as sulphate. This operation is conducted as in the foregoing potassium salt. Calculate the percentage of calcium, and the amount of acid (carbon and oxygen) combined with very often ts of the metal.

its mode o*tion of Ammonium Salt.*—Neutralise about to a sufficien oxalic acid with ammonium hydroxide,

evaporate to crystallisation, and determine the ammonia in a sample of the salt carefully dried between filter paper.

To determine the Ammonia:—Weigh off 0·2–0·3 gram into a small Wurtz flask furnished with a caoutchouc stopper, wash down the sides of the flask with a little water, and connect with the condensing arrangement shown in Fig. 22. The flask, of about 200 ccm. capacity, and connected air-tight with the condenser, contains 50 ccm. of standard $\frac{N}{10}$ sulphuric or nitric acid. The flask also carries the small upright tube, containing fragments of broken glass moistened

Fig. 22.



with water or a few ccm. of the standard acid. When matters are properly arranged, the caoutchouc stopper is removed from the Wurtz flask, and a small fragment (about half an inch) of solid caustic potash added; the stopper is quickly replaced, and the contents submitted to careful distillation. After about half an hour, disconnect the apparatus, wash down the condenser

and side tube into the flask, and proceed to titrate with standard alkali.

During the preparation and analysis of the foregoing salts, the necessary apparatus for estimating the carbon and hydrogen in the oxalic acid may be got ready. See Analysis, p. 21.

In particular cases a modification of the programme may be here introduced. The oxalic acid can be titrated by a standard solution of potassium permanganate. From the information gained in the analysis of the potassium, calcium, and ammonium salts, it will readily appear that one atom of oxygen suffices to oxidise one molecule of oxalic acid completely into carbon dioxide and water—

$$C_2H_2O_4 + O = 2CO_2 + H_2O.$$

A standard solution of potassium permanganate is to be prepared, and its value determined by the usual methods. About 0·2 gram of the pure crystallised acid is dissolved in a little water, a few ccm. of dilute sulphuric acid added, and the permanganate run into the solution (warmed up to 60° C.) until a slight permanent tint is developed.

Knowing the amount of oxygen available from each ccm. of the permanganate, calculate from your experiments the quantity of oxygen required for 100 parts of the acid. Compare the experimental numbers with those demanded by the foregoing equation.

Note.—The water of crystallisation in the crystallised

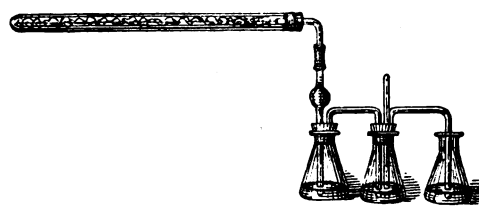
acid is not represented in the equation, as it is not concerned in the oxidation, but it must be taken into account in the calculations.

With the standard permanganate we may estimate the acid (and also the base) in the *salts* of oxalic acid. A weighed quantity of the salt is digested with dilute sulphuric acid, and titrated with the permanganate. Determine the amount of acid and base in the foregoing potassium and calcium salts. The details of the calculations need no explanation.

Synthesis of Oxalic Acid from Cyanogen:—

A. *Formation of Oxamide.*—Into a hard glass tube, about 8 inches long by ½ inch wide, sealed and rounded at one end like a test tube, introduce a sufficient quantity

Fig. 23.



of mercuric cyanide * to occupy three-fourths of the length of the tube. The cyanide is kept in position by a loosely-fitting plug of asbestos. Fit in a cork and connect up with glass tube, as in Fig. 23. The three

* Instead of mercuric cyanide, a mixture of two parts of thoroughly dried potassium ferrocyanide and three of mercuric chloride may be employed.

small flasks contain strong hydrochloric acid. Gently tap the tube on the table so as to make a passage for the evolved gases. Place the tube in a small furnace, and gradually heat it along its entire length, beginning at the end nearest the flasks. The heat must be sufficient to cause a steady evolution of gas, which bubbles through the acid in the flasks.

$$Hg(CN)_2 = Hg + (CN)_2.$$

When the evolution of gas is finished, the apparatus is disconnected at A (note the residue in the tube), and the flasks allowed to stand in a cool place for a few hours. A beautiful white crystaline compound will gradually separate out. This substance is called "Oxamide," and its formation from cyanogen may be expressed by the following equation:—

$$C_2N_2 + 2H_2O = C_2O_2(NH_2)_2.$$

Pour off the acid and wash the oxamide on a filter with cold water until free from acid. Dry in the air-oven. With portions of the product thus obtained make the following experiments. (*a*) Examine the substance for carbon, hydrogen, and nitrogen. (*b*) Test its solubility in water and alcohol. (*c*) Ascertain what happens when heated. Determine quantitatively the carbon, hydrogen, and nitrogen in a sample of the oxamide.

B. *Conversion of Oxamide into Oxalic Acid.*—Place some oxamide in a small flask with a little water; heat, and add a few drops of potassium hydroxide.—

What gas is given off? When the oxamide has dissolved, evaporate the solution to crystallisation, and compare the crystals by the aid of a powerful lens or microscope with those obtained by adding potassium carbonate to oxalic acid (p. 57).

On applying the usual tests for an oxalate, the product obtained by the action of potash on oxamide will be found to be identical with ordinary potassium oxalate.

The conversion of oxamide into ammonium oxalate may also be effected by heating with water in a sealed tube to 200° C.

$$C_2O_2(NH_2)_2 + 2H_2O = C_2O_4(NH_4)_2.$$

Preparation of Ethyl Oxalate $C_2O_4(C_2H_5)_2$.—Method I. —Mix 80 ccm. of strong alcohol with 80 ccm. of concentrated sulphuric acid, employing for this operation the apparatus described on page 77. When cold, pour on to 40 grams of potassium oxalate contained in a Wurtz flask attached to a condenser; mix well, and distil over about one-third; return this to the distilling flask and again distil, changing the receiver when about one-third has distilled over. The distillation must be pushed almost to dryness. The first distillate consists of water, alcohol, and a small quantity of ethyl oxalate. To this solution add a little concentrated aqueous ammonia, when oxamide will separate out in the form of a white crystalline powder.

$$C_2O_4(C_2H_5)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2C_2H_5OH.$$

The second part of the distillate is washed with a little water containing a small quantity of sodium carbonate to remove acid, separated from the aqueous liquid, dried over $CaCl_2$, and distilled from a small Wurtz flask furnished with a thermometer. Pure ethyl oxalate boils at 186°; sp. gr., 1·082.

Method II.—To about 50 ccm. of absolute alcohol add 30 grams of oxalic acid dehydrated at 100°; warm gently so as to dissolve most of the acid, and into the warm solution pass a current of dry hydrogen chloride. The operation is most conveniently conducted in a tubulated retort to the neck of which is attached a reflux condenser. When the oxalic acid has disappeared, continue to pass the gas for some time and then allow the mixture to stand for some hours. Rearrange the apparatus for distillation and distil off (from a water bath) about a third of the volume. This portion, when treated with ammonia, will furnish a small quantity of oxamide. The residue in the retort is poured into water containing a little sodium carbonate, when the ethyl oxalate will separate out in oily droplets, which can be separated from the aqueous liquid and dried over calcium chloride, or may be converted into oxamide by treatment with ammonia.

Note.—The samples of oxamide accumulating in the preparation of ethyl oxalate must be carefully examined and compared with the specimen prepared by the action of hydrochloric acid on cyanogen.

Action of Phosphorus Pentoxide on Oxamide.—Place

two or three grams of dry oxamide in a test tube fitted with a cork and delivery tube; cover the oxamide with a thick layer of P_2O_5; heat gently, and collect the gas given off in a small test-tube over mercury. The gas is inflammable, burning with a purple flame which will be recognised as cyanogen.

Note to Student.—What change has the phosphoric anhydride effected?

Preparation of Formic Acid, H–COOH.—100 grams of ordinary crystallised oxalic acid and 100 grams of commercial glycerol (glycerine) dehydrated at 175° C. are heated in a retort of 1½ litre capacity, placed in a brine bath, and provided with condenser and receiver. At about 80° to 90° a brisk reaction begins, carbon dioxide is evolved, and aqueous formic acid distils. When the temperature has been maintained for some time at 90° to 105° and the evolution of carbonic anhydride has nearly ceased, the contents of the retort are cooled to almost 80° and a further quantity of 100 grams of oxalic acid added. The reaction recommences with the formation of more aqueous formic acid. A quantity of formic acid remains in the retort as glycerol monoformin.

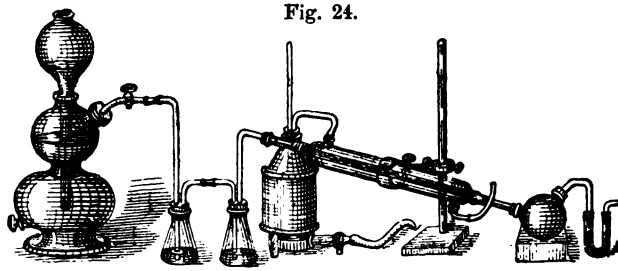
$$C_3H_5(OH)_3 + C_2H_2O_4 = \underset{\text{Glycerol monoformin}}{C_3H_5\overset{(OH)_2}{O.CO.H}} + CO_2 + H_2O.$$

In order to recover this formic acid, the contents of the retort are diluted with about half a litre of hot water

and distilled in a brisk current of steam until the distillate has only a faintly acid reaction.

$$C_3H_5\begin{matrix}(OH)_2\\O.COH\end{matrix} + H_2O = \underset{\text{Formic acid}}{H\text{–}COOH} + C_3H_5(OH)_3.$$

Fig. 24.



On neutralising the united acid distillates by boiling with excess of copper carbonate and concentrating the filtered solution, the copper salt of formic acid is obtained in large bright blue monoclinic prisms. From the salt we may obtain the anhydrous acid by decomposing with sulphuretted hydrogen. A portion of the powdered salt, well dried at 100–110°, is introduced in a long layer into the inner tube (as wide in the bore as possible) of a condenser loosely stoppered at the lower end by a plug of glass-wool or asbestos. To the end of the condenser a receiver is attached, which is guarded from moisture by a drying tube. The salt is heated by passing steam into the outer tube of the condenser. Sulphuretted hydrogen, washed and dried by passing first through water and then concentrated sulphuric acid, is passed over the salt in not too rapid

a stream. The arrangement of the apparatus is shown in Fig. 24. The copper formate blackens and is slowly converted into copper sulphide and formic acid, the latter flowing down into the receiver. The acid, which retains a strong smell of SH_2, is further purified by a second distillation over dry copper formate.

Formic acid when pure boils at 99° C.; it has the specific gravity 1·223 at 0°, and solidifies below 0° C. to colourless plates, melting at 8°·6 C.

PROGRAMME II.

ETHYL ALCOHOL AND ITS REACTIONS.

Preparation of Alcohol from Malt.—Procure about two quarts of recently crushed and freshly *malted* barley, and mix with about 50 grams of powdered starch. Stir up this mixture with cold water in a large evaporating dish until a thin cream is formed. Now place the dish on a sand-bath and apply a gentle heat, which is to be so regulated that a temperature of 65–70° C. may be maintained for some time. Withdraw a few drops of the extract at intervals by means of a pipette, and test with a dilute solution of iodine.

Note that the colour produced changes as the heating proceeds until the liquid no longer causes a blue tint with iodine, and only affords a reddish brown colouration. The *diastase* present in the malt, has converted the starch into dextrine and a fermentable sugar termed *maltose*,

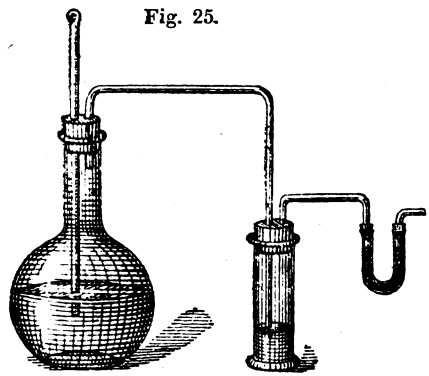
$$3C_6H_{10}O_5 + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrine.}}{C_6H_{10}O_5}.$$

When this conversion is complete, the solution is no longer coloured by iodine; but a few drops when

warmed with alkaline copper tartrate solution* cause a precipitate of cuprous oxide, Cu_2O. (Fehling's test.)

The solution in the basin ("sweet wort") is now strained off, the filtrate being received in a large flask. When the contents of the flask have cooled down to 30° C. add a little fresh brewer's yeast or "barm," and mix thoroughly. Fit a cork, carrying a thermometer and a gas delivery tube, to the flask, and let the tube dip under the surface of some clear lime water contained in a cylinder, and protect the latter from the

Fig. 25.



air by means of a tube containing caustic potash (Fig. 25). Let the whole stand in a warm place so that the contents of the flask may be maintained at a temperature of about 25° C.

* Prepared by adding tartaric acid to a solution of copper sulphate and rendering strongly alkaline by caustic soda. A clear blue solution is obtained if sufficient tartaric acid be added.

After some time the process of fermentation commences, the mixture develops a frothy "head," and much gas is evolved, and, as this passes through the lime water, a precipitate of calcium carbonate will be formed.

The evolution of gas ceases after some hours, and fermentation is at an end. Now, observe that the contents of the flask are rather more turbid than they were at first; in other words, the quantity of yeast has *increased* during the process of fermentation.

Connect the flask which contains the fermented liquid with a condenser, and rapidly distil over about one-third the total volume of liquid. The unpleasant smelling distillate contains the alcohol formed during the process of fermentation.

The dilute spirit obtained in this experiment may be concentrated by redistillation. Place the distillate obtained as above in a small flask, add a few drops of caustic potash (to neutralise any acid formed during fermentation), and distil over quickly about half the total volume of liquid.

In order to detect the alcohol, warm a small quantity of the distillate in a test tube and apply a light to the escaping vapour. To about 30 ccm. of the distillate add 4 or 5 drops of a dilute solution of potassium bichromate and then a few drops of sulphuric acid, and warm gently. Note appearance and odour produced. (See "Preparation of Aldehyde," p. 85).

A good way to detect alcohol in a dilute solution is

as follows:—Warm the solution to be tested, add a small crystal of iodine and then a solution of caustic potash until the colour is destroyed. On cooling a yellow crystalline powder of iodoform, CHI_3, is deposited, having a very characteristic appearance and odour.

The production of alcohol and carbon dioxide from maltose during fermentation may be represented as follows:—

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

Purification of Alcohol.

The dilute spirit prepared in the foregoing experiment owes its unpleasant smell to a small proportion of a liquid termed "fusel oil"; it also contains many other impurities. The quantity of alcohol obtained is usually too small to attempt a complete purification; it may, however, be shaken up with a little recently ignited charcoal, decanted off, allowed to stand over quicklime, and then distilled from a water-bath. By this treatment it will be found to have lost much of its bad odour and to have increased in strength. This latter can be tested by taking its specific gravity and reference to tables.

Separation of Water from Alcohol by Fractional Distillation.—Mix 100 ccm. of strong alcohol, of known

specific gravity and boiling point, with 100 ccm. of distilled water.

Note to Student.—What happens when the liquids are mixed? Determine the specific gravity of the mixture by means of the "gravity bottle" and, employing a dephlegmating apparatus, proceed to fractionally distil, carrying out the operation as indicated on p. 9.

Measure the various fractions obtained, and determine the percentage of alcohol in the principal ones. The strongest spirit obtained by fractional distillation still contains 8–10 per cent. of water. To obtain a stronger spirit the principal fractions are poured into a flask containing small lumps of fresh quicklime and allowed to stand over the lime for about 24 hours; the dehydrated liquid is then distilled off with the aid of a water-bath. The first few ccm. are collected apart; the rest of the liquid which distils over may then be preserved as a specimen of nearly anhydrous (its specific gravity should be recorded on the label) alcohol.

Purification of Methylated Spirit.—This useful substance is a mixture of about 90 parts ethyl alcohol and 10 parts crude methyl alcohol (wood spirit); in addition it contains water, "fusel oil," acetaldehyde and acetone. It may be freed from aldehyde and acetone by boiling with 4–5 per cent. of solid potash on the water-bath in a flask fitted with an upright condenser for an hour or two, and then distilling. The alkali converts the aldehyde and acetone into resinous bodies, so that after distilla-

tion it contains little besides methyl and ethyl alcohols. The spirit may be dehydrated by allowing it to stand over quicklime for 24 hours and then distilling. By repeated treatment with good quicklime, and subsequent distillation, all but a trace of water may be removed; such spirit is said to be "absolute." Methylated spirit, purified as described, may generally replace the more expensive ethyl alcohol as a solvent.

The presence of water in alcohol may be shown by agitating a sample with a little *anhydrous* copper sulphate, when the salt will become blue if a notable quantity of water be present.

A more delicate test is to add a crystal of potassium permanganate; the formation of a pink colouration indicates water.

It may here be added that an excellent process for the complete dehydration of alcohol consists in allowing the spirit, after distilling from lime, to stand over some anhydrous oxide of barium (BaO) contained in a stoppered bottle; after the latter has removed all the water, the dry alcohol then dissolves some of the oxide, the solution acquiring a yellow colour; it is then distilled.

Note to Student.—Great care has to be exercised in the selection of a dehydrant. Many substances having an affinity for water cannot be used for drying alcohol; zinc chloride, calcium chloride, &c., are not suitable, inasmuch as they either combine to form alcoholates or effect decomposition.

Separation of Fusel Oil from Ethyl Alcohol.—Redistil from a Wurtz flask fitted with a thermometer, about 200 ccm. of the purified "absolute" methylated spirit which you have prepared in a former operation. Mix 150 ccm. of the distillate, which will be found to boil near 80° C., and for the purpose of this experiment may be regarded as ethyl alcohol, with 50 ccm. of "fusel oil," or amyl alcohol, of which you have previously determined the boiling point (it will lie somewhere near 130° C.) Pour the mixture into a flask of 400 or 500 ccm. capacity, introduce a few pieces of broken tobacco pipe or scrap platinum foil (to prevent "bumping"), insert cork with fractionating column and thermometer, and proceed to fractionate, employing a small "rose" burner, and so regulate the flame that steady and continuous, but not violent, ebullition shall be maintained. Collect in bottles or flasks having blank labels, three or four fractions of about 50 ccm. each, marking them "No. 1 fraction," &c. Be careful to record temperatures. The degree of separation effected by the distillation can be roughly tested by treating the various fractions with water. Put about 5 ccm. of each fraction into separate test tubes, add about 25 ccm. of water to each, and mix thoroughly. State in note-book the result of each experiment.

Determination of Alcohol by Distillation.—Into a *tared* flask which can be connected air-tight to a condenser, *weigh* about 50 grams of the sample to be tested (beer,

wine, &c.), neutralise any free acid by cautious addition of sodium hydroxide solution, sufficient being added to impart a slightly alkaline reaction. Now add about 0·1 gram tannin (to prevent frothing) and make up the liquid with water to about 150 ccm. Connect flask to condenser, and distil by a gentle heat, collecting the

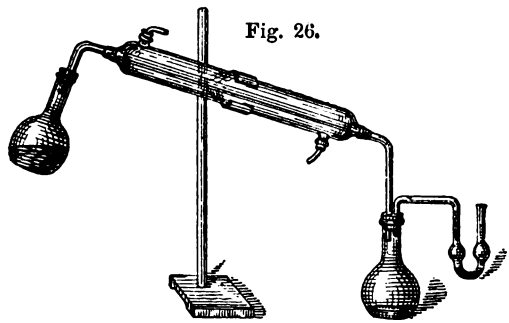


Fig. 26.

distillate in a *tared* flask of about 150 ccm. capacity, furnished with an india-rubber stopper pierced with two holes through one of which passes the end of the condensing tube, while the other carries a safety tube or funnel, closed by mercury (see Fig. 26). The retort and receiver are thus connected air-tight with the condenser, a certain contraction and expansion of the contained air is permitted, while all loss is prevented. When the distillate has a volume of about 100 ccm. the operation is arrested, and the receiver with its contents carefully weighed. Now thoroughly mix the contents, cool to 15°·5 C. (= 60° F.), and determine

the density by specific gravity bottle. Refer to alcohol tables for corresponding percentage of alcohol, when

$$\frac{\text{Weight of distillate} \times \text{percentage of alcohol found in distillate by table}}{\text{Weight of sample taken.}}$$

= percentage of absolute alcohol by weight contained in *the sample.*

Action of Reagents on Alcohol.

Action of Sodium.

Preparation of Sodium Ethylate, C_2H_5ONa.—Into a small flask containing about 10 ccm. of absolute alcohol throw a small pellet of clean sodium (note what happens), continue the addition of sodium until it no longer dissolves. (What gas is given off?) Apply gentle heat to effect solution of last particle of metal and distil off excess of alcohol. When dry, heat gently in a current of hydrogen, and preserve in a stoppered bottle.

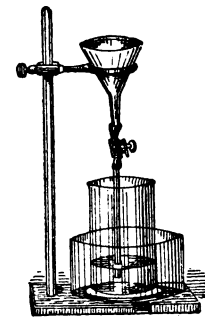
Note.—Potassium acts on alcohol in the same way as sodium.

Action of Sulphuric Acid at different Temperatures.

Preparation of Potassium Ethyl Sulphate, $C_2H_5KSO_4$. —To 200 grams conc. sulphuric acid, contained in a beaker or small earthenware jar, add slowly 250 grams commercial absolute alcohol. A reference to Fig. 27 will show how this operation is to be conducted.

The alcohol is contained in the funnel, which is connected to a piece of glass tube by means of india-rubber tube having a screw-clip, by which the flow of spirit can be regulated. The sulphuric acid is contained in the beaker, which in its turn stands on a pad of paper, the whole standing in an outer vessel in case of an accident. The manner in which the glass tube is connected to the funnel allows of a stirring motion during the addition of the alcohol. It is unnecessary to cool the beaker, but care must be taken that the end of the glass tube dips well beneath the surface of the sulphuric acid. During the mixing the temperature rises to 80–90°. After all the alcohol is added, heat the mixture for an hour on the water-bath, and then allow to stand a few hours. Pour the cold liquid into some water contained in a pan, and add chalk ground into a thin paste with water until all acid is neutralised. It is now filtered and the filtrate, after the *addition of lime water* until slightly alkaline, is concentrated on the water-bath. When somewhat evaporated a concentrated solution of potassium carbonate is added until the calcium is all precipitated. The soluble potassium salt of ethyl sulphate is formed and the solution, after filtering from the precipitated calcium carbonate, can be concentrated over

Fig. 27.



the water-bath until crystallisation begins. By slowly concentrating the liquid, a well-crystallised product may be obtained.

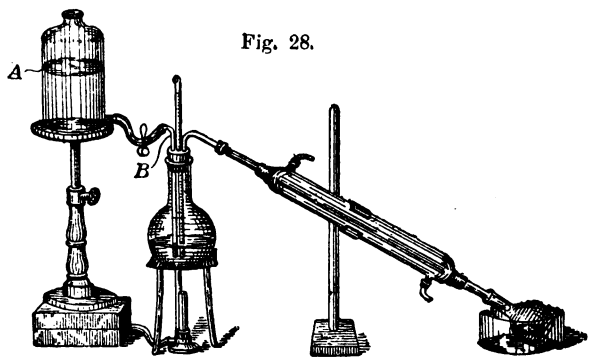
The product is collected on a funnel fitted with filter and parchment-cone. After draining thoroughly it is wrapped in drying paper and allowed to dry on a porous tile. Weigh the product obtained, and test its solubility in water and alcohol.

Note to Student.—Write out all reactions involved in the preparation of this salt.

Preparation of Ethyl Ether, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$. (Action of sulphuric acid at about 140° C.)

Mix 100 grams 90 per cent. alcohol with 180 grams

Fig. 28.



conc. sulphuric acid, employing funnel, clip, &c., as in foregoing experiment. Allow mixture to cool down.

Arrange an apparatus as shown in Fig. 28. The

flask containing the mixture is closed with a cork pierced with three holes; through one of these holes a thermometer is inserted and dips into the liquid; through the second a tube is fitted which reaches beneath the surface of the mixture, and is connected at its upper end with a vessel containing alcohol. A bent tube passing through the third hole connects the flask with a long condenser and receiver, both of which must be kept well cooled during the experiment. Commence the operation by heating the mixture, (this must be done cautiously, the flask standing on one or two plates of wire gauze), until the thermometer indicates 140°. At this point the mixture boils, and ether begins to distil over. As soon as this is noticed cautiously open the stop-cock of the vessel A, and let a slow stream of alcohol pass into the distilling flask through the tube B. Regulate this stream so that the temperature remains constant at 140–145°. In this way the operation can be kept up for a considerable time, the alcohol admitted to the flask passing out as ether, and being collected together with some alcohol in the receiver. After about half a litre has been collected, stop the operation. *Note.*—The mixture in the distilling flask is to be kept in a stoppered bottle; it will be useful in subsequent experiments.

Pour the distillate into a stoppered separating-funnel and shake up with a dilute solution of sodium hydroxide. The ether will rise to the surface, and the aqueous portion may be run off. It should now be

shaken up a few times with water, separated, and allowed to stand over fused calcium chloride, poured off into a dry flask fitted with a thermometer, and distilled over a water-bath. Note the temperature.

The ether thus purified still contains traces of alcohol and water, which it obstinately retains. To further purify the ether, it is digested in the cold for some time with fresh metallic sodium, cut into thin slices (*pure* ether has no action upon sodium). When the sodium has no further action, the ether is distilled off over the water-bath.

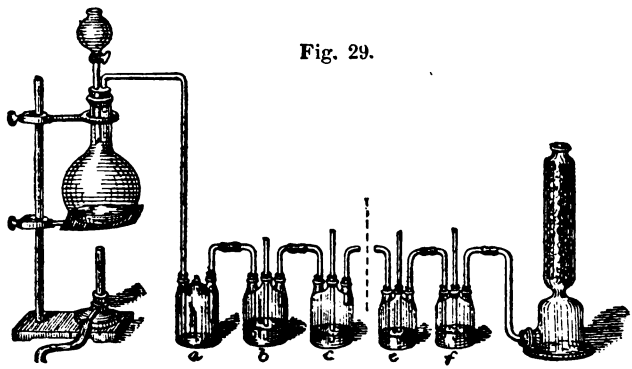
N.B.—*Great care must be taken when working with ether. Never distil directly over a flame; always use a water-bath, and do not heat the water to boiling. Carefully avoid the neighbourhood of flames.*

Preparation of Ethylene Dibromide, $\left\{\begin{matrix}CH_2Br\\CH_2Br\end{matrix}\right.$ (Action of sulphuric acid on alcohol at about 160–180°).

Into a flask of 2 to 3 litres capacity put a mixture of 25 grams alcohol (strong methylated spirit may be substituted), and 150 grams concentrated sulphuric acid. Heat on a sand-bath or wire gauze until ethylene is evolved in a steady stream. Now add gradually through a tap-funnel a mixture of one part alcohol and two parts concentrated sulphuric acid at such a speed that the evolution of gas continues without interruption, and at the same time without causing the contents of the flask to froth up too violently. The gas is purified from alcohol, ether, sulphurous acid, and carbon dioxide,

by conducting it through a series of Woulfe's bottles fitted with safety tubes, and connected with the generating flask (Fig. 29). The first of these bottles (*a*) is empty, the second (*b*) contains concentrated sulphuric acid, the third (*c*) and fourth (*d*)—not shown in

Fig. 29.



the sketch—dilute caustic soda solution. Thus purified, the ethylene passes into two smaller bottles (*e*) and (*f*), containing bromine covered with a layer of water. The last bromine bottle is connected with an arrangement for absorbing bromine vapours. This is half filled with pieces of broken brick (moistened with soda solution), and then filled up with lumps of common washing soda.

The corks of the bromine bottles must be well soaked in melted paraffin before use, to protect them from the action of bromine vapour. The bromine bottles are cooled, if necessary, in cold water.

Continue to pass the gas until the bromine is decolourised and converted into ethylene dibromide, then remove and shake up with dilute caustic soda solution. After washing with water to remove soda solution, separate the aqueous portion as far as possible by means of the separating-funnel and dehydrate over calcium chloride. After decanting from the calcium chloride the product is rectified.

Note.—The student should have a measured quantity of bromine given to him, and must state in his note book the yield of ethylene dibromide obtained.

Action of Hydrochloric Acid on Alcohol.

Preparation of Ethyl Chloride, C_2H_5Cl (affording practice in the preparation and isolation of a substance gaseous at ordinary temperatures).

Into a small retort, which is connected to a reflux condenser (Fig. 30), introduce 50 ccm. of absolute alcohol and about 20 grams of fused zinc chloride. Now pass a rapid current of dry hydrogen chloride into the alcohol, which is at first kept cool by cold water. A large volume of the gas is absorbed. When nearly saturated the contents of the retort are gently warmed, the current of hydrochloric still maintained, and the ethyl chloride which is given off, together with hydrochloric acid, led through the reflux condenser, where any alcohol vapour is condensed. The ethyl chloride is freed from acid by passing through one or two wash

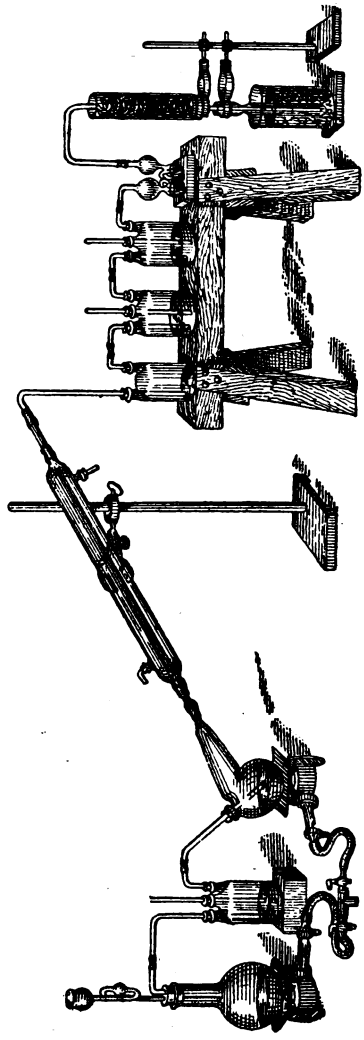


Fig. 30.

bottles containing *dilute* caustic soda solution, and afterwards dried by bubbling through strong sulphuric acid, conveniently contained in a set of Geissler bulbs. It is now condensed by passing through the spiral condenser containing ice and salt, and is finally led nearly to the bottom of a piece of moderately broad tube, sealed at one end and constricted at the upper part in the manner shown in the sketch. This tube is also kept in a freezing-mixture of ice and salt. When the tube is about half full of ethyl chloride, the narrow leading tube is withdrawn, and the tube carefully sealed up at the constricted part. It is advisable to keep the tube in the freezing-mixture as much as possible during the process of sealing. When properly sealed the tube may be preserved as a specimen in a box containing cotton wool.

Ethyl chloride boils at 12° C.

When a specimen has been obtained in the manner indicated, the operation should be continued, and the following experiments made:—(*a*) Collect a little ethyl chloride in a narrow test-tube, remove from freezing-mixture, and apply a light to the mouth of the test-tube; note colour of the flame, and bring a rod moistened with ammonia close to the burning gas. This experiment will serve to demonstrate the presence of chlorine in the substance. (*b*) To an aqueous solution of ethyl chloride (it is sparingly soluble in water) add a few drops of silver nitrate; no turbidity is produced if the ethyl chloride is pure.

Note.—The alcoholic residue in the retort may be preserved in a stoppered bottle, and used again when needed.

Preparation of Ethyl Bromide.—Dilute 17 ccm. of strong sulphuric acid with 10 ccm. of water, and cool thoroughly: add this to 20 ccm. of strong alcohol contained in a flask of 200 ccm. capacity. Shake contents of flask, and when cold add 16 grams of powdered potassium bromide; connect flask to condenser, and distil carefully from a sand-bath. Ethyl bromide passes over along with some water. Frothing takes place at the end of the operation, but this does not give trouble if a flask of sufficient size be employed.

The ethyl bromide is formed in accordance with the equation—

$$H_2SO_4 + KBr + C_2H_5OH = C_2H_5Br + KHSO_4 + H_2O.$$

Wash the ethyl bromide with dilute soda solution, dry over calcium chloride, and rectify from a dry flask over the water bath, noting the temperature.

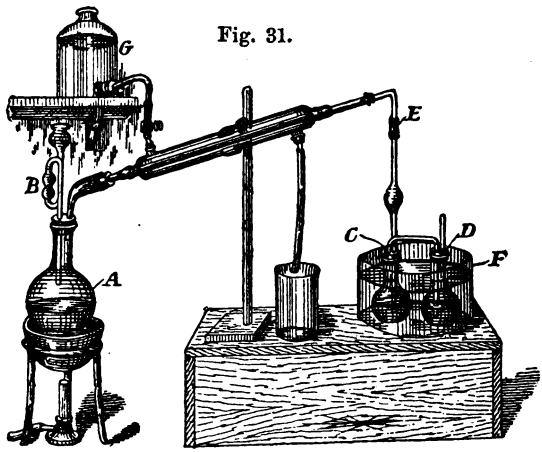
Note to Student.—Weigh the resulting ethyl bromide and see if the yield corresponds to that demanded by the above equation.

Action of Oxidising Agents on Alcohol.

Preparation of Acetaldehyde, CH_3–COH.—Arrange an apparatus as shown in Fig. 31. Into the flask A, which must have a capacity of 1½ to 2 litres, put

120 grams granulated potassium bichromate (made by dissolving the salt in a little hot water and evaporating to dryness with constant stirring). Make a mixture of 160 grams conc. sulphuric acid, 480 grams water, and

Fig. 31.



120 grams alcohol (methylated spirit). Cool the mixture down to the ordinary temperature, and then pour it slowly through the funnel-tube B into the flask containing the potassium bichromate. The flask stands in a water-bath containing cold water. The flasks C and D are half filled with ordinary ether; they are placed in an outer vessel F containing ice water. A considerable evolution of heat occurs, the liquid becomes green, and water, alcohol, and aldehyde distil over into the receiver. By conducting the vapours through the inverted

condenser, which is maintained at a temperature of 25–30°, most of the alcohol and water condense, while the aldehyde (B.P. 21°) passes over and is absorbed by the ether. The reaction is assisted by gently warming the flask, and when completed the apparatus is detached at E, and connection is made with an apparatus furnishing *dry* ammonia gas. The gas is passed into the cold ethereal solution of aldehyde to the point of saturation. The aldehyde separates out in the form of a beautifully white crystalline deposit of aldehyde-ammonia. It is separated from the mother-liquor by draining well on the filter-pump, washed with ether, and finally dried on bibulous paper over calcium chloride. From this compound the aldehyde may be isolated by dissolving in a little water, adding dilute sulphuric acid (1½ parts of acid to 2 parts of water), and distilling on the water-bath, the receiver being kept cool with ice. The distillate is dehydrated over coarse calcium chloride, poured off into some fresh calcium chloride and distilled from the same, the temperature of the water bath being about 30°. The anhydrous acetaldehyde is kept in sealed tubes.

Experiments with Aldehyde.—After a sample of anhydrous aldehyde has been secured in the manner indicated, the following experiments may be performed with it and its solution in water.

(*a*) Add a few drops to solution of ammoniacal nitrate of silver, in a test-tube, and heat. The tube becomes coated internally with a beautiful specular

layer of *metallic silver*. (What is the explanation of this?)

(*b*) Shake up 10 ccm. with about 50 ccm. of a nearly saturated solution of hydrogen sodium sulphite, $HNaSO_3$. On standing crystals separate, which consist of $C_2H_4O, HNaSO_3$. Heat a little of this compound with sodium carbonate and note what comes off.

(*c*) Add a few drops of the solution of aldehyde to some strong caustic potash and warm the mixture in a test-tube; a peculiar resinous-looking body, termed aldehyde resin, is formed. (See application of this reaction to the purification of alcohol, page 72.)

Oxidation of Alcohol to Acetic Acid. Determination of small quantities of Alcohol.

Into a 3–4 oz. narrow-necked bottle, 20 ccm. of *weak* alcohol (containing 0·1–0·2 gram of pure alcohol) are introduced, together with 10 ccm. of a solution of chromic acid, made by adding 10 grams of potassium bichromate to 12 ccm. of strong sulphuric acid and making up to 100 ccm. The bottle is then securely closed by an india-rubber stopper, tied down, wrapped in cloth, and suspended in a bath of boiling water for two hours, by which time all the alcohol will have been oxidised to acetic acid. After cooling, the bottle is opened and sulphuric acid and granulated zinc added to reduce the excess of chromic acid. The green liquid is then transferred to a flask, a few pieces of

pumice or tobacco-pipe added to prevent bumping, and the liquid carefully distilled. When nearly dry, water is added and the distillation repeated. The acetic acid in the distillate is determined by standard decinormal soda, phenol-phthaleïn being used as indicator. It is desirable before titrating to add a drop or two of barium chloride as a test for sulphuric acid. Any precipitate must be filtered off, and 46 parts of alcohol subtracted for every 233 of $BaSO_4$ found.

1 ccm. of $\frac{N}{10}$ soda = ·0046 gram of C_2H_5OH in sample.

Action of Chlorine on Ethyl Alcohol. Preparation of Chloral.

Pass a current of dry chlorine gas* through about 100 ccm. of absolute alcohol contained in a retort, which can be cooled in water containing ice if necessary, so that the temperature shall not rise above 10°. The chlorine is quickly absorbed, and, after a short time, *aldehyde* can be detected in the liquid when a few drops are removed, diluted with water, and warmed with ammoniacal nitrate of silver. In testing the liquid for aldehyde an excess of ammonia must be added in order to prevent the precipitation of silver chloride. The primary action of chlorine is therefore one of oxidation. The retort being connected with a reflux con-

* The chlorine is generated by gently warming a mixture of manganese dioxide in lumps and concentrated hydrochloric acid. The gas is dried by passing through strong sulphuric acid.

denser (Fig. 30), gently warm the liquid to 60° C. and continue to pass the gas as long as any of it is absorbed. The liquid is then boiled gently for a short time and allowed to cool (it ought to have a density of 1·400); after which it is cautiously mixed with an equal volume of strong sulphuric acid. Hydrochloric acid and ethyl chloride are evolved, and the mixture is distilled from a water-bath. The distillate is neutralised with chalk and again distilled, afterwards fractionated. Chloral is a colourless mobile liquid, B.P. 94°·5 C. It reduces ammonio-silver nitrate like aldehyde, and forms crystalline compounds with the acid sulphites; it acts generally like an aldehyde; the formula is $CCl_3.COH$, or trichloraldehyde.

When mixed with about one-fifth of its weight of water, the mixture slowly solidifies to a crystalline mass of chloral hydrate which has probably the formula

$$CCl_3-CH<\begin{matrix}OH\\OH\end{matrix}$$

Dissolve about half a gram of chloral or its hydrate in a little water; then add a few drops of caustic soda solution. The mixture soon becomes milky, owing to the separation of minute drops of *chloroform*, while the liquid in which it is produced will give the characteristic reactions of a formate. (Try it.)

The following equation explains the change brought about by the alkali:—

$$NaOH + CCl_3.COH = CCl_3H + H.COONa.$$

Preparation of Chloroform, $CHCl_3$.—Mix 430 grams of good bleaching powder with 100 grams quicklime, introduce into a capacious flask and add about 100 ccm. of ordinary methylated spirit diluted with $1\frac{1}{2}$ litres of water. Agitate the contents of the vessel so as to secure complete mixture, connect the flask with a condenser, and distil from a water-bath. A mixture of alcohol, water, and chloroform collects in the receiver, where the chloroform settles to the bottom as a heavy oil. The chloroform is freed from alcohol by shaking with water and dehydrated over calcium chloride. It is finally rectified on the water bath. Pure chloroform boils at 62° C.; the specific gravity is 1·525 at 0°; it does not readily burn.

The formation of chloroform is here due to a secondary reaction. By the action of bleaching powder on alcohol, chloral is first formed, which, in presence of the calcium hydrate, decomposes into chloroform and calcium formate. (See preparation of chloral and its decomposition, p. 90.)

The ultimate change which takes place is represented by the equation:—

$$4C_2H_6O + 8Ca(OCl)_2 = CCl_3H + 3Ca(OOCH)_2 + 5CaCl_2 + 8H_2O.$$

Reactions of Chloroform.—Shake up a few drops of chloroform with a little water in a test-tube; to the aqueous solution add a drop or two of aniline and a

little alcoholic potash. Either immediately, or on gently warming the mixture, a strong and peculiar smell will be observed, due to the formation of phenyl-carbamine (phenyl isocyanide) C_7H_5N. In the absence of chloral and similarly constituted bodies, the reaction with aniline is a very delicate test for chloroform. (See also p. 124.)

Another delicate test for chloroform is the formation of cuprous oxide when heated with Fehling's alkaline copper solution, the following reaction taking place:—

$$CHCl_3 + 5KOH + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O.$$

PROGRAMME III.

A STUDY OF THE PREPARATION AND DECOMPOSITION OF ETHYL ACETATE, AND OF THE COMPOSITION AND REACTIONS OF SOME OF THE NATURAL FATS AND OILS.

Preparation of Ethyl Acetate.—Mix 60 grams of strong alcohol (97 per cent.) with 150 grams of ordinary concentrated sulphuric acid. (This operation must be done with care, see p. 77.) Allow to stand some time, and when quite cold pour into a half-litre flask; now add slowly 100 grams of fused and coarsely powdered sodium acetate. After standing a few hours distil first from a water-bath, and finally from a sand-bath. Shake up the distillate with a strong solution of brine containing a little sodium carbonate. Remove the upper layer of liquid by means of a separating-funnel, and distil from calcium chloride in a water-bath. Redistil from water-bath, employing a thermometer. The portion distilling below 74° contains ether, that coming over at 74–79° is principally ethyl acetate. This is separately collected and purified by redistillation.

Ethyl acetate boils at 77° and has a specific gravity

of ·9068 at 15°. Determine the boiling-point of the sample prepared as above, and also its specific gravity at 15°.

Write out the reactions involved in the foregoing preparation.

Decomposition of Ethyl Acetate.—Into a half-litre flask put about 20 ccm. of ethyl acetate and 50 grams of potassium hydroxide dissolved in 200 ccm. of water. Connect the flask with a reflux condenser and boil gently for an hour or so. Now arrange the condenser for distillation and distil off about 50–60 ccm. Examine distillate for alcohol. Acidify the contents of the flask with dilute sulphuric acid and again distil. What now passes over?

Note.—The student must thoroughly understand the nature of the decomposition which the foregoing ethereal salt undergoes by treatment with caustic potash. All ethereal salts, or as they are now sometimes called, *esters*, are decomposed by boiling with caustic alkalies. Nearly all natural fats are ethereal salts, or esters. Now, when these fats are boiled with alkalies they are decomposed in the same way as the ethyl acetate, an alcohol and the salt of a fatty acid being produced. As this decomposition is best known on the large scale in the preparation of soaps, it is commonly called *saponification*. Hence, to *saponify* an ester, means to decompose it into the corresponding alcohol and the alkali salt of the acid contained in it.

Saponification of a Natural Fat. Preparation of Stearic Acid.—Cut up about ½ lb. of mutton or beef suet, and throw the pieces into a little boiling water contained in a basin; the fat soon melts, and can be squeezed out from the animal membrane, the latter being thrown away. Put the fat into a large iron saucepan, add a little water, and then a moderately strong solution of commercial caustic soda, and boil gently for two or three hours, stirring frequently. Water may be added from time to time to replace the loss by evaporation. The boiling must be continued until the fat is decomposed.

After cooling, add a strong solution of sodium chloride. The soap will separate out and rise to the top of the solution, where it will form a curd. Collect and wash with a little cold water.

When suet is boiled with a solution of a caustic alkali, its component ethereal salts, *stearin* $(C_{17}H_{35}COO)_3.C_3H_5$; *palmitin* $(C_{15}H_{31}COO)_3.C_3H_5$; and *oleïn* $(C_{17}H_{33}COO)_3.C_3H_5$, are decomposed according to the following scheme:—

$$C_3H_5'''(O\bar{A})_3 + 3NaOH = C_3H_5'''(OH)_3 + 3NaO\bar{A}.$$

A sodium or potassium salt, or "soap" of the fatty acid, is produced, together with glycerol.

Note to Student.—Write out in detail the equations representing the saponification of stearin, palmitin, and oleïn by caustic potash.

Most of the glycerol $C_3H_5'''(OH)_3$ in the experiment,

remains in solution in the brine, from which however it cannot be economically separated.

For the preparation of stearic acid, take about half the soap formed as above, dissolve in hot water and filter if necessary. To the hot solution add a slight excess of moderately strong hydrochloric acid. The soap is decomposed, and an oil rises to the surface which solidifies in cooling. This mass, consisting of a mixture of stearic, palmitic, and oleic acids [*Note to Student.*—Write out the reaction here brought about by the decomposition of the foregoing soap by hydrochloric acid] is collected, and washed by stirring up with hot water once or twice. It is now separated from the aqueous portion and digested with a *small* quantity (about an equal bulk) of hot methylated spirit, allowed to cool, well drained on the filter-pump and washed with a little cold spirit. This operation is to be repeated, the object being to remove oleic acid, which is much more soluble in alcohol than stearic or palmitic acid. Now remove the mass from the funnel and press thoroughly between folds of blotting paper. The well pressed acids are now dissolved up completely in hot methylated spirit (employ for this purpose a flask attached to a reflux condenser, see "Operations," p. 4), and allowed to crystallise. Collect the crystalline deposit, drain well on the filter-pump and press between blotting-paper. The degree of purity effected by the successive crystallisations should be ascertained by determining the melting-point of the different

fractions. (See p. 7.) The well pressed mass is now dissolved up in a large excess of spirit, and to this is added, while hot, a boiling alcoholic solution of magnesium acetate. The latter salt is added in the proportion of one part of the acetate to four parts of the mixed acids. By this treatment a precipitate of almost pure magnesium stearate is obtained; most of the magnesium palmitate, being more soluble, remains in solution. The precipitate is collected when cold, well drained, pressed, and decomposed by boiling for some time with dilute hydrochloric acid. After cooling and filtering, the stearic acid is again crystallised from alcohol, and the melting-point determined. Pure stearic acid melts at 69°·2. If the sample of stearic acid has a much lower melting-point, recrystallise until pure. When pure, determine carbon and hydrogen.

The foregoing separation of stearic from palmitic acid is an example of *fractional precipitation.* An alcoholic solution of other salts can be employed instead of magnesium. In general, the acid richest in carbon is thrown down first, if care be taken only to add sufficient to precipitate a small proportion of the acids present. The filtrate is again treated with more of the alcoholic solution of the salt, and so on. The various precipitates are decomposed, examined, and the process of fractional precipitation repeated. The acids obtained are crystallised until a pure substance is obtained, this being ascertained by a determination of melting-point and other characteristics.

Experiments with Stearic Acid. Preparation of Potassium Salt.—To a hot alcoholic solution of stearic acid add alcoholic potash until neutral, this point being ascertained by using phenol-phthaleïn as an indicator. On concentrating the solution and allowing it to cool, the potassium salt separates out in shining needles or thin plates. Or the salt may be obtained by dissolving one part of stearic acid in ten parts of water containing one part of caustic potash. The resulting mass may now be dissolved up in hot alcohol and allowed to crystallise. Determine the potassium in a sample of the salt.

Dissolve one part of potassium stearate in ten parts of water, heat until clear and largely dilute with cold water, when an acid stearate will separate out, having the composition $C_{17}H_{35}COOK$, $C_{17}H_{35}COOH$ (determine the potassium in a sample), which crystallises in white pearly laminæ, while the solution becomes more or less alkaline. (Test it.) This hydrolysis of the salt of a higher fatty acid is important, and has an intimate relation to the detergent properties of soap. (See paper by Wright and Thompson, *Jour. Soc. Chem. Ind.*, iv. 630.)

Preparation of Lead Stearate.—Dissolve some potassium stearate in water, and add a clear solution of lead acetate. Collect the precipitate on a filter, and wash with cold water; dry at 100° and estimate lead. Test solubility of lead salt in alcohol, ether, and petroleum. Determine the melting-point of a sample of the salt.

Action of Bromine and Iodine on Stearic Acid.—To

an aqueous solution of the salt add a few drops of bromine water drop by drop, and note what happens. Repeat this experiment, substituting an aqueous solution of iodine for the bromine. Dissolve a little of the *pure stearic acid* in carbon tetrachloride or ether, and add the foregoing reagents also dissolved in tetrachloride or ether. (See p. 106.)

Titration of Stearic Acid with Standard Alkali.—Weigh off about one gram of pure stearic acid into a stoppered ¼-litre flask, and wash down with about 50 ccm. of *neutralised* methylated spirit.* Immerse the flask in hot water, and effect as complete solution of the acid as possible by agitating thoroughly. Add a few drops of phenol-phthaleïn solution, and titrate with a semi-normal solution of sodium hydroxide (= 20·0 NaOH per litre). The addition of the alkali is continued, with vigorous shaking, until a permanent pink coloration is obtained :—

$$C_{17}H_{35}COOH + NaOH = C_{17}H_{35}COONa + H_2O.$$

Calculate the percentage of pure stearic acid.

Saponification of Olive Oil.—Isolation of Glycerol.—Into a porcelain basin put about 100 grams of pure olive oil (which consists largely of the glyceride *oleïn* $[C_{17}H_{33}COO]_3C_3H_5$), together with about three times

* Some of the purified methylated spirit prepared in accordance with the directions given on p. 72 is treated with a few drops of an alcoholic solution of phenol-phthaleïn, and then *dilute* sodium hydroxide added drop by drop until the solution retains a faint pink tint after shaking.

the volume of water. Heat on a water-bath, stir in gradually 50 grams of finely powdered litharge (PbO), and continue to heat for several hours, adding water from time to time to replace loss by evaporation. A pasty mass is finally obtained (this is lead oleate; the principal constituent of the "lead plaster" of pharmacy).

Pour off the aqueous portion which contains the glycerol, wash the residue in the dish with hot water, and pass sulphuretted hydrogen to remove any lead in solution; filter, and evaporate to a small bulk on the water-bath. A sweet syrupy liquid is left, which is glycerol or glycerine. The lead soap obtained should be preserved; it is useful for the preparation of oleic acid. (See p. 104.)

Note to Student.—Express in the form of an equation the decomposition of the oleïn contained in olive oil, by lead hydroxide.

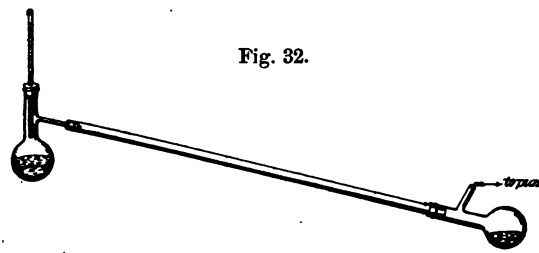


Fig. 32.

Experiments with Glycerol.—(*a*) Heat a little of the glycerol quickly in a small test-tube, and note the acrid tear-exciting odour produced. This is due to

the formation of *acroleïn*, and constitutes a test for glycerol.

(*b*) Put 20 ccm. of glycerol into a flask with 200 ccm. of water, connect with a condenser and boil briskly, passing in a current of steam. Prove that glycerol passes over with the water vapour. Into a 4-oz. Wurtz flask connected air-tight to a similar flask by means of a glass tube (see Fig. 32) put 30 grams of glycerol. Exhaust by means of an air-pump, and distil over *in vacuo* half the glycerol. From the appearance and odour of the distillate, what conclusions do you draw?

Determination of Carbon and Hydrogen in Glycerol.—Heat some glycerol nearly to its boiling-point, to render it anhydrous, and allow it to cool in a *small* desiccator over sulphuric acid. Weigh out into a porcelain or platinum boat 0·2 to 0·3 gram glycerol, and determine carbon and hydrogen by combustion.

Note.—The weighing-out of the glycerol must be done with expedition, as it is very hygroscopic.

Determination of Glycerol by Oxidation with Alkaline Permanganate.—When glycerol is treated with permanganate in the presence of excess of caustic alkali, it is converted into oxalic acid, carbon dioxide, and water, in accordance with the following equation:—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + H_2O.$$

From this equation it will be seen that one molecule of oxalic acid corresponds to one of glycerol.

The details are as follows:—Weigh off about 0·5 gram

of the anhydrous glycerol, prepared as above, transfer to a porcelain basin, and dilute with cold water to about 300 ccm. Then a strong solution of caustic potash, containing at least 12 grams of potash, is added: now pour in a saturated solution of potassium permanganate, until the solution is no longer green, but blackish. The liquid is then heated to the *boiling-point* for an hour or so; a strong solution of sodium sulphite is then added to the hot liquid until all greenish colour is destroyed. The liquid containing the precipitated oxide of manganese is then poured into a 500 ccm. flask: the basin is washed out with hot water. The liquor and washings in the flask are made up to 15 ccm. above the 500 ccm. mark, the excess being an allowance for the volume of the precipitate and hot liquid. The solution is passed through a dry filter, and when cold 400 ccm. of the filtrate are measured off, acidified with acetic acid, and the oxalic acid precipitated with calcium chloride.

The solution must be kept in a warm place for two or three hours, in order to insure complete precipitation of the oxalate. The precipitate, which consists of calcium oxalate and sulphate, is well washed. After washing, the filter is pierced and the precipitate rinsed into a beaker, the filter-paper well washed with hot dilute sulphuric acid (which of course is added to the contents of the beaker), the liquid diluted to 200 ccm., warmed up to 60°, and titrated with standard permanganate. If decinormal permanganate be employed, each ccm.

corresponds to ·0045 oxalic acid, or ·0046 gram glycerol.

Preparation of Allyl Alcohol, $CH_2:CH.CH_2.OH$.—Into a retort of about 500 ccm. capacity, provided with a condenser and arranged for distillation, introduce 50 grams of oxalic acid and about 200 ccm. of glycerol. Pass a thermometer through the cork of the retort, and let the bulb dip well under the liquid. If commercial oxalic acid is employed, it is necessary to add to the contents of the retort about a half per cent. of sodium chloride and a quarter per cent. of ammonium chloride.

When the temperature has reached 130°, much carbon dioxide gas is evolved and a little formic acid distils over; continue to heat gradually up to 200°, when more gas is evolved. At 200–210°, oily streaks are observed to run down the neck of the retort and a peculiar, somewhat irritating, but highly characteristic odour is perceptible; at this stage the receiver is changed. By gently heating the contents of the retort, a temperature of about 220–230° is maintained for some time, and when it has finally risen to 260° the distillation is stopped. Excess of glycerol remains behind in the retort, and may be used again by repeating the operation with a smaller quantity of oxalic acid (20–30 grams). The whole of the allyl alcohol, together with a small quantity of formic acid and acrolein, is obtained by submitting the distillate to rectification. The distillation is this time continued until, on treating the

last portions, coming over at about 105°, with potassium carbonate, no oily layer separates. Now add to the distillate solid potassium carbonate, when the allyl alcohol separates out as an oil. This is separated from the aqueous portion and allowed to stand for 24 hours in contact with 5 to 10 per cent. of powdered potassium hydroxide; the liquid loses the smell of acrolein, and at the same time assumes a brown colour. (Compare the purification of ethyl alcohol from acetaldehyde, p. 72.) The liquid is decanted off and distilled. In order to abstract the last traces of water, which are obstinately retained, the alcohol is left in contact with anhydrous baryta and then distilled.

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3} = \underset{\text{Monoformin.}}{C_3H_5(OH)_2\text{–O–CHO}} + H_2O + CO_2.$$

$$C_3H_5(OH)_2\text{–O–CHO} = \underset{\text{Allyl alcohol.}}{C_3H_5OH} + H_2O + CO_2.$$

Allyl alcohol, when pure, is a colourless liquid boiling at 96°; sp. gr. 0·858 at 0°.

The foregoing preparation is an example of the conversion of a trihydric alcohol (glycerol) into a monohydric alcohol.

Preparation of Oleic Acid, $C_{17}H_{33}COOH$.—Introduce some of the lead oleate (free from water) obtained in the preparation of glycerol, into a flask, and agitate repeatedly with petroleum spirit, which dissolves the lead oleate and free oleic acid, leaving the palmitate

and stearate of lead unchanged. (Note this fact carefully.) The solution is separated from insoluble salts and thoroughly shaken with an excess of hydrochloric acid. The aqueous portion now contains chloride of lead, while the spirit will retain the oleic acid. It is separated from the acid aqueous liquid, washed by agitation with water, carefully separated, and the spirit distilled off rapidly and at as low a temperature as possible. The oily residue is dissolved in moderately strong ammonia, solution of barium chloride added, the precipitate of barium oleate collected, washed with water and crystallised from alcohol. (Determine the barium in a sample of the salt).

The barium oleate is finally decomposed by boiling with a strong solution of tartaric acid, the oleic acid extracted with ether, and the ether distilled off as quickly as possible. The residual oleic acid may be further purified by allowing to crystallise from alcohol, or by cooling down to about 7° C., when it solidifies to a crystalline mass, which is quickly pressed between folds of filter paper, or drained on a vacuum-filter, (see p. 21); by repeatedly melting, cooling, and pressing the crystalline portion, and finally crystallising from alcohol, the impurities are completely removed.

Oleic acid crystallises from alcohol in brilliant white needles melting at 14° C.

Action of Reagents on Oleic Acid.

Action of Bromine.—Dissolve a little oleic acid in ether or chloroform, and add drop by drop a dilute solution of bromine dissolved in the same solvent. Note what happens.

The foregoing reaction can be made approximately quantitative, and is of great technical importance. Iodine can be used instead of bromine. The iodine absorption of an oil has been thoroughly studied by Baron Hübl.*

On p. 99 it was found that pure stearic acid does not readily combine with bromine; this was because the acid is a "saturated compound," inasmuch as it is a higher homologue of acetic acid, the general formula of the acids of this series being $C_nH_{2n+1}COOH$. Oleic acid belongs to the series $C_nH_{2n-1}COOH$.

Oleic acid, $C_{18}H_{34}O_2$, forms $C_{18}H_{34}Br_2O_2$, and $C_{18}H_{34}I_2O_2$.

From the foregoing considerations we can approximately estimate oleic acid from the amount of halogen assimilated. About 0·1–0·2 gram of pure anhydrous oleic acid is placed in a stoppered bottle of about 100 ccm. capacity, and dissolved in 50 ccm. of carbon tetrachloride previously dried by calcium chloride. An approximately $\frac{N}{10}$ solution of (8 grams per litre)

* Dingl. Polyt. Jour., ccliii, 281, Jour. Soc. Chem. Ind., iii. 641 See also Allen's 'Commercial Organic Analysis,' vol. ii., page 48.

bromine in dry carbon tetrachloride, having an exactly known strength, is then gradually added to the solution, until after standing a few minutes it is no longer decolourised. The excess of bromine is then estimated by adding an aqueous solution of potassium iodide and starch, and titrating back with a standard solution of sodium thiosulphate. Repeat the above, substituting pure olive oil for the oleic acid. Express the results in percentages of bromine assimilated.

Action of Nitrous Acid on Oleic Acid.—Pass, for a few minutes only, a gentle current of the nitrous fumes generated by the action of nitric acid on sugar or arsenious oxide (see Fig. 34, p. 129), into about 10 grams of well-cooled oleic acid; after some time a crystalline mass separates out, called elaïdic acid (which is considered an isomer of oleic acid). The acid may be purified by washing with hot water, and crystallisation from alcohol. From this solvent it crystallises in fine pearly laminæ, melting at 45°. It has strongly acid characters, forming well-defined salts. (Prepare the sodium and potassium salts by dissolving in alcohol and adding the necessary quantity of alkaline hydroxides.)

The property of forming an isomer of higher melting point under the influence of nitrous acid is not peculiar to oleic acid, but is exhibited by its homologues. The glyceride triolein also, when similarly treated, gives a solid modification termed *Elaïdin*. Experiment: Pass a current of nitrous acid through some well-cooled olive oil, and allow to stand for some time.

Note.—The drying oils, which consist chiefly of linolein and its homologues, are not visibly affected by treatment with nitrous acid. Upon this property is based the important "Elaidin test," described in works treating of the analysis of fats and oils.

Determination of Oleic Acid by Standard $\frac{N}{2}$ *Sodium Hydroxide.*

This operation is carried out as in the titration of stearic acid. (See p. 99.)

$$C_{17}H_{34}COOH + NaOH = C_{17}H_{34}COONa + H_2O.$$

Determination of the Percentage of Caustic Potash required for Saponification of an Oil.

Before commencing this operation, the following standard solutions must be prepared :—

(*a*) Dissolve 14 grams of good stick potash in 500 ccm. of good rectified methylated spirit (distilled from potash), and allow the liquid to stand till clear. This solution will be approximately seminormal.

(*b*) A standard solution of hydrochloric or sulphuric acid of approximately seminormal strength.

About 2 grams of pure olive oil are accurately weighed into a flask fitted to a reflux condenser. 25 ccm. of the prepared alcoholic potash are added, and the flask is heated on a water-bath, with frequent rotatory agitation for about half an hour, or until

saponification is judged to be complete. After cooling, about 1 ccm. of an alcoholic solution of phenol phthaleïn is added, and the liquid is titrated with the seminormal hydrochloric or sulphuric acid. 25 ccm. of the same alcoholic solution of potash, without the fat, should then be carefully titrated with the standard acid. The difference between the volumes of standard acid used in the two titrations gives the number of ccm. corresponding to the alkali neutralised in saponifying the oil.

$$1 \text{ ccm. of } \frac{N}{2} \text{ acid} = 0{\cdot}02805 \text{ of KOH.}$$

Calculate the percentage of KOH required to saponify 100 parts of the oil.

$$C_3H_5(O\overline{F})_3 + 3KOH = C_3H_5(OH)_3 + 3K(O\overline{F}).$$

From the foregoing general equation it appears that one molecule of glyceride requires three molecules of potassium hydroxide for its saponification. The amount of glyceride saponified by one molecule of potash will therefore be one-third of the molecular weight (in the case of a monohydric alcohol the number will be identical with the molecular weight).

The number of grams of any oil saponified by one litre of any normal alkali is designated the "saponification-equivalent," and it is found by dividing the percentage of alkali required for saponification into 5610 for KOH and into 400 for NaOH. (See Allen's 'Commercial Organic Analysis,' vol. ii. p. 40.)

PROGRAMME IV.

COAL-TAR AND COAL-TAR PRODUCTS.

Distillation of Coal-tar.—Into a tubulated glass retort of about 1½ litre capacity, introduce about 500 ccm. of good gas-tar (to be obtained from any gas-works). Close the tubulure with a cork fitted with a thermometer. The retort is supported on a cup-shaped piece of wire-gauze, placed in an aperture cut in a plate of sheet-iron, conveniently supported in position by four bricks. Over the retort is placed a dome of thin sheet-iron, so cut as to allow the neck of the retort to pass through. (See Fig. 33.)

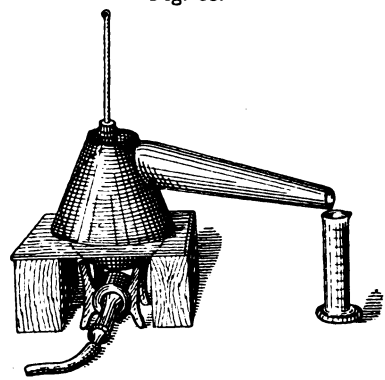
This latter contrivance confines the heat, and so prevents condensation in the upper part of the retort.

No condensing arrangement is necessary, the neck of the retort acting in this capacity.

The retort is heated very gently and carefully at first (one of Fletcher's powerful ring burners should be used, as towards the close of the operation it is necessary to maintain the wire-gauze at a red heat). There is usually much frothing, and if great care is not taken, the distillate will be spoilt.

The burner being lighted, the ammoniacal liquor and "light oils" are collected together in a graduated cylinder, which is changed when a drop of the distillate

Fig. 33.



collected in a test-tube begins to sink. After standing, to allow perfect separation of the ammoniacal liquor and light oils, the volume of each is observed. The strength or amount of ammonia contained in the former, is to be determined by distilling an aliquot portion with caustic alkali and titration of the distillate. (See Fig. 22, p. 59).

The quantity of light oils (containing benzene, toluene, &c.) is usually too small to admit of further fractionating, but can be preserved as a specimen.

The next fraction of the distillate (200–240°) consists of "creosote oil"; at first it will contain much naphthalene, and will probably solidify on cooling; but

as the distillation proceeds it will become more fluid. When a drop of the distillate received on a cool surface deposits solid matter of a yellow or greenish-yellow colour, the receiver is changed. (The temperature will be about 270°. Pull the bulb of the thermometer up into the cork). Measure the fraction, and label it "Creosote oils."

The next fraction is rich in anthracene, and mostly condenses in the neck of the retort as a yellow waxy substance, which may be melted by the cautious application of a small Bunsen flame. The operation is continued until no more distillate can be obtained, and the pitch intumesces and gives off heavy yellow fumes. This last fraction is measured, cooled thoroughly, and the resulting pasty mass pressed between folds of thick filter paper and weighed. Label it "Anthracene cake," and preserve for future experiments. (See p. 141.)

When the distillation is complete, the retort is allowed to cool down, and when almost cold, its body is plunged into cold water. This operation causes a rapid surface cooling and shrinking of the pitch from the glass of the retort, which may then be broken by gently tapping, leaving the pitch clean and ready for weighing. Preserve a specimen.

In this experiment it will be seen that the retort (costing about one shilling) is sacrificed; it is therefore recommended that the experiment be performed by a group of three or more students.

The following table will give some idea as to how

the results of the foregoing operation should appear in the note-book:—

DISTILLATION OF A SAMPLE OF LONDON TAR.

	per cent.
Ammoniacal water	4·5
Total light oils	3·5
Carbolic and creosote oils	26·2
Anthracene oils	14·5
Pitch (grams per 100 ccm.)	58·6
	107·3

The apparent excess is due to the tar having been measured and the pitch weighed.

Fractionation of Light Oil. Isolation of Benzene and Toluene.—Shake up in a capacious flask a measured quantity (say 250 ccm.) of light oil, procured from some tar distillery, with an equal bulk of dilute sulphuric acid (1 of acid to 3 of water), connect flask to condenser, and distil in a current of steam. Collect, and separate oil from aqueous distillate, and repeat foregoing operation, substituting a 20 per cent. solution of caustic soda for the sulphuric acid. The purified oil is separated, dried over calcium chloride, and fractionated. It will be observed that there is a tendency to an accumulation of the distillates in the parts boiling near 80° (B.P. of benzene, 80°·5) and 110° (B.P. of toluene, 110–111°). The portion which passes over below 90° C. is digested at 100° in a flask furnished with an upright condenser, with 5 per cent. by measure of concentrated sulphuric acid for several hours, in order to separate thiophene and

hydrocarbons of the C_nH_{2n-2} and C_nH_{2n} series. This treatment is continued with successive portions of acid as long as any blackening takes place. The oil is separated as far as possible from acid, and distilled in a current of steam. The oil is separated from water and submitted to a freezing mixture of ice and salt, when the benzene crystallises out, and may be separated from the more fusible hydrocarbons by draining on a vacuum pump. (See p. 21.)

Pure benzene melts at 5°·5, and boils at 80°·5.

The fraction boiling above 90°, together with the mother-liquors accumulated during the purification of benzene, are carefully fractionated by means of the bulb apparatus, and the portion which finally comes over at 110–111° is collected. This will be nearly pure toluene. Submit a sample to a powerful refrigerating mixture; it does not solidify (distinction from benzene).

Action of Reagents on Benzene and its Derivatives.

Action of Sulphuric Acid. Preparation of Potassium Benzene-Sulphonate, $C_6H_5SO_3K$.—Into a flask of about ½-litre capacity introduce 100 grams pure commercial benzene and 200 grams of concentrated sulphuric acid; attach a reflux condenser, and keep the mixture gently boiling on a sand-bath for about twenty-four hours. When about four-fifths of the benzene have dissolved, and more prolonged heating produces no further change, distil off any residual benzene, cool,

and pour the dark-coloured liquid into about a litre of water contained in an earthenware pan. The acid liquid is now neutralised whilst hot with powdered chalk mixed into a thin cream with water. The mass is filtered through calico (conveniently stretched on a wooden frame), and the residue well washed with water. The brown-coloured filtrate, together with the wash-water, is concentrated over a small flame until a sample withdrawn on the end of a glass rod solidifies on cooling. From the solution the calcium salt of benzenesulphonic acid separates out on cooling, forming an almost solid mass of small white crystals, which, after being well drained from the mother-liquor, are almost pure. *Note.*—Press some of the well-drained crystals between filter-paper, and when dry, determinine the calcium (as sulphate) in a sample.

In order to prepare the corresponding potassium salt from the calcium compound, dissolve the latter in hot water and add a moderately concentrated solution of potassium carbonate until the calcium is completely precipitated as carbonate. The aqueous solution of the potassium salt is filtered from the calcium carbonate and evaporated down, first over a small flame, and finally on the water-bath, until a sample crystallises on cooling.

The potassium salt crystallises in the form of colourless crystalline plates, which, after collecting and draining, may be dried on a porous tile or plate.

Note to Student.—Write out equations explaining all

chemical reactions involved in the preparation of the foregoing compound. Is the action of sulphuric acid on benzene a typical one? How is ethyl-sulphonic acid obtained?

Action of Fused Potassium Hydroxide on Potassium Benzene-Sulphonate. Preparation of Phenol, C_6H_5OH. —In an iron crucible (or small gluepot) melt 40–50 grams of potassium hydroxide, after adding a few ccm. of water. Now add gradually, and with constant stirring, 10–15 grams of finely powdered potassium benzene-sulphonate. Do not heat to a very high temperature. *Note.*—A narrow piece of iron tube, closed at one end and containing a little mercury, and sufficiently large in bore to admit of the insertion of a thermometer, is a useful adjunct in conducting fusions with potash; by employing a thermometer, protected as described, the temperature in the present experiment may be maintained at about 290–295°. During fusion the mass is first thick and pasty, but soon becomes semi-fluid, and remains in this condition until towards the end of the operation, when it regains its original consistency.

After the mass has been kept in a state of fusion for about an hour, allow it to cool, and dissolve in about 200 ccm. of water; transfer to a porcelain basin and acidify with concentrated hydrochloric acid. (What gas comes off?) When the liquid has cooled down, shake up with ether in a glass separating-funnel. After separating, distil off the ether; the residue consists of

impure phenol, which may be detected by the following reactions, for which a solution in water should be prepared :—

(*a*) A few drops of ferric chloride give a beautiful violet colour.

(*b*) To another portion add some ammonia and then a few drops of a solution of bleaching powder; a blue colour is produced.

(*c*) Bromine water gives a yellowish white precipitate of tribromphenol.

Now repeat and compare the above reactions with a sample of commercial phenol.

Separation of Phenol from Coal-tar.—Procure about two litres of the fraction from coal-tar boiling at 150-200° C. This is transferred to a separating funnel or Winchester quart bottle, and agitated with successive quantities of caustic potash solution (25 per cent). The aqueous portion is now drawn off and concentrated to a small bulk over a sand-bath, allowed to cool completely, separated from any further stratum of oil, and treated with a slight excess of dilute sulphuric acid (one of conc. acid to three of water). The oily layer obtained is separated as completely as possible from the aqueous portion, and distilled from a small Wurtz flask; the portion coming over at about 182° is fairly pure phenol. It may be further purified by freezing, pressing, and redistillation.

Estimation of Phenol.—The reaction which bromine gives with phenol may be utilised in approximately

determining the amount of the latter in aqueous liquids. The precipitate of tribromphenol may be collected on tared filter papers, dried in the desiccator, and weighed; or the estimation may be effected by adding standardised bromine water *in excess*, followed by potassium iodide, and then titrating back with a standard solution of sodium thiosulphate.

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Action of Nitric Acid on Phenol.—Preparation of Ortho- and Para-nitrophenol.—To a mixture of 80 grams nitric acid, sp. gr. 1·34, and 164 grams of water, contained in a porcelain basin, and kept cool by standing in a vessel of water, 40 grams of melted phenol are gradually added in small quantities, and the contents of the basin well stirred. On the addition of the phenol the liquid changes to a deep brown or black colour, and a heavy dark brown oil separates out. When all the phenol has been added, the mixture is allowed to stand for about twelve hours.

The oil, which for the most part collects at the bottom of the vessel, is washed two or three times with water by decantation. The black oily product is now put into a flask and distilled in a current of steam. (See "Operations," p. 12.) Yellow crystals pass over and appear in the receiver. The distillation is continued until the distillate is almost colourless. The volatile substance is ortho-nitrophenol, which can be further purified by crystallisation from dilute alcohol. Deter-

mine the melting-point of a sample after well pressing and drying between filter-paper.

The residue in the flask contains the other isomer, the non-volatile para-nitrophenol, which can be extracted from the black, pitchy, contaminating substance by repeatedly exhausting with boiling water. The united portions of the aqueous extract are boiled with animal charcoal and filtered, the filtrate concentrated to a small bulk and allowed to crystallise, further purification being effected by recrystallisation from hot dilute alcohol.

After pressing and drying the crystals between filter-paper, determine the melting-point, and also point out any further distinguishing properties by which the compound is distinguished from its isomer.

Action of Phosphorus Pentachloride on Potassium Benzene-Sulphonate.—In a dry evaporating dish mix 15 to 20 grams potassium benzene-sulphonate and an equal weight of phosphorus pentachloride, by means of a dry pestle. The mass beomes hot and semi-liquid, and hydrochloric acid is given off. Hence the operation should be performed under a hood or out of doors. The reaction which takes place is represented by the equation:—

$$C_6H_5SO_2OK + PCl_5 = C_6H_5SO_2Cl + POCl_3 + KCl.$$

When the action is over and the mass has cooled down to the ordinary temperature, add about a litre of cold water. Everything will dissolve except the

sulphon-chloride, $C_6H_5SO_2Cl$, which will remain as a heavy oil at the bottom of the basin. Pour off the greater part of the water, and add 30–40 grams of powdered ammonium carbonate. The chloride is thus converted into the corresponding sulphon-amide, thus:—

$$C_6H_5SO_2Cl + 2NH_3 = C_6H_5SO_2NH_2 + NH_4Cl.$$

After cooling, filter off the sulphon-amide; wash well with cold water and crystallise from water. The compound crystallises in needles, melting at 153°.

Note to Student.—Refer to the manufacture of *saccharin*, and compare its mode of formation with the foregoing.

Action of Potassium Cyanide on Potassium Benzene-Sulphonate.—Mix 20 grams of dry potassium benzene sulphonate with an equal weight of potassium cyanide (or, preferably, dry ferrocyanide), and distil from a small retort. The distillate is impure phenyl cyanide, C_6H_5CN.

$$C_6H_5SO_2OK + KCN = C_6H_5CN + K_2SO_3.$$

Put the phenyl cyanide into a flask of 250 ccm. to 300 ccm. capacity, and add 150 ccm. of a moderately strong solution of potassium hydroxide. Connect with an inverted condenser and boil for two or three hours. What is given off? After cooling, acidify with hydrochloric acid. A solid substance is precipitated. Filter off, wash slightly, and crystallise from water,

or sublime between watch-glasses. This substance is benzoic acid.

Write out the reactions showing its formation from the phenyl cyanide. (See also p. 134, on the application of Sandmeyer's reaction.)

Action of Nitric Acid on Benzene. Preparation of Nitrobenzene.

Into a flask of about ½-litre capacity containing 50 grams of benzene introduce a well-cooled mixture of 100 grams concentrated nitric acid and 150 grams strong sulphuric acid. The acid must be very slowly added from a tap-funnel and the contents of the flask *well shaken.* Nitrous fumes are evolved and a considerable amount of heat developed. Care must be taken that the temperature does not exceed 40–50°, by immersing the flask in cold water. The nitrobenzene separates out as a brown, oily layer on the surface of the acid. When all the acid has been added—an operation which should last about half-an-hour—heat the mixture for half-an-hour to 60° on the water-bath with frequent agitation; then pour slowly into about a litre of cold water. The nitrobenzene will sink to the bottom as a yellow oil. Pour off the acid and wash three or four times with water, then add a dilute solution of sodium carbonate, and distil in a current of steam. The nitrobenzene, separated as carefully as possible from water, is allowed to stand over a little granulated

calcium chloride and shaken occasionally until the liquid is perfectly clear. The yellow liquid is now decanted from the calcium chloride and distilled from a dry distilling-flask, noting the temperature. Nitrobenzene has the formula $C_6H_5NO_2$, and distils at 205–207° C.

Show by means of an equation the reaction which has taken place in its formation from benzene and nitric acid. Why is sulphuric added to the nitric acid?

Action of Nitric Acid on a Mixture of Benzene and Petroleum.—To a mixture of 10 ccm. benzene and 5 ccm. of petroleum contained in a small flask fitted with an inverted condenser, add twice its measure of fuming nitric acid of 1·50 sp. gr. If a vigorous action occur, no extraneous heat need be applied, but if the reaction be sluggish the liquid should be well agitated and moderately heated for a few minutes. Cool the flask, transfer the contents to a tapped funnel, and run off the bottom layer into water, when nitrobenzene will be seen to have formed. The top layer in the funnel will be found to be unaltered paraffin. This experiment is to demonstrate the difference in behaviour towards reagents, between hydrocarbons of the benzene series and those of the paraffin series. Its application to technical purposes will readily appear.

Action of Reducing Agents on Nitrobenzene.

Preparation of Aniline, $C_6H_5NH_2$.—(1.) Sixty grams nitrobenzene and 100 grams granulated tin are placed in a flask of about 1 litre capacity connected with a reversed condenser; 360 grams of strong commercial hydrochloric acid are gradually added in small quantities, the amount being regulated by the reaction, which should proceed steadily. Should the contents of the flask boil up violently, the flask is cooled in water until the reaction has somewhat slackened; towards the conclusion of the operation the flask is gently heated for about an hour. When nearly the whole of the tin has dissolved, the contents of the flask (which solidify on cooling to a crystalline mass consisting of a double salt of stannic chloride and aniline hydrochloride) are submitted to distillation in a current of steam (see "Operations," p. 12), so long as any unaltered nitrobenzene comes over. The contents of the flask are now cooled and neutralised with quicklime ground into a thin paste with water, a small quantity of sodium hydroxide solution being added until slightly alkaline. The contents of the flask are again distilled in a current of steam. Aniline and water collect in the receiver, the former as an almost colourless oil. When no further condensation of oil is observed, the operation is discontinued and the oil separated from the aqueous distillate by means of the separating funnel. The aqueous portion of the distil-

late contains aniline in suspension and in solution. The latter may be extracted with ether, the ethereal solution separated as far as possible from water, and the ether distilled off.* The residue in the flask, together with the oil in the separating-funnel, is dehydrated over solid caustic potash, decanted, and distilled. Aniline, when pure, distils at 181–182°, and has usually a faint amber colour.

(2.) Dissolve a further quantity of nitrobenzene in alcoholic ammonia, and saturate the solution with hydrogen sulphide, keeping it slightly warm. On the water-bath distil off the excess of ammonium sulphide and some of the alcohol. (Operation to be conducted in fume cupboard.) To the residue add dilute hydrochloric acid. This will combine with and dissolve the aniline, but leave any unchanged nitrobenzene undissolved. Separate the latter; evaporate to dryness on the water-bath, mix with a little lime and soda solution, and distil as in process No. 1. Aniline will pass over.

Experiments with Aniline.—To an aqueous solution of a little of the aniline in a test tube add a clear solution of bleaching powder. A beautiful purple colour is produced.

Heat a few drops of the base with a little alcoholic

* An alternative method for recovering the aniline from its aqueous solution is to evaporate the latter, rendered slightly acid by the addition of dilute hydrochloric acid, nearly to dryness on the water-bath. Aniline hydrochloride is formed, which may be collected and used for subsequent experiments.

potash and a drop or two of chloroform in a test tube. Phenylcarbamine is produced, a substance possessing a most unpleasant odour. (Hofmann's reaction for primary amines.)

Salts of Aniline.—Put a few ccm. of aniline into a test-tube containing an equal bulk of water, and add hydrochloric acid. Note that the aniline slowly disappears on shaking the liquid; the solution contains aniline hydrochloride, $C_6H_5NH_2HCl$, which can be obtained as a solid by evaporating the solution. Repeat with dilute sulphuric and nitric acids.

Note.—It is necessary to point out here that aniline is by no means the sole product of the reduction of nitrobenzene, and that intermediate compounds are known, one of which, *azobenzene*, is next described. The manner in which these compounds are related to nitrobenzene and aniline must be fully explained by the teacher, or by reference to a good text-book.

Preparation of Azobenzene, $C_6H_5.N_2.C_6H_5$. — Dissolve 16 grams of powdered sodium hydroxide in 100 ccm. of boiling methylated spirit, contained in a flask of about half-litre capacity connected to an inverted condenser, and add gradually to the hot solution 20 grams of nitrobenzene (can be introduced down the condenser). Heat for two to three hours. Now add, in small portions, 8 grams of zinc dust, and continue the heating for one or two days. Distil off the alcohol, add water, and filter; wash the residue with a little water and boil up with hydrochloric acid and alcohol;

filter hot. Azobenzene crystallises out on cooling in large red crystals melting at 67°. Determine the nitrogen in a sample of the azobenzene.

Preparation of Acetanilide, $C_6H_5NH.COCH_3$.—Equal weights of aniline and glacial acetic acid are mixed in a flask of about 250 ccm. capacity connected with a reversed condenser, and gently boiled for about twelve hours. The liquid on cooling solidifies. The contents while warm are therefore at once distilled until excess of acetic acid has been expelled, and the liquid which passes over begins to solidify. The contents of the flask are allowed to cool somewhat and then poured into some cold water. The crystals are collected on a filter, washed with a little water, and crystallised from boiling water. The compound forms colourless tabular crystals, melting when pure at 114°, and the purity of the preparation under consideration must be ascertained by pressing a sample between filter-paper, drying in the water-oven, and carefully observing the melting-point. When pure, determine percentage of carbon, hydrogen, and nitrogen.

Acetanilide is an important compound. The aromatic amido-compounds are readily acted on by glacial acetic acid or acetic anhydride, and form acetyl derivatives or acid amides. The introduction of the acid radicle into the NH_2 group confers stability on the compound; for instance, aniline cannot be readily nitrated without undergoing decomposition, acetanilide is easily nitrated. The acetyl group can afterwards be removed

by heating with hydrochloric or sulphuric acid, or with caustic alkalies (saponification or hydrolysis).

$$R\text{-}NHC_2H_3O + H_2O = RNH_2 + C_2H_4O_2.$$

Action of the Halogens on Benzene.

Preparation of Monobrom- and Dibrombenzene.—Into a flask of about 300 ccm. capacity pour 50 grams of benzene, then measure out 28 ccm. of bromine. (Bromine is more readily measured than weighed: the operation must be conducted in a good draught-chamber.) The quantities given are in the proportion of nearly two atoms of bromine for one molecule of benzene. Place the flask in cold water and gradually add the bromine to the benzene. What gas is given off? Note that the mixture remains highly coloured by the bromine. (Refer to the action of bromine on ethylene.) Now connect the flask, by means of an asbestos stopper * well luted with plaster of Paris, to an upright condenser, and heat the contents of the flask over wire gauze, with a small flame, until the evolution of hydrobromic acid fumes from the top of the condenser have nearly ceased.†

The product, which has a deep red colour, is poured into water containing a little caustic potash; the liquid

* A strip of thin sheet asbestos-board, rendered pliable by moistening with water, and wrapped round the condensing-tube until of sufficient thickness to form a tightly-fitting stopper.

† By attaching a glass tube to the top of the condenser, the hydrobromic acid may be absorbed in a little weak caustic potash; on evaporating to dryness, igniting, and subsequent crystallisation, the bromine may be recovered as potassium bromide.

monobrombenzene settles to the bottom of the vessel as a heavy oil. On shaking in a stoppered funnel with a little weak caustic potash, the liquid gradually loses its red colour. Separate the oil from the aqueous liquid, place in a flask connected with a condenser, and distil in a current of steam.

The oil quickly passes over with the steam and is collected in a receiver. Separate the oil from the aqueous distillate as carefully as possible by means of the separating funnel, and dehydrate over a few pieces of fused calcium chloride.

The clear liquid decanted from the calcium chloride is distilled over wire gauze from a Wurtz flask provided with a thermometer. A small quantity of benzene first passes over and the temperature then rises rapidly, the chief portion which comes over between 150–155°, being separately collected. The colourless distillate is nearly pure monobrombenzene.

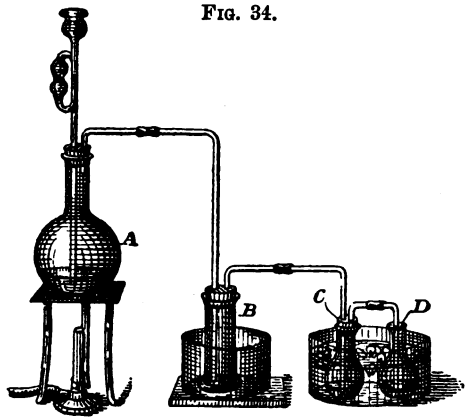
A small quantity of a crystalline residue remains in he flask; this is para-dibrombenzene. This compound may be submitted to steam distillation, when it will solidify in the condenser in prismatic crystals, melting at 89°. Collect a sample, and after well pressing between filter paper and allowing to remain for a few hours in the desiccator, determine percentage of bromine.

Now express in the form of an equation the action of bromine on benzene. What is the general action of the halogens on the hydrocarbons of the aromatic series?

Action of Nitrous Acid on Aniline (a study of the Diazo-Reaction).

Preparation of Diazobenzene Nitrate.—Prepare some aniline nitrate by mixing 15 grams of aniline with 16 grams strong nitric acid previously diluted with about 20 ccm. of water. Drain the crystalline mass of nitrate from the acid liquid, and wash once or twice with a little cold water. Introduce into each of the

Fig. 34.



flasks C and D an equal quantity of the nitrate, and sufficient water to form a stiff paste. Now pass a current of the oxides of nitrogen, generated from nitric acid (60 ccm.) and arsenic trioxide (60 grams) until the material in the flasks dissolves. Special care must be taken that the temperature of the liquid does

not exceed 10° C. To this end the flasks are kept in ice water, and the current of gas is cooled by passing through the empty cylinder B surrounded by ice water.

Filter, if necessary, and add to the filtrate an equal volume of strong alcohol, previously cooled to 0° C., and then a little cold ether. If the operation has been properly carried out, a copious precipitate of crystals of *diazobenzene nitrate* is formed. Filter off with the aid of a filter pump, and proceed without delay to study the properties of the compound.

(*a*) Dissolve a little in cold water and allow the solution to stand. Decomposition, indicated by change of colour, will take place.

(*b*) Boil a little with water in a small flask, and notice the odour of phenol. Connect flask to condenser, and distil over a few ccm. Test distillate with bromine water.

(*c*) Boil a few grams with strong alcohol in a small flask attached to a reversed condenser, and notice the odour of aldehyde. After boiling for some time add excess of water, and notice the light, nearly colourless oil, having the odour of benzene, at the top of the liquid. The oil can be separated by means of a separating funnel, and distilled with a little water, when it will be obtained quite colourless, and can be shown to be benzene.

(*d*) Boil a few grams with strong hydrochloric acid in a small flask attached to a reversed condenser. Add

water, when an oil will sink to the bottom of the flask; this is chlorbenzene. *Note.*—If hydrobromic acid is used instead of hydrochloric, brombenzene will be formed.

(*e*) Dissolve about a gram in a little cold water, and add either aqueous hydriodic acid, or an aqueous solution of potassium iodide. The diazo-compound is rapidly decomposed, and iodobenzene separates from the aqueous solution as a heavy oil, which can be purified by distilling with steam. It is obtained as a colourless liquid, which soon turns red on standing. (B.P. 188°, sp. gr. 1·69.)

(*f*) If to another portion dissolved in a little cold water, a little bromine, dissolved in potassium bromide, be added, a brown oil separates out, which, after pouring off the water and adding ether, solidifies; this is diazo-benzene perbromide. This compound, boiled with alcohol or glacial acetic acid, furnishes brombenzene.

(*g*) In all the foregoing experiments a gas is given off when the diazo-compound is decomposed; this gas can be shown to be nitrogen. Boil a little of the diazo salt with water in a test-tube, and collect some of the gas; show that it does not support combustion.

(*h*) Place a very small quantity of the compound, carefully dried by pressing between filter paper, on an anvil, and strike it sharply with a hammer. It explodes.

Now write out equations for the above experiments, and show how, having a nitro-compound, we can convert it into an amido-derivative; and, by employing the diazo reaction, convert the latter into—(1) the corresponding hydroxyl derivative; (2) into the corresponding chlorine, bromine, or iodine derivative; (3) and finally how the amido-group can be eliminated and replaced by hydrogen.

Sandmeyer's Modification of the Diazo Reaction for the substitution of Chlorine, Bromine, and Cyanogen in Aromatic Compounds.

Traugott Sandmeyer has found * that diazo-compounds are very readily decomposed in the presence of cuprous salts, giving rise to corresponding chlorine, bromine, or cyanogen derivatives, according to the salt of copper employed. In this modification the diazo-compound is not isolated, as will be seen in the following preparations.

Preparation of Monochlorbenzene from Aniline.—Prepare a solution of diazobenzene-chloride by dissolving 30 grams aniline in 67 grams strong acid diluted with 200 grams water; thoroughly cool in ice water, and add very slowly 23 grams sodium nitrite dissolved in 60 grams of water. Now, into a flask of about a litre capacity connected to an upright condenser, place

* Berichte der Deutschen Chemischen Gesellschaft Jahrg., xvii., 1633.

150 grams of a 10 per cent. solution of cuprous chloride,* heat to the boiling-point, and allow the diazobenzene chloride to flow from a separating-funnel, drop by drop, down the condenser, the flask meanwhile being kept well shaken. Each drop of the diazobenzene solution, as it meets the copper solution, produces a yellow precipitate, which, however, at once decomposes with evolution of nitrogen into an oil. When all the diazo-solution has been added, arrange the apparatus for distillation, and distil over the chlorbenzene, separate the oil from the aqueous distillate, dry over calcium chloride, and fractionate from a small flask. The chlorbenzene should distil over at about 130°.

Preparation of Brombenzene from Aniline.—25 grams of crystallised copper sulphate and 72 grams potassium bromide are dissolved in 160 grams of water; 24 grams of strong sulphuric acid and 40 grams of copper turnings are now added, and the whole boiled up in a flask furnished with a reversed condenser until the solution is almost decolourised; cool down, and add

* The cuprous chloride solution is prepared as follows:—25 parts (by weight) of crystallised copper sulphate and 12 parts sodium chloride are boiled together in a flask, with 50 parts water, until decomposition is complete, i. e. until sodium sulphate crystallises out. 100 parts of concentrated hydrochloric acid and 13 parts of copper turnings are now added, and the whole gently boiled until all colour is discharged, the flask meanwhile being loosely stoppered. Now, so much concentrated hydrochloric acid is added as is sufficient to make up the total solution to 203·6 parts. Of the copper added only 6·4 parts go into solution, so that we have 197 parts of a solution which contains 19·7 parts, that is one-tenth of the molecular weight, of anhydrous cuprous chloride.

19 grams of aniline; heat again to the boiling-point, and add from a dropping-funnel a solution of 14 grams sodium nitrite dissolved in 80 grams of water. The solution must be added drop by drop down the condenser, the flask in the meanwhile being kept well agitated. When all the nitrite has been added, arrange the apparatus for distillation. Separate the aqueous portion of distillate, and wash the oil with a little weak sodium hydroxide solution, then once or twice with water; extract with ether, carefully distil off the ether from a water-bath, dry the residue over a little calcium chloride, and proceed to carefully fractionate. The monobrombenzene should distil over at about 150–152°.

Preparation of Phenyl-cyanide from Aniline (replacement of the Amido-group by Cyanogen).—50 grams of copper sulphate are dissolved in 150 grams of hot water contained in a flask, and to the hot solution 56 grams of 9 per cent. potassium cyanide solution are added. The precipitate which at first forms quickly dissolves, a quantity of prussic acid being generated (for this reason the operation must be carried out in a fume cupboard or in the open air). When all the cyanide has been added, the flask is attached to a reversed condenser, the contents heated to about 90° C., and a solution of diazobenzene-chloride slowly added drop by drop down the condenser, the flask being kept well agitated. The diazobenzene-chloride solution is prepared as follows:—19 grams of aniline are dissolved in

200 ccm. of dilute hydrochloric acid (160 grams water and 40 grams strong hydrochloric acid), to this solution 14 grams of sodium nitrite dissolved in 40 grams of water are slowly added, care being taken to keep the mixture quite cold.

After all the solution of diazobenzene-chloride has been added to the copper solution, the apparatus is arranged for distillation. The oil which distils over with the water is separated as far as possible by means of a small separating-funnel, and the aqueous portion carefully extracted with ether. The latter is distilled off over the water-bath, and the residue mixed with the portion separated by means of the funnel. The whole of the oil is now dissolved in about four times its volume of ether, and the ethereal solution washed by agitation, first with a dilute solution of sodium hydroxide, then once or twice with water, and finally with a little dilute sulphuric acid. The ethereal liquid is carefully separated and allowed to stand some time over fused calcium chloride. The ether is distilled off over the water-bath, and the residue carefully distilled, noting the temperature. It should boil near 184°. *Experiment.*—Into a small flask provided with a cork and a long tube to act as a condenser, place about 2 ccm. of the phenyl cyanide and a little alcoholic potash. Digest at a gentle heat for some time, and notice the odour of the gas which is given off. After heating for about an hour, evaporate off the alcohol on a water-bath; to the residue add a little dilute hydrochloric acid, collect the precipitate on a

filter, wash with a little cold water, dry by pressing between filter paper, and sublime between watch-glasses. On determining the melting-point of the sublimate, it will be found to be that of benzoic acid. Confirm by the ordinary reagents.

Appendix to Diazo-Reaction.—Ludwig Gattermann has lately published (Ber. d. Deut. Chem. Ges. 1890, p. 1218), a modification of the diazo-reaction for the replacement of NH_2 by other radicles. The amido compound is diazotised in the usual way, and mixed with the salt whose acid radicle is to be substituted. Finely divided copper is then added, which brings about decomposition of the diazo-compound and the formation of the desired compound, which is isolated in an appropriate manner.

The application of this method to the preparation of *Phenylisocyanate*, $C_6H_5-N=CO$, from aniline will next be considered.—10 grams of aniline are dissolved in a mixture of 100 grams water and 20 grams concentrated sulphuric acid. To this solution 7·5 grams of sodium nitrite are added, in small portions at a time, and with all necessary precautions. The diazotised solution is then poured into a porcelain dish and mixed with a concentrated aqueous solution of 9 grams of pure potassium cyanate.*

* *Preparation of pure Potassium Cyanate* (Chichester, A. Bell, *Chem. News*, 32, § 99).—100 grams of dehydrated and finely-powdered potassium ferrocyanide are intimately mixed with 75 grams of finely-powdered and anhydrous potassium bichromate. This mixture is slowly, and in portions of 3–5 grams, introduced into a large iron crucible

Now add, with vigorous stirring, about 5 grams of copper powder.* An energetic reaction takes place, nitrogen is evolved, and the well-known pungent smell of the isocyanates is perceptible. (*Note.*—The operation must be conducted in a fume closet). When

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(or glue pot) which is heated *nearly* to low redness over a large Bunsen gas-burner. As the mixture is introduced it becomes black, and care must be taken not to heat to fusion. During the introduction of the mixture, an operation that should occupy about fifteen minutes, the contents of the crucible are kept well stirred by means of an iron spatula. The product of the reaction should present a loose porous appearance. After cooling, it is powdered and boiled up with five times its volume of 80 per cent. alcohol (dry methylated spirit). The alcoholic solution can be poured off quite clear from the heavy residue. In order to separate the potassium cyanate from its alcoholic solution, the containing vessel is placed in cold water and the contents vigorously stirred with a glass rod. The heavy white precipitate is collected on a filter, and the alcoholic filtrate employed again for extracting a further quantity of the cyanate. This is repeated until nothing further separates from the alcohol. On distilling off the alcohol an additional quantity of cyanate may be obtained. The various portions of cyanate are collected on the same filter, washed with a little absolute alcohol, well drained on the filter-pump, and finally washed with a little ether. The dry salt is preserved in a stoppered bottle.

* *Preparation of Copper-powder.*—To a cold saturated solution of copper sulphate, contained in a capacious porcelain basin, dust in, by the aid of a fine sieve, some recently-prepared zinc dust, and keep the solution well stirred throughout the operation. The addition of zinc is discontinued when only a faint blue colour remains. By this means we avoid a large excess of zinc. The hot supernatant liquid is allowed to cool down and then removed by decantation, the heavy precipitate of finely divided copper is then repeatedly washed with cold water. In order to remove a trace of zinc, the precipitate is treated with some *very* dilute hydrochloric acid until no further evolution of hydrogen is observed. The acid liquid is removed, the metallic precipitate collected on the filter-pump, well washed with water, and whilst in a moist state transferred to a stoppered bottle. It cannot be dried in the air without oxidising.

the reaction has somewhat moderated, add a further quantity of 5 grams copper powder. The oily layer which rises to the surface, consisting of phenyl-isocyanate, is removed as far as possible, by means of a glass spoon, from the decomposing action of the aqueous solution, and dissolved in ether. The addition of copper powder is continued until there is no further evolution of nitrogen. The whole of the ethereal solution is then filtered through cotton wool, carefully separated from aqueous liquid by means of a separating funnel, and dried over anhydrous potassium carbonate. The residue left after distilling off the ether is submitted to distillation over a small flame, and that portion coming over at about 163° C. collected. It is nearly pure phenylisocyanate.

Action of Oxidising Agents upon Aromatic Compounds.

Preparation of Benzoquinone (*Quinone*), $C_6H_4O_2$.—Fifty grams of commercial aniline are dissolved in a mixture of 400 grams strong sulphuric acid and 1500 grams water, contained in a large flask of about 4 litres capacity. To the well-cooled solution of aniline sulphate, 175 grams of finely-powdered potassium bichromate are slowly added in small portions at a time. After each addition of the bichromate the flask must be well shaken, and care must be taken that the temperature of the mixture does not rise above

the ordinary atmospheric temperature. The mixture changes from dark green to violet-black. When all the bichromate has been added the mixture is heated for a short time to 35° C. on the water-bath, and, after well cooling, extracted with small quantities of ether.

On distilling off the ether, quinone remains in the form of yellow needle-shaped crystals, which are usually discoloured by the presence of a substance called quinhydrone. The quinone may be further purified by distilling in a current of steam and extracting the distillate with ether, or by crystallisation from petroleum spirit.

Note.—The formation of quinone from aniline shows that the reaction consists in the elimination of the amido group and an atom of hydrogen, and the simultaneous substitution of two atoms of oxygen. The nitrogen is removed in the form of ammonia. The changes taking place cannot well be expressed in the form of an equation.

Quinone, when pure, melts at 116° C. It readily dissolves in ether and alcohol, sublimes on heating, and volatilises at the ordinary temperatures.

Preparation of Phthalic Acid, $C_6H_4<\begin{matrix}COOH\\COOH\end{matrix}$, *from Naphthalene.*—Mix 40 grams powdered naphthalene with 80 grams of powdered potassium chlorate and add this mixture gradually to 400 grams concentrated hydrochloric acid. Naphthalene tetrachloride, $C_{10}H_8Cl_4$, is formed in this reaction. Wash with water.

Now add gradually 400 grams of concentrated nitric acid (sp. gr. 1·45), and boil in a flask connected to an inverted condenser. When all is dissolved, distil off the excess of nitric acid, pour into a porcelain basin, add water, and continue evaporation in order to expel nitric acid; finally distil the residue. Phthalic *anhydride* passes over. Recrystallise from water. Determine melting-point. Sublime some of the phthalic acid, and determine the melting-point of the phthalic anhydride formed ($C_6H_4<^{CO}_{CO}>O$).

Phthalic anhydride reacts with phenols, giving rise to compounds known as phthaleïns.

Phenol-phthaleïn, $C_{20}H_{14}O_4$.—This interesting substance, now so extensively used as a substitute for litmus in alkalimetry, is prepared in the following manner:—Ten grams phthalic anhydride, 20 grams phenol, and 8 grams conc. sulphuric acid (dehydrating agent), are heated together in a small flask to 115–120° C. in an oil-bath for ten hours. The dark red and semi-fluid mass is poured into water and boiled until the smell of phenol has disappeared. When cool the yellow granular precipitate is separated by filtration, and washed with water. It is then dissolved in *dilute* sodium hydroxide solution, filtered from undissolved residue, and the filtrate acidulated with acetic acid and a few drops of hydrochloric acid. The solution, after standing a few hours, deposits phenol-phthaleïn as a light yellow crystalline powder. It is further purified

by dissolving in dry methylated spirit, adding about half its weight of freshly ignited animal charcoal, and digesting in a flask fitted to an inverted condenser on the water-bath for about an hour. The solution is filtered hot, the charcoal washed with a little hot alcohol, and the filtrate concentrated to about two-thirds of its bulk by evaporation or distillation. To the cooled solution water is added until it becomes turbid (about eight times the quantity of water will be required). The liquid is stirred and filtered to separate it from the resinous matter, and the filtrate evaporated down on the water-bath to expel alcohol. Phenol-phthalien will separate out as a white crystalline powder.

Determine the melting-point of a sample, and examine its behaviour with pure sodium carbonate, sodium and potassium hydroxide, and with ammonium hydroxide.

Explain fully the following equation :—

$$2C_6H_5OH + C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O = C_6H_4{<}\begin{matrix}C{=}(C_6H_4OH)_2\\CO\end{matrix}{>}O + H_2O$$

Special Note for Student.—Phenol-phthaleïn has been shown to be a derivative of triphenylmethane. The manner in which this relationship has been established forms a nice exercise for the earnest student.

Preparation of Anthraquinone. Estimation of Anthracene.—The most satisfactory method of assaying

crude anthracene is based on the conversion of the hydrocarbon into anthraquinone by the action of oxidising agents. The operation is carried out as follows:—1 gram of the carefully sampled specimen is placed in a flask of about 500 ccm. capacity connected to an inverted condenser. 45 ccm. of glacial acetic acid are then added, and the contents of the flask brought to the boiling-point, and while boiling a solution of chromic acid is added to it gradually, drop by drop, see Fig. 35. The chromic acid solution is prepared by dissolving 15 grams of the pure acid in 10 ccm. water and 10 ccm. glacial acetic acid. The addition of the chromic acid should occupy about two hours, and the contents of the flask should be kept gently boiling for two hours longer, four hours in all, this being necessary to insure complete oxidation of the impurities. The flask is then allowed to remain at rest for twelve hours, after which the contents are diluted with 400 ccm. of cold water and again left at rest for another three hours. The precipitated anthraquinone is now filtered off and well washed with cold water. It is next washed on the filter with a boiling hot solution of *dilute* caustic soda (1 part of soda to 100 parts water), and finally thoroughly washed with hot water until the filtrate exhibits no alkaline reaction. The precipitate is now washed from the

Fig. 35.

filter by means of a jet of water into a tared platinum dish, the water evaporated off at 100°, and the residue weighed. The weight of anthraquinone thus obtained ought not to be regarded as representing pure quinone, as it usually contains a certain proportion of inorganic impurities. Hence, the dish should be gradually heated, so as to completely sublime the anthraquinone, and the residue obtained deducted from the weight previously found. *Note.*—If a funnel be placed over the dish during sublimation, the anthraquinone will condense on the glass; the sublimate can be collected and preserved as a specimen. Its melting-point should be determined.

Preparation of Alizarin.—Weigh out 50 grams of fuming sulphuric acid (45 per cent. anhydride) into a small dry flask, and introduce in small portions an equal weight of finely divided anthraquinone. Keep the contents of the flask at about 160° for 3–4 hours. Dissolve the product in about 1½ litre of water, and neutralise with finely powdered chalk made into a thin cream with water; filter. To the filtrate add a solution of sodium carbonate until no further precipitate is produced, filter, and evaporate to dryness. The salt thus obtained is impure sodium anthraquinone sulphonate. In an iron crucible (a glue-pot will answer as well) prepare a strong syrupy solution of caustic potash; heat up to about 200° C. (see p. 116), and add in small portions about 20 grams of the sulphonate.

The heating is continued for some hours, and care

must be taken not to exceed a temperature of 260° C. If the crucible is heated in an oil-bath there is less risk of exceeding this temperature, and the operation is more under control.

The formation of alizarin during the fusion of the salt with caustic potash is shown by the dark purple colour of the mass. When a little of this is dissolved in water it should form a beautiful purple-red solution. Continue the fusion until the mass acts in this way. Dissolve in a litre of water and acidify; alizarin is thrown down in brown amorphous flocks. Filter off, dry, and sublime between watch-glasses.

Note.—On a commercial scale the sulphonate is heated with strong potash solution under pressure. The fusion requires a long time, and is conducted at a lower temperature.

Preparation of Cinnamic Acid, $C_6H_5CH : CH . CO_2H$, *from Liquid Storax.*—Into a capacious flask connected with a condenser introduce about 30 grams of *liquid storax*, along with 15 grams of ordinary crystallised sodium carbonate and 250 ccm. of water. Heat to boiling and pass in a rapid current of steam. When about 200 ccm. have been collected, the operation is discontinued. The distillate contains some oily drops of styrene (what is its formula?) which can be separated and preserved. The residual liquid in the retort is poured off from the resinous residue.*

* This residue contains an oily substance named "styracin," which is cinnyl cinnamate, $C_6H_5-CH=CH-COOC_9H_9$. If then the whole

The filtrate is mixed at first with just so much dilute sulphuric acid that a very small quantity of cinnamic acid is precipitated along with dissolved resin, and the liquid filtered from this precipitate is treated with excess of sulphuric acid, which precipitates cinnamic acid of a tolerably white colour. It is further purified by dissolving in a large quantity of water with as little sodium carbonate as possible, and again precipitating, first with a little sulphuric acid, and then, after filtration, with an excess of acid, by which treatment a white precipitate is obtained. Collect and wash with a little water and crystallise from alcohol. Pure cinnamic acid melts at 133° C. Determine melting-point of sample obtained as above.

Reactions of Cinnamic Acid.—(1) Dissolve a little of the acid in water with the aid of ammonia, boil off the excess of the latter so as to obtain a solution of neutral ammonium cinnamate, and add a few drops of ferric chloride to the solution. A buff coloured precipitate is obtained very like that produced by a benzoate; the two acids are, however, sufficiently distinguished by many other reactions, e. g. manganous chloride

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material in the flask be distilled with a strong solution of caustic potash or soda, the ethereal salt is saponified and cinnylic alcohol passes over. The milky distillate is saturated with common salt, in whose solution the alcohol is less soluble than in pure water; an oily layer is formed which afterwards solidifies. Cinnylic alcohol crystallises from water in soft silky crystals, having a sweet taste and an agreeable odour of hyacinths, melting at 33° C., and when carefully oxidised affords first the aldehyde and then cinnamic acid.

produces a whitish precipitate with a cinnamate, but not with a benzoate. (Try it.)

(2) A solution of cinnamic acid boiled with peroxide of lead or chromic acid gives the odour of cinnamon and bitter almond oil (benzoic aldehyde).

Synthesis of Cinnamic Acid.—A knowledge of the fact that cinnamic acid affords benzoic aldehyde on decomposition enabled Dr. W. H. Perkin to successfully employ this substance in conjunction with acetic-anhydride and sodium acetate in the synthesis of cinnamic acid. This method, which is known as "Perkin's reaction," is applicable to substituted aromatic aldehydes on the one hand and a large number of fatty acids on the other.

12·5 grams benzaldehyde, 6·5 grams sodium acetate previously fused and powdered, and 19 grams acetic anhydride, are mixed together in a small flask fitted to a reversed condenser and kept at a gentle boil for about eight hours. After cooling add water and a slight excess of sodium carbonate and distil off any unchanged benzaldehyde. After removing resinous by-products by filtration add at first a *small* quantity of dilute sulphuric acid, filter, and treat the filtrate with excess of acid, and proceed exactly as in the purification of cinnamic acid from liquid storax.

Compare the acid prepared above with that obtained from storax.

The manufacture of cinnamic acid has being considerably simplified by Dr. Caro, of Mannheim.

Toluene is converted into benzylene dichloride by the action of chlorine on the boiling hydrocarbon, and this is heated directly with sodium acetate, when the following reaction takes place—

$$C_6H_5.CHCl_2 + CH_3{-}CO{-}ONa = C_6H_5CH = CH{-}COOH + NaCl + HCl.$$

The cinnamic acid thus obtained is the starting point for the production of *artificial indigo.*

Preparation of Indigotin, C_8H_5NO, *from Commercial Indigo.* (*Operation to be made roughly quantitative.*)—About five grams of *finely* powdered indigo are well mixed in a mortar with an equal weight of pure recently-slaked lime. The mixture is transferred to a stoppered bottle of known capacity (about one litre), the mortar being well rinsed with water which is added to the contents of the bottle. The latter is now heated in a water-bath for some hours and a quantity of powdered ferrous sulphate is added; the bottle is now filled up with *hot* water, the stopper inserted, and after the contents have been well shaken the whole is left at rest for about 12 hours, till the indigo is reduced and the sediment has sunk to the bottom. A portion of the clear liquor is then drawn off with a siphon, and the quantity of liquid having been accurately measured (say 250 ccm.), it is mixed with an excess of hydrochloric acid and oxidised by forcing a gentle current of air through the solution; the precipitate is collected on a tared filter and washed with water.

It is then dried in the water-oven and weighed, and the quantity of indigotin obtained calculated on the total quantity of indigo employed.

Experiments with Indigo.—The yellow supernatant liquid obtained in the reduction of indigo represents the "cold vat" of the dyer.

(1) Take a small piece of white calico, and having cleansed thoroughly in boiling water, soak it in the clear liquid left in the bottle, and then remove into the air. It soon acquires a blue colour.

Note.—Explain the changes brought about in the foregoing experiments.

(2) Drop a little of the pure indigotin obtained as above on a piece of heated platinum foil; notice that it volatilises in purple vapours, leaving little or no residue. Repeat, using commercial indigo, and notice residue left.

(3) Stir up a little indigotin with water into a thin paste and test separate portions with (*a*) chlorine water, (*b*) bromine water, and (*c*) nitric acid, strong and dilute.

(4) Treat separate portions of indigotin with strong sulphuric acid and with fuming acid.

Preparation of Isatin, $C_8H_5NO_2$, *from Indigo.*—250 grams of *finely* powdered good commercial indigo are stirred up in a large dish to a thin paste with water; the mixture is then placed over a water-bath and heated up to 90–95° C. Commercial nitric acid is now added in successive portions of about 10 ccm.,

until the blue colour has disappeared (from 150 to 180 grams of acid will be required). After each addition of nitric acid it is necessary to wait until the effervescence which is produced is over before adding more acid. If no effervescence takes place, in consequence of the indigo being mixed with too much water or not sufficiently heated, and the addition of nitric acid is continued, a violent reaction suddenly ensues when the solution has reached a certain concentration, the mass overflowing the vessel. The operation must not therefore be hurried, and the contents of the dish must be kept well stirred. Hot water must also be added from time to time, to replace that lost by evaporation.

When the necessary amount of nitric acid has been added, the solution is mixed with about four times its volume of hot water, and the whole boiled up and filtered as rapidly as possible; after standing 12 hours the isatin separates in reddish crystalline nodules. The mother-liquor is again boiled up with the undissolved residue and filtered, the operation being two or three times repeated. The mother-liquor yields more isatin on evaporation.

In order to purify the crude isatin it is neccessary to moisten the crystals with water containing a little ammonia (to remove resinous matter); then wash with a little cold water and crystallise from hot alcohol. Another method of purification, when the isatin is contaminated with much resinous matter, is as

follows:—The crude isatin is dissolved in moderately strong caustic potash, and dilute hydrochloric acid added to the solution as long as it forms a black or brown precipitate; when a portion on filtering is of a pure yellow colour, and gives a highly red precipitate with hydrochloric acid, the whole solution is filtered off and the precipitation completed by the further addition of hydrochloric acid. The precipitate is collected, washed with water, and crystallised, if necessary, from alcohol.

Properties of Isatin.—Isatin does not unite with acids, but plays the part of an acid, exchanging an atom of hydrogen for an equivalent of metal. Of the salts of isatin we may prepare that of silver, which is obtained as a wine-red crystalline precipitate by mixing silver nitrate with an alcoholic solution of isatin. Collect and wash with a little alcohol, and allow to dry in the desiccator. When dry determine percentage of silver.

Isatin dissolves in strong sulphuric acid, and this solution is used as a test for thiophene in benzene.

Experiment.—Agitate a few ccm. of commercial benzene with the solution of isatin in strong sulphuric acid: a deep blue colouration is produced, due to the formation of *indophenin*,—

$$C_8H_5NO_2 + C_4H_4S = C_{12}H_7NSO + H_2O.$$

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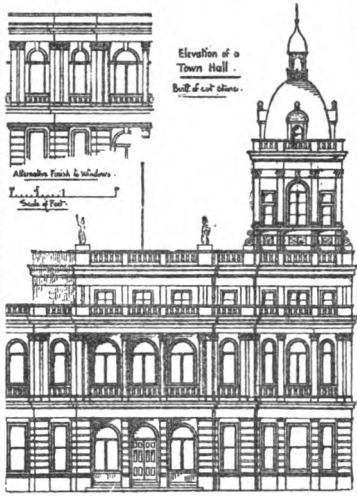

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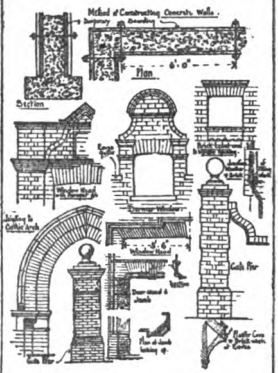

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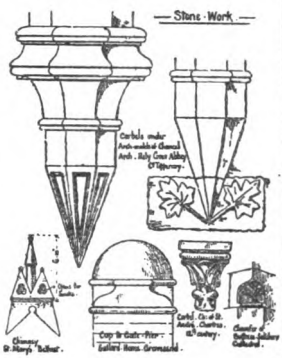

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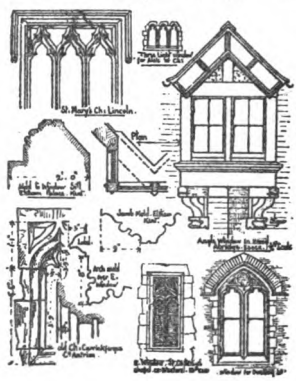

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