



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

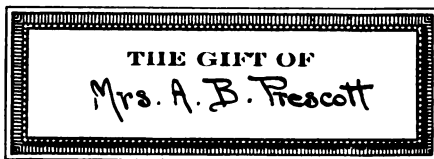
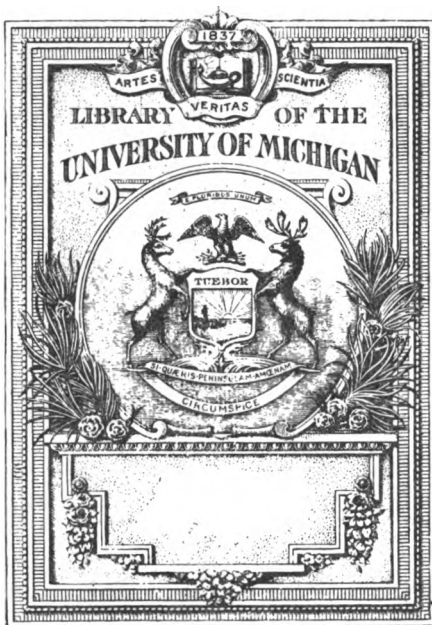
### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

# An elementary course of practical organic chemistry

Frederic Charles  
Garrett, Arthur  
Harden

# **An elementary course of practical organic chemistry**



QD  
261  
.G24





# **PRACTICAL ORGANIC CHEMISTRY**





AN ELEMENTARY COURSE  
OF  
PRACTICAL ORGANIC CHEMISTRY

BY  
*F. C. Garrett*  
F. C. GARRETT, M.Sc. (VICT. et DUNELM.)

ASSISTANT LECTURER AND DEMONSTRATOR IN CHEMISTRY  
THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE

AND

ARTHUR HARDEN, M.Sc. (VICT.) PH.D.

ASSISTANT LECTURER AND DEMONSTRATOR IN CHEMISTRY  
THE OWENS COLLEGE, MANCHESTER

LONGMANS, GREEN, AND CO.

89 PATERNOSTER ROW, LONDON

NEW YORK AND BOMBAY

1897

All rights reserved

20

8-5-22 M.H.13.

## PREFACE

---

10.10.22 : P. 6-24 : 7

IN order to be of the highest educational value, it is necessary that the practical work of a student commencing the study of Organic Chemistry should deal, as far as possible, with the very substances and subjects which are being treated in the lecture room. The compounds which are there described, and of which the constitution and properties are discussed, should as soon as possible be actually prepared and their behaviour experimentally examined by the student himself. The advantage, and at the same time the difficulty, of arranging a suitable practical course to thus accompany the theoretical instruction in Organic Chemistry, has been deeply felt by the authors in their teaching experience, and it is hoped that the following selection of preparations and experiments, the details of which have been carefully tested, may provide, at all events, a partial solution of the problem.

As will be seen from the Table of Contents, the course of the work follows the arrangement now adopted in most

of the elementary text-books, and, presumably, in most of the elementary lectures dealing with theoretical Organic Chemistry.

With the view of rendering the work suitable for use in Technical Schools and Colleges, for which it is specially intended, care has been taken to describe only such experiments as can be successfully carried out in the somewhat limited periods of time which are at the disposal of students in such institutions; the important question of expense has also been borne in mind, and every endeavour has been made to avoid the use of costly materials and apparatus.

The authors are indebted to many friends for assistance in the preparation of this book, and to Dr. H. G. Colman for kindly reading the proof-sheets.

F. C. GARRETT.

ARTHUR HARDEN.

# CONTENTS

CHAPTER	PAGE
I. PRELIMINARY . . . . .	1
Purification of Methylated Spirit	
II. QUALITATIVE DETECTION OF CARBON, HYDROGEN, NITROGEN, SULPHUR, AND CHLORINE . . . . .	3
III. DETERMINATION OF PHYSICAL CONSTANTS . . . . .	6
Melting-Point.	
Boiling Point	
IV. DETERMINATION OF MOLECULAR WEIGHTS . . . . .	8
Dumas' Vapour Density Method	
Victor Meyer's Vapour Density Method	
Determination of the Molecular Weight of Acetic Acid	
V. THE PARAFFINS . . . . .	13
Preparation of Marsh Gas from Sodium Acetate, and of Ethane from Ethyl Iodide	
VI. UNSATURATED HYDROCARBONS . . . . .	16
Preparation of Ethylene and Ethylene Dibromide	
Preparation of Acetylene	
Copper Acetylide	
VII. HALOGEN DERIVATIVES OF THE PARAFFINS . . . . .	20
The Preparation and Properties of Ethyl Bromide and Methyl Iodide	
VIII. THE ALCOHOLS . . . . .	23
Preparation of Ethyl Alcohol by Fermentation	
Fractional Distillation. Reactions of Ethyl Alcohol, and of Methyl Alcohol	
IX. THE ETHERS . . . . .	28
Synthesis of Ethyl Ether. Preparation and Properties of Ethyl Ether and of Potassium Ethyl Sulphate	
X. THE ALDEHYDES AND THEIR DERIVATIVES . . . . .	33
Preparation and Properties of Acetaldehyde	
Reactions of Aldehyde and of Chloral	
Preparation of Chloroform and Iodoform	
XI. THE KETONES . . . . .	37
Preparation of Acetone. Reactions of Acetone	

## CHAPTER

XII.	THE FATTY ACIDS AND THEIR DERIVATIVES . . . . .	39
	Preparation of Acetic Acid from Alcohol	
	Reactions of Acetic Acid	
	Ethyl Acetate. Hydrolysis of Ethyl Acetate and Recognition of the Products	
XIII.	THE FATTY ACIDS AND THEIR DERIVATIVES ( <i>continued</i> ) . . . . .	43
	Preparation and Properties of Acetyl Chloride, Acetic Anhydride, Acetamide, and Acetonitrile	
	Hydrolysis of Acetonitrile	
	Preparation and Properties of Formic Acid	
XIV.	ETHEREAL SALTS OF THE ALCOHOLS . . . . .	49
	Ethyl Nitrite. Amyl Nitrite (See also Chapters VII. and IX.)	
XV.	PREPARATION AND PROPERTIES OF GLYCOL . . . . .	50
XVI.	THE DIBASIC ACIDS . . . . .	51
	Preparation of Oxalic Acid from Sugar. Reactions of Oxalic Acid. Methyl Oxalate. Oxamide	
	Reactions of Tartaric Acid	
XVII.	GLYCEROL AND ITS DERIVATIVES . . . . .	54
	Preparation of Glycerol from Fats. Saponification	
	Soap. Tests for Glycerol	
	Acrolein. Preparation of Allyl Alcohol	
XVIII.	THE CARBOHYDRATES . . . . .	56
	Reactions of Glucose, Fructose, Lactose, Maltose, Cane-sugar, Starch, and Cellulose	
	Preparation of Glucose and Fructose from Cane-sugar	
	Glucosazone. Production of Glucose from Starch and Cellulose. Parchment Paper	
XIX.	THE CYANOGEN COMPOUNDS . . . . .	62
	Preparation and Properties of Cyanogen	
	Preparation of Dilute Hydrocyanic Acid. Reactions of Hydrocyanic Acid	
XX.	SYNTHESIS OF UREA . . . . .	64
	Preparation of Urea and Urea Nitrate	
	Tests for Urea	

## APPENDIX

QUALITATIVE TESTS REQUIRED FOR THE ELEMENTARY STAGE OF THE SCIENCE AND ART DEPARTMENT'S EXAMINATION . . . . .	66
---	----

INDEX . . . . .	71
-----------------	----

# AN ELEMENTARY COURSE OF PRACTICAL ORGANIC CHEMISTRY

---

## CHAPTER I

### PURIFICATION OF METHYLATED SPIRIT

ORDINARY commercial methylated spirit, which is a mixture of ethyl and methyl alcohols, usually contains, in addition to water, small amounts of aldehyde and other substances which yield a dark brown mass when the alcohol is boiled with potash. It is best to purify a moderately large quantity of the spirit, and it can then be used for recrystallisations, &c., and for certain preparations in which the presence of methyl alcohol is not a disadvantage.

Place two litres of methylated spirit in a large flask connected with a back-flow condenser (fig. 1), add fifty grams of solid caustic potash (in sticks), place a small piece of unglazed porous plate in the flask in order to ensure steady boiling, and heat

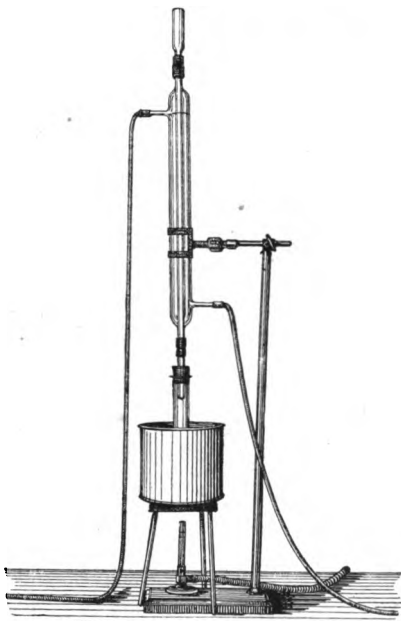


Fig. 1

\*B



the whole in the water-bath for three hours. Then arrange the condenser in the ordinary way (fig. 2), distil off the alcohol, wrapping the head of the flask in a towel to prevent unnecessary cooling. The dehydration of the distillate is effected by placing it in a tin can or glass bottle almost one-quarter filled with small lumps of good quicklime (about the size of a marble), and

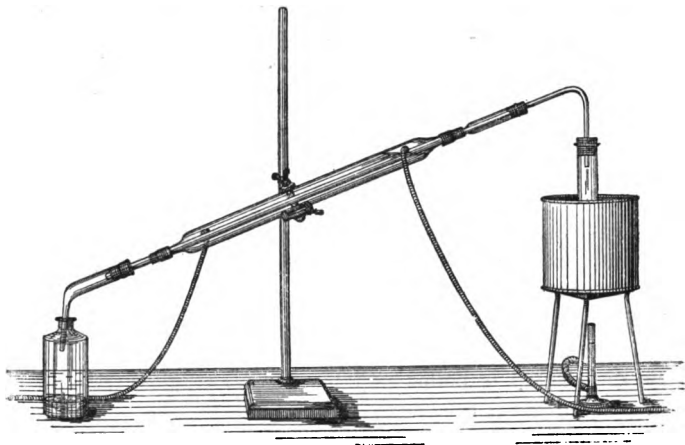


FIG. 2

allowing to stand for forty-eight hours. If a tin can is used, this may then be placed in the water-bath, a duster being arranged between the bottom of the bath and the can, the latter connected with a condenser, and the alcohol distilled off. If not, the liquid is poured into a flask, with the addition of a piece of porous plate, and distilled on the water-bath.

Commercial methylated spirit sometimes contains light petroleum, which separates out as a distinct layer when water is added. Such spirit is quite unsuitable for use in the following preparations.

## CHAPTER II

## THE DETECTION OF THE COMMONER ELEMENTS IN ORGANIC COMPOUNDS

**Detection of Carbon and Hydrogen.**—Make a test-tube, about six inches long and half an inch internal diameter, of infusible glass, and fit it with a good cork and a delivery-tube bent at right angles. Dry some copper oxide by heating it in a small porcelain dish over the Bunsen burner for about ten minutes, and allow it to cool in a desiccator. (Copper oxide is hygroscopic.)

Fill the test-tube to the depth of about three-quarters of an inch with copper oxide, add about a quarter of a gram of powdered sugar intimately mixed with about ten times as much copper oxide, and then copper oxide until the tube is about two-thirds full, taking care not to pack it too tightly; insert the cork, support the apparatus with the delivery-tube dipping under lime water (fig. 8), and heat the contents of the tube strongly, commencing at the end nearest to the cork. The sugar deprives part of the oxide of copper of its oxygen, and is itself burnt to carbon dioxide and water, the former turning the lime water milky, and the latter condensing on the cold parts of the tube.

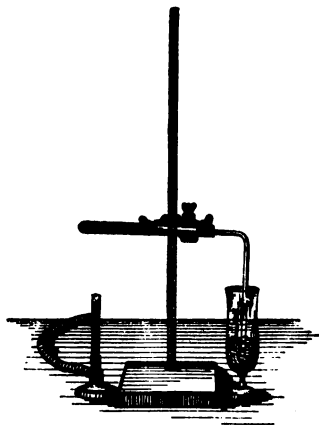
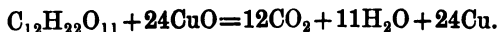


FIG. 8



\* 2 2

**Detection of Nitrogen.**—I. The nitrogen of many organic bodies is driven off as ammonia when they are heated with soda-lime.

Mix a small fragment of cheese or of urea with five or six parts of soda-lime, and heat in a test-tube; ammonia is given off and may be recognised (*a*) by its turning a wet piece of red litmus paper blue; (*b*) by its giving white fumes when a drop of strong hydrochloric acid is brought to the mouth of the tube; (*c*) by its smell.

II. Most organic compounds which contain nitrogen, when heated with metallic potassium or sodium, give potassium or sodium cyanide.

In a *dry* test-tube place a small fragment of gelatine, add two or three chips of *dry* potassium (or sodium), and heat cautiously. The reaction is at first a violent one, but must be completed by heating rather strongly; when it is at an end break the tube by placing the hot end in cold water. An alkaline solution is thus obtained, which must be filtered and tested for a cyanide. Dissolve some ferrous sulphate in cold water, and add a drop or two of ferric chloride solution; on adding this to the alkaline cyanide solution and boiling, a thick precipitate is obtained, consisting of ferrous and ferric hydrates, whilst sodium ferrocyanide is formed in solution. Add dilute hydrochloric acid until the solution is strongly acid, when the hydrates are dissolved and Prussian blue formed, which indicates the presence of a cyanide.

**Detection of the Halogens.**—Fix a fragment of copper oxide in a loop of platinum wire, and heat it strongly until it no longer colours the Bunsen flame green; allow to cool, and then add to the oxide a small quantity of the substance to be tested (chloroform will do very well), and heat in the outer Bunsen flame. The substance first burns, and then the copper halide colours the flame green.

**Detection of Sulphur.**—When non-volatile substances are fused with a mixture of potassium nitrate and sodium carbonate, they are destroyed, and any sulphur they may contain is oxidised and converted into sodium sulphate.

Mix about a quarter of a gram of gelatine with five or six

parts of this mixture (having first carefully tested both the salts for sulphates) on platinum foil, and heat over the Bunsen burner until the mixture melts to a clear liquid ; allow to cool, dissolve the melt in warm water, acidulate with nitric acid, and then test for sulphuric acid by adding barium chloride.

## CHAPTER III

## DETERMINATION OF PHYSICAL CONSTANTS

**Determination of the Melting Point of a Substance.**—The melting point is usually determined by bringing a small quantity of the substance under examination into a capillary-tube attached to the bulb of a thermometer, and slowly heating it in a bath of water, of sulphuric acid, or of paraffin wax, according to the temperature required. Fit up an apparatus similar to that shown in

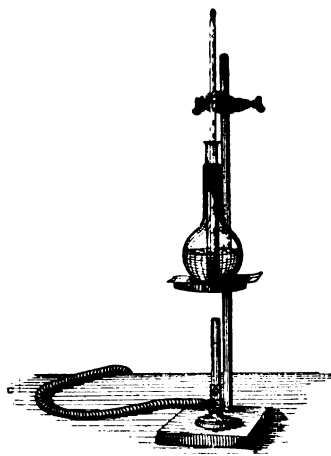


FIG. 4

fig. 4. A thermometer is fixed in a test-tube by means of a cork, a nick being filed down the side of the cork so that the joint may not be air-tight. The tube is then supported in an eight-ounce flask by a ring of cork or of rubber, taking care that this joint also is not air-tight. Fill the flask about two-thirds full of strong sulphuric acid, and arrange the thermometer so that the whole of the bulb is below the surface of the acid. Prepare a capillary tube two to two and a half inches long, sealed at one end; introduce a few small fragments of

iodoform, fasten the tube to the thermometer by an india-rubber ring (a fragment of small tubing is best), so that the solid is about on a level with the centre of the mercury bulb, put the thermometer in position in the bath, and heat the acid with a

small flame until the iodoform melts. The heating must be done very gradually, and the temperature should rise very slowly. Note the temperature at which the iodoform melts, and also note that it melts *suddenly*. Impure substances usually melt gradually. Repeat the experiment twice, with fresh quantities of iodoform, and compare the results.

**Determination of the Boiling Point of a Liquid.**—The boiling point of a volatile liquid can usually be determined with sufficient accuracy by simply distilling a small quantity of it.

Fill a two-ounce distilling flask half full of chloroform (or water), connect the side tube with a condenser by means of a well-fitting cork, close the neck of the flask by a good cork carrying a thermometer, arrange the thermometer so that the *whole* of the bulb is below the level of the side tube, heat on the sand-bath or wire gauze, and distil about 15 cc. of the liquid, noting the temperature frequently. If the liquid is pure the temperature should be practically constant.

For accurate work a more elaborate apparatus may be used, and corrections must be introduced for variations of the atmospheric pressure, &c.; but for these the student must be referred to the larger treatises.

## CHAPTER IV

## DETERMINATION OF MOLECULAR WEIGHTS

**I. Determination of the molecular weight of Acetic Acid by ignition of Silver Acetate.**—Prepare some silver acetate by dissolving 2.7 grams of sodium acetate in 20 cc. of hot water, and adding 8.4 grams of silver nitrate, also dissolved in 20 cc. of hot water; silver acetate ( $2\frac{1}{2}$  to 3 grams) gradually separates in small white or greyish plates. Filter (preferably by the pump), wash three times with *small* quantities of cold water, press the solid lightly between filter papers, and place in the desiccator until perfectly dry.

Weigh out about half a gram of the dry salt into a weighed porcelain crucible, heat over the Bunsen burner for ten minutes with the cover on, and weigh again; repeat the heating and weighing until the weight becomes constant. The residue in the crucible is pure silver.

Acetic acid being a monobasic acid, a molecule of the silver salt must contain 108 parts of silver (108 being the atomic weight of silver), and, therefore, if  $x$  gram of the salt yield  $y$  gram of silver, the molecular weight of silver acetate must be  $\frac{108x}{y}$ . But if an atom of silver (108) be replaced by an atom of hydrogen (1) we shall obtain a molecule of the acid, so the molecular weight of the acid is  $\frac{108x}{y} + 1 - 108$ .

**Example.**—0.6485 gram of salt gave 0.4185 gram of silver; then the molecular weight of the silver salt will be  $\frac{108 \times 0.6485}{0.4185} = 169.4$ . The molecular weight of the acid then



## DETERMINATION OF MOLECULAR WEIGHTS

will be  $169.4 + 1 - 108 = 62.4$ . The molecular weight calculated from the formula  $C_2H_4O_2$  is 60.

**II. Determination of the molecular weight of ether by observing its vapour density.**—The most direct way to determine the vapour density of a volatile liquid is by Dumas's method.

Take a glass bulb of about 150 cc. capacity drawn out to a fine neck, and weigh it exactly; introduce about 10 cc. of ether by first warming the bulb, then dipping its neck into ether and allowing the bulb to cool; as the air inside the bulb contracts, ether is driven up into the bulb. Now fix the bulb in a bath of hot water at about  $70^\circ$ , taking care that only the narrow neck projects above the surface (fig. 5). The ether boils, and the escaping vapour can be lighted at the end of the fine tube; when no more vapour escapes (which is known by the flame dying down and going out), quickly seal the neck of the bulb by means of the blow-pipe, taking care not to lose the bit of glass that is drawn off in the sealing. At once notice the temperature of the bath ( $T$ ), remove the bulb from the bath, dry it, and while it is cooling observe the height of the barometer ( $P$ ), and the temperature ( $t$ ) of the balance case or room. Then weigh the bulb and the fragment of tube drawn off during the sealing—this gives the weight of the bulb full of ether vapour.

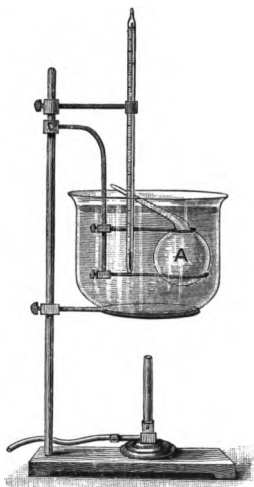


FIG. 5

After weighing, break the point of the tube under water, when, if the operation has been properly done, the water rushes in and almost completely fills the globe, a very small bubble of air being usually left; now weigh again, the increase shows the weight of water that has entered, and hence gives the capacity of the globe ( $v$ ).

Having thus obtained the weight of the bulb when full of air at  $t^\circ$  and under  $P$  mm. pressure, the weight of the same bulb full of ether vapour at  $T^\circ$  and under  $P$  mm. pressure; and the

capacity of the bulb, the calculation of the vapour density is not difficult.

The capacity of the bulb is  $v$  cc., and hence if the bulb were to be exhausted at the air-pump and then sealed up and weighed, its weight would be that of the open bulb *minus* the weight of  $v$  cc. of air at the temperature ( $t^\circ$ ) and pressure ( $P$ ) of the balance case. The weight of vapour contained in the bulb after the experiment is, of course, equal to the weight of the bulb full of vapour *minus* the weight of the exhausted bulb, and hence this difference gives the weight of  $v$  cc. of vapour at the temperature of the bath ( $T$ ), and the pressure of the air.

This must then be divided by the weight of an equal volume of air or hydrogen at the same temperature and pressure, and the result is the relative density of the vapour.

**III. Determination of the Vapour Density by Victor Meyer's method.**—This is the most convenient method for determining the density of the vapour of a volatile substance, and consists in measuring the volume of air displaced by the vapour produced from a known weight of the substance. The apparatus consists of a glass cylinder, to which is sealed a long and rather narrow glass stem, closed at the top by a cork, and provided with a narrow side tube ;

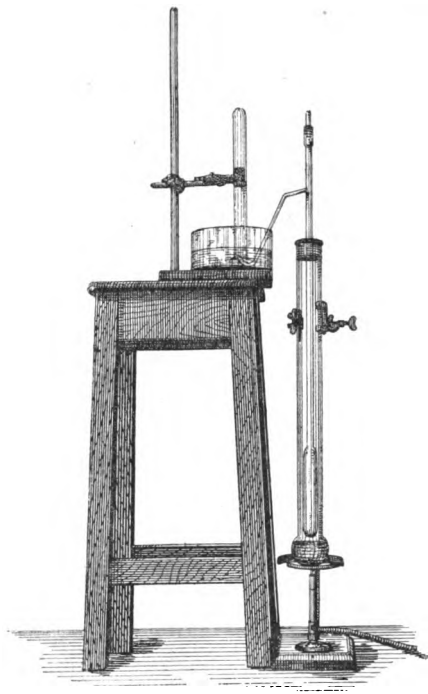


FIG. 6

a little asbestos or clean dry sand is placed in the cylinder to break

the fall of the bulb to be introduced later, and the whole apparatus must be perfectly dry. This is placed in a metal or glass boiling tube, and heated by the vapour of water, or some other substance placed in the latter; the side tube dips into the water of a small glass dish, and the apparatus is heated until the air in the cylinder has attained the temperature of the bath and no more bubbles escape from the side tube. About 0.2 gram of the liquid to be examined (pure chloroform for example) is introduced into a small weighed glass tube, sealed at one end and drawn to a point at the other; the point sealed, and the tube again weighed; the point is then cut off—care being taken that none of the liquid is lost—the tube dropped into the Meyer apparatus, the cork being *instantly* replaced, and a graduated tube full of water immediately brought over the end of the side tube. The liquid rapidly evaporates and expels a quantity of air which is collected in the graduated tube. It is not necessary that we should know the temperature of the bath, as what has to be found is the weight of air displaced by the vapour, and of course this weight will be the same whether its volume is observed at the temperature of the bath or at that of the room; the temperature of the bath should, however, be at least forty degrees above the boiling point of the liquid under examination.

The escape of air usually continues for a minute or two, and after it has ceased the tube is transferred to a cylinder of water, and the volume of the gas, the temperature of the water, and the atmospheric pressure read off and noted, taking care that the level of the water is the same in the tube and in the cylinder. The weight of this air is then calculated, and the vapour density found by dividing the weight of liquid taken by the weight of air displaced.

**Example.**—0.1008 gram of chloroform (heated by water vapour) displaced 20 cc. of air, measured at 15°C. and 770 mm. over water.

This volume of air would therefore =  $\frac{20 \times 273 \times (770 - 18)}{288 \times 760}$  cc.  
 = 18.9 cc. of dry air at NTP (18 mm. being the tension of aqueous vapour at 15°). The weight is :  
 $18.9 \times 0.001293 = 0.0244$  gram.

The vapour density of  $\text{CHCl}_3$  is therefore  $\frac{1008}{0244} = 4.18$  compared with air, or  $4.18 \times 14.39 = 59.4$  compared with H. The molecular weight is accordingly  $59.4 \times 2 = 118.8$ , and this agrees with that calculated from the empirical formula  $\text{CHCl}_3$ —118.5.

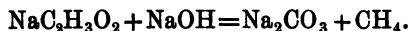
## CHAPTER V

## THE PARAFFINS

**Preparation of Methane, CH<sub>4</sub>.**—Methane is most easily prepared by heating together anhydrous sodium acetate and soda-lime.

Sodium acetate crystals contain three molecules of water, and are converted into the anhydrous salt by the action of heat; the heating must be done very carefully, as if the salt is heated too strongly it is decomposed. Place the salt in a metal or porcelain dish, heat carefully, and stir; the salt melts in its water of crystallisation, and resolidifies when most of this is driven off. On now heating more strongly the remainder of the water is driven off and the salt melts a second time. As soon as the mass commences to darken stop heating it; if bubbles of inflammable gas appear the salt has been over-heated.

Mix fifteen grams of the *anhydrous* acetate with sixty grams of soda-lime, grind the mixture to a fine powder, place it in a small dry flask fitted with a cork and delivery tube, and heat carefully, but strongly. Impure methane is evolved, and can be collected over water (fig. 7); collect two jars of the gas.



Methane is a colourless, tasteless, and odourless gas; it is lighter than air, burns with a non-luminous flame, and is incapable of combining directly with the halogens.

To the first jar apply a light; the gas burns,<sup>1</sup> but as it is not pure the flame is slightly luminous.

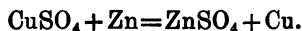
The gas in the second jar may be shown to be lighter than air by 'pouring it up' into another jar, as in the familiar experi-

<sup>1</sup> When examining the combustion of a gas the burning gas should be driven from the jar by pouring in water. A much larger flame is then obtained.

ment with hydrogen; the gas collected in the upper jar is mixed with air and forms an explosive mixture.

The paraffins may be obtained in a much purer condition by reducing an alcoholic solution of a mono-halogen substitution product (such as ethyl iodide) by a 'copper-zinc couple.'

**Preparation of Ethane,  $C_2H_6$ .**—Fill a small flask with granulated zinc, and wash the zinc, first with very dilute sulphuric acid, then three times with water; then add a three-per-cent. solution of copper sulphate and allow the mixture to stand. Copper is deposited on the zinc, forming a 'copper-zinc couple,' and the solution becomes colourless:



As soon as this is the case pour off the liquid and refill the flask with copper sulphate solution. Finally, wash the couple

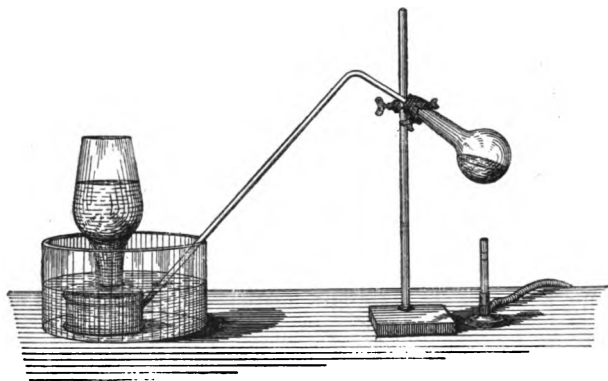
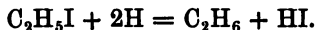


FIG. 7

twice with water, and once with strong methylated spirit, after which it is ready for use.

Dissolve four grams of ethyl iodide in about the same quantity of strong methylated spirit, pour it into the flask, insert a cork fitted with a glass delivery tube and collect the escaping gas over water.



The reaction sets in at once, and a steady stream of the gas

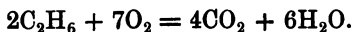
continues to be evolved for about fifteen minutes; time may be saved by warming the flask *gently*, but much less gas is obtained in this way, and it is also less pure.

About 500 cc. of gas can be obtained from four grams of ethyl iodide, and should be collected in two bottles.

Ethane is a colourless gas without taste or smell, which burns with a bright, luminous flame, and does not combine directly with the halogens.

To the first bottle add about 5 cc. of bromine water and shake. The colour of the bromine is not destroyed (cf. Ethylene and Acetylene).

To the remainder of the gas apply a light; the gas burns with a bright, luminous flame.

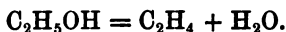




## CHAPTER VI

## UNSATURATED HYDROCARBONS

**Ethylene,  $C_2H_4$ , and Ethylene Dibromide,  $C_2H_4Br_2$ .**—Place a mixture of 25 grams of alcohol and 150 grams of strong sulphuric acid in a 30-oz. flask fitted with a dropping funnel and a delivery tube; heat on a sand bath until ethylene is steadily evolved; then run in from the dropping funnel a mixture of one part of alcohol to two of sulphuric acid, regulating the flow so that the gas may be steadily evolved without the liquid frothing excessively.



Collect two jars of the gas over water, and then remove the delivery tube and connect the flask with the apparatus shown in the figure (fig. 8).

The first wash-bottle contains water, the second caustic soda solution (to remove sulphur dioxide and acid vapours from the gas); the two large test-tubes stand in beakers of cold water, and the first of them contains forty grams, the second twenty grams of bromine, covered by a layer of water. As any escaping gas will carry with it some bromine vapour it is finally passed through a tube filled with granulated soda lime. The corks of the tubes should be coated with paraffin wax by dipping them in a little paraffin melted in a basin, to protect them from the bromine vapour.

The mixture in the generating flask must be heated carefully, as if allowed to get too hot there is considerable charring which gives rise to the evolution of sulphur dioxide and carbon dioxide, and increases the risk of 'frothing.'

A steady stream of gas is passed through the apparatus until the bromine in the first tube is completely decolorised, and that

in the second tube nearly so; this usually requires about two hours. In the meantime examine the two jars of gas.

Ethylene is a colourless gas, with a rather sweet smell, is only slightly soluble in water, burns with a luminous flame, and combines directly with the halogens.

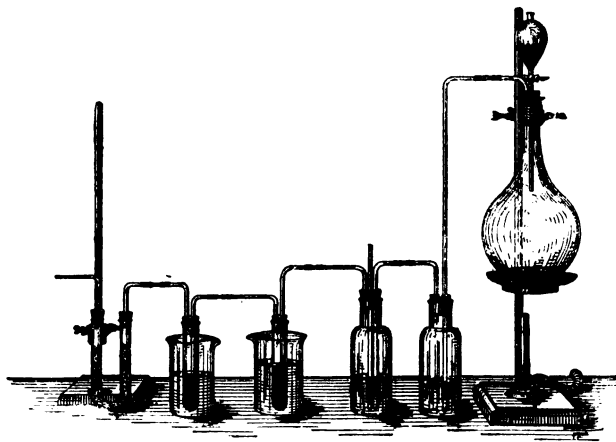
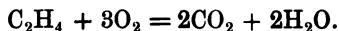
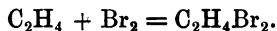


FIG. 8

To the first jar apply a light; the gas burns with a brightly luminous flame.



To the second add 5 or 10 cc. of bromine water, and shake well; the water is decolorised (cf. Ethane) and a few drops of a colourless sweet smelling oil (ethylene dibromide) are formed.



When the bromine in the large apparatus is almost decolorised remove it from the test-tubes and shake with weak caustic soda solution to remove any excess of bromine, repeating the operation, if necessary, until the liquid becomes quite colourless. When one liquid has to be treated with another the operation is best performed in a 'tap funnel.' On allowing the mixture to stand in this apparatus the two liquids separate, the

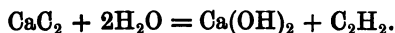
c

heavier one (in this case ethylene bromide) sinking to the bottom, and being drawn off by the tap. After treatment with caustic soda the bromide is washed three times with water, separated from the water as completely as possible, and allowed to stand in contact with some lumps of dry calcium chloride in a corked flask for at least six hours. At the end of this time the chloride should not appear damp, if it does some more lumps must be added, and a second six hours allowed. When quite dry the bromide is poured off into a small distilling flask, and distilled, the temperature at which it passes over being noted.

Ethylene bromide is a colourless liquid, with a sweet, sickly odour; its boiling point is  $131^{\circ}$ , and its specific gravity at  $0^{\circ}$  is 2.21.

The yield depends chiefly on the length of time during which the gas has been passed into the bromine; about 60 grams should be obtained.

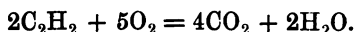
**Acetylene,  $C_2H_2$ .**—Acetylene is most easily prepared by the action of water on calcium carbide, one gram of the carbide yielding about 200 cc. of gas:



Drop a piece of calcium carbide, about the size of a bean into a basin of water, and bring over it a jar filled with water; collect three small jars of the gas.

Acetylene is a colourless and—when pure—almost inodorous gas; it burns with a brightly luminous flame, unites directly with the halogens, and gives a red precipitate with cuprous chloride.

To the first jar apply a light, and note the bright but very smoky flame (see note 1, p. 13):



To the second jar add about 5 cc. of bromine water, and shake well; the brown colour of the bromine disappears, and small yellow or colourless oily drops (a mixture of bromides) having a sweet smell appear in the water.

To the third jar add about 15 or 20 cc. of an ammoniacal

solution of cuprous chloride<sup>1</sup> and shake; a red-brown precipitate of copper acetylene ( $C_2H_2Cu_2O$ ) is obtained. This compound, when dry, is explosive, and is decomposed by hydrogen chloride with evolution of acetylene. Filter the liquid, place the paper and precipitate in a small beaker, add strong hydrochloric acid, and warm gently; on applying a light the acetylene takes fire.

<sup>1</sup> *Preparation of cuprous chloride solution.*—Place 25 grams of copper sulphate crystals, 12 grams of sodium chloride, 13 grams of copper turnings, 50 cc. of water, and 100 cc. of strong hydrochloric acid in a flask, cover the neck with a crucible lid, and boil until the liquid turns a light brown, then pour into a large dish of water, when cuprous chloride is precipitated. Pour off the liquid and preserve the mud in a well stoppered bottle in the dark.

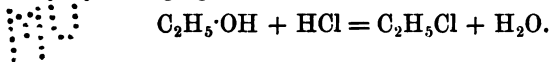


## CHAPTER VII

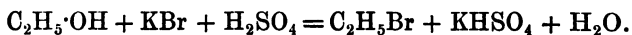
## THE HALOGEN DERIVATIVES OF THE PARAFFINS

THE mono-halogen substitution products of the paraffins are best prepared from the corresponding alcohols by one of the following methods :

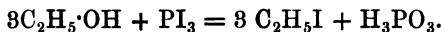
- (1) Heat the alcohol with the halogen acid in presence of a dehydrating agent :



- (2) Heat the alcohol with sulphuric acid and the potassium salt of the halogen :



- (3) Heat the alcohol with a halogen compound of phosphorus, or with a mixture of phosphorus and the halogen :



(1) This method is not a convenient one, and usually gives a very poor yield (see p. 26).

(2) This method is better adapted for use in the case of a chloride or bromide than of an iodide.

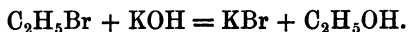
**Preparation of Ethyl Bromide.**—In a distilling flask, of about 700 cc. capacity, place 60 grams of absolute alcohol, then add a *cold* mixture of 120 grams of sulphuric acid and 86 grams of water, and finally 60 grams of powdered potassium bromide. Shake the mixture well, connect the flask with a good condenser, and distil as rapidly as possible from a sand bath ; the distillation requires about three-quarters of an hour, and towards the

close the mixture froths a great deal. Ethyl bromide, being a very volatile liquid, is difficult to condense.

Fix an adaptor to the end of the condenser, half fill the receiver with cold water (adding, if possible, some broken ice), and arrange the apparatus so that the beak of the adaptor just dips below the surface of the water (fig. 9); the bromide collects below the water as a heavy opalescent liquid. When the distillation is completed fill the receiver with water, transfer the distillate to a tap funnel, and wash the ethyl bromide—once with weak caustic soda solution and three times with water. Finally place the ethyl bromide in a small distilling flask with some granulated calcium chloride, cork tightly, allow to stand for at least six hours, and distil from the water bath; the boiling point of the bromide being so low it is not necessary to remove the calcium chloride before distilling. The bromide passes over at about 38°, and must be received in a dry bottle cooled by melting ice or water. Note the yield obtained, which should be about 50 grams.

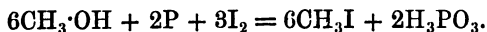
Ethyl bromide is a colourless sweet smelling liquid; boiling point 39°, specific gravity 1.47. It is not soluble in water, and burns with the green mantled flame which is characteristic of organic halogen derivatives.

When boiled with caustic potash it yields alcohol:



Dissolve 10 grams of potash in 15 grams of water in a small flask, add 5 grams of ethyl bromide, and connect with a back-flow condenser, boil gently on the water bath for half an hour, remove some of the *upper* layer by means of a pipette, and test for alcohol by the iodoform reaction (p. 26).

(8) **Preparation of Methyl Iodide.**—Methyl iodide is prepared by the action of iodine on methyl alcohol in presence of red phosphorus:



In a flask, of about 200 cc. capacity, place 5 grams of red phosphorus and 18 grams of methyl alcohol, and then add

gradually 50 grams of powdered iodine. The reaction is tolerably vigorous, so that the flask must be connected with a back-flow condenser, and only momentarily disconnected whilst the iodine is added; the mixture must then be allowed to stand over-night, the flask being still attached to the condenser. After this period disconnect the flask, insert a cork and bent glass tube, connect with a condenser and distil off the water-bath, using the same precautions for preventing loss of the iodide as in the case of ethyl bromide (p. 21).

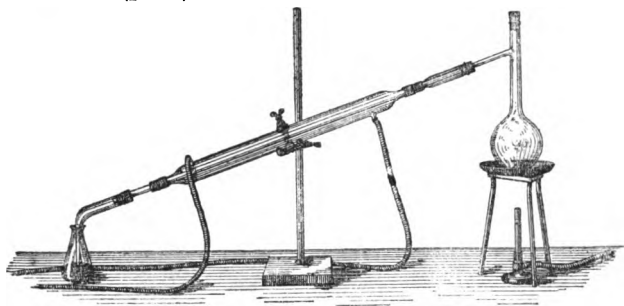


FIG. 9

Wash the distillate in a tap funnel with weak caustic soda solution to remove hydriodic acid and free iodine, and if it is not quite decolorised repeat the washing. Place the colourless liquid in a small distilling flask with some granulated calcium chloride, cork it up tightly and allow to stand for at least six hours, then insert a thermometer, and distil from the water-bath, noting the boiling point of the liquid.

Methyl iodide is a colourless liquid, of specific gravity 2.27 at 15°, and boils at 44°.

Yield: 45 to 50 grams.

## CHAPTER VIII

## THE ALCOHOLS

**Preparation of Ethyl Alcohol by Fermentation.**—Ethyl alcohol is easily prepared by the fermentation of sugar, although to obtain it quite free from water is a tedious operation. Dissolve 100 grams of cane sugar in one litre of water, place the solution in a flask or 'Winchester quart' bottle, and add about 50 grams of yeast. Fit into the neck of the bottle a cork carrying a thermometer, so arranged that the bulb is completely immersed in the fermenting liquor, and a delivery tube, bent twice at right angles and dipping into a small flask containing lime water (fig. 10).

Place the bottle in a warm place (the alcoholic fermentation proceeds best at about  $24^{\circ}$ ), and allow to stand for about a week; fermentation goes on during this time with the formation of ethyl alcohol, and evolution of carbon dioxide, roughly in accordance with the equation:

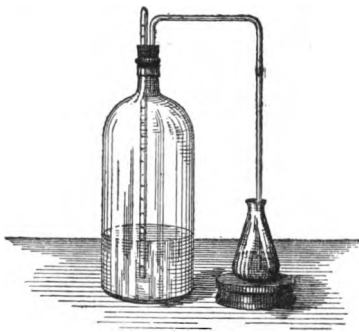
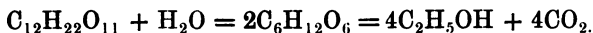


FIG. 10



Small quantities of several other substances are however formed at the same time. In this way a solution containing four or five per cent. of alcohol may be obtained, from which, with careful work, a small quantity of pure alcohol can be



isolated. A considerable portion of the water can be removed from the spirit by *fractional distillation*. When a mixture such as this is heated, the vapour which is given off at first contains a large proportion of the vapour of the more readily volatile constituent (in this case alcohol), accompanied by a smaller proportion of the less readily volatile constituent. By condensing the vapour in fractions, therefore, it is possible to obtain one fraction which is rich in alcohol, an intermediate fraction of

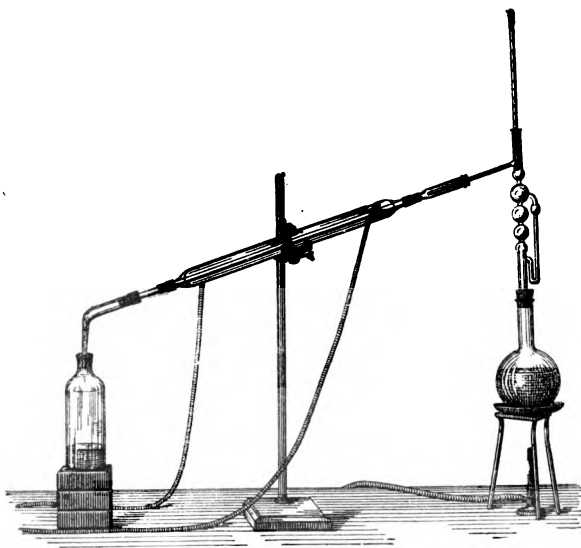


FIG. 11

about the same composition as the original mixture, and a third one which is rich in water and almost free from alcohol. Strain the liquor through linen and pour it into a large flask fitted with a fractionating column, carrying a thermometer and connected with a condenser (fig. 11). The large quantity of carbon dioxide dissolved in the liquid renders it very liable to froth, and it must, therefore, be heated slowly and with frequent shaking: the addition of a small piece of platinum foil or clean pipe stem reduces the risk of bumping during the distillation.

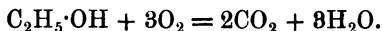
Boil the liquid until about 250 cc. have distilled over ; then measure the volume of the distillate and determine its specific gravity. Reference to a table then gives the percentage of alcohol, from which the total amount present may be calculated. The distillate should contain 15 to 20 per cent. of alcohol, and must be further rectified by treatment with potassium carbonate. Dry some potassium carbonate by heating it in a basin over a Bunsen burner, add to the distillate  $\frac{1}{2}$  gram of the salt for each cubic centimetre of the weak spirit, shake well, and allow to stand for about twenty minutes. The carbonate dissolves, and alcohol, being insoluble in a strong solution of potassium carbonate, separates as a light layer above the heavy solution. When the separation appears to be complete, carefully remove the spirit—which should now contain about 50 per cent. of alcohol—by means of a pipette, and determine its specific gravity as before.

Repeat the treatment with potassium carbonate, using the same proportion as before ; the salt should not this time dissolve, but should form a pasty mass, and the spirit obtained should contain about 75 per cent. of alcohol. A third treatment gives a spirit containing about 90 per cent. of alcohol.

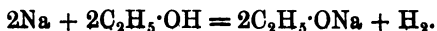
Potassium carbonate will not remove the last traces of water, and it is therefore necessary to have recourse to quicklime. Place the alcohol in a small flask, add small pieces of quicklime until they appear above the surface of the liquid, cork well, allow to stand for two days, and then distil off the water-bath.

The yield is very variable, but about 20 grams of spirit, containing 96 per cent. of alcohol, ought to be obtained.

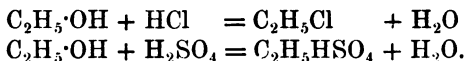
Ethyl alcohol is a colourless mobile liquid, which boils at  $78^{\circ}$ , and has the specific gravity 0.8062 at  $0^{\circ}$ . It burns with a pale non-luminous flame, forming carbon dioxide and water :



It is attacked by the alkali metals, with liberation of hydrogen and formation of a soluble *ethoxide* :



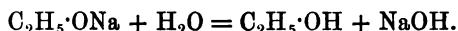
It is neutral to test-paper, but reacts with acids in a very similar manner to caustic soda :



**Experiments with Alcohol.**—(For these experiments use as far as possible the absolute alcohol you have prepared.)

(1) Pour a few drops of alcohol into the cup of a deflagrating spoon, apply a light, and introduce the burning spirit into a glass jar. Moisture is deposited on the walls of the jar, and carbon dioxide is formed ; test for the latter with lime water.

(2) Place a few cubic centimetres of alcohol in a test-tube and add a small fragment of sodium ; the metal reacts with the alcohol as with water, but less vigorously. Test the alkalinity of the solution formed by litmus paper. Add fragments of sodium until no further action occurs, and then allow the liquid to cool ; the whole mass solidifies, owing to the separation of the sodium ethoxide. This substance is decomposed by water :



(3) The most convenient test for alcohol is the iodoform reaction. Place a few cubic centimetres of the liquid to be tested in a test-tube, add a small piece of iodine and then caustic soda, shake well, and warm to about 60° C. ; if the iodine does not dissolve add more caustic soda. If there is much alcohol present an immediate yellow crystalline precipitate of iodoform is produced, but the precipitation requires some time in a very weak solution. Note the very characteristic odour of iodoform.

These reagents give no precipitate with methyl alcohol, but iodoform is produced from many other compounds containing two or more atoms of carbon, such as aldehyde, acetone, &c.

(4) Place about 20 cc. of alcohol in a large test-tube and saturate it with dry hydrochloric acid gas, keeping the tube cool by a current of water throughout the operation. Place the solution in a small flask, fitted with a cork and delivery tube, boil, and collect the escaping gas (ethyl chloride) over water. When a light is applied the gas burns with the peculiar green mantled flame characteristic of the organic halogen derivatives.

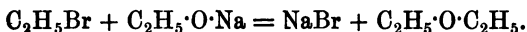
**Methyl Alcohol**,  $\text{CH}_3\cdot\text{OH}$ , is a liquid which closely resembles ordinary ethyl alcohol in its properties. It boils at  $66^\circ$  and has the specific gravity 0.8142 at  $0^\circ$ . It reacts like ethyl alcohol with most reagents, but does not give the iodoform reaction (see p. 71).

*Experiments.*—Repeat experiments 1, 2, 3 and 4 on p. 26, using methyl alcohol, and note the results.

## CHAPTER IX

## THE ETHERS

**Synthesis of Ethers.**—The ethers may easily be synthesised by boiling a mono-halogen derivative of a paraffin with a sodium derivative of an alcohol :



In a two-ounce distilling flask place 40 cc. of absolute alcohol, and add gradually 3 grams of sodium cut into thin slices ; the reaction is at first vigorous, but towards the end becomes feebler and may then be assisted by very cautious warming. When the sodium is all dissolved cool the liquid, add 10 grams of ethyl bromide, connect the flask with a reversed condenser, close the side tube of the flask (by rubber tubing and a glass stopper), and boil gently on the water-bath until ethyl bromide can no longer be smelt at the top of the condenser (this usually requires about 15 or 20 minutes) ; then allow to cool, remove the flask from the condenser, insert a cork and thermometer in the neck of the flask, connect the side tube with a condenser, and distil on the water-bath, stopping the distillation when the thermometer rises above 70°.

On adding an equal bulk of water to the distillate (which contains a good deal of alcohol) the ether rises to the top, and may be removed by a small pipette. If the yield is large enough the ether may be dried over calcium chloride and distilled. Yield : 6 or 7 cc. of wet, 4 grams of dry, ether.

Ether is a colourless, mobile liquid, with a sweet smell ; boiling point 35°, specific gravity 0.736 at 0°. It is very volatile and exceedingly inflammable, and must therefore be handled

with the utmost care. It is miscible with alcohol, and dissolves in about nine times its volume of water.

The solid residue in the distilling flask is chiefly sodium bromide, and should be dissolved in water and tested qualitatively.

**Preparation of Ether.**—In a flask of about 800 cc. capacity place a mixture of 100 grams of absolute alcohol and 180 grams of strong sulphuric acid; insert a cork carrying a thermometer, a tap funnel, and a bent tube connected with a condenser; place the flask on a piece of wire gauze (fig. 12), and heat carefully, taking care that the bulb of the thermometer is completely

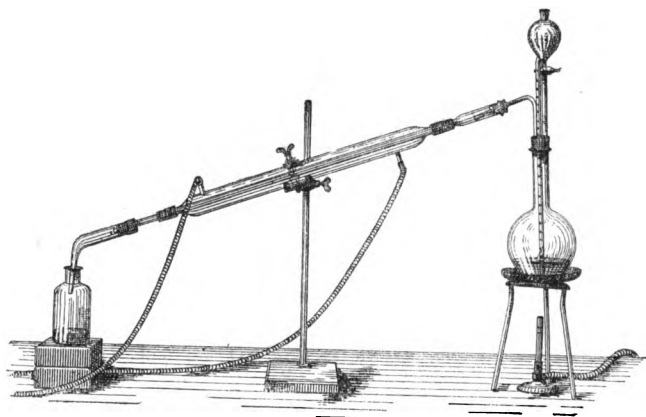


FIG. 12

immersed in the liquid. The receiver must be cooled by cold water, and its mouth loosely closed with cotton-wool. When the temperature reaches  $140^{\circ}$  impure ether begins to distil over, and alcohol must now be run slowly in from the dropping funnel, about as fast as the ether distils over, the temperature being kept between  $140^{\circ}$  and  $145^{\circ}$ . Remember that ether vapour is very inflammable, and that it forms explosive mixtures with air. The receiver should therefore be placed at a lower level than the burner used for heating the flask, or, if this is not possible, a towel should be hung up so as to direct the stream of uncondensed ether vapour to the edge of the bench.

Continue the operation until about 250 cc. have passed over. The distillate is chiefly composed of water, ether, and alcohol, but contains also sulphur dioxide, &c. ; it separates into two layers, the upper one containing the ether.

Remove the lower layer by means of a separating funnel, and to the ether in the funnel add an equal volume of very weak caustic soda solution ; then wash twice with about half as much water, run the wet ether into a distilling flask containing some lumps of calcium chloride, cork tightly, allow to stand six hours, and distil off a bath of hot water without using a flame. If the calcium chloride looks wet, treat the ether a second time with a fresh quantity, and again distil. The ether still contains small quantities of alcohol and water, and must finally be purified by adding slices of bright sodium, allowing to stand over-night (the flask being closed by a cork carrying a calcium chloride tube to permit the escape of hydrogen), and again distilling.

**Ethyl Hydrogen Sulphate or Sulphovinic Acid,  $C_2H_5 \cdot HSO_4$ .** This acid is most conveniently prepared by warming a mixture of absolute alcohol and sulphuric acid. Place 30 cc. of absolute alcohol in a small flask, and add gradually with constant shaking 30 cc. of strong sulphuric acid ; when the acid has all been added, place the flask in a bath of boiling water for about an hour :

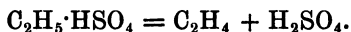


Allow the mixture of alcohol, sulphuric acid, and sulphovinic acid to cool, and then pour it slowly into 500 cc. of cold water, stirring well during the mixing. The two acids must now be neutralised by barium carbonate ; this is best done by making the carbonate into a cream with water, and adding it little by little to the solution with vigorous stirring, until the liquid is quite neutral to test-paper. A considerable quantity of barium sulphate is precipitated, together with any excess of barium carbonate, and the mixture can only be filtered with great difficulty ; the best plan, therefore, is to pour the solution into a tall cylinder, and allow it to stand over-night, when the mud settles down and the supernatant liquid can be syphoned off, though, of course, there is considerable loss.

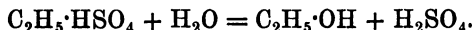
From the solution of barium ethyl sulphate so obtained prepare the potassium salt by carefully adding just sufficient potassium carbonate (dissolved in water) to precipitate all the barium as carbonate. The precipitate can easily be filtered off, and on carefully evaporating the filtrate on the water bath, fine transparent crystals of potassium ethyl sulphate,  $\text{C}_2\text{H}_5\cdot\text{KSO}_4$ , are obtained. These must be filtered off, and 'air dried' by loosely wrapping in filter paper and exposing them to the air. The free acid is only prepared with great difficulty, as when boiled with water it is decomposed.

Ethyl sulphuric acid gives three very important reactions, and is formed as an intermediate product in the preparation of ethylene and of ether from alcohol.

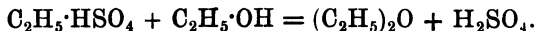
(1) When heated it gives ethylene and sulphuric acid :



(2) When heated with water it gives alcohol and sulphuric acid :



(8) When heated with alcohol, by a similar reaction it gives ether and sulphuric acid :



In each of the following experiments sufficient sulphuric acid is added to liberate the ethyl hydrogen sulphate and to form potassium hydrogen sulphate.

(1) Make 10 grams of the potassium salt and 10 grams of sulphuric acid into a paste in a mortar, and, after well mixing, transfer them to a small flask ; insert a cork and delivery tube, heat carefully, and collect the resulting gas over water. The ethylene so prepared is not quite pure, as there is always a certain amount of charring and consequent evolution of sulphur dioxide, but it will answer to the same tests as that formerly prepared (p. 17). Divide the gas into two portions : to the first apply a light—it burns with a luminous flame ; to the second add 5 cc. of bromine water—the brown colour of the bromine disappears.

(2) Dissolve 5 grams of the salt in 30 cc. of water in a small



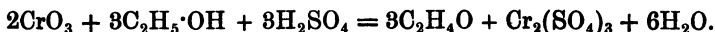
flask, add 4 grams of strong sulphuric acid, and insert a cork carrying a delivery tube dipping into some cold water contained in a test-tube. Boil the mixture in the flask for several minutes, when alcohol passes over and is condensed in the cold water. Test the distillate for alcohol by the iodoform reaction (p. 26).

(8) To prove the formation of ether is not so easy. Mix together (in a mortar) 8 grams of potassium ethyl sulphate, and 8 grams of strong sulphuric acid, then add 5 cc. of absolute alcohol, and again mix thoroughly; transfer the mixture to the apparatus described in the last experiment, using, however, a test-tube instead of a flask, and heat very carefully. After heating for three or four minutes the water in the receiver will be found to smell strongly of ether.

## CHAPTER X

## THE ALDEHYDES AND THEIR DERIVATIVES

**Aldehyde,  $\text{CH}_3\cdot\text{CHO}$ .**—Place 140 grams of roughly powdered potassium bichromate and 550 cc. of water in a litre flask (a distilling flask if possible) provided with a cork and tap funnel; connect it with a condenser and a receiver, the latter being placed in a freezing mixture of ice and salt. By means of the funnel slowly add a mixture of 148 grams of strong ethyl alcohol with 184 grams of concentrated sulphuric acid, which has been well cooled under the tap, and shake the flask repeatedly. The heat evolved in the oxidation of the alcohol is sufficient to cause the distillation of a mixture of water, alcohol, and aldehyde:



In order to purify the distillate thus obtained, it is redistilled over wire gauze in a flask connected with a back-flow condenser, from the upper end of which a conducting tube (a 50 cc. pipette) leads to two small wash flasks, half filled with pure dry ether (fig. 18). Fill the condenser with water at  $30^\circ$ , close the lower exit of the condenser jacket and heat the flask gently. The water and alcohol are condensed and pass back into the flask, whilst the aldehyde escapes condensation, and is rapidly absorbed by the ether. If the ether rises rapidly in the tube the heat applied to the flask must be increased, so as to prevent it from passing over into the flask. The ethereal solution is then placed in a beaker, well cooled by ice, and ammonia gas, dried by solid caustic soda contained in a U-tube or small tower, is passed in until the liquid is saturated. Aldehyde ammonia  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}_2$ , is thus formed as a white crystalline mass, which can be filtered off on the pump, washed with ether and dried.

\*D

In order to finally obtain pure aldehyde, 1 part of aldehyde ammonia is dissolved in an equal weight of water,  $3\frac{1}{2}$  parts of well cooled sulphuric acid ( $1\frac{1}{2}$  of acid to 2 of water) added, and the whole distilled, the receiver being well cooled with ice and salt. (Yield : 28.5 grams of aldehyde ammonia, 10 of aldehyde.) Aldehyde is a colourless liquid, with a characteristic unpleasant odour, boils at  $21^{\circ}$ , and has the specific gravity 0.807.

The following reactions are characteristic of all aldehydes :

(1) To a few drops of the aqueous solution of aldehyde add a little ammoniacal silver nitrate solution, and warm gently. Metallic silver is deposited and the aldehyde oxidised to acetic acid.

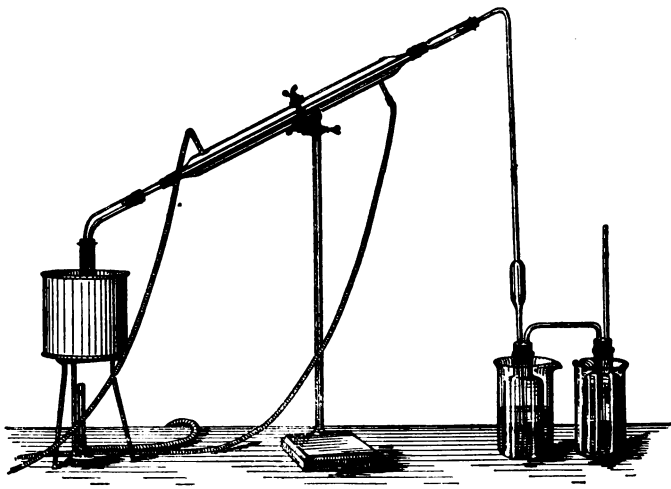


FIG. 13

(2) When heated with a little Fehling's solution (see p. 56) a red precipitate of cuprous oxide is formed, whilst the aldehyde is converted into acetic acid.

(3) Add a little aldehyde to two or three cubic centimetres of concentrated sodium bisulphite solution in a test-tube, shake well, and cool. White sparingly soluble crystals of a double compound of the aldehyde with this salt separate out.

(4) Add a drop of concentrated sulphuric acid to a little pure aldehyde in a test-tube. A considerable evolution of heat occurs, and the aldehyde is converted into the polymeric paraldehyde, which boils at 124°.

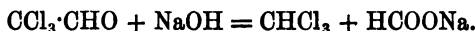
(5) Warm a little aldehyde with aqueous caustic soda. A yellowish resinous mass is produced.

(6) Dissolve a little aldehyde in water, add dilute sulphuric acid and a dilute solution of potassium permanganate. The latter is rapidly decolorised.

(7) Make a very dilute solution of the colouring matter known as magenta, and add sulphurous acid until the liquid after shaking is colourless. A drop or two of aldehyde added to this solution restores the characteristic colour of magenta (Schiff's reaction).

**Chloral**,  $\text{CCl}_3\cdot\text{CHO}$ .—Chloral is trichlor-acetaldehyde, and reacts in most respects like acetaldehyde. Repeat the experiments, given under aldehyde, with a solution of chloral hydrate in water, and note the results.

**Decomposition of Chloral by Alkalis.**—When treated with an alkali, chloral yields chloroform and a formate (hydrolysis):



Dissolve 6 grams of chloral hydrate in 5 grams of water, add  $1\frac{1}{2}$  grams of caustic soda dissolved in 8 cc. of water, shake well, and allow to stand. Chloroform is precipitated and sinks to the bottom of the tube. Separate, dry, and if possible determine its boiling point. Acidify the aqueous layer with sulphuric acid, distil, and test the distillate for formic acid (p. 48).

**Preparation of Chloroform from Alcohol.**—Chloroform may be prepared directly from alcohol as follows. In a very large flask (of at least 2 litres capacity) place 150 grams of bleaching powder, ground up to a thin cream with 100 cc. of water, 400 cc. of water and 95 cc. of methylated spirit; place on a water-bath, connect with a condenser, and heat until the mixture boils. When the reaction has commenced the lamp may be withdrawn, and only replaced when the distillation slackens. The mixture usually froths a good deal. To the distillate add water, remove the heavy layer of chloroform, wash with dilute caustic soda

solution until the smell of chlorine has disappeared, and then again with water; dry over calcium chloride and distil. The chloroform thus prepared is not so pure as that obtained from chloral. Chloroform is a heavy, colourless liquid of specific gravity 1.498, boils at  $61^{\circ}$ , and has a sweet and characteristic odour.

**Iodoform,  $\text{CHI}_3$ .**—Iodoform is prepared by the action of iodine on ethyl alcohol in presence of an alkali, the reactions being complicated.

Dissolve 20 grams of crystallised sodium carbonate in 100 cc. of water, and add 20 cc. of absolute alcohol; heat the liquid in a water bath to about  $70^{\circ}$ , and add gradually 10 grams of powdered iodine; stir well, and keep the mixture at about  $70^{\circ}$  until all the iodine dissolves. Allow the liquid to cool, filter off the iodoform which crystallises out, wash it with a little cold water, press between filter papers, and finally 'air dry' the crystals—that is to say, wrap the powder loosely in filter paper and allow it to stand until perfectly dry. Determine its melting point.

Iodoform is a yellow solid, which crystallises in six-sided plates, melts at  $119^{\circ}$ , and has a peculiar and very characteristic odour.

Yield: about 2 grams.

## CHAPTER XI

## THE KETONES

**Acetone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ .—Acetone is very easily prepared by strongly heating barium or calcium acetate :



Prepare a tube of infusible glass about ten inches long and half an inch internal diameter, sealed at one end. In it place 25 grams of powdered barium acetate,<sup>1</sup> insert a cork and connect with a condenser, taking care that the tube to be heated is horizontal. Heat the acetate strongly, by means of a Bunsen burner, commencing at the sealed end and gradually working along the tube. Seven or eight cubic centimetres of impure acetone (together with water, &c.) will distil over, leaving barium carbonate in the retort ; the quantity of the distillate is too small to allow of the separation of pure acetone, but the impure liquid serves perfectly well to show the characteristic reactions of acetone.

Acetone is a colourless mobile liquid of specific gravity 0.792, and boiling at  $56.5^\circ$  ; it has a faint, pleasant odour, is soluble in water or alcohol, forms a crystalline compound with sodium hydrogen sulphite, and gives the 'iodoform reaction.'

Dissolve 5 grams of sodium bisulphite in a very small quantity of hot water, and add the hot solution to the distillate ; on cooling, fine colourless crystals of acetone sodium bisulphite ( $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3\cdot\text{NaHSO}_3$ ) appear. Filter these off and dry between filter paper. This compound is easily decomposed by alkalis, giving acetone once more. Place a gram of the compound in a test-

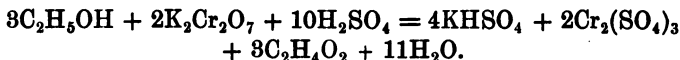
<sup>1</sup> Prepared, if necessary, by dissolving barium carbonate or hydrate in acetic acid, evaporating and heating gently to remove the water of crystallisation.

tube with an equal quantity of sodium carbonate and 10 cc. of water; insert a cork fitted with a delivery tube and arrange the apparatus so that the delivery tube dips below the surface of a little cold water in a second tube. On boiling the solution acetone vapour escapes, and is condensed in the second tube; after boiling for three or four minutes test the liquid in the receiver by the iodoform reaction (p. 26).

## CHAPTER XII

## THE FATTY ACIDS AND THEIR DERIVATIVES

**Acetic acid,  $\text{CH}_3\cdot\text{COOH}$ .**—Acetic acid can be readily prepared by the oxidation of alcohol, the best oxidising agent to employ being potassium bichromate and sulphuric acid :



Place 30 grams of coarsely-powdered potassium bichromate in a round-bottomed flask, and add a cold mixture of 30 grams of sulphuric acid with 18 cc. of water ; place the flask on a sand bath and connect it with a back-flow condenser, and then add gradually 5 cc. of alcohol diluted with an equal volume of water. After each addition, a vigorous reaction takes place, and the liquid becomes very hot ; allow all action to cease before adding the next quantity, but do not cool the flask. When all the alcohol has been added, boil for ten minutes, then connect the flask with the other end of the condenser and distil over wire gauze, until about 20 cc. of distillate have come over. This consists of aqueous acetic acid, but usually also smells slightly of acetic ether and aldehyde. The acid can readily be recognised by the ordinary tests, or can be concentrated. For this purpose add solid sodium carbonate to the heated distillate until effervescence no longer occurs, and evaporate the solution to dryness ; dry the sodium acetate thus obtained by gently heating it over the flame, in a distilling flask or retort ; carefully add concentrated sulphuric acid and distil until white fumes begin to appear in the retort.

**Properties.**—Acetic acid is a colourless liquid, which boils at  $118^\circ$ , and has an extremely pungent odour, not unlike that of sulphur dioxide. It freezes at  $14^\circ$ , and mixes with water in all



proportions. It is an excellent solvent for many organic substances.

**Tests for Acetic Acid.**—The acetates are almost all soluble in water, the least soluble being silver acetate, which, however, dissolves in hot water; its salts with weak bases ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) are decomposed when their solutions are boiled; free acetic acid and an insoluble basic acetate being formed. The acid is further characterised by its smell, its volatility, and its reaction with alcohol in presence of sulphuric acid to form the fragrant acetic ether. It should be tested for in complex mixtures of substances by distilling with dilute sulphuric acid and examining the distillate. The following tests are based upon these properties:

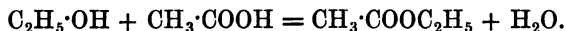
(1) Acetates are decomposed by free mineral acids, and the acetic acid thus liberated can be detected by its smell, especially when the liquid is gently warmed.

(2) Add to a solution of an acetate or acetic acid about a quarter of its volume of alcohol and half its volume of concentrated sulphuric acid and mix well. Acetic ether is formed, and may be recognised by its smell (care must be taken to distinguish this from the smell of alcohol vapour).

(3) To a concentrated *neutral* solution of an acetate add silver nitrate. A white precipitate is obtained, soluble in hot water without decomposition.

(4) Ferric chloride added to a *neutral* solution gives a red coloration, which is destroyed by acids. When the red solution is boiled, a basic ferric acetate is precipitated, and a colourless solution containing free acetic acid is left.

**Preparation of Ethyl Acetate,  $\text{CH}_3\cdot\text{COOC}_2\text{H}_5$ .**—Ethyl acetate (acetic ether), like many other ethereal salts, may be prepared by the direct action of acetic acid on alcohol in the presence of sulphuric acid:

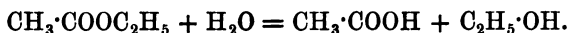


Fit a 10-oz. distilling flask with a tap funnel; connect the side tube with a condenser; in the flask place 25 cc. of alcohol and 25 cc. of strong sulphuric acid, and heat in a paraffin or oil bath to  $140^\circ$ . Then add from the funnel, fairly rapidly, a mixture of 100 cc. of alcohol and 100 cc. of acetic acid, and continue

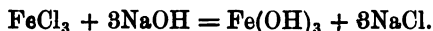
the heating until the temperature reaches 160°. Wash the distillate with a solution of 8 grams of caustic soda in 100 cc. of water (to remove acetic acid), and if the layer of acetic ether which rises to the top reddens litmus paper, wash again until it is neutral. Then shake well with 100 cc. of a 33 per cent. solution of calcium chloride (which removes alcohol); run the ethyl acetate into a flask, allow to stand over calcium chloride for at least six hours, pour, or if necessary filter through a dry paper, into a dry distilling flask, and distil from the water-bath.

Ethyl acetate is a mobile and very fragrant liquid, which boils at 78°, and is slightly lighter than water, in which, however, it is fairly easily soluble. In presence of moisture it gradually decomposes, forming acetic acid and alcohol.

**Hydrolysis of Ethyl Acetate by Aqueous Caustic Soda Solution.**—When ethyl acetate is boiled with water it is gradually decomposed with formation of alcohol and acetic acid:



The change takes place more rapidly and more completely when caustic soda solution is used instead of water, since this neutralises the acetic acid and prevents it from reacting with the alcohol to reproduce ethyl acetate. A decomposition of this kind, in which the elements of water (or caustic soda) are shared between the two products, is termed 'hydrolysis.' The change is quite analogous to that which occurs when caustic soda is added to a metallic salt:



Place in a small distilling flask connected with a back-flow condenser 20 grams of ethyl acetate, and a solution of 11 grams of solid caustic soda in 60 cc. of water. Close the narrow side tube by means of a rubber tube and glass rod, add a small piece of porous plate and boil on the water-bath, shaking repeatedly to prevent bumping. As soon as the layer of ethyl acetate disappears, remove the flask, connect it with an ordinary condenser, insert a thermometer and distil over wire gauze, collecting everything that comes over below 90°. The distillate may be shown to contain

alcohol by saturating it with solid potassium carbonate, when the alcohol rises to the top and may be removed and identified by the usual tests. The acetic acid may be obtained from the residue in the flask by continuing the distillation carefully until the mass is dry, cooling, and slowly adding concentrated sulphuric acid, the flask being well cooled by a current of water during this process. Then again distil. Acetic acid passes over, and may be recognised by its strong smell, &c., &c.

## CHAPTER XIII

THE FATTY ACIDS AND THEIR DERIVATIVES (*continued*)

**Preparation of Acetyl Chloride,  $\text{CH}_3\cdot\text{COCl}$ .**—When acetic acid or an anhydrous acetate is treated with a chloride of phosphorus, the hydroxyl group is displaced by chlorine and acetyl chloride obtained :



As large volumes of hydrogen chloride are evolved, this preparation must be carried out in the draught cupboard. Fit a quarter

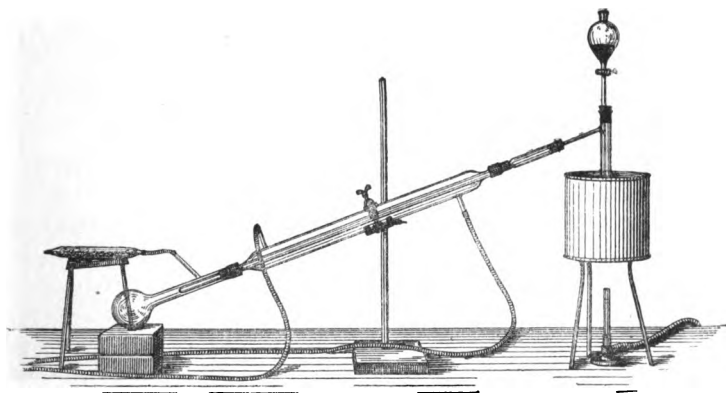


FIG. 14

litre distilling flask with a tap funnel, and connect the side tube with a condenser : as a receiver use a pump bottle or distilling flask with a calcium chloride tube attached to the side tube

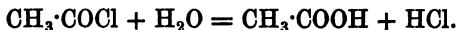
(fig. 14); in the flask place 100 grams of glacial acetic acid, and immerse it in a bath of cold water. By means of the funnel run in gradually, though not too slowly, 80 grams of phosphorus trichloride (weigh in the draught cupboard); when this has been added replace the cold water of the bath by water at about 40°, warm gently until the reaction ceases, and then heat to the boiling point. The distillate must be fractionally distilled, using the same apparatus as before, and the acetyl chloride preserved in a well-stoppered bottle, as it is decomposed by moisture.

Yield: 80–90 grams.

Acetyl chloride is a colourless liquid, boiling at 55°, and fuming very strongly in the air.

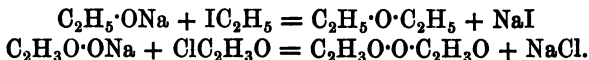
Try the following experiments with the chloride (the residue boiling above 60° contains sufficient acetyl chloride for these tests).

1. Add a very little acetyl chloride to 5 cc. of water in a test-tube and shake well: the chloride rapidly dissolves, and a considerable amount of heat is evolved:



2. Add drop by drop 1 cc. of the chloride to 1 cc. of alcohol in a test-tube surrounded by cold water; then add 2 cc. of cold water, and make alkaline with caustic soda; ethyl acetate separates and floats on the surface of the liquid.

**Acetic Anhydride,  $(\text{CH}_3\cdot\text{CO})_2\text{O}$ .**—Acetic anhydride is prepared from the chloride and sodium acetate by a reaction which is precisely similar to that by which ether is prepared from sodium ethylate and ethyl iodide:

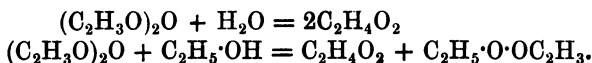


Dehydrate 120 grams of crystallised sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ ) by heating it on a clean sand tray over a Bunsen burner (*see* p. 18), and place 70 grams of the powdered salt in a retort which is connected with the same condenser and receiver as were used in the preparation of acetyl chloride. The tubulure of the retort is closed by a cork carrying a tap funnel, in which 50 grams of acetyl chloride are placed. Allow the chloride

to drop slowly on to the anhydrous acetate, and as soon as half of it has been added remove the cork from the retort, and carefully break up the mass of salt with a stout glass rod; then slowly add the second half of the chloride. If anything distils over, pour it back into the funnel and again let it drop into the retort. Remove the funnel, close the retort by a cork, and distil carefully with a slightly smoky flame, taking care not to heat too strongly at any one spot, as otherwise the retort will crack. Redistil the product from a small flask over wire gauze.

Yield: 45 grams.

Acetic anhydride is a colourless liquid boiling at  $138^{\circ}$ , the vapour of which irritates the membrane of the eyes and nose. It reacts with water and alcohol much less vigorously than acetyl chloride. Repeat the two experiments described under acetyl chloride, and note that the reactions only proceed when the liquid is *heated*:



**Acetamide**,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$ , may be prepared in several different ways:

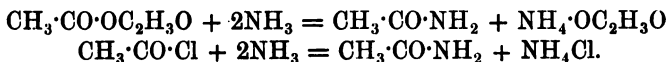
(1) When ammonium acetate is heated it loses 1 molecule of water and forms acetamide:



This reaction is best carried out by heating ammonium acetate in a sealed tube at  $230^{\circ}$ , but a small amount of the amide can be obtained by heating the salt under the ordinary pressure. Melt 50 grams of ammonium acetate in a basin, pour it into a small distilling flask, and distil at a moderate rate, a simple wide glass tube being used as condenser instead of the ordinary Liebig's condenser, and the distillate collected in a beaker. Stop the distillation as soon as the thermometer rises to  $180^{\circ}$ , and pour the residue into a small basin; pour the distillate back into the flask, and repeat the distillation as before, collecting all that passes over between  $140^{\circ}$  and  $180^{\circ}$ , and pouring the residue into the basin. Repeat as often as is found practicable, and then place the united

residues on a porous plate until the mass is white and dry. Only a few grams will be obtained.

(2) Ammonia reacts directly with acetyl chloride or acetic anhydride to form acetamide and ammonium chloride or acetate :



Place 80 grams of acetic anhydride in a small distilling flask, and pass in a current of *dry* ammonia (see p. 33) until the liquid is saturated. The flask must be cooled at first, but afterwards allowed to get warm in order to prevent solidification. As soon as the ammonia is no longer absorbed, disconnect the ammonia apparatus, connect the flask with the condensing tube used in the previous experiment, and distil, collecting the fraction between 180° and 230°. Place this on a porous plate until it is white and dry.

(For a third general method of preparation of an acid amide see oxamide, p. 52.)

Acetamide forms white silky needles, and boils without decomposition at 223°. As prepared by the methods described above it smells like the excrement of mice, but when purified by recrystallisation from ether it is odourless.

When boiled with water it is reconverted into ammonium acetate, whilst if caustic soda be used instead of water ammonia is given off.

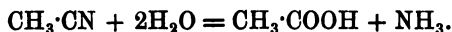
Experiment:—Boil a little acetamide with caustic soda in a test-tube, and test for ammonia and for acetic acid.

**Acetonitrile**,  $\text{CH}_3\cdot\text{CN}$ .—Acetonitrile is very readily formed when acetamide is heated with phosphorus pentoxide. To prepare it in this way, place in a very small distilling flask connected with a condenser 15 grams of phosphorus pentoxide. (This is best weighed out in a conical tube, corked at each end; the narrow end should fit the neck of the distilling flask, and the oxide may then be easily transferred to the flask with the aid of a glass rod). Add 10 grams of dry acetamide, as finely powdered as possible, shake well, and distil with a small smoky flame. Care must be taken to heat uniformly by moving the flame about, or the flask will break. Add to the distillate 2 cc. of water and solid

potassium carbonate until no more dissolves. Remove the upper layer of liquid, and distil it over a little phosphorus pentoxide. Acetonitrile is a liquid having a characteristic odour, and boils at 82°.

Yield : About 5 grams.

**Hydrolysis of Acetonitrile.**—Acetonitrile reacts with alkalis or acids to form acetic acid and ammonia; this reaction is another instance of hydrolysis :



Boil 2 or 3 cc. of acetonitrile with 5 cc. of concentrated caustic potash for half an hour in a small flask provided with an air condenser in the shape of a long glass tube. When the layer of acetonitrile has disappeared, remove the cork, and notice the strong smell of ammonia. Acidify the liquid with dilute sulphuric acid, distil, and test the distillate for acetic acid by the usual tests.

**Formic Acid, H·COOH.**—Formic acid is easily prepared by heating glycerine and oxalic acid, carbon dioxide being liberated at the same time. The glycerine is found unchanged at the end of the operation, and can be used many times :



In a good-sized retort, fitted with a condenser, place 100 cc. of glycerine and 50 grams of oxalic acid, arrange a thermometer with its bulb immersed in the liquid, and heat on a sand-bath to between 100° and 110°. Distillation proceeds quietly, and an aqueous solution of formic acid passes over. When the distillation slackens add a further 50 grams of oxalic acid and heat again, repeating the operation, if necessary, until 50 to 100 cc. of dilute formic acid are obtained.<sup>1</sup> The distillate is now to be neutralised by boiling with lead carbonate, the clear liquid being decanted off and allowed to cool, when long colourless prisms of lead formate are obtained. Convert a portion of this salt into sodium formate by boiling with a solution of sodium carbonate; filter, concentrate, allow to cool, filter from any lead formate that may separate, and use the solution for the following experiments :

<sup>1</sup> The residue may be used for the preparation of allyl alcohol; for details refer to p. 55.



(1) Add a little silver nitrate; a white precipitate of silver formate is obtained, which on carefully warming turns grey, and then deposits a silver mirror on the tube.

(2) Ferric chloride gives a dark red solution, which on boiling gives a rusty red precipitate (compare acetic acid).

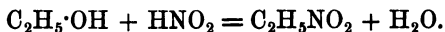
(3) Heat a little lead formate with strong sulphuric acid; pure carbon monoxide is evolved, and can be burnt at the mouth of the tube (compare oxalic acid).

Formic acid is a colourless liquid of specific gravity 1.24 (at 0°), boiling at 101°, solidifying when cooled, and melting at 8°. It is a fairly strong acid, blisters the skin, and smells like sulphur dioxide.

## CHAPTER XIV

## ETHEREAL SALTS OF THE ALCOHOLS

**Ethyl Nitrite,  $C_2H_5NO_2$ .**—Ethyl nitrite is readily prepared by the action of nitrous acid on alcohol :



The operation must be carried on at a low temperature, as the nitrite boils at  $18^\circ$ . Dissolve 34 grams of sodium nitrite in cold water, make up the solution to 120 cc., and place it in a tall cylinder surrounded by a freezing mixture. Mix together 32 cc. of ethyl alcohol and 32 cc. of water, and add 13.5 cc. of strong sulphuric acid; make up to 120 cc. with water, and cool well. Add this liquid very gradually and with constant stirring to the sodium nitrite solution, pouring it through a thistle funnel so that it may be delivered at the bottom of the cylinder. Ethyl nitrite rises to the top, forming a yellow layer. This is then separated, washed, and dried over solid potassium carbonate, a little of which should also be kept in the bottle with the liquid. Ethyl nitrite is a colourless liquid, boiling at  $18^\circ$ , and having the specific gravity 0.7 at  $15^\circ$ ; it has a sweet, apple-like odour and a burning taste, and is not soluble in water.

**Amyl Nitrite,  $C_5H_{11}NO_2$ .**—Dissolve 30 grams of amyl alcohol in an equal weight of sulphuric acid, and to the well-cooled mixture add very gradually and with constant shaking a solution of twenty-six parts of potassium nitrite in fifteen of water. Connect the flask with a condenser, distil, dry the distillate over calcium chloride, and purify by fractional distillation. Yield : about 15 grams. Amyl nitrite is a pale yellow liquid boiling at  $96^\circ$ , and having the peculiarly penetrating smell characteristic of the amyl compounds.

For the preparation of other 'esters' see p. 20.

E

## CHAPTER XV

## PREPARATION AND PROPERTIES OF GLYCOL

**Preparation of Ethylene Glycol,  $C_2H_4(OH)_2$ .**—Ethylene glycol is prepared by boiling ethylene dibromide with potassium carbonate solution, but the process is tedious and the yield very small.

In a flask of about half a litre capacity place 250 cc. of hot water, 35 grams of potassium carbonate, and 47 grams of ethylene bromide, connect the flask with a reflux condenser, and keep the liquid gently boiling on a sand-bath until all the oil disappears (8 to 10 hours). The liquid 'bumps' a good deal, but this 'bumping' may be diminished by placing a spiral of platinum wire in the flask. When all the oil has dissolved, add a further 35 grams of potassium carbonate and 47 grams of ethylene bromide, and repeat the boiling. Work up as many batches of bromide as possible in the one quantity of water; if crystals of potassium bromide separate when the liquid cools, filter before reheating, rinse the crystals with strong alcohol, and add the rinsings to the filtrate. When all the ethylene bromide has disappeared pour the liquid into a basin, and evaporate on the water-bath until crystals of potassium bromide appear in considerable quantity; allow to cool, add an equal bulk of anhydrous methylated spirit (which precipitates potassium bromide), filter by means of the pump, rinse the crystals with alcohol, and add the washings to the filtrate. Place the filtrate in a flask, heat in an oil-bath, and fractionally distil. Glycol comes over between  $180^\circ$  and  $200^\circ$ .

Ethylene glycol is a colourless, syrupy liquid boiling at  $197.5^\circ$ ; it is soluble in alcohol or water in all proportions.

## CHAPTER XVI

## THE DIBASIC ACIDS

**Preparation of Oxalic Acid from Sugar.**—Place 120 grams of strong nitric acid in a beaker, add 20 grams of powdered sugar, and heat in a water-bath. The moment brown fumes appear lift the beaker out of the bath and place it in a draught cupboard, as the reaction is vigorous and torrents of fumes are evolved. When the reaction ceases, concentrate the liquid on the water-bath to about two-thirds of its bulk; on cooling, colourless crystals of oxalic acid are obtained. Pour off the mother liquor (or strain through a filter plate), concentrate further, and obtain a further crop of crystals. Recrystallise from a little hot water.

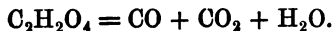
Oxalic acid crystallises with two molecules of water in colourless prisms; it is easily soluble in alcohol and fairly soluble in water; it melts at  $100^{\circ}$ , and gradually loses its water of crystallisation; at  $150^{\circ}$  the anhydrous acid sublimes.

When heated with strong sulphuric acid, oxalic acid gives off equal volumes of carbon monoxide and carbon dioxide without charring. The escaping gas turns lime water milky, and can be ignited at the mouth of the tube.

When a solution of oxalic acid is acidulated with dilute sulphuric acid and warmed with potassium permanganate (or manganese dioxide), carbon dioxide is evolved and the solution is decolorised.

Try both these experiments.

**Tests for Oxalic Acid.**—(1) Heated with strong sulphuric acid carbon monoxide and carbon dioxide are evolved without any charring :



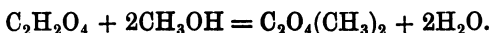
(2) Silver nitrate with neutral solutions gives a white precipitate of silver oxalate, which is soluble in nitric acid, and does not blacken when boiled.

(3) Calcium chloride gives a white precipitate of calcium oxalate, insoluble in acetic acid, but soluble in hydrochloric or nitric acids.

(4) When a solution of an oxalate is warmed with manganese peroxide and sulphuric acid, carbon dioxide is given off.

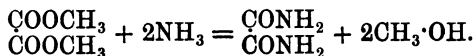
**Methyl Oxalate and Oxamide.**—Dehydrate 80 grams of oxalic acid by heating it to  $110^{\circ}$  in an air-bath for some time. Place 20 grams of the anhydrous acid in a small flask, add an equal weight of absolute methyl alcohol, connect with a back-flow condenser, and boil for fifteen minutes. Filter, if necessary, through a hot water funnel containing water at about  $50^{\circ}$ , and cool. Filter the crystals which separate out, drain at the pump, and dry.

Methyl oxalate forms soft white needles, melting at  $54^{\circ}$  :



Prove that on hydrolysis it yields methyl alcohol and oxalic acid.

**Oxamide,  $(\text{CO.NH}_2)_2$ .**—When treated with strong ammonia methyl oxalate is at once converted into oxamide. To the filtrate from the crystals obtained as described above, add an equal volume of *strong* ammonia. Filter on the pump, wash with cold water until the mass is free from ammonia, and dry in the air :



Oxamide is very sparingly soluble in water, and may thus be separated from ammonium oxalate.

(1) Heat a little dry oxamide in a tube. A portion of it sublimes, ammonia and cyanogen being given off (smell cautiously).

(2) Boil a little of the oxamide with caustic soda solution. It slowly dissolves, with evolution of ammonia. Test the solution for oxalic acid.

**Reactions of Tartaric Acid.**—Tartaric acid forms large transparent crystals melting (though not sharply) at about  $167^{\circ}$ . It

is easily soluble in water and in alcohol, and gives two series of salts.

(1) Tartaric acid or a tartrate, when heated, chars and gives the peculiar smell of burnt sugar.

(2) Calcium chloride gives with neutral solutions of tartrates a white precipitate of calcium tartrate, soluble in the mineral acids or caustic soda or potash.

(3) Place some calcium tartrate in a test-tube with a few drops of ammonia solution and a crystal of silver nitrate, and warm gently; metallic silver is deposited on the glass as a mirror, whilst the tartrate is oxidised.

(4) When heated with strong sulphuric acid the mixture is charred, and carbonic acid gas, carbonic oxide, and sulphur dioxide are evolved.



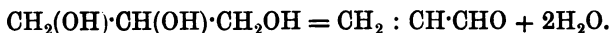
## CHAPTER XVII

## GLYCEROL AND ITS DERIVATIVES

**Glycerol, or glycerine**,  $C_3H_5(OH)_3$ , can readily be obtained by hydrolysis or 'saponification' of the natural fats (cf. p. 41); on the small scale this can be done by boiling 50 grams of olive oil with 10 grams of caustic soda and 100 cc. of water until on cooling a solid cake of sodium oleate forms on the surface. In order to separate this soap completely, add 100 grams of common salt to the boiling liquid, stir well, and allow to cool. When cold, filter on the pump, neutralise the filtrate with hydrochloric acid, and evaporate on the water-bath; the residue consists of sodium chloride and glycerol. Extract with absolute alcohol, filter, and evaporate to dryness on the water-bath, when crude glycerol is obtained as a thick brown liquid.

Pure glycerol is a thick colourless liquid, which has a sweet taste, and boils at  $290^\circ$ . It does not volatilise with steam at  $100^\circ$ , and is therefore left as a thick liquid when its solution is evaporated. It is miscible with water and alcohol in all proportions, but is insoluble in ether.

**Tests.**—(1) The chief reaction by which glycerol can be detected is its decomposition into acryl aldehyde (acrolein) and water when it is heated with dehydrating agents, potassium hydrogen sulphate being the most suitable:



The test is best carried out in a moderately large test-tube provided with a conducting tube dipping into water. An aqueous solution of acrolein is thus obtained, which shows all the tests for an aldehyde (ammoniacal silver nitrate, magenta, p. 84). It

is also characterised by the irritating effect of its vapour, which causes a flow of tears, this property alone being often sufficient to indicate the presence of acrolein.

(2) When a borax head is dipped into a neutral solution of glycerol (free from ammonium salts) and then brought into a flame, a green coloration due to boric acid is produced.

(3) When 2 drops of glycerol are heated with an equal amount of phenol and of concentrated sulphuric acid to  $120^{\circ}$ , a mass is obtained which, after cooling, gives a red coloration when it is diluted with water and a few drops of ammonia are added (Reichl's test).

**Allyl Alcohol.**— Fifty grams of crystallised oxalic acid, 200 grams of glycerine, and  $\frac{1}{4}$  gram of ammonium chloride are placed in a half litre retort, which is connected with a condenser. A thermometer dipping into the mixture is inserted through the tubulure of the retort, and the mixture is heated slowly until the effervescence of carbon dioxide has ceased and the temperature has reached  $195^{\circ}$ . The receiver is then changed, and the distillate collected until the temperature has risen to  $260^{\circ}$ . A further quantity may be obtained by adding about 80 grams of oxalic acid to the contents of the retort, and repeating the distillation. The crude allyl alcohol is then redistilled from a distilling flask, until a sample of the distillate no longer yields an oily layer when treated with potassium carbonate. The distillate is then treated with solid potassium carbonate, the oily layer dried over caustic potash, and distilled with caustic baryta.

Allyl alcohol is a colourless liquid, having a pungent odour, and boiling at  $96^{\circ}$ .

It behaves towards reagents in a similar manner to ethyl alcohol, but also behaves as an unsaturated compound.

(1) To 1 cc. of allyl alcohol add bromine drop by drop. The colour of the bromine at first disappears, heat is evolved, and dibromopropyl alcohol,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{OH}$ , is produced.

(2) Compare allyl alcohol and ethyl alcohol with respect to their behaviour towards sodium, phosphorus trichloride, acetyl chloride, and potassium bichromate and sulphuric acid.

(3) Allyl alcohol gives the 'iodoform reaction.'



## CHAPTER XVIII

## THE CARBOHYDRATES

**The Glucoses or Hexoses.**—These are solid bodies having a sweet taste; they are easily soluble in water, less so in alcohol, and insoluble in ether; most of them are crystalline, and are optically active. They have the formula  $C_6H_{12}O_6$ .

**Glucose, Dextrose, or Grape-sugar.**—Glucose is usually met with in irregular lumps, containing 1 molecule of water of crystallisation, melting at  $86^\circ$ ; the anhydrous substance melts at  $146^\circ$ . It is soluble in its own weight of water, is less sweet than cane sugar, and does not crystallise readily.

Dissolve some glucose in water, and try the following experiments:

(1) Add a little strong sulphuric acid to the cold solution; no change occurs at first, but on warming the solution turns yellow, and gradually darkens (compare cane-sugar).

(2) Glucose is a reducing agent, and with solutions of cupric salts gives a red or yellow precipitate of cuprous oxide. Make the solution alkaline with caustic soda, and add 2 drops of copper sulphate solution; a violet solution is obtained, and, on heating, an immediate precipitate of cuprous oxide. This is known as 'Trommer's test.'

(3) Add a few drops of 'Fehling's solution,'<sup>1</sup> and warm; cuprous oxide is precipitated as before.

(4) 'Barford's solution' is also reduced by glucose, with precipitation of cuprous oxide (compare 'maltose'). Barford's

<sup>1</sup> Fehling's solution does not keep well, and should be prepared as it is wanted by mixing equal volumes of the following stock solutions: (a) 34.6 grams of copper sulphate crystals dissolved in water and the solution made up to 500 cc.; (b) 178 grams of Rochelle salt (sodium potassium tartrate) and 60 grams of caustic soda dissolved in water and made up to 500 cc.

solution is made by dissolving 1 part of cupric acetate in 15 of water, and then acidulating with acetic acid (0.75 gram of acid to 100 cc. of the solution).

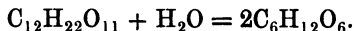
(5) When warmed with phenyl-hydrazine, glucose gives a yellow precipitate of glucosazone. Dissolve one gram of glucose and three grams of sodium acetate in 20 cc. of water; add two grams of phenyl-hydrazine hydrochloride and heat the liquid in the water-bath for twenty minutes. On cooling (or even in the hot liquid) an abundant yellow crystalline precipitate is obtained. Filter, wash, and dry the precipitate, and determine its melting point ( $204^{\circ}$ ).

(6) With lime water glucose gives no precipitate (compare 'fructose').

**Fructose, Levulose, or Fruit Sugar.**—Fructose crystallises with great difficulty, and is usually obtained as a gummy syrup; from alcohol it can be obtained in small crystals melting at  $95^{\circ}$ . It has a sweet taste, and is more soluble in water and in alcohol than is glucose. With sulphuric acid, with Trommer's, Fehling's, or Barford's test it acts like glucose, though rather more quickly; and it yields the same glucosazone with phenyl-hydrazine.

It can be distinguished from glucose by its optical properties, and by giving a white precipitate on the addition of lime water.

**The Cane Sugar Group.**—The sugars of this group, also known as the saccharoses or diglucoses, are optically active bodies having a sweet taste and crystallising fairly readily. In solubility they resemble the glucoses, but they are more stable than the latter, and with the exception of maltose they are not directly fermentable, but must first be converted into glucoses. They have the formula  $C_{12}H_{22}O_{11}$ , and when heated with dilute acids take up the elements of water yielding two molecules of sugars of the glucose series:



In some cases two molecules of the same glucose are formed, whilst in others two different members of this series are obtained.

**Cane Sugar, or Saccharose.**—Cane sugar crystallises in transparent monoclinic prisms, melting at about  $160^{\circ}$ . It dissolves very readily in water, but only very sparingly in alcohol. When

heated it melts at 160°, between 200° and 215° it gradually loses water and is converted into caramel, and on heating more strongly it chars.

With an aqueous solution of sugar try the following experiments :

(1) Add an equal bulk of strong sulphuric acid ; the solution blackens immediately, and if there is much sugar present a spongy mass of carbon is formed.

(2) Cane sugar does not reduce Fehling's or Barford's solution, and does not give a precipitate with Trommer's test.

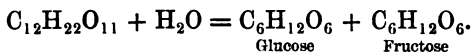
(3) Boil the solution with a little dilute hydrochloric acid for a few minutes ; glucose and fructose are formed. Neutralise the liquid with caustic soda, and test with Fehling's solution.

(4) When treated with yeast the sugar is first of all converted into glucose by the enzyme invertase. Add a little yeast to the solution, allow to stand for ten minutes, and filter (the filtrate need not be quite clear) ; test the filtrate for glucose.

(5) Heat some powdered sugar carefully, in a crucible, and observe the changes it undergoes.

#### **Preparation of Glucose and Fructose from Cane Sugar.—**

Dissolve 10 grams of sugar in 50 cc. of water, add 15 cc. of dilute sulphuric acid, and heat in a water-bath to about 70° for fifteen minutes ; neutralise the acid with chalk, and filter off the precipitated calcium sulphate. The filtrate contains equal quantities of glucose and fructose, and on evaporation would yield 'invert sugar' :



To the filtrate add 6 grams of calcium hydrate (slaked lime) suspended in 50 cc. of cold water, stir *well* and allow to stand ; a stiff paste is obtained, the lime compound of fructose being precipitated and that of glucose remaining in solution. Filter the paste and wash with the aid of the pump. Suspend the precipitate in water, and pass carbon dioxide through the mixture until it is no longer alkaline (or the lime may be precipitated by oxalic acid, any excess of acid being afterwards neutralised by lime water), filter off the precipitated chalk, and evaporate the filtrate to dry-

ness on the water-bath. Fructose is obtained as a yellow syrup. Prepare glucose by treating the filtrate in the same manner as the lime precipitate. Dissolve the two glucoses in water and compare their behaviour with Fehling's solution, and with lime water.

**Lactose, or Milk Sugar.**—Lactose crystallises in rhombic prisms with one molecule of water ; it is less sweet than cane sugar, and dissolves in about six parts of cold water. When heated to  $186^{\circ}$  it is converted into a caramel. It gives a red precipitate when warmed with copper sulphate and caustic soda, and reduces Fehling's solution, but does not reduce Barford's solution.

Try these three tests.

**Maltose, or Malt Sugar.**—Maltose crystallises in needles containing one molecule of water, is very soluble in water, and is less sweet than cane sugar. Unlike the other members of the group, it undergoes direct fermentation. It reduces Fehling's solution and gives a red precipitate with Trommer's test, but does not reduce Barford's solution.

**The Amyloses.**—These are amorphous bodies having the composition  $(C_6H_{10}O_5)_n$  ; they are not soluble in alcohol or ether, do not reduce Fehling's solution, and are not attacked by yeast, though dilute acids and certain ferments convert them into glucoses. Most of them are optically active, and some of them give characteristic colours with iodine.

**Starch.**—Starch forms a soft white powder composed of microscopic granules ; it is not soluble in cold water, but when heated in water the granules burst, their contents dissolve, and the husks remain in suspension, giving an opalescent solution. To prepare starch solution make a gram of starch into a paste with 8 or 4 cc. of cold water in a mortar and pour it into 20 cc. of boiling water.

The cold solution is coloured an intense blue by the addition of a drop of iodine solution (1 gram of iodine and 2 grams of potassium iodide in 100 cc. of water) ; the colour disappears when the solution is heated, and reappears (though more feebly) on cooling.

With cold starch solution baryta water gives a white precipitate.

Starch is very easily converted into other carbohydrates.

**Preparation of Glucose from Starch.**—Dissolve 10 grams of starch in 200 cc. of water, place in a flask of about 700 cc. capacity, add 10 cc. of dilute sulphuric acid, connect with a back-flow condenser, and boil gently. At intervals of five minutes pour two or three drops into a tube half full of water, and test with one drop of iodine solution. The first sample should give the fine blue characteristic of starch, while successive samples will give various shades of purple gradually passing into the deep red due to erythrodextrin. After about half an hour's boiling a sample should only show the faint yellow colour due to the iodine.

After boiling for one hour, pour the liquid into a basin, neutralise the acid by adding chalk until litmus paper is no longer reddened; filter off the precipitated calcium sulphate, and evaporate the filtrate to dryness on the water-bath. A clear yellow gum is left which consists chiefly of glucose, but contains also dextrins and maltose—these bodies being formed as intermediate products. Test the residue for glucose, and taste it.

**Cellulose.**—Cellulose is a white solid, insoluble in all ordinary solvents, but soluble in an ammoniacal solution of copper oxide (Schweitzer's reagent), from which it is reprecipitated by acids. It gives no coloration with iodine. Moderately strong sulphuric acid converts it into amyloid, a substance coloured blue by iodine.

Mix 20 cc. of strong sulphuric acid with 10 cc. of water, and when quite cold place the acid in a small basin. Take a strip of filter paper ten inches long by a quarter of an inch wide, draw it once through the acid (pressing it below the surface with a glass rod), drop it into a large basin of water, and wash it a second time in water containing a trace of ammonia. The superficial cellulose is converted into amyloid, and 'parchment paper' is obtained. Test the parchment paper with iodine.

Place the two ends of a strip (which need not be dry) between the finger and thumb; through the loop of the paper pass a glass rod, and from this suspend a box or the pan of a pair of scales; put weights in the pan until the strip breaks. Note the weight used, and then test a similar strip of untreated filter paper. Good filter paper will carry 250 to 300 grams.

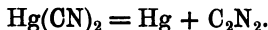
The parchment paper, even though wet, should be very much stronger than the original paper.

When heated with more dilute acid cellulose is converted into glucose. Grind a pinch of cotton wool with a few drops of strong sulphuric acid in a mortar, until a sticky mass is formed. Add strong caustic soda solution until the mass is alkaline (the mixture gets very hot); dissolve in water, and test for glucose by Trommer's or Fehling's test.

## CHAPTER XIX

## THE CYANOGEN COMPOUNDS

**Cyanogen**,  $C_2N_2$ , is readily prepared by heating mercuric cyanide, and may be collected over mercury :



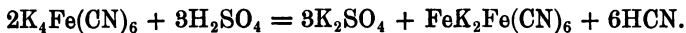
Cyanogen is a colourless gas with a peculiar and characteristic smell ; it is soluble in four volumes of cold water, burns with a beautiful purple flame, and is very poisonous.

**Experiment.**—Heat a little mercuric cyanide in a tube of infusible glass, and ignite the gas at the mouth of the tube.

**Hydrocyanic Acid (HCN)** may be prepared by distilling potassium cyanide with a mineral acid :



or (more cheaply) by heating potassium ferrocyanide with weak sulphuric acid :



Pure anhydrous hydrocyanic acid is a colourless liquid, smelling like bitter almonds ; it boils at  $26.5^\circ$ , is soluble in water, burns with a violet flame, and is a most violent poison.

*Great care must be taken in all experiments with the cyanides, and they should not be attempted by a solitary student, as these substances are all dangerous.*

**Preparation of dilute Hydrocyanic Acid.**—In a small flask place 10 grams of potassium ferrocyanide, and add a cold mixture of 7 grams of strong sulphuric acid with 14 grams of water ; connect the flask with a Liebig's condenser, and distil in a draught cupboard. The receiver must contain a little distilled water, and the condenser must be fitted with an adaptor dipping

below the surface of this water. In this way a weak solution of hydrocyanic acid is obtained, which may be used for the following tests :

(1) Note the characteristic smell, but do not inhale very much of the vapour.

(2) Silver nitrate gives a white precipitate of silver cyanide, insoluble in nitric acid, but soluble in ammonia.

(3) In a small porcelain dish place a drop of the solution, add one drop of ammonia solution, and one of ammonium sulphide, and evaporate to dryness on the water-bath ; ammonium thiocyanate is formed, and on adding water and then a drop of ferric chloride solution the well-known deep red colour is obtained.

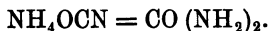
(4) Make the solution alkaline with caustic soda, and add ferrous sulphate solution containing a little ferric chloride ; on addition of an acid Prussian blue is formed (*see* p. 4).



## CHAPTER XX

## SYNTHESIS OF UREA

**Urea**,  $(\text{CO}(\text{NH}_2)_2)$ .—Urea is prepared by boiling a solution of ammonium cyanate :

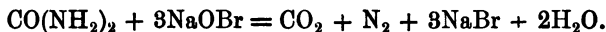
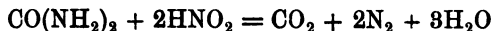


Powder some crystallised potassium ferrocyanide finely and dry it by gently heating it on a flat iron dish. Dry some finely powdered manganese dioxide in a similar manner and mix together 70 grams of the dried manganese dioxide with 140 grams of dried potassium ferrocyanide. Heat this mixture 70 grams at a time on a flat iron dish and stir it constantly until the mass glows throughout. Extract with a small quantity of warm water, filter, and to the warm solution add 104 grams of ammonium sulphate (finely powdered) and shake up well ; on cooling, a quantity of potassium sulphate crystallises out. Pour off and evaporate the liquid to dryness on the water-bath. Extract the urea with boiling methylated spirit, filter from the residual potassium sulphate, and allow to cool. Recrystallise the urea once from methylated spirit, and finally from absolute alcohol, which removes the yellow colour due to traces of potassium ferrocyanide. Determine its melting point.

Yield : 20 to 30 grams.

Urea forms colourless needles melting at  $132^\circ$ , and is easily soluble in water or alcohol ; it possesses basic properties, combining with one equivalent of an acid to form salts, the most characteristic being the nitrate. It is decomposed by nitrous

acid, by a hypochlorite, or by a hypobromite to nitrogen and carbon dioxide.



**Preparation of Urea Nitrate.**—Utilise the alcoholic mother liquors for the preparation of the nitrate. For this purpose dilute with water, evaporate most of the liquid, cool, and add an equal volume of strong nitric acid. By dissolving the precipitated nitrate of urea in warm water, adding a little nitric acid, and allowing to cool slowly, the salt may be obtained in good crystals.

Yield: 15 to 20 grams.

Instead of strong nitric acid, a strong solution of oxalic acid may be used, giving urea oxalate.

**Tests for Urea.**—1. Add strong nitric acid to a strong solution, when a *crystalline* precipitate of urea nitrate is obtained.

2. Add caustic soda to the solution and then bromine water; on warming gently the liquid effervesces briskly, nitrogen being evolved.

## APPENDIX

---

THE first step in the identification of an organic substance is the determination of the elements which it contains. This process, however, which is in most cases sufficient for the complete identification of an inorganic substance, only enables us to classify the organic substance as a member of one of several large groups, such as the nitrogenous or the non-nitrogenous substances, &c., &c. Further evidence must, then, be sought as to the type of compound to which the substance belongs, whether acid, ether, salt, alcohol, &c., and finally it must be identified by special tests which distinguish it from all members of the same class. Thus, for example, a substance like acetic acid would first of all be found to belong to the large group of compounds which only contain C, H, O.

(2) It would be found to be an acid by its action on alkalis.

(3) An examination of the salts would show that—

(1) The barium and calcium salts are soluble in water.

(2) The silver salt is only sparingly soluble in cold water, and is not blackened on boiling with water.

(3) The ferric salt is decomposed when its solution is boiled, and a red precipitate is produced.

All these reactions are only given by acetic acid, and this evidence would usually be taken as sufficient to show the identity of the substance.

A more complete proof would be afforded by—

(1) Analysing the acid quantitatively.

(2) Determining its physical properties (boiling point, melting point, density, smell, &c.) and comparing them with those of acetic acid.

Since very many different types of organic compounds exist, it is impossible to draw up a simple plan of qualitative analysis which shall

apply to *any* organic substance, but it is often possible to ascertain which out of a certain number of substances is present, this being a very frequent problem in practical organic work; and the lists drawn up by the Science and Art Department are no doubt intended to be representative of some such actual case. It must be remembered, then, that the principles of qualitative recognition of organic substances are: first, the recognition of the class to which the compound belongs, and secondly, the identification of the particular substance by special tests. In the particular list of substances before us (see below) we have only two types of organic compounds to distinguish—alcohols and acids. These may, however, form compounds with inorganic substances, the acids forming salts and the alcohols combining with various salts to form double compounds. The first step, then, is to try to find out whether the substance is: (1) an alcohol; (2) an acid; (3) a salt; (4) a compound of an alcohol and an inorganic compound; (5) a mixture of two of these. Having done this, the next step is to ascertain which of the special alcohols and acids are present.

This can be done by carrying out the following tests in order. A scheme can, of course, be arranged for any other special list of substances based on the same principles.

‘Required to recognise in a powder soluble in water or dilute acid, the following bodies: methyl and ethyl alcohols, glycerine, formic acid, acetic acid, oxalic acid, tartaric acid, citric acid, salicylic acid; not more than two of them being present.’

1. Heat a little of the powder on a small piece of platinum foil until no further change occurs.

A. No residue is left. Ammonium or mercury salts or no inorganic substances present.

(1) Test for ammonia by heating with caustic soda solution.

(2) Test for mercury by heating in a dry tube with potassium cyanide and sodium carbonate, and seeing whether a sublimate of mercury is produced.

If *no* inorganic substance is present, the substance must be either oxalic, tartaric, citric, or salicylic acid, or a mixture of these, since all the other substances in the list are liquids when in the pure state.

B. If a residue is left, or if ammonia or mercury be found, the substance is either a salt or a compound of an alcohol with an inorganic compound.

2. Heat in a dry tube.

(1) The substance gives off inflammable vapours without charring (alcohols, glycerine, oxalate, formate).

(2) The substance chars (acetate, tartrate, citrate, salicylate).

8. Heat with strong sulphuric acid.

(1) CO evolved alone (formate).

(2) CO and CO<sub>2</sub> evolved.

(a) Without charring (oxalate).

(b) With charring (tartrate, citrate).

(3) Inflammable gas, burning with luminous flame (alcohols).

(4) Smell of vinegar (acetate).

4. Test solubility of substance in water. If it dissolves, make a solution and test with litmus. Make neutral by caustic soda or nitric acid, if necessary, and use for the following tests. If the substance is insoluble in water, boil with sodium carbonate solution, filter, and neutralise the boiling filtrate with nitric acid.

With this (after cooling) try the following tests, taking separate portions for each.

A. Make acid with acetic acid.

White crystalline precipitate (salicylic acid).

Filter if a precipitate is produced, and—

(a) Add calcium chloride. White precipitate (oxalic acid).

B. To the neutral solution add—

- |                      |                       |                        |
|----------------------|-----------------------|------------------------|
| (1) Calcium chloride | (a) White precipitate | [Phosphate, sulphate,  |
| (equal bulk and      | in the cold. .        | arsenate, &c., if pre- |
| scratch the sides    | (b) White precipitate | sent also come         |
| of the glass).       | on boiling—cit-       | down] Oxalate, tar-    |
|                      | rate . . .            | trate.                 |
| (2) Ferric chloride. | (a) Red coloration    | Formate, acetate.      |
|                      | and precipitate       |                        |
|                      | on boiling. .         |                        |
|                      | (b) Purple colour. .  | Salicylate.            |

Having ascertained the general nature of the substances which are present, special tests must be applied.

1. Detection of Glycerine.—If inorganic matter be present, extract with alcohol, filter, and evaporate to dryness. Test the residue.

(1) A bead of borax brought into a neutral solution of glycerine and then held in the flame produces a green coloration.

(2) Heat with potassium hydrogen sulphate; irritant vapours of acrolein are evolved.

2. Detection of Methyl and Ethyl Alcohols.—Add a little water to the powder and distil from a small distilling flask or retort. To the

distillate add solid potassium carbonate, and allow to stand. If an inflammable liquid separates at the top, alcohols are present.

To a separate portion of the distillate add dilute caustic soda and then a crystal or two of iodine; shake until this has dissolved, and warm gently. Yellow precipitate of iodoform indicates *ethyl alcohol*.

If ethyl alcohol is not present, the inflammable liquid must be methyl alcohol.

Confirm by boiling the liquid with dilute sulphuric acid and a little potassium bichromate; both alcohols turn the solution green and give an odour of aldehyde.

### 3. Detection of Tartaric and Citric Acids in Presence of Oxalic Acid.—

If oxalic acid be found by means of calcium chloride in acetic acid solution, it will be precipitated along with any tartaric acid by calcium chloride in neutral solution. Filter after allowing to stand for ten minutes, and boil the filtrate. A dense crystalline white precipitate indicates *citric acid*.

Test the precipitate produced by calcium chloride (in the cold) for tartrate by placing in a test tube, adding a *crystal* of silver nitrate and a few drops of ammonia solution, and warming. If a tartrate be present a mirror of metallic silver will be produced.

The precipitate obtained by boiling with calcium chloride should be tested in a similar way, since calcium tartrate is sometimes precipitated in this way.

### 4. Detection of Formic and Acetic Acids.—

In the presence of salicylic acid, either of these acids is best tested for by acidifying the solution with sulphuric acid, filtering off the crystals of salicylic acid and distilling the solution. In the distillate the acids may be tested for by ferric chloride, silver nitrate, &c., in the usual way.

Formic acid can always be recognised by its behaviour with concentrated sulphuric acid. Acetic acid can be detected in the presence of formic acid by shaking the acid distillate obtained as described above with pure litharge. Acetic acid forms a basic acetate which turns red litmus paper blue. The litharge must be tested by itself, as it is often alkaline.

### Reactions of Citric Acid and the Citrates.

- (1) Citric acid or a citrate, when heated, chars and evolves irritating fumes.
- (2) Calcium chloride produces no precipitate in a cold, neutral solution of a citrate. On boiling a crystalline white precipitate of calcium citrate is produced.

- (3) Calcium citrate does not reduce silver nitrate in the presence of ammonia.
- (4) When heated with strong sulphuric acid, carbonic acid gas and carbonic oxide are at first evolved without any charring, but on continued heating blackening takes place, and sulphur dioxide is evolved.

**Reactions of Salicylic Acid.**

- (1) Salicylic acid is precipitated in white crystals when a solution of one of its salts is acidified.
- (2) Ferric chloride produces a deep violet coloration, which is destroyed by acids.
- (3) When heated with soda lime, a characteristic smell of phenol is produced.

**Reactions of Methyl Alcohol.**

- (1) Methyl alcohol mixes with water in all proportions.
- (2) It burns with a flame resembling that of ethyl alcohol.
- (3) It does not yield the iodoform test.
- (4) It is oxidised by a mixture of sulphuric acid and potassium bichromate, the liquid becoming green.

# INDEX

---

**Acetamide**, 45  
**Acetic acid**, 39  
— — detection of, 68-70  
— — molecular weight of, 8  
— — reactions of, 40  
— anhydride, 44  
**Acetone**, 37  
— sodium bisulphite, 37  
**Acetonitrile**, 46  
— hydrolysis of, 47  
**Acetyl chloride**, 43  
**Acetylene**, 18  
**Acrolein**, 54  
**Alcohol**, oxidation of, 33, 39  
**Aldehyde**, 33  
**Aldehyde-ammonia**, 33  
**Aldehyde sodium bisulphite**, 34  
**Allyl alcohol**, 55  
**Amyl nitrite**, 49  
**Amyloid**, 60  
**Amyloses**, the, 59  
  
**Barford's solution**, 56  
**Barium acetate**, preparation of, 37  
**Boiling point**, determination of, 7  
  
**Cane sugar**, 57  
— — group, 57  
**Caramel**, 58  
**Carbon**, detection of, 3  
**Cellulose**, 60  
**Chloral**, 35  
**Chloroform**, from chloral, 35  
— preparation of, 35  
— vapour density of, 10

**Citric acid**, detection of, 69  
— — reactions of, 69  
**Copper acetylene**, 19  
**Cuprous chloride**, preparation of, 19  
**Cyanides**, test for, 4  
**Cyanogen**, 62

**Dextrose**, 56  
**Dibromopropyl alcohol**, 55  
**Dumas' method of vapour density**  
determination, 9

**Ethane**, 14  
**Ether**, from ethyl sulphuric acid, 32  
— preparation of, 29  
— synthesis of, 28  
— vapour density of, 9  
**Ethyl acetate**, 40  
— — hydrolysis of, 41  
— alcohol, 23  
— — detection of, 68-70  
— bromide, 20  
— chloride, 26  
— hydrogen sulphate, 30  
— nitrite, 49  
— sulphuric acid, 31  
**Ethylene**, 16  
— dibromide, 16  
— from ethyl sulphuric acid, 31  
— glycol, 50

**Fehling's solution**, 56  
**Fermentation**, 23  
**Formic acid**, 47



Formic acid, detection of, 68-70

— — from chloral, 35

— — reactions of, 48

Fractional distillation, 24

Fructose, 57

— preparation of, from cane sugar, 58

Fruit sugar, 57

Glucosazone, 57

Glucose, 56

— preparation of, from cane sugar, 58

— — from cellulose, 61

— — from starch, 60

Glucoses, the, 56

Glycerine, 54

— detection of, 68-70

— reactions of, 55

Glycol, 50

Grape sugar, 56

Halogens, detection of, 4

Hexoses, the, 56

Hydrocyanic acid, 62

— — reactions of, 63

Hydrogen, detection of, 3

Hydrolysis, 35, 41

Iodine reaction for starch, 59

Iodoform reaction, 26

— preparation of, 36

Lactose, 59

Levulose, 57

Malt sugar, 59

Maltose, 59

Melting point, determination of, 6

Methane, 13

Methyl alcohol, 27

— — detection of, 68-70

— — reactions of, 70

— iodide, 21

Methyl oxalate, 52

Methylated spirit, purification of, 1

Milk sugar, 59

Nitrogen, detection of, 4

Oxalic acid, 51

— — detection of, 68-70

— — reactions of, 51

Oxamide, 52

Paraldehyde, 35

Parchment paper, 60

Prussian blue, formation of, 4

Reichl's test for glycerine, 55

Saccharose, 57

Salicylic acid, detection of, 68-70

— — reactions of, 71

Saponification, 54

Schiff's reaction, 35

Silver acetate, preparation of, 8

Sodium acetate, dehydration of, 13

— ethoxide, 25, 26

Starch, 59

Sugar, oxidation of, 51

Sulphovinic acid, 30

Sulphur, detection of, 4

Tartaric acid, detection of, 68-70

— — reactions of, 52

Trommer's test for sugars, 56

Urea, 64

— nitrate, 65

— oxalate, 65

Victor Meyer's method of vapour  
density determination, 10





UNIVERSITY OF MICHIGAN



3 9015 03107 4936

QD  
261  
.G24

Garrett, Frederic

An elementary course  
of practical organic  
chemistry.

384349

*Ernest Gary  
Mich. Municipal League*

8-6-38

AUG 5  
1938

AUG 5  
1938

