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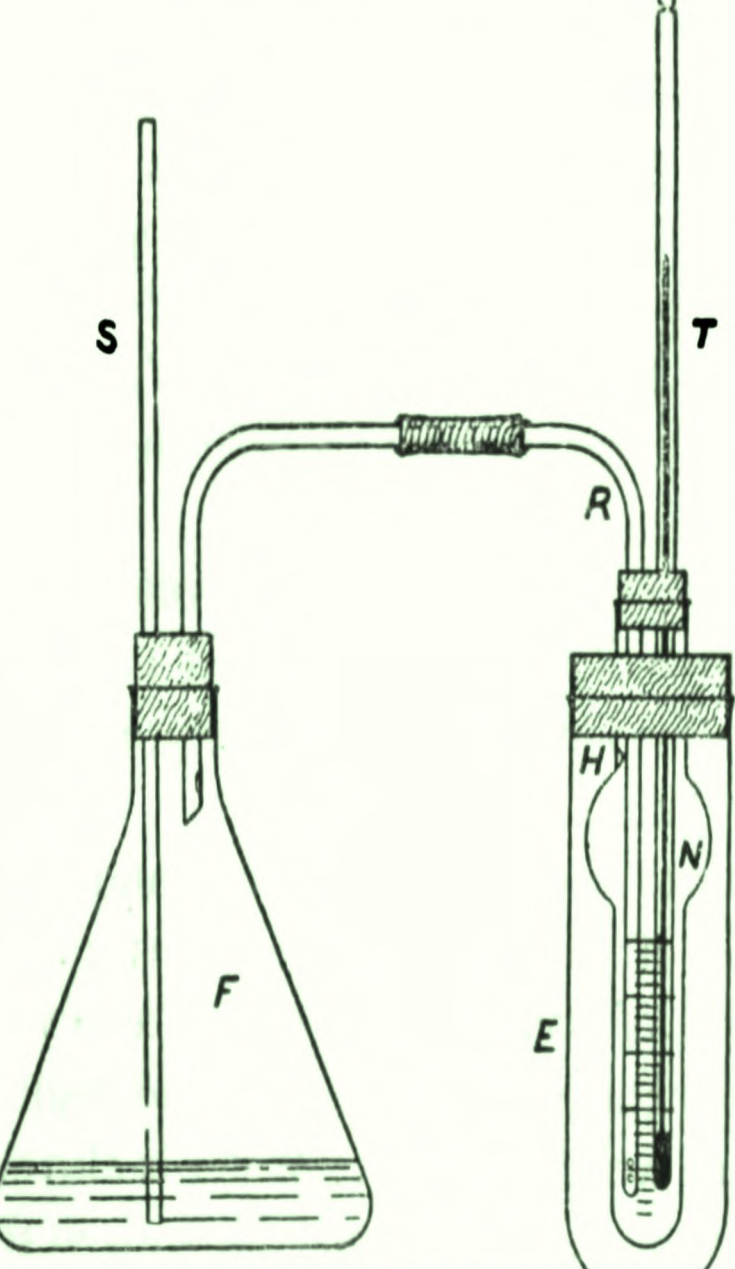
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*A course of practical
organic chemistry*

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**A COURSE OF
PRACTICAL ORGANIC CHEMISTRY**

A COURSE OF PRACTICAL ORGANIC CHEMISTRY

BY

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PREFACE

THE recent revision of the Board of Education syllabus for Practical Organic Chemistry is undoubtedly to be welcomed by all teachers of that subject, although they may not be in complete agreement with the details. It has naturally created the necessity for a text-book which will cover the complete syllabus, since hitherto the student has had to refer to different books for different parts of the subject.

The students of Organic Chemistry in the Birmingham Municipal Technical School, as in most other Technical Schools, comprise those working for

- (1) The Board of Education examinations,
- (2) The B.Sc. degree,

and during the past few years the course has been arranged to suit both classes of students. It has consequently been very similar in character to the revised syllabus, and the present book really consists of an amplification of the notes which have been given to our own students.

In drawing up a scheme of work we have had to bear in mind the fact that the classes in the Birmingham Technical School are, with few exceptions, held only in the evening, and consequently many lengthy preparations have been omitted. At the same time, we have endeavoured to arrange the course so that the student will get a completely satisfactory practical acquaintance with Organic Chemistry. The number of preparations given in each stage is far more than the individual student in an evening school can get through in the course of one session, so that the teacher will have to exercise his judgment in the choice of exercises; at the same time, a good deal of ground can be covered in a limited time if the students work in groups of three, each member of a group doing a different preparation; each student will then be able to follow the manipulative details of the other preparations which are being performed at the same time.

In the qualitative portions of the book are given the tests for the individual substances mentioned in the syllabus of Practical Organic Chemistry (Stages I. and II.) and of Theoretical Organic Chemistry (Stage III.). Some of the substances are so expensive that it is not likely that the student will often come in contact with them, but they are included for the sake of completeness.

It has not been deemed advisable to give tables for the separation of mixtures of the commoner compounds, since there are now very few examinations which require such operations. In case of necessity the student should be able to devise methods of separation by making use of the tests given in the book.

It is with great pleasure we acknowledge the assistance received from our colleague Mr. W. Russell, F.I.C., and from Dr. R. C. Farmer, of the Royal Arsenal, Woolwich, in the preparation of the manuscript, and from our colleague Mr. A. W. T. Hyde, who has drawn the majority of the diagrams; especially are we indebted to Dr. Farmer for the main ideas of the scheme for the identification of an organic compound. These three gentlemen have also assisted in the reading of the proofs.

For portions of the practical quantitative work in Part III. we are greatly indebted to Dr. Findlay, of the Birmingham University, who has allowed us to make free use of his "Practical Physical Chemistry."

In the preparations and qualitative and quantitative work we have used the notes which we have compiled in previous years from the literature and various larger text-books which are available to the chemist.

We also have to acknowledge the permission granted to us by the Chemical Society and the Society of Chemical Industry to reproduce the diagrams on pp. 195 and 163 respectively.

T. S. P.
D. F. T.

BIRMINGHAM,
September, 1907.

NOTE

Since this book was written a change has been made in the Board of Education Syllabus. **Allyl alcohol, trimethylamine, methyl- or ethyl-ammonium salts, chloracetic acids, and palmitic acid** have been transferred from Stage I. to Stage II. The Student should bear this in mind when working through the Identification Tables.

INTRODUCTION

ARRANGEMENT OF SUBJECT MATTER

IN drawing up a scheme of work for practical organic chemistry three points have to be borne in mind, viz. (1) the compounds prepared should follow each other in logical sequence, (2) the easier preparations should come first, and (3) the tests for individual compounds, or groups of compounds, should come immediately after the preparation of those compounds.

It is impossible, however, to comply satisfactorily with all three conditions at the same time, so that a compromise has to be made.

CONTENTS

PART I

(STAGE 1)

CHAPTER I

| | PAGE |
|------------------------------------------------------------------------------------------------|------|
| DETERMINATION OF: MELTING POINTS; BOILING POINTS; SPECIFIC GRAVITY OF LIQUIDS | I |
| DETECTION OF THE ELEMENTS: CARBON, HYDROGEN, HALOGENS, NITROGEN, SULPHUR, PHOSPHORUS | 7 |
| PRELIMINARY NOTES ON PREPARATIONS | 10 |

CHAPTER II

| | |
|-----------------------------------------------------------------------------------------|----|
| PREPARATION OF METHANE. | 14 |
| PURIFICATION OF ETHYL ALCOHOL, AND SPIRIT DETERMINATION OF A FERMENTED LIQUOR | 15 |

(The tests for ethyl alcohol should come next, but a number of these presuppose a knowledge of the tests for acetaldehyde and acetic acid. These therefore follow, with those for formic acid, etc., for the sake of comparison. The preparations of acetaldehyde and formic acid are too difficult for the student to do at the commencement of his course, so that they are postponed till later.)

| | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| TESTS FOR: FORMATES, ACETATES, FORMALDEHYDE, ACETALDEHYDE, METHYL ALCOHOL, ETHYL ALCOHOL | 17 |
| PREPARATION OF THE FOLLOWING COMPOUNDS, WITH ETHYL ALCOHOL AS THE STARTING POINT: POTASSIUM ETHYL SULPHATE, ETHER, ETHYL ACETATE, ETHYL BROMIDE, ETHYL IODIDE, ETHYLENE AND ETHYLENE DIBROMIDE, ACETALDEHYDE | 23 |

CHAPTER III

| | PAGE |
|----------------------------------------------------------|------|
| TESTS FOR ACETONE | 36 |
| PREPARATION FROM ACETONE OF: ACETOXIME, CHLOROFORM . . . | 36 |
| TESTS FOR CHLOROFORM, CHLORAL HYDRATE, IODOFORM . . . | 37 |

CHAPTER IV

MONOBASIC ACIDS, ETC.

| | |
|------------------------------------------------------------------------------------------------------------------------------------------|----|
| TESTS FOR PALMITIC ACID | 40 |
| SAPONIFICATION OF A FAT AND PREPARATION OF STEARIC ACID . | 40 |
| PREPARATION OF SUBSTANCES WITH ACETIC ACID AS STARTING POINT: MONOCHLORACETIC ACID, ACETAMIDE, ACETONITRILE, METHYLAMINE | 42 |
| TESTS FOR: CHLORACETIC ACIDS, METHYLAMINE AND TRIMETHYL- AMINE | 43 |

POLYBASIC ACIDS

| | |
|-------------------------------------------------------------------------------------------------------------|----|
| PREPARATION OF OXALIC ACID | 49 |
| TESTS FOR: OXALATES, TARTRATES, CITRATES, SUCCINATES . . | 49 |
| PREPARATIONS WITH OXALIC ACID AS THE STARTING POINT: ETHYL OXALATE, METHYL OXALATE, OXAMIDE, FORMIC ACID | 54 |

(The preparation which comes naturally after formic acid is that of *Allyl Alcohol*, although this compound is not a derivative of oxalic acid. It is at the same time convenient to take the tests for glycerol.)

ALCOHOLS

| | |
|------------------------------------------------|----|
| PREPARATION OF ALLYL ALCOHOL | 58 |
| TESTS FOR ALLYL ALCOHOL AND GLYCEROL | 60 |

(The above list contains acetamide and oxamide. It is therefore convenient, at this stage, to take the preparation of urea, the amide of the dibasic carbonic acid.)

AMIDE OF CARBONIC ACID

| | |
|-----------------------------------------------|----|
| UREA, PREPARATION OF, AND TESTS FOR | 60 |
|-----------------------------------------------|----|

CHAPTER V

| | PAGE |
|---------------------------------------------------------------|------|
| TESTS FOR: CYANIDES, FERROCYNANIDES, AND FERRICYNANIDES . . . | 63 |

CHAPTER VI

| | |
|--------------------------------------------------------|----|
| TESTS FOR: DEXTROSE, CANE SUGAR, LACTOSE, STARCH . . . | 68 |
| PREPARATION OF GLUCOSAZONE | 69 |

CHAPTER VII

| | |
|-----------------------------------------------------------------------------------------------------------------|----|
| SCHEME FOR THE IDENTIFICATION OF ANY COMPOUND CONTAINED IN THE BOARD OF EDUCATION SYLLABUS, STAGE I. | 73 |
|-----------------------------------------------------------------------------------------------------------------|----|

PART II

(STAGE II)

CHAPTER VIII

| | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| FRACTIONAL DISTILLATION OF A MIXTURE OF BENZENE AND TOLUENE. DISTILLATION UNDER REDUCED PRESSURE | 86 |
| PREPARATION OF: NITROBENZENE; m-DINITROBENZENE; ANILINE (AND TESTS); ACETANILIDE; m-NITRANILINE; SULPHANILIC ACID (AND TESTS); THIOCARBANILIDE, PHENYL MUSTARD OIL, AND TRIPHENYLGUANIDINE | 90 |

CHAPTER IX

| | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| PREPARATIONS DEPENDING ON DIAZOTIZATION: BENZENE DIAZONIUM SULPHATE; IODOBENZENE; CHLOROBENZENE BY SANDMEYER'S REACTION; o-BROMTOLUENE BY GATTERMANN'S REACTION; PHENOL (AND TESTS); BENZENE (AND TESTS); p-TOLUYL NITRILE; p-TOLUIC ACID AND TEREPHTHALIC ACID | 100 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

CHAPTER X

| | |
|-----------------------------------------------------------------------------------------|-----|
| PREPARATION OF: BROMBENZENE; BENZYL CHLORIDE; BENZOIC ACID AND BENZYL ALCOHOL | 112 |
| TESTS FOR: BENZOIC ACID; SALICYLIC ACID; BENZALDEHYDE | 116 |

| | PAGE |
|-----------------------------------------------------------------------------------------------------|------|
| PREPARATION OF: BENZOYL CHLORIDE; BENZAMIDE; PHENYL BENZOATE; BENZANILIDE; ETHYL BENZOATE | 118 |
| DISTINCTION BETWEEN PRIMARY, SECONDARY, AND TERTIARY AMINES | 122 |

CHAPTER XI

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| PREPARATION OF: o- AND p-NITROPHENOL; PICRIC ACID (AND TESTS); ANISOL; β -NAPHTHALENE SULPHONIC ACID; β -NAPHTHOL; PHTHALIC ACID; ANTHRAQUINONE | 125 |
| TESTS FOR: NAPHTHALENE, ANTHRACENE | 129 |

PART III

(STAGE III)

CHAPTER XII

| | |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| SPECIAL PREPARATIONS: DIAZOAMINOBENZENE; AMINOAZOBENZENE; p-NITROSO DIMETHYLANILINE; BENZOIN, BENZIL, AND BENZILIC ACID; ACETOPHENONE BY FRIEDEL AND CRAFTS' REACTION; ACETOPHENONE MONOXIME; ACETANILIDE FROM ACETOPHENONE OXIME BY THE BECKMANN REARRANGEMENT; ETHYL BENZENE BY FITTIG'S REACTION; CINNAMIC ACID BY PERKIN'S REACTION; DIPHENYL CARBINOL (BENZHYDROL) BY THE GRIGNARD REACTION; HELIANTHINE AND METHYL ORANGE; MALACHITE GREEN; QUINOLINE BY SKRAUP'S REACTION | 136 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

CHAPTER XIII

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| QUANTITATIVE DETERMINATION OF THE ELEMENTS: CARBON; HYDROGEN; NITROGEN (DUMAS, VACUUM, AND KJELDAHL METHODS); HALOGENS, SULPHUR, AND PHOSPHORUS BY CARIUS' METHOD | 155 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

CHAPTER XIV

| | |
|------------------------------------------------------------------------|-----|
| DETERMINATION OF THE MOLECULAR WEIGHT OF AN ORGANIC COMPOUND | 173 |
|------------------------------------------------------------------------|-----|

Contents

xiii

| | PAGE |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| CHEMICAL METHODS : MOLECULAR WEIGHT OF AN ACID BY ANALYSIS OF THE SILVER AND BARIUM SALTS, AND BY TITRATION ; MOLECULAR WEIGHT OF A BASE BY ANALYSIS OF THE PLATINICHLORIDE, AND BY TITRATION OF THE SALTS | 173 |
| PHYSICAL METHODS : VAPOUR DENSITY AND MOLECULAR WEIGHT BY THE METHODS OF DUMAS AND VICTOR MEYER. CRYOSCOPIC AND EBULLIOSCOPIC METHODS | 177 |

CHAPTER XV

| | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| SPECIAL QUANTITATIVE WORK : QUANTITATIVE SAPONIFICATION OF ETHYL BENZOATE AND APPLICATION TO THE DETERMINATION OF $-OH$ GROUPS BY ACETYLATION AND BENZOYLATION. DETERMINATION OF $-NH_2$ AND $=NH$ GROUPS. PERKIN'S MODIFICATION OF ZEISEL'S METHOD FOR THE DETERMINATION OF METHOXYL AND ETHOXYL. DETERMINATION OF THE $-CN$ AND $-CO.NH_2$ GROUPS | 192 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

CHAPTER XVI

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| TESTS FOR URIC ACID, PYRIDINE, QUINOLINE, PIPERIDINE, CONINE, MORPHINE, QUININE, CINCHONINE, STRYCHNINE, BRUCINE, PIPERINE, CAFFEINE, AND THEOBROMINE | 199 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

CHAPTER XVII

| | |
|-------------------------------------------------------------------------------------|-----|
| SCHEME FOR THE DETECTION OF AN ORGANIC COMPOUND (STAGES I., II., AND III) | 211 |
| APPENDIX | 228 |
| INDEX | 235 |

ORGANIC CHEMISTRY

PART I

CHAPTER I

Determination of the Melting Point.—The temperature at which a substance melts is important, not only for the identification of the substance, but also as a test of the purity, since the presence of impurities nearly always causes a lowering of the melting point, and also renders it indistinct.

For the determination the substance is, if necessary, reduced to a powder and introduced into a thin-walled glass tube of about 1 mm. diameter.¹ The tube, containing as much of the solid as will occupy, when closely packed, about one centimetre of the lower end, is clipped by a narrow rubber band (cut from a piece of indiarubber tubing) to the side of a thermometer so that the portion containing the solid is against the bulb; the thermometer bulb is then completely immersed in a small beaker of glycerine, or strong sulphuric acid, which is heated by a small flame (Fig. 1). As the temperature rises, the liquid in the beaker should be agitated by a glass stirrer, to ensure the temperature being the same throughout. At the instant the solid melts the thermometer is read, the reading giving the melting point; the more slowly the heating is performed, the more accurate is the determination.

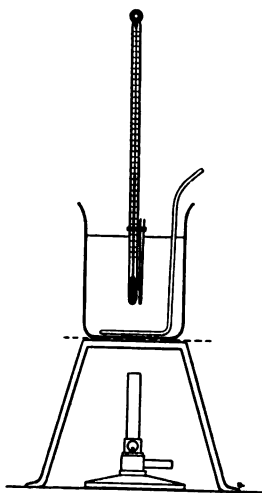


FIG. 1.

¹ Such tubes are easily made by heating a dry test-tube in a bunsen flame, and when soft, drawing it out to the correct diameter; the long tube thus obtained is broken into lengths of about 6 cms., and each piece is sealed at one end.

As a general rule, the same small quantity of substance should not be used for several determinations of the same melting point. This precaution is advisable for several reasons, *e.g.* some substances undergo slight decomposition at their melting point, other substances separate from the molten state in an unstable crystalline form (*cf.* chloracetic acid, p. 43), while others on melting change to a greater or less extent into a dynamic isomer; an example of this last is thiourea, which on melting isomerizes to some extent into ammonium thiocyanate. These changes nearly always cause the melting point to be lower than that of the original substance; it is obviously necessary, therefore, to use a fresh quantity of the substance for each determination.

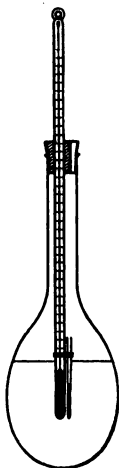


FIG. 2

The beaker can with advantage be replaced by a glass bulb with a fairly wide neck, as in Fig. 2. In this case

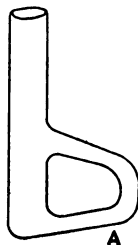


FIG. 3.

the stirring can be dispensed with. The rubber band is also not required if the bulb of the thermometer is not wider than the stem, because when the latter is wetted with the liquid in the bulb the narrow tube will cling to it by surface tension.¹

¹ The apparatus may be improved thus. A long tube of thin glass, of such diameter that it will slip easily into the neck of the bulb, is sealed at one end, and as much of the heating liquid is introduced as will suffice for the complete immersion of the thermometer bulb. This tube is then fitted by a ring of cork into the neck of the glass bulb, so that the lower end reaches down into the liquid. The thermometer and the attached tube containing the substance are then immersed in the liquid in this inner tube, and the heating is performed in exactly the same manner as before. By using this modification, the possibility of inaccuracy in the determination, due to local variation in the temperature of the liquid in different portions of the bulb, is almost completely removed.

A very convenient form of melting-point apparatus (Thiele's) is shown in Fig. 3. It consists of a tube about 2 cms. wide and 12 cms. long, to which a side tube of 1 cm. diameter is so fused that it connects the lower end of the main tube with the middle. In order to use it, just enough sulphuric acid is put into it to close the upper end of the side tube; the thermometer is placed so that the bulb is midway between the two openings of the side tube. On heating the tube at the point A, the sulphuric acid begins to circulate in the apparatus in such a way that it passes downwards in the main tube. The thermometer then rises very steadily and uniformly.

The apparatus works much more uniformly than any other apparatus in which there is not a mechanical stirring arrangement; the heating takes place rapidly, and is under complete control. If it is heated up quickly, the particles of substance remaining in the upper parts of the capillary melt first, owing to the direction in which the acid circulates, and this indicates when the temperature is approaching that of the true melting point. The heating is then proceeded with very cautiously until the substance at the bottom of the capillary tube melts.

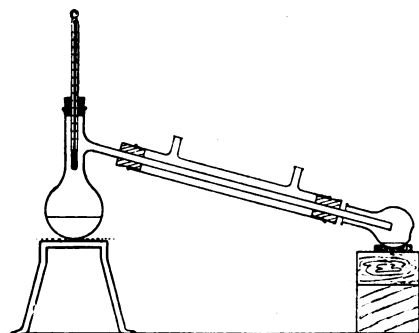


FIG. 4.

The following substances might be taken for practice in the above determination: salol (43° C.), m-dinitrobenzene (90° C.), acetanilide (112° C.), urea (132° C.), hippuric acid (187° C.), and phthalimide (238° C.).

Determination of the Boiling Point.—If several cubic centimetres of the liquid be available, the most suitable apparatus to use is that represented in Fig. 4. A clean, dry, distilling flask (capacity 1 oz.) is about one-third filled with the liquid, and the neck is fitted with a cork carrying a thermometer; the bulb of the thermometer should reach just below the side tube, and

must not touch the walls of the neck. The side tube can, if necessary, be attached to a small condenser.¹

The liquid is gently boiled over a small flame; the thermometer column at first rapidly rises, but, if the liquid is a pure substance, soon becomes stationary; the reading then gives the boiling point. If the boiling point does not appear fixed, but continues to rise slowly for several minutes, it is an indication that the liquid is not pure, or consists of a mixture of substances.

For smaller quantities of liquids the apparatus can be modified as in Fig. 5.

A fairly narrow dry test-tube is fitted with a cork, thermometer, and escape tube. It is advantageous to fit the tube, near the bottom, with a piece of asbestos cardboard. This protects the upper part of the tube from the hot gases rising from the flame (Fig. 5). The liquid is gently heated over a *small* flame, and the boiling point registered as above.

For even smaller quantities of liquid—less than 1 c.c.—a third method is convenient (Silowski). A small ignition tube is attached to a thermometer bulb, the liquid is introduced into the tube, and a small capillary tube, sealed at about 1 cm. from the lower end, is placed in it (Fig. 6). The thermometer and tube are heated slowly in a bath of glycerine or sulphuric acid, and at the boiling point a regular stream of bubbles rises from the end of the capillary in the liquid. The results of this method, however, are not so accurate as those of the preceding ones.

The boiling point as recorded by the above methods is generally a little lower than the correct, partly because the mercury column of the thermometer is as a rule not completely immersed in the vapour, and partly because the standard boiling points are

¹ For the distillation of small quantities of liquid, it is of great advantage to use the side tube of the flask as the inner tube of the condenser by fitting over it, by means of two bungs, a small outer jacket carrying two side tubes (see Fig. 4). It may be necessary to lengthen the side tube of the flask by fusing on to it a piece of glass tubing of the same diameter. Any trouble incurred in making this apparatus will be amply repaid by its use in later work. A small distilling flask extremely suitable for use with small quantities of liquid can be made from any old distilling flask whose bulb has been broken. The neck is heated near the broken portion and the latter is drawn off; the neck is then sealed up and a small bulb blown on the end.

² It is essential to this method that the flame should be as small as possible, because, otherwise, the vapour easily becomes superheated. Even when great care is taken, the results are sometimes inaccurate from this cause.

recorded under an atmospheric pressure of 760 mm., which in most cases is greater than the ordinary pressure.

The boiling point of water may be used as a check on the accuracy of the thermometer. In order to calculate the boiling point of water

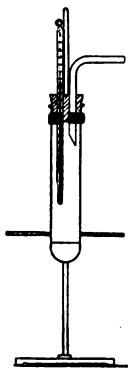


FIG. 5.

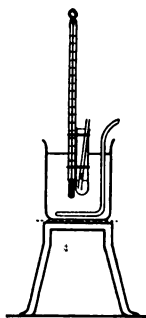


FIG. 6.

at pressures other than the normal, 1° should be added to or subtracted from 100° for every 27 mm. (approx.) above or below the pressure of 760 mm.

The boiling points of the following liquids might be determined for practice : ethyl alcohol (78.3° C.), toluene (110.3° C.), aniline (184° C.), and nitrobenzene (209° C.).

Specific Gravity of Liquids.—The specific gravity of a liquid is an important property, since not only can it be used, if necessary, for the identification of the liquid, but it is frequently used to test its purity (see the preparation of pure alcohol).

To determine the specific gravity, the usual procedure is to find the relation between the mass of a volume of the liquid and the mass of an equal volume of water, the volume in each case being measured at 15° . The essential part of the apparatus, therefore, is some vessel by which equal volumes of different liquids can be accurately obtained; this vessel is generally either a specific-gravity bottle or a pycnometer.

There are two common forms of specific-gravity bottle—

(a) The one is a small flask with a narrow neck, on which a horizontal mark is etched. If the weight of water necessary to fill the flask has not previously been determined, the flask (previously weighed dry) is filled roughly to the mark with distilled

water, and immersed up to its neck in a bath of water at 15° ; it is allowed to stand for at least 20 minutes, when the level of the water is adjusted by means of a narrow dropping tube, so that the lower portion of the meniscus is at the level of the mark on the neck. The flask is then withdrawn from the bath, carefully wiped dry, and weighed.

The flask is then emptied and carefully dried; the liquid whose specific gravity is required, is introduced, and the above procedure repeated.

Subtracting the weight of the flask from the two weighings, we get the weight of equal volumes of water and liquid at 15° ; dividing the latter by the former, we get the required specific gravity.

(b) The second form is a small bottle with a ground-glass stopper, which is perforated by a narrow hole. The procedure is exactly as above, except that the bottle is filled with water or other liquid in such a way that the liquid completely fills the neck and the whole of the perforation in the stopper. This is ensured by filling the bottle with liquid below the temperature of the bath, inserting the stopper tightly, and immersing up to the neck in the bath. After standing for 20 minutes, the liquid which has expanded through the stopper is removed, the bottle carefully wiped, and weighed.

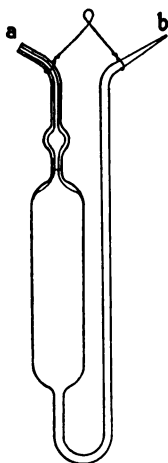


FIG. 7.

The pycnometer in its simplest form consists of a bulb blown in the centre of a bent piece of glass tubing of narrow bore; the tubing is drawn out to a jet at one end, while on the other end is etched a circular mark perpendicular to the axis of the tube (Fig. 7).

Attached to the pycnometer is a copper or platinum loop for suspension during weighing. The dried pycnometer is weighed, and completely filled with liquid by inserting the end *a* in the liquid in a porcelain crucible, and sucking at *b* by means of a piece of rubber tubing. It is then suspended in a bath of water at 15° , so that only the extremities project above the surface. When the liquid has reached the temperature of the bath, a piece of filter paper is placed against the tip *b*, and, if

necessary, the pycnometer is tilted till the liquid touches the paper; the liquid is cautiously withdrawn till the meniscus in the other limb is situated just on the mark; the pycnometer is then removed, wiped dry, and weighed. For very accurate work it should be allowed to stand in the balance case for 20 minutes before the weighing is performed.

From the results of two such experiments, one with the liquid and the other with water, the specific gravity is easily calculated.

N.B.—In all the above methods, the weight of water required to fill the flask or pycnometer obviously need only be determined once, and the result should be kept for use in future experiments.

Frequently the specific gravity of a liquid is measured at other temperatures than 15° . In these cases, the pycnometer is filled with the liquid at the required temperature and the weight of the liquid obtained; this weight is then compared with the weight of an equal volume of water at the standard temperature (either 4° or 15°) to obtain the specific gravity. Such specific gravities should have stated immediately after them the relative temperatures at which they were determined, e.g. for alcohol, $d. \frac{20^{\circ}}{15^{\circ}} = 0.7901$.

Tests for the Elements.—Carbon.—The presence of carbon in a substance does not, as a rule, require any special test: the fact that a supposed organic substance on heating will burn or char is sufficient proof. In cases where the heating does not give any satisfactory evidence, the substance should be intimately mixed with finely divided dry copper oxide, and placed at the closed end of a hard glass tube, a layer of coarse, dry copper oxide being introduced into the tube above the mixture. The tube, clamped in a horizontal position, is then fitted with a delivery tube passing into a test-tube containing lime water. The solid in the tube is raised to a dull red heat, commencing heating at the part nearest the mouth and slowly working back to the sealed end. During this heating, the oxide of copper oxidizes any carbon present in the substance to carbon dioxide, which is detected by the lime water. Any deposit of moisture in the cooler parts of the tube at the same time shows the presence of hydrogen in the substance; this is only reliable when the copper oxide has been very carefully dried.

Nitrogen.—1. On heating most nitrogenous organic compounds with soda-lime, the nitrogen present is expelled as ammonia. The test is most satisfactorily performed by introducing an intimate mixture of the substance and soda-lime into an ignition tube, covering the mixture with a layer of soda-lime and heating, beginning at the soda-lime layer and slowly proceeding downwards towards the sealed end; the evolved ammonia should be tested for by moistened litmus-paper.

The most important classes of nitrogenous substances which do not respond to this test are the nitro bodies and azo compounds.

2. A more delicate and trustworthy test, applicable to all compounds of carbon containing nitrogen, is with metallic potassium or sodium. A little of the substance is introduced into a small ignition tube, and a piece of clean sodium or potassium of approximately the same weight added.¹ The mixture is heated in a bunsen flame, gently at first, but more strongly afterwards, till all action has ceased, and no more fumes are emitted from the tube. After the lower part of the tube has become red hot and looks incapable of withstanding much more heating, allow it to cool somewhat, and then drop it into about 15 c.c. of water in a porcelain basin. (Great caution is necessary during this operation.) The charred mass is stirred well with the water, and the aqueous extract filtered off. To the filtrate add a few drops of caustic soda solution, a little ferrous sulphate solution, and then one or two drops of ferric chloride solution. Shake the mixture well, warm gently, and then acidify with dilute hydrochloric acid. A precipitate of Prussian blue proves the presence of nitrogen in the original substance. If the formation of Prussian blue is doubtful, filter the liquid, when the presence of any trace of blue colour is easily detected on the white filter-paper.

The formation of the Prussian blue depends on the fact that the nitrogen and carbon in contact with sodium combine together, giving sodium cyanide. The last-named substance, on the addition of ferrous sulphate, forms sodium ferrocyanide, which reacts with ferric chloride in the usual way (see p. 65).

¹ If insufficient alkali metal be used, a nitrogenous substance containing sulphur will often yield a sulphocyanide by the above treatment, and so the rest of the above test will not be satisfactory. An excess of alkali metal prevents the formation of sulphocyanide, and the test proceeds in a normal manner.

The Halogens.—1. The flame of a combustible substance containing a halogen is generally tinged with green.

2. A delicate test, requiring very little substance, is Beilstein's. A small piece of copper gauze (1 cm. by 2 cms.) is wrapped round the end of a stout piece of copper wire. The gauze is heated in a bunsen flame till it no longer gives any green coloration; the oxidized gauze is then allowed to cool somewhat, a little of the substance is placed on it, and it is again heated, first in the inner and then in the outer flame of the bunsen burner. A green coloration of the flame shows the presence of a halogen. This test is successful even with volatile halogen compounds such as chloroform or ethyl iodide; it depends on the formation of the volatile copper halide.

3. A second test for a halogen, which can also be used for distinguishing between the three elements, is performed with sodium. A little of the substance is heated with an approximately equal weight of clean sodium, and the product extracted with water, just as in the nitrogen test. The filtered solution is acidified with nitric acid, and a little of it tested with silver nitrate solution. If nitrogen is also present in the substance, the liquid should be boiled with the dilute nitric acid for several minutes, in order to remove any hydrocyanic acid before the addition of the silver nitrate. To find which halogen is present, a little more of the acidified solution can be treated with a few drops of chlorine water, and the resultant liquid tested with starch solution, or extracted with carbon bisulphide.

Sulphur.—The best method for the detection of sulphur is to heat with sodium or potassium in the manner already described under nitrogen and the halogens. Sodium sulphide is formed. The filtered solution can be tested by placing a drop on a silver coin; or by adding dilute sulphuric acid, when, on warming, sulphuretted hydrogen is evolved (test with lead acetate paper). The presence of sodium sulphide in the alkaline filtered solution can also be detected by the addition of a solution of sodium nitroprusside, which gives a permanganate colour with an alkali sulphide. For this test the nitroprusside solution must be freshly prepared, because it rapidly deteriorates, with discoloration, on keeping.

NOTE.—In all the tests with metallic sodium, whether for nitrogen, halogen, or sulphur, if the substance is very volatile, a modification of the process is necessary. The ignition tube should be clamped in

an upright position, the sodium introduced, and heated till it begins to boil. The usual amount of substance is then added in small quantities (if a liquid, from a dropping tube), so that each time it falls directly on the sodium, the latter being reheated after each addition. When all the substance has been added, the tube is strongly heated; the remaining procedure is as in the preceding descriptions.

Phosphorus.—1. On strongly heating a compound containing phosphorus with an equal bulk of magnesium powder, some magnesium phosphide is formed. If the cooled mass be powdered up and moistened with water, the odour of phosphine will be observed.

2. If an organic substance containing phosphorus be fused with a mixture of equal portions of potassium nitrate and anhydrous sodium carbonate, the phosphorus will be oxidized to phosphate. Dissolve the product in water, acidify with nitric acid, and test for phosphate in the usual way with ammonium molybdate.

PREPARATIONS—PRELIMINARY NOTES.

Corks.—Whenever using apparatus for which corks are required, great care should be taken in choosing and boring the latter. The cork chosen should always be a sound one, and before boring it should always be well pressed; good corks treated in this way are generally more suitable than indiarubber bungs. The latter are obviously unsuited for closing flasks in which liquids like benzene or carbon bisulphide are to be distilled, because these liquids dissolve rubber; also indiarubber bungs should not be used for distillations at temperatures much above 100°, because they soften, and may even melt.

Salting Out.—In the preparation of substances appreciably soluble in water, it frequently happens that the substance is obtained mixed with a fairly large quantity of that liquid. This would evidently cause a considerable decrease in the yield, and so, whenever possible, the water is made to give up a great deal of its solute by the process of "salting out."

It is a well-known fact that an electrolyte is generally less soluble in a solution containing a common ion than it is in pure water.¹ In the preparation of sodium stearate (which is an electrolyte), the solution which is obtained is treated with common salt; this dissolves in the water, and the solubility of the sodium stearate is thereby decreased to such an extent that most of it separates out from the solution.

¹ See any modern text-book on physical or inorganic chemistry.

For solutions of non-electrolytes in water, the method of salting out is to add an electrolyte which is soluble in the water, but insoluble in the non-electrolyte; the latter then separates out, generally forming a layer above the surface of the aqueous solution of the electrolyte. Thus, if a mixture of alcohol and water be shaken with anhydrous potassium carbonate, the alcohol is salted out. Various salts can be used for the purpose, and their application can be seen in the preparation of ethyl acetate, acetonitrile, aniline, etc.

Recrystallization.—To purify a solid substance, the usual procedure is to make a hot concentrated solution, from which, on cooling, a large proportion of the substance crystallizes out, while the impurities remain to a large extent in the mother liquor; by repeating the process as many times as may be necessary, the substance is obtained pure. As a rule, this operation need only be performed once or twice.

It is generally necessary to filter the hot solution before allowing it to crystallize; the filtration must be performed rapidly, in order to prevent cooling. A filter-paper, folded in the way illustrated in the

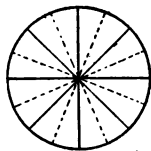


FIG. 8.

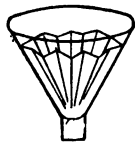


FIG. 9.

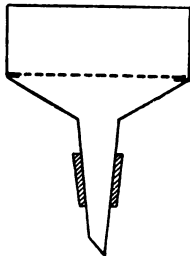


FIG. 10.

diagram (Fig. 8) greatly hastens the filtering (the paper is first doubled along the lines marked, and then each section is doubled back at its centre in the opposite direction). If a small quantity of liquid is to be filtered, the folded paper is placed in an ordinary funnel, which preferably has had its stem cut short (Fig. 9); for filtering large quantities it is necessary to use a funnel with a hot-water jacket, which keeps the solution hot, and so prevents it from crystallizing in the funnel and choking it.

Filtering under Reduced Pressure.—In filtering off bulky precipitates, the weight of the liquid is often insufficient to give a reasonable rate of filtration, and so the process is hastened by causing the pressure of the atmosphere to assist in forcing the liquid through the paper. In order that the paper may withstand the pressure, it is placed on a flat, perforated porcelain plate fitted in an ordinary funnel; or a Buchner funnel (Fig. 10), made especially for this purpose, may be used. The funnel is fitted into the neck of a stout-walled flask with a side-tube, which is attached to a water-pump

by a piece of pressure tubing. When a filtration is to be performed, a filter-paper¹ is fitted carefully into the funnel to cover all the holes, the pump is set working, and the liquid is poured into the funnel.

Extraction from Aqueous Solution with Ether.—When a substance soluble in ether is obtained in aqueous solution, a simple method of isolating the substance is to extract with ether. The process, however, is only rapid in the case of substances which are much more soluble in ether than in water. The extraction consists in

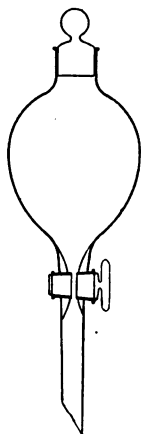


FIG. 11.



FIG. 12.

shaking the aqueous solution with a suitable quantity of ether, when the dissolved substance divides itself between the ether and the water; the mixture is then allowed to settle into two layers, and the upper layer of ether is separated from the aqueous layer; the shaking and separation are most conveniently performed in a "separating funnel" (see diagram, Fig. 11). The aqueous layer is again extracted several times more with fresh quantities of ether, when almost all the substance will be removed from the water; three extractions are, as a rule, sufficient for ordinary purposes. The combined ethereal extracts are dried (p. 13), and the ether is distilled off. In order to avoid using too large a flask in the distillation, a small distilling flask should have a small tap funnel fitted into its neck by means of a cork; a suitable quantity

¹ Hardened filter-papers can be obtained which are especially suited for such work, since they can withstand a higher pressure than the ordinary papers, and the solid can easily be removed from them without being contaminated by paper fibre.

of the ethereal extract is placed in the flask, and the ether distilled from a water-bath ; as rapidly as distillation occurs, fresh quantities of the ethereal solution are run in from the tap funnel. When all the solution has been introduced, and no more ether distils over, the residue, if liquid, is fractionally distilled over wire gauze, the tap funnel being replaced by a thermometer ; if the residue is solid, it is recrystallized from a suitable solvent.

When small quantities of liquid have to be manipulated, the extraction is better performed in a test-tube ; the lower aqueous layer is then withdrawn by means of a pipette with a rubber tube attached (see diagram, Fig. 12). The passage of the liquid into or out of the pipette can easily be checked by pinching the tube.

Other liquids can be used for extracting, the only necessary conditions being that the extracting liquid must be a solvent for the substance to be extracted, and at the same time must be practically insoluble in the other solvent.

Drying the Prepared Substance.—If the substance obtained is a liquid, the dehydration is usually performed by the addition of a solid which will combine with water, but which is at the same time insoluble in, and without action on, the organic liquid. The drying agents which are most frequently used are fused calcium chloride, anhydrous potassium carbonate, anhydrous sodium sulphate, quicklime, and caustic soda. Calcium chloride is not suitable for alcohols and amines, because it forms compounds with them. Potassium carbonate, quicklime, and caustic soda can be used for basic bodies, but not for esters or acidic substances. Sodium sulphate can be applied in practically all cases.

If the substance is solid, the crystals are dried by pressing between absorbent paper or upon a porous tile ; most of the adherent moisture is thus withdrawn, and the remainder is removed by allowing the substance to stand for several days on absorbent paper or on a porous tile, exposed to air but protected from dust. The drying can be accelerated by the use of a vacuum exsiccator.

Quantities and Yields.—In every preparation the student should calculate from the equation for the reaction the relative quantities of the substances theoretically required, and compare them with those actually used ; in this way he will note some of the conditions essential for the achievement of success in the experiment.

Also, after the completion of the experiment, the student should find the weight of the pure dry product. This weight should be compared with that which would be expected if the whole of the substance which was originally taken in the least proportion had been entirely converted into the pure product of the action. The "percentage yield," calculated from the actual yield and the one which is theoretically possible, should be entered in the notebook in each case.

CHAPTER II

Methane—Marsh Gas, CH_4 .

This simplest of all hydrocarbons is most conveniently made by a general method for the preparation of saturated hydrocarbons. The sodium salt of the carboxy acid containing one more atom of carbon than the hydrocarbon itself is made to react with caustic soda by heating, when a change takes place according to the equation—



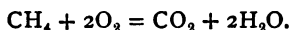
For the actual preparation of the gas, pure caustic soda is not taken, since on account of its ready fusibility it rapidly attacks glass; but a much less fusible mixture of caustic soda with slaked lime, known as "soda-lime," is used. About 10 grams of powdered anhydrous sodium acetate¹ are taken and well mixed with 20 grams of dry soda-lime, by grinding together in a mortar; the mixture is placed in a hard glass tube (about 9" \times $\frac{5}{8}$ "), sealed at one end, while the other end is fitted with a previously pressed and carefully bored cork carrying a delivery tube of the usual shape for collecting gases over water. The tube containing the mixture is gently tapped to ensure a free passage throughout its length, and then clamped so that the mouth of the tube is slightly lower than the sealed end, while the delivery tube passes to a pneumatic trough. The heating is then begun, first at the front of the tube, slowly moving backward as necessary. The evolved gas is collected in the usual way.

¹ If a supply of anhydrous sodium acetate is not available, the ordinary crystalline solid can be dehydrated as follows. Place 25 grams of the crystals on a tin tray and heat gently; the crystals first dissolve in their water of crystallization, but owing to the expulsion of the water the liquid soon sets to a solid again. The heating is continued till this solid once more melts; on cooling, a solid mass of anhydrous sodium acetate is obtained, which is removed from the tray, and the 10 grams weighed out.

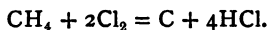
Properties.—The gas is evidently only very slightly soluble in water.

It burns with a feebly luminous flame. In reality the flame of pure methane is still less luminous, since the gas, as prepared above, contains impurities, especially acetone, which increase the brightness of the flame.

A mixture of methane and oxygen, in the proportion of one volume to two, explodes vigorously when fired—



If methane be mixed with twice its volume of chlorine, and a light applied, a flame passes through the mixture, the gases reacting with the formation of hydrochloric acid and free carbon. If a similar mixture be exposed to bright sunlight, the same products are obtained with explosion—



Preparation of Pure Alcohol ($\text{C}_2\text{H}_5\text{OH}$) from Methylated Spirit, or Spirits of Wine.—The methylated spirit for this purpose must not contain added mineral naphtha; a sample of it should remain clear on mixing with water. The chief impurities present are acetone, methyl alcohol, aldehydic substances, and water. If spirits of wine be taken, only the latter two impurities will be present. The acetone and aldehydic substances are removed by boiling with caustic soda, which converts them into non-volatile compounds; the water is removed by treatment with quicklime. The methyl alcohol is not removed.

Take a litre of methylated spirit in a tin can, and add approximately 30 grams of caustic soda. Place the can in a bath of hot water, on the bottom of which are a few pieces of glass tubing, and boil the alcohol gently for an hour under reflux condenser, as in diagram (Fig. 13). The adapter in the neck of the can is then replaced by a still-head, or suitably bent glass tube, the position of the condenser is altered, and the alcohol distilled off into a large bottle containing 500 grams of fresh quicklime.¹ The residue in the can is rejected. The distillate is allowed to stand in contact

¹ In all such distillations it is not sufficient to merely insert the delivery tube from the flask loosely into the condenser; it should be fixed there by a bored cork. If this precaution is omitted, the condensation of the vapour does not take place nearly so completely, because the jet of vapour then shoots straight down the condenser, carrying much air with it (*cf.* the action of a steam injector), and the mixture reaches the other end of the condenser so rapidly that much of the alcohol is uncondensed.

with the lime for at least twenty-four hours (preferably much longer), and is then distilled off, using a water-bath. During this distillation the boiling point of the alcohol should be registered by a

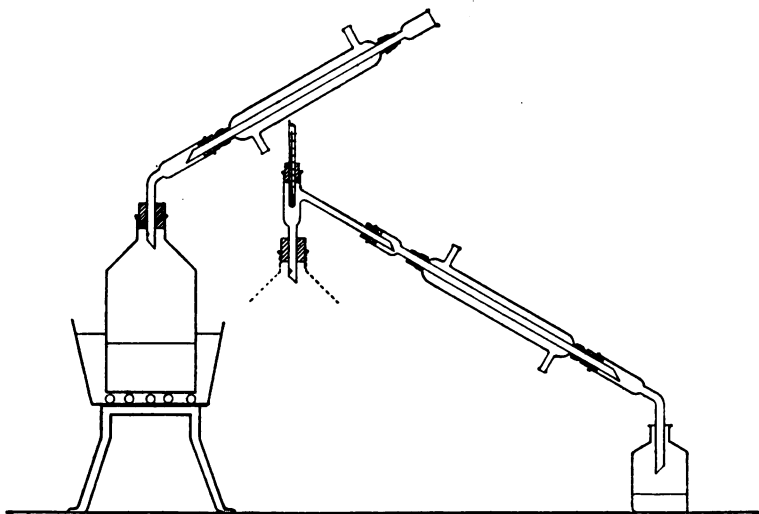


FIG. 13.

thermometer fitted into the adapter, and should be constant (78.3° at 760 mm.).

The ethyl alcohol thus obtained should be practically pure, except for a little methyl alcohol (if methylated spirit was originally taken), which will not interfere in its use for most chemical purposes.

To test if alcohol is absolute, *i.e.* completely free from water and other impurities, the specific gravity at 15° should be measured as described on pp. 5, 6. From the specific gravity, a reference to the table in the appendix gives the percentage of alcohol.

The alcohol obtained by this treatment is never quite anhydrous, but it may be considered so for all ordinary purposes. To remove the last traces of water, special dehydrating agents, such as metallic calcium, are often used.

The Determination of the Amount of Alcohol in a Fermented Liquor.—The alcoholic liquor is distilled and the amount of alcohol in the distillate determined by a measurement

of the specific gravity.¹ It is assumed in the experiment that all the alcohol has come over when two-thirds of the liquor has been distilled.

Fill a 100 c.c. measuring flask to the mark with a cheap wine, and transfer the wine completely to a distilling flask, rinsing the wine clinging to the walls of the measuring flask into the distilling flask with a little distilled water. Distil the liquid through a condenser till two-thirds of the contents of the flask have distilled over; transfer the distillate completely to the 100 c.c. flask, rinsing out the last drops as before, and make up to 100 c.c. with distilled water. Determine the specific gravity of the dilute alcohol in the manner described previously; from the specific gravity a reference to the spirit table in the appendix gives the amount of alcohol in the distillate, and therefore in 100 c.c. of the wine.

FORMIC ACID,



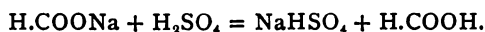
The anhydrous acid is a colourless liquid at ordinary temperatures, with a pungent and characteristic odour; very corrosive, and attacks the skin. The solid acid melts at $8\cdot6^{\circ}$, and the liquid boils at $100\cdot6^{\circ}$. Miscible with water and alcohol in all proportions.

The formates are readily soluble in water, with the exception of the silver, mercury, and lead salts, which are sparingly soluble.

1. Heat the solid formate with *soda-lime*. Hydrogen is evolved.



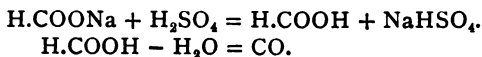
2. To a little of the solid formate contained in a mortar add a few drops of *strong sulphuric acid*, and grind up the mixture with a pestle. The characteristic pungent odour of formic acid will be perceived. The same odour is obtained by warming a formate with dilute sulphuric acid.



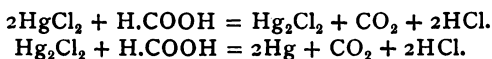
3. Formates, or formic acid, are decomposed on being gently warmed with *strong sulphuric acid*, carbon monoxide, which may be

¹ In the case of an alcoholic liquor containing appreciable quantities of volatile acid (acetic), *e.g.* a sour wine, the above procedure would give a distillate containing both the alcohol and the acid. In order to avoid this, the measured quantity of acid liquor is carefully neutralized by the addition of a solution of caustic soda before distillation, using turmeric paper as indicator. The distillate then contains only the alcohol, the amount of which is determined in the manner described above.

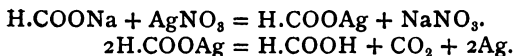
burnt at the mouth of the test-tube, being evolved ; no charring takes place, and no carbon dioxide is evolved (*cf.* oxalates).



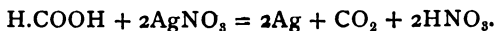
4. *Mercuric chloride*, on boiling with formic acid, or formates, is reduced to white mercurous chloride, and this becomes further reduced to grey metallic mercury, if the formate is in excess. In the case of formates the reaction goes best if hydrochloric acid is added to liberate the formic acid.



5. *Silver nitrate* gives a white precipitate of silver formate with strong solutions of formates, or with free formic acid. On standing for some time, or quickly on warming, the silver formate is reduced to grey metallic silver.

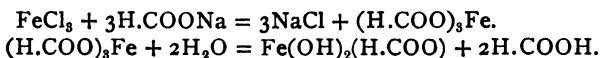


The final result is—

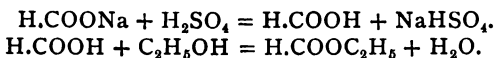


NOTE.—Ammoniacal solutions of silver salts are also reduced.

6. *Ferric chloride*¹ gives a red coloration with neutral solutions of formates. The red colour is changed to yellow by hydrochloric acid. On boiling the red solution a brown basic formate is precipitated.²



7. On warming formic acid, or a formate, with *concentrated sulphuric acid* and *ethyl alcohol*, ethyl formate is produced, and can be detected by its characteristic pleasant odour.



In reactions of this kind the sulphuric acid (1) liberates the formic acid ; (2) acts as a dehydrating agent, and thus enables the formation

¹ The ordinary solution of ferric chloride is strongly acid, because of hydrolysis. $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$. Before use add very dilute ammonia until the precipitate just redissolves, or, better still, the solution should be saturated with freshly precipitated ferric hydrate.

² The precipitation of a basic salt on boiling is due to the fact that a rise in temperature increases very considerably the hydrolytic action of water.

of the ester to proceed to a greater extent than it otherwise would do, since the reaction is a reversible one;¹ (3) accelerates the formation of the ester by acting catalytically.²

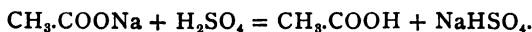
ACETIC ACID,



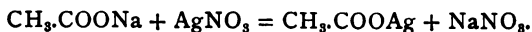
The anhydrous acid is known as "glacial acetic acid"; it is an ice-like solid, melting at 16.7° , and boiling at 118.1° . The liquid is colourless, possessing a pungent odour, and attacks the skin as formic acid does. Miscible with water, alcohol, and ether in all proportions. The vapour burns with a pale blue flame. The normal acetates are soluble in water. On ignition they give off inflammable vapours, consisting chiefly of acetone; the residue contains the base as carbonate, oxide, or metal.



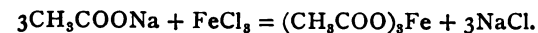
1. To a little of the solid acetate contained in a mortar add a few drops of *strong sulphuric acid*, and grind up the mixture with a pestle. The characteristic odour of acetic acid will be perceived.³ The same odour is obtained when an acetate is warmed with sulphuric acid, either dilute or strong, since sulphuric acid does not decompose acetic acid.



2. *Silver nitrate* gives a white crystalline precipitate of silver acetate with concentrated *neutral* solutions of acetates. There is no reduction on heating (*cf.* formates).



3. *Ferric chloride* gives a red coloration with neutral solutions of acetates. The red colour is changed to yellow by the addition of hydrochloric acid. On boiling the red solution a brown basic acetate is precipitated out, the smell of acetic acid is noticed, and the solution becomes colourless.

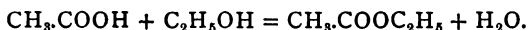


¹ In a reversible reaction, if one of the products of reaction is removed as fast as it is formed, the reaction will proceed to completion.

² Compare the preparation of ethyl acetate.

³ At the same time as this test is carried out the corresponding one for formates should be repeated, so that the different odours of the two acids will be made evident.

4. On warming acetic acid, or an acetate, with *concentrated sulphuric acid* and *ethyl alcohol*, ethyl acetate is produced, and can be detected by its characteristic pleasant odour.



5. On heating a mixture of a dry acetate with a small quantity of *arsenious oxide*, the extremely obnoxious odour of cacodyl oxide is produced.



NOTE.—Cacodyl oxide is extremely poisonous, so that this test should only be carried out on a small scale. If the finger is held over the mouth of the test-tube during the heating, and then put to the nose, the smell will be very evident.

6. Acetates, unlike formates, do not reduce mercury salts.

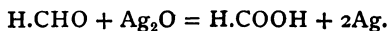
FORMALDEHYDE,



Formaldehyde is a gas with a peculiar pungent odour. It is readily soluble in water, and a 40 per cent. solution comes into the market as a disinfectant and antiseptic, and is known as *formalin*.

1. Readily polymerizes, with the formation of *paraformaldehyde* (or *trioxymethylene*), which compound is left as a white solid on evaporating down some of the formalin solution on the water bath.

2. An *ammoniacal solution of silver nitrate* is reduced by formaldehyde, the silver being deposited as a mirror on the sides of the test-tube. In order to obtain a good mirror, the test-tube should be previously cleaned with caustic soda, nitric acid, and distilled water respectively. If the tube is not clean, a brown precipitate of silver is produced; or, if a mirror is formed, it is very imperfect. The test-tube should be heated in a beaker of boiling water, and not with the direct flame of the bunsen burner.



3. *Schiff's reagent* is coloured pink by formaldehyde. With very dilute solutions the colour develops slowly. [Schiff's reagent is prepared by decolourizing a solution of *fuchsine* (rosaniline hydrochloride) by the careful addition of sulphurous acid.] In carrying out the test the solution should not be warmed, otherwise SO_2 may be driven off, and thus cause the pink colour to appear.

4. On oxidation with *potassium bichromate* and *sulphuric acid*, formic acid is produced.

A solution of 10 grams of *sodium* (or *potassium*) *bichromate* in

100 c.c. of 1 : 3 (by volume) sulphuric acid may be used for the oxidation. The formaldehyde is mixed with an excess of this solution in a small distillation flask. The mixture is allowed to stand for a few minutes and then distilled. The distillate will contain the formic acid produced by oxidation of the formaldehyde. Neutralize with sodium hydrate or sodium carbonate,¹ and test for a formate in the usual manner.

ACETALDEHYDE,

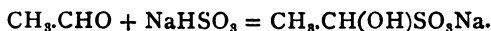


Colourless liquid, possessing a peculiar and very characteristic odour. It is very volatile, boiling at 20·8°. Mixes with water and alcohol in all proportions.

1. *Ammoniacal silver nitrate* is reduced on warming with acetaldehyde, a silver mirror being produced (*cf.* formaldehyde).

2. Acetaldehyde restores the pink colour to *Schiff's reagent*.

3. On shaking up with a cold concentrated solution of *sodium hydrogen sulphite*,² a crystalline precipitate of an additive compound is produced. The aldehyde may be regenerated by warming with sodium carbonate solution.



4. On warming with a strong solution of *caustic soda*, acetaldehyde gives a yellowish-brown mass (aldehyde-resin).

5. Acetaldehyde is not oxidized to acetic acid by potassium bichromate and sulphuric acid (*cf.* formaldehyde).

METHYL ALCOHOL,



Methyl alcohol is a colourless mobile liquid, boiling at 66°. It is miscible with water in all proportions, with evolution of heat. With anhydrous calcium chloride it forms a crystalline compound, $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$.

1. Methyl alcohol is inflammable, burning with a pale blue, smokeless flame.

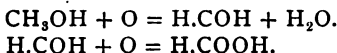
2. Methyl alcohol is readily oxidized to formic acid.

¹ In carrying out the neutralization, it is convenient to add a small piece of litmus-paper to the solution.

² The solution of sodium hydrogen sulphite should be saturated with sulphur dioxide before use.

Carry out the oxidation and distillation as described under test 4 for formaldehyde. The distillate will contain the formic acid produced by oxidation of the methyl alcohol, together with small quantities of formaldehyde (and acetaldehyde, if ethyl alcohol was also present) which may have been formed. Neutralize with sodium hydroxide or sodium carbonate,¹ and boil for a short time to drive off the aldehydes. Then carry out the usual tests for formates, as given on pp. 17-18.

The oxidation of the alcohol takes place in stages, according to the equations—



3. On warming methyl alcohol with a few drops of *strong sulphuric acid* and a *salicylate*, methyl salicylate (oil of wintergreen) is produced, which has a characteristic odour.

4. Methyl alcohol does *not* give the *iodoform* reaction. (Distinction from ethyl alcohol.)

NOTE.—Commercial methyl alcohol often contains acetone, which gives the iodoform reaction.

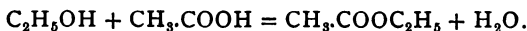
ETHYL ALCOHOL,



Ethyl alcohol is a colourless mobile liquid, boiling at 78.3° . It is miscible with water in all proportions, with evolution of heat.

1. Ethyl alcohol is inflammable, burning with a pale luminous flame. It is not necessary that it should be anhydrous before it will burn.

2. On warming ethyl alcohol with *strong sulphuric acid* and an *acetate*, the characteristic fruity odour of ethyl acetate will be perceived.



3. Add a little *iodine solution* (5 gms. iodine + 10 gms. KI in 250 c.c. water) to an aqueous solution of ethyl alcohol; then add *caustic soda* solution drop by drop till the colour of the iodine nearly disappears. Warm to about 80° and then cool. A yellow crystalline precipitate of iodoform is produced; if the alcohol solution is very dilute, precipitation only takes place after standing for some time, but the characteristic odour of the iodoform will be observed.



NOTE.—Other substances besides ethyl alcohol, *e.g.* acetaldehyde, acetone, lactic acid, isopropyl alcohol, give the iodoform test; methyl

¹ In carrying out the neutralization, add a piece of litmus *paper* to the solution.

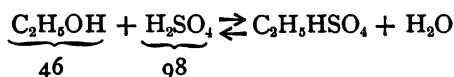
alcohol, ethyl ether, acetic acid, and normal propyl alcohol do not respond to the test.

4. On oxidation with *potassium bichromate* and *sulphuric acid*, ethyl alcohol gives acetaldehyde, and not acetic acid.

Carry out the oxidation and distillation as described under test 4 for formaldehyde. (The characteristic odour of acetaldehyde will be perceived before the distillation is carried out, especially on warming slightly.) The distillate is tested for aldehyde by means of *Schiff's reagent*, and the reduction of an ammoniacal silver solution. (See tests for aldehyde, pp. 20-21.)

Potassium Ethyl Sulphate, $C_2H_5OSO_2OK$.

The group C_2H_5 behaves in many ways like a metal atom, and will replace the hydrogen of acids forming "esters;" thus, if alcohol and sulphuric acid are heated together, ethyl hydrogen sulphate is obtained, which compound is most conveniently isolated as the potassium salt—



As the equation shows, the sulphuric acid reacts with approximately half its weight of alcohol, but as there are several side-reactions (such as the formation of ethylene and ether) in which alcohol is lost, it is advantageous to take an excess of alcohol.

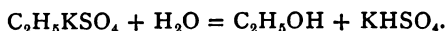
Take 100 c.c. (c. 80 grams) of alcohol in a half-litre flask, and pour carefully into it 40 c.c. (c. 70 grams) of concentrated sulphuric acid. Heat for an hour under reflux condenser on the water-bath, and then allow to cool. Pour the cold liquid into 500 c.c. of water, contained in a large porcelain dish (or earthenware trough), and stir into it precipitated chalk, a little at a time, till no further effervescence occurs. By this treatment the excess of sulphuric acid is precipitated as calcium sulphate, while soluble calcium ethyl sulphate remains in solution. The mixture is filtered, either through canvas or through a porcelain Buchner funnel (in the latter case with the aid of a filter-pump). Concentrated potassium carbonate solution is then carefully added to the filtrate till all the calcium is precipitated (excess must be avoided), and the calcium carbonate is filtered off. The filtrate, a sample of which should give no effervescence on the addition of a little hydrochloric acid, is evaporated on a water-bath till a drop will

crystallize when withdrawn on the end of a cold glass rod ; it is then allowed to cool, and the potassium ethyl sulphate crystals are filtered off, and dried between filter-paper or on a porous tile. A second less pure crop of crystals can be obtained by further evaporation of the filtrate. The yield should be about 45 grams.

Potassium ethyl sulphate is a deliquescent crystalline solid. It is very soluble in water, but insoluble in alcohol or ether.

Hydrolysis.—A fresh solution of potassium ethyl sulphate does not respond to the ordinary sulphate test with barium chloride solution, but on boiling with a little dilute hydrochloric acid, hydrolysis rapidly takes place, with formation of alcohol and potassium hydrogen sulphate.

Place a few grams of the potassium ethyl sulphate in a small flask, add 50 c.c. of dilute hydrochloric acid, and boil for about ten minutes with a reflux condenser ; distil over about one-third of the liquid, when alcohol can be tested for in the distillate and sulphate in the residue—



It should be noted that caustic alkali solution is far less effective than dilute acid for the hydrolysis of the salts of ethyl sulphuric acid ; in fact, the addition of a small quantity of alkali to a solution of a salt of ethyl sulphuric acid increases the stability of the latter.

Ether, $(\text{C}_2\text{H}_5)_2\text{O}$.

When ethyl alcohol is heated with an equal bulk of strong sulphuric acid, the alcohol (ethyl hydroxide) loses water and forms ether (ethyl oxide). The mechanism of the process will be explained later ; at present it may be represented by the equation—



Carefully add 100 c.c. of strong sulphuric acid to 100 c.c. of alcohol with constant shaking and cooling, and place the mixture in a 500 c.c. distilling flask. Fit the flask with a doubly bored cork ; through one hole of this pass the stem of a tap funnel, to which is attached a glass tube¹ of such length that, when the bung is in position, it will reach down under the liquid ; the other hole is fitted with a thermometer, which *should dip into the liquid* in the

¹ The glass tube must be firmly wired on, or else it will fall off during the preparation.

flask. The flask is then fitted with a condenser¹ (the longer the better) and carefully heated over a sand-bath or wire gauze. When the temperature of the liquid approaches 140° the liquid will begin to boil, and from this point alcohol should be run into the flask from the tap funnel as fast as the liquid distils, the temperature being maintained at about 140° ; this should be continued till about 150 c.c. more alcohol have been added.²

The distillate containing ether, alcohol, water, and some dissolved sulphur dioxide, is placed in a separating funnel with about 50 c.c. of dilute caustic soda solution and shaken; the alkali solution is then run off from below, and the ether is again shaken with 50 c.c. of saturated salt solution; the latter is then run off. The ether thus freed from the sulphur dioxide and most of the alcohol and water, is poured into a flask and allowed to stand several hours over about 20 grams of fused calcium chloride, in order to dry it; after this it is poured off from the calcium chloride into a distilling flask and carefully distilled from a bath of warm water (at about 45°). The distillate will be fairly pure ether, and should distil over at 35° .

To obtain ether absolutely free from alcohol and water, it requires further treatment with metallic sodium (see p. 147), but for all ordinary purposes the above product will prove satisfactory.

Pure diethyl ether boils at 34.6° , and has a specific gravity of 0.720 at 15° . At 17° it is soluble in water to the extent of 1 part in 11.5 parts of water.

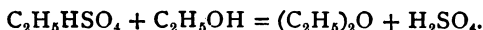
Mechanism of the Etherification of Alcohol.—Ethyl hydrogen sulphate probably plays an extremely important part in the preparation of ether from alcohol and sulphuric acid. The action of the acid was once supposed to be a simple dehydrating one, but this

¹ For condensing the vapour of very volatile liquids, such as ether, double-surface condensers are especially efficient; they will condense as completely as ordinary condensers of about three times their length, and they are far less clumsy.

² In all distillations of ether, care should be taken to keep all flames as far as possible from the receiver, since the liquid, on account of its volatility, will often catch fire from a flame at a distance. Since ether vapour is very heavy, it flows about on the surface of the bench; a barrier of dusters round the burner, therefore, greatly assists in keeping the vapour away from the flame. It is also advisable either to wrap a duster round the neck of the receiver, or to fit the latter to the condenser by means of a two-holed cork, from the second hole of which a tube leads over the side of the bench to carry off uncondensed vapour.

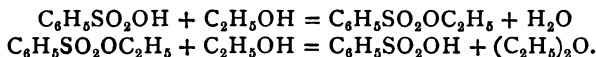
is obviously a false idea, because water distils over with the ether ; also the sulphuric acid will convert many times its own volume of alcohol into ether, and probably would convert much more still, except for the fact that secondary processes take place with formation of sulphur dioxide ; if the action were simply dehydration, we should expect it to stop as soon as the acid had abstracted water from a small amount of alcohol.

The action of etherification probably consists of two stages. In the first, the alcohol forms ethyl hydrogen sulphate as described in the previous preparation, and this then reacts with more alcohol, forming ether and regenerating sulphuric acid.



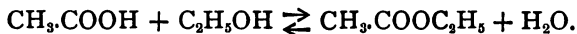
The sulphuric acid is thus free to form more ethyl hydrogen sulphate, and so the cycle of actions proceeds.

A confirmation of this theory lies in the fact that the sulphuric acid can with advantage be replaced by benzene sulphonic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$, which will convert more alcohol into ether than sulphuric acid itself. In this case ethyl benzene sulphonate is first formed, and then reacts with alcohol, giving ether and free benzene sulphonic acid once more.



Ethyl Acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$.

Theory.—When an alcohol is allowed to stand in contact with any acid an ester is formed, but as these esters are hydrolyzed by water, the water formed in the reaction prevents the process becoming complete, and the esterification stops before all the alcohol or acid has been used up ; the equation is therefore represented by—



In whatever proportions the alcohol and acid be taken, the final concentrations of the four substances, when equilibrium is reached, are such that—

$$\begin{aligned}\text{Conc. (acid)} \times \text{conc. (alcohol)} &= \text{const.} \times \text{conc. (ester)} \\ &\quad \times \text{conc. (water)}\end{aligned}$$

If equimolecular proportions of acetic acid and ethyl alcohol are taken, the final equilibrium is reached when two-thirds of each is esterified. When an alcohol is expensive, it is advisable to make use of the principle expressed in the above equation,

and get a higher percentage of it esterified by increasing the proportion of acid; conversely, we can get a higher percentage of an expensive acid esterified by increasing the proportion of alcohol. Another method of obtaining a better yield is to introduce into the mixture more or less anhydrous sulphuric or hydrochloric acid; these exert a catalytic effect, and cause the final equilibrium to be reached more rapidly; they also increase the percentage of ester obtained, in that their dehydrating action diminishes the reverse hydrolysis and consequently causes the esterification to approach more nearly to completion.

Method of Procedure.—From the equation above it is clear that the theoretical proportions of acid and alcohol necessary are 60 grams to 46; as both are cheap, there is no great advantage in increasing very largely the relative amount of either of the reagents.

Mix carefully 25 c.c. of absolute alcohol with 25 c.c. of concentrated sulphuric acid, and heat the mixture in a distilling flask fitted with condenser, by means of an oil-bath. Have fitted into the neck of the flask a tap funnel, and when the oil-bath reaches 140° allow a mixture of 75 c.c. of alcohol with 75 c.c. glacial acetic acid to flow slowly in, at about the same rate as ethyl acetate distils. When all the mixture has been added, shake the distillate well with about 20 c.c. of strong sodium carbonate solution, to remove the acetic acid which is present. After a few minutes, remove the sodium carbonate solution (bottom layer) by means of a separating funnel, and shake the ethyl acetate with a solution of 30 grams of calcium chloride in 30 c.c. of water, in order to abstract the alcohol present. Again separate the two layers, and allow the ethyl acetate to remain overnight standing over a few lumps of anhydrous calcium chloride. The ethyl acetate is then poured off into a dry flask, a thermometer is fitted into the neck, and the liquid distilled on a water-bath; the portion coming over between 74° and 79° being practically pure. The yield is 80 per cent. of the alcohol and acid taken. To further purify the product, it may be redistilled, and the fraction from 76° to 78° collected separately.

Pure ethyl acetate is a colourless liquid, boiling at 77.5° ; its specific gravity is 0.907 at 15° .

Hydrolysis of Ethyl Acetate.—Place in a small flask about 10 c.c. of ethyl acetate, add roughly 75 c.c. of caustic soda solution (10 per cent.),

and boil under reflux condenser over wire gauze for half an hour.¹ At the end of this time the odour of the ester should have almost disappeared, the liquid in the flask now containing ethyl alcohol, sodium acetate, and excess of caustic soda. Distil off a quarter of the liquid through a condenser—the distillate will contain the alcohol; add to it 10 grams of anhydrous potassium carbonate and shake; by this means the alcohol is salted out, and forms a separate layer on the surface of the aqueous solution of the carbonate. Draw off the alcohol by a pipette, and prove its identity by a boiling-point determination and any of the tests on pp. 22–23.

To the residual liquid in the flask add dilute sulphuric acid till the liquid is strongly acid; again distil, when the distillate will be an aqueous solution of acetic acid; identify by odour and suitable tests (or the residue in the flask may be neutralized by dilute nitric acid and the tests performed on this solution).

Detection of Hydroxyl Groups.—The most convenient method for detecting the presence of alcoholic hydroxyl groups in an organic compound depends on the formation of some ester, frequently the acetate, the usual reagents being acetyl chloride or acetic anhydride. For the illustration of the method proceed as follows.

Take 10 c.c. amyl alcohol, add 10 c.c. acetyl chloride or acetic anhydride, and boil for about 15 minutes under a small reflux condenser; if acetyl chloride is used, the boiling should be performed in a fume-chamber. After the 15 minutes have expired, allow the liquid to cool, pour into water, and stir well; an oil smelling of pear-drops separates on the surface.² Pour the mixture into a small tap funnel and run off the water from below. Shake the liquid again with about 15 c.c. of dilute sodium carbonate solution, and once more run off the lower layer. The ester—amyl acetate—is then poured into a test-tube and dried by the addition of a lump of fused calcium chloride; when dry (gentle warming will hasten this), it is poured into a small distilling flask and its boiling point noted. The boiling point should be 139°.

Proceeding in the above way with an unknown substance, the formation of an acetic ester not only proves the presence of an alcoholic OH group, but the boiling point of the ester formed provides an important step towards the actual identification of the original alcohol.

NOTE.—Primary and secondary amines also give acetyl derivatives in a similar way, but in this case the substances formed are generally

¹ The addition of a small fragment of porous tile (about the size of a pea) will obviate trouble caused by irregularity or bumping in the boiling.

² Amyl acetate is almost insoluble in water; in the case of esters of lower molecular weight, salt solution should be used in place of water, to prevent the ester dissolving, and so being lost.

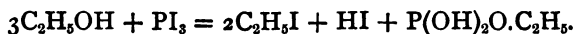
solids ; also it is not difficult to distinguish between an alcohol and an amine before the acetylation is performed.

Ethyl Iodide, C_2H_5I .

This ester is most conveniently prepared by the action of iodine on alcohol in the presence of phosphorus¹; the latter first forms iodide of phosphorus, and this reacts with the alcohol if the latter be present in excess, giving phosphorous acid and ethyl iodide.



If only the theoretical quantity of alcohol be present, only two-thirds of it is converted into ethyl iodide, hydriodic acid and monoethyl phosphorous acid also being formed.



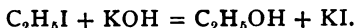
Evidently, therefore, it is important to use an excess of alcohol.

Place 5 grams of amorphous phosphorus in a small flask, pour on to it 40 grams (50 c.c.) of absolute alcohol, and add slowly in small portions, with constant shaking, 50 grams of powdered iodine. The addition of the whole of the iodine should take $\frac{1}{4}$ hour, and the flask should be cooled occasionally during this process. Fit the flask with a reflux condenser, and allow it to stand for at least 4 hours (preferably overnight). Then heat the flask on a water-bath, gently boiling the contents for $1\frac{1}{2}$ hours. Distil off from the water-bath through a long condenser (or a double-surface condenser). The distillate consists of ethyl iodide mixed with some alcohol, and contains a little dissolved iodine; it is shaken with an equal bulk of dilute sodium carbonate solution, and the lower layer of ethyl iodide, which should now be colourless, is separated by means of a tap funnel; it is again washed with water, separated off, and dried by standing a few hours over some lumps of anhydrous calcium chloride. The impure iodide is then poured from the calcium chloride into a small dry distilling flask, a thermometer is placed in the neck, and the liquid is distilled off on a water-bath; the portion distilling between 69° and 73° should be collected separately. Yield *c.* 50 grams.

Pure ethyl iodide is a colourless liquid, boiling at 72.3° ; it has a specific gravity of 1.943 at 15° .

¹ For preparation on a large scale, the best method is that given by James Walker (*Journ. Chem. Soc. Trans.*, 1892, 61, 717), to which the student should refer.

Hydrolysis.—On boiling a little ethyl iodide with a dilute aqueous caustic potash solution under a reflux condenser, hydrolysis occurs, and the products may be separated in the same way as with ethyl acetate.

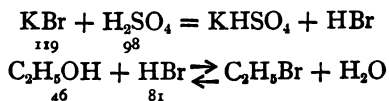


If an alcoholic solution of caustic potash be used for the hydrolysis, potassium iodide and ethylene are obtained.



Ethyl Bromide, $\text{C}_2\text{H}_5\text{Br}$.

This ester is conveniently prepared by the direct interaction of the alcohol and acid in the presence of sulphuric acid. The sulphuric acid, which is taken in excess, plays a part similar to that in the preparation of ethyl acetate, and in addition serves to liberate the hydrobromic acid from the potassium salt taken—

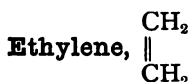


In order to esterify the more expensive hydrobromic acid as completely as possible, an excess of the cheaper alcohol is taken. In a half-litre distilling flask mix 50 grams (27 c.c.) of concentrated sulphuric acid and 30 grams (approx. 40 c.c.) of absolute alcohol. Place the flask on a sand-bath, fit its side tube with a double-surface condenser, and attach to the end of the latter an adapter, so that any distillate may be collected below the surface of a suitable quantity of water placed in the receiving flask. Introduce into the distilling flask 50 grams of coarsely powdered potassium bromide. Cork the flask and heat carefully; the mixture begins to boil and the ethyl bromide collects in oily drops under the water in the receiver (care must be taken to keep the receiver as cold as possible). The heated mixture must not be allowed to froth over into the condenser. When no more oily drops distil over, the distillate is poured into a separating funnel and the lower layer of ethyl bromide separated off; it is then shaken in the funnel with an equal bulk of weak sodium carbonate solution, again separated, and once more shaken with water. The ester, which is now milky (due to moisture), is placed in a corked flask and dried by standing with calcium chloride till clear; it is then poured into a distilling flask, a long condenser is attached, and

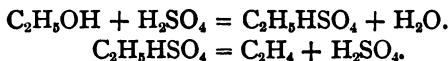
the ester is heated gently on the water-bath. The fraction distilling at 35° to 40° is ethyl bromide. Yield *c.* 35 grams.

Pure ethyl bromide is a colourless liquid, boiling at 38·4°; its specific gravity at 15° is 1·450.

Hydrolysis.—Carry out the hydrolysis on a small scale, as with ethyl iodide.



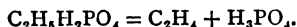
If the elements of water are abstracted from an alcohol, an unsaturated hydrocarbon is formed; with the higher alcohols mere heating is often sufficient to cause the dehydration, but with the lower ones the addition of sulphuric acid is also necessary. The reaction then takes place in two stages, the ethyl hydrogen sulphate first formed being decomposed at the high temperature into ethylene and sulphuric acid.



However, the sulphuric acid soon begins to char and oxidize the alcohol, and some sulphur dioxide and carbon dioxide are evolved with the ethylene.¹

(a) **Preparation of Ethylene Dibromide, CH₂Br.CH₂Br.**
—Mix 12 grams (15 c.c.) of alcohol with 75 grams (42 c.c.) of strong sulphuric acid in a litre flask. Place the latter on a sand-bath and fit the neck with a three-holed bung, one hole of which is occupied by a thermometer, the second by a dropping funnel, and the third by a right-angle delivery tube. To the stem of the dropping funnel attach a glass tube² drawn out at the lower end, of such a length that the jet reaches into the liquid. Attach the

¹ The sulphuric acid can with great advantage be replaced by phosphoric acid, when the ethyl dihydrogen phosphate first formed decomposes into ethylene and phosphoric acid.



The alcohol is merely dropped into syrupy phosphoric acid heated to 200° in a distilling flask; in this case no charring takes place, and a small quantity of phosphoric acid will convert an indefinite quantity of alcohol; the action can be continued for several days. See Newth, *Journ. Chem. Soc. Trans.*, 1901, 79, 915.

² See note, p. 24.

delivery tube, by means of a piece of rubber tubing, to a pair of bottles, the first being empty, to act as a trap in case of the liquid in the large flask frothing over, the second being a wash-bottle of caustic soda solution, to remove any sulphur dioxide and carbon dioxide from the gas evolved. Then arrange for the gas to bubble through two test-tubes, the first containing 5 c.c., the second 1 c.c. of bromine, in each case covered with a layer of water;¹ these should be kept cool in a trough of cold water. To the latter of these tubes attach a U-tube of soda-lime, to prevent the bromine fumes from escaping into the air.

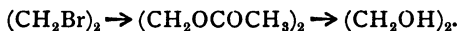
Having made sure that all the joints are gas-tight, heat the flask on the sand-bath to 165° , when a brisk evolution of gas commences; a mixture of 60 c.c. of alcohol with 55 c.c. of concentrated sulphuric acid (*i.e.* a proportion of roughly 1 : 2 by weight) is allowed to run slowly from the dropping funnel (keeping the latter stoppered if necessary) through the long tube, and so is introduced under the surface of the hot liquid. The action is continued, keeping the temperature constant, till the bromine is reduced to a pale yellow colour. The impure ethylene dibromide is poured from the tubes into a small separating funnel, shaken with an equal bulk of dilute caustic soda solution, and run off from below the aqueous layer, which is rejected. The dibromide is returned to the funnel, shaken with water, and the lower layer, which is milky from the presence of moisture, is run off into a flask and dried over calcium chloride; when dry, it is poured into a small dry flask and distilled. The fraction between 130° and 132° is practically pure.

Ethylene dibromide is a colourless liquid, boiling at 131° to 132° . On cooling in ice, it freezes to a crystalline mass, which melts at 8° . The specific gravity of the liquid at 15° is 2.189.

It is important as being the usual source of glycol. To obtain this substance, the ethylene dibromide is first boiled with dry potassium acetate, when ethylene diacetate is formed; this, on boiling

¹ Indiarubber bungs should not be used with the bromine tubes, but well-pressed corks which have been soaked in paraffin wax. If larger quantities of bromine are to be converted into ethylene dibromide, the special bottles made for the purpose are most suitable; in these, the bubbling tube, the exit tube, and the stopper are all blown to make one piece of glass, which is ground to fit into the neck of the bottle. The use of these bottles precludes any danger of impurities being introduced into the ethylene dibromide from the cork.

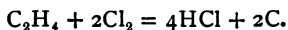
with a solution of caustic alkali, is hydrolyzed to glycol and an alkali salt of acetic acid.



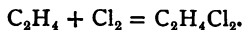
(b) **Experiments with Ethylene Gas.**—After the decolorization of the bromine in the previous experiment, from the same apparatus several cylinders and a 250 c.c. flask should be filled over water with ethylene gas. The following tests should then be performed :—

1. The gas burns with a bright luminous flame ; the flame is observed more easily if water is poured into the cylinder as the gas burns.

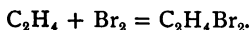
2. Mix one volume of ethylene with two volumes of chlorine and apply a light. The mixture burns with a red flame, giving a copious liberation of soot ; the chlorine combines with the hydrogen and liberates the carbon.



3. Mix equal volumes of ethylene and chlorine in a cylinder, and allow the mixture to stand over brine. The volume of the mixed gases gradually decreases on account of the formation of ethylene dichloride as small oily drops.

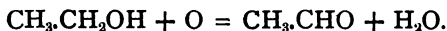


Pour $\frac{1}{2}$ c.c. of bromine into the 250 c.c. flask of ethylene ; insert the stopper and shake well. The colour of the bromine disappears and ethylene dibromide is formed as a colourless liquid. On opening the flask under water, the disappearance of the ethylene is apparent.



Acetaldehyde, CH_3CHO .

When ethyl alcohol is carefully oxidized, acetaldehyde is formed—



The oxidation is usually carried out with a mixture of sulphuric acid and potassium bichromate. A gram molecular weight of the latter substance (294 grams) contains 3 atomic weights of available oxygen, and so should be capable of oxidizing 138 grams of alcohol. In practice an excess of alcohol is taken.

Fit up an apparatus as illustrated in the diagram (Fig. 14), taking great care that all the joints are air-tight. A large flask (capacity $1\frac{1}{2}$ to 2 litres) is placed in a bath of cold water and fitted with a reflux condenser by means of an adapter. The top of the condenser is attached by a glass bend to a 100 c.c. pipette, which reaches down to the bottom of a 4-oz. flask arranged

D

wash-bottle fashion; this flask is connected with a second similar flask fitted in the same way, both flasks standing in a glass dish.

The reservoir of the condenser is filled with water at 25° to 30° , which is allowed to run slowly through the condenser. The small flasks are both half filled with dry ether, and ice is placed in the dish to keep them cool. Into the large flask are introduced 120 grams of potassium bichromate broken into small pieces (*not powder*), and then a well-cooled mixture of 480 grams of water, 160 grams (90 c.c.) of strong sulphuric acid, and 120 grams (150 c.c.) of alcohol is slowly added through the tap

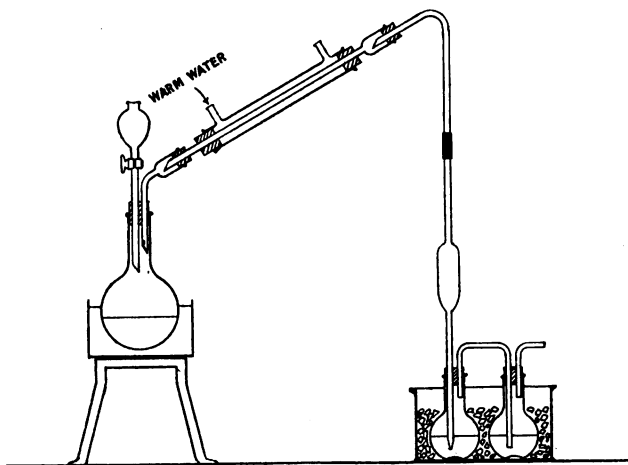


FIG. 14.

funnel. An action soon commences, and considerable heat is evolved as the oxidation proceeds, the liquid becoming green. All vapours are returned to the large flask by the condenser, with the exception of the aldehyde, which passes on and is dissolved by the ether. When the reaction slackens, it is aided by gently warming the water-bath until the water just boils. When the action has ceased, the flasks containing the ethereal solution of aldehyde are disconnected from the condenser, and dry ammonia¹ gas is carefully passed down the pipette into the flasks, which are

¹ This can be easily made by gently warming a concentrated solution of ammonia and drying the evolved gas by passing it through a tower or U-tube containing quicklime.

still kept cooled, till no more ammonia is absorbed ; the compound—aldehyde-ammonia—separates in white crystals, and should be quickly filtered on the pump, washed with a little ether, and dried. Yield of aldehyde-ammonia *c.* 30 grams.

To obtain pure aldehyde the crystals are dissolved in an equal weight of water, and dilute sulphuric acid added ; the mixture is then distilled from a water-bath, which should be slowly raised to boiling, through a double-surface condenser, the distillate being collected in a receiver cooled in ice. The distillate is poured into a distilling flask, and an equal bulk of anhydrous calcium chloride is added ; the flask is then tightly corked, the side-tube stopped, and the whole allowed to stand for a few hours. The dry aldehyde is then distilled off from the calcium chloride on a bath of water at 30° ,¹ again taking care to condense the vapour as completely as possible.

Pure acetaldehyde is a colourless liquid, boiling at 20.8° . Its specific gravity at 15° is 0.789.

¹ In almost all cases it is necessary to remove a liquid from the desiccating agent before distillation, because the temperature at which the latter occurs is often such as would drive off the water from the desiccating agent ; *e.g.* anhydrous sodium sulphate, which is often used for drying liquids, will not retain water above 32.5° . In the above distillation the temperature is so low that the hydrated calcium chloride is not affected.

CHAPTER III

Acetone, $\text{CH}_3\text{CO.CH}_3$.

Acetone is a colourless liquid, having a pleasant and characteristic odour. It is miscible with water and alcohol in all proportions. It boils at 56.5° . It does not form a compound with calcium chloride, and use is made of this in the separation from methyl alcohol.

1. Acetone gives the *iodoform* reaction. The test is carried out in exactly the same way as with ethyl alcohol (*q.v.*).

Iodoform is also produced when *iodine* and *ammonia* are used. The solution of acetone is made alkaline with ammonia, and then a solution of iodine in ammonium iodide is added carefully until a black precipitate of nitrogen iodide is formed. On warming, the black precipitate goes into solution and iodoform crystallizes out.

NOTE.—Ethyl alcohol does *not* give iodoform with iodine and ammonia.

2. On being shaken up with a concentrated solution of *sodium bisulphite*, acetone yields a crystalline addition product (*cf.* acetaldehyde).

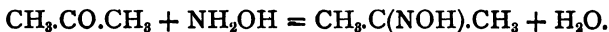
3. Acetone does *not* reduce *ammoniacal silver nitrate*.

4. Acetone dissolves precipitated (yellow) *mercuric oxide*.

Make a solution of *mercuric chloride* alkaline with *caustic soda* or *potash* in excess, and then shake up with the acetone solution. Filter till clear, acidify the filtrate with *hydrochloric acid*, and add *stannous chloride* solution. A white or grey precipitate denotes the presence of mercury, which has been taken into solution by the acetone.

Acetoxime, $(\text{CH}_3)_2\text{C}:\text{NOH}$.

Hydroxylamine is a useful reagent for aldehydes and ketones, since it forms crystalline compounds with these substances; the resulting compounds are termed oximes, *e.g.* acetone gives acetoxime—



According to this equation, 58 grams of acetone require 69.5 grams of hydroxylamine hydrochloride; 40 grams of caustic soda

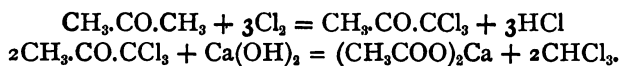
are necessary to liberate the hydroxylamine. In order to ensure as complete conversion of the hydroxylamine as possible, a slight excess of the acetone is used.

Dissolve 7 grams of hydroxylamine hydrochloride in 15 c.c. of water, and add a solution of 4 grams of caustic soda in 1 c.c. of water; to the mixture add 8 grams (10 c.c.) of acetone, and allow to stand 24 hours in a closed flask. During this time the oxime will separate out. The contents of the flask are mixed with ether, shaken, poured into a separating funnel, and the ethereal extract separated; the aqueous residue is extracted twice more with ether. The combined ethereal extracts are poured into a distilling flask, and most of the ether is distilled off; the remainder is poured into a porcelain dish and allowed to evaporate in the air, the last traces of ether being expelled by warming on the water-bath at about 50°. Recrystallize from petroleum ether. The melting point of the pure substance is 60°.

Hydrolysis of Acetoxime.—Oximes are readily hydrolyzed by dilute mineral acids. Distil a mixture of a little acetoxime with dilute sulphuric acid, using a small distilling flask, and a short condenser. The oxime is hydrolyzed to acetone and hydroxylamine. The presence of the former in the distillate can be detected by the iodoform reaction; the presence of the latter in the residue is shown by its reduction of Fehling's solution.

Chloroform, CHCl₃.

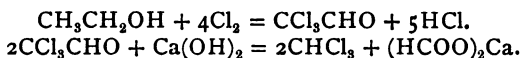
Chloroform is most conveniently prepared by the action of bleaching powder on acetone; the mechanism of the action appears to be that the bleaching powder yields its chlorine to form trichloroacetone, which is then hydrolyzed, by the calcium hydroxide remaining, into calcium acetate and chloroform.



Grind 150 grams of fresh bleaching powder to a paste with water, and rinse it into a two-litre flask, using about 400 c.c. of water. Fit the neck of the flask with a reflux condenser (double surface), and add 60 c.c. of acetone. Place a trough of cold water handy, shake the flask to agitate its contents, warm gently if necessary (by immersion in hot water), and as soon as an action starts, moderate it by cooling in the cold water. When the action has ceased, alter the position of the condenser

and distil the contents of the flask through it till a sample of the distillate collected in a test-tube contains no drops of a heavy liquid. Shake the distillate with an equal bulk of *dilute* caustic soda solution in a separating funnel, and run off the *lower* layer of chloroform. Dry by allowing to stand in contact with a few pieces of calcium chloride, and then redistil from a water-bath, noting the boiling point. The fraction distilling at a constant temperature of 61° is the chloroform. Yield *c.* 60 grams.

For anæsthetic purposes chloroform is prepared by the action of bleaching powder on ethyl alcohol; chloral is supposed to be first formed, and subsequently to undergo hydrolysis by the calcium hydroxide. Prepared by this method, the chloroform contains a small quantity of ethyl chloride, which increases its value as an anæsthetic. The yield, however, is not so satisfactory as that obtained from acetone.



Chloroform is a colourless, heavy, oily liquid (sp. gr. 1.501 at 15°) possessing a peculiarly sweet odour, and boiling at 61.2° . It dissolves readily in alcohol, but only to a very slight extent in water (enough to give the water a sweet taste). Beilstein's test shows the presence of a halogen.

1. Chloroform does not burn unless it is very strongly heated. On mixing with an excess of alcohol, it burns, the borders of the flame being tinged with green.

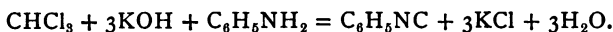
2. Chloroform dissolves *iodine*, giving a violet solution. (Alcohol gives a brown solution.)

3. Chloroform is decomposed by warming with *zinc* and *dilute sulphuric acid*. The solution then reacts with *silver nitrate*, giving a precipitate of silver chloride. Chloroform itself does not react with silver nitrate.

4. On boiling with *alcoholic potash solution*, chloroform gives potassium chloride and formate, which can be tested for in the usual manner after neutralizing the solution.



5. When heated with *alcoholic potash* and *aniline*, chloroform gives the extremely unpleasant and characteristic smell of phenyl isonitrile. (Isonitrile or carbylamine reaction.)



NOTE.—Only very small quantities should be used in carrying out this test, otherwise the odour is overpowering.

Chloral Hydrate, $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$.

Chloral hydrate forms colourless crystals, which melt at 57° , and boil at 96° – 98° , with decomposition into chloral and water. It possesses a peculiar sharp smell. Soluble in water and alcohol. It is readily dehydrated by means of strong sulphuric acid.

1. If chloral hydrate is warmed with *caustic potash* or *soda* solution it is decomposed, giving chloroform (recognized by its odour), and potassium formate.



If the chloral hydrate solution is very strong, the chloroform separates out in oily drops and makes the solution appear milky.

2. *Ammoniacal silver nitrate* is reduced, with the formation of a silver mirror.

3. Chloral hydrate gives the *carbylamine reaction* (phenyl isonitrile) exactly as does chloroform (see test 5, for chloroform).

4. On boiling with *zinc* and *dilute sulphuric acid*, a chloride is formed, which responds to the test with *silver nitrate* (see test 3, for chloroform). The presence of a halogen may also be detected by Beilstein's test (p. 9).

Iodoform, CHI_3 .

Iodoform crystallizes in the form of hexagonal yellow plates, which are insoluble in water, but soluble in alcohol and ether. The melting point is 120° . It possesses a characteristic odour. An alcoholic solution is readily decomposed by light.

1. Heated in a dry tube, it melts, and at temperatures above its melting point it partly decomposes, giving off iodine. (Hydriodic acid is also given off, but its presence is masked by the iodine.)

2. On boiling with *alcoholic potash*, potassium iodide and formate¹ are formed, and may be tested for in the neutralized solution (*cf.* chloroform).



¹ Methylene iodide is formed as an intermediate product.

CHAPTER IV

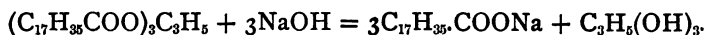
Palmitic Acid, $C_{15}H_{31}COOH$, crystallizes from alcohol—it is insoluble in water—in the form of white needles, which melt at 62° . The melted acid gives a greasy stain to paper. The alcoholic solution reddens litmus, and discharges the colour from pheno phthalein which has been turned just red by the addition of a drop of caustic soda solution. It is soluble in *caustic soda* (forming a soap), but, by the addition of *hydrochloric acid*, it is precipitated again as a flocculent solid; if the temperature of the solution is higher than the melting point of palmitic acid, the acid separates out in the form of oily drops, which rise to the surface of the liquid. All soluble palmitates behave in this manner with hydrochloric acid.

Stearic Acid, $C_{17}H_{35}COOH$, behaves similarly to palmitic acid. It melts at 69° .

Oleic Acid, $C_{17}H_{33}COOH$, is a liquid at ordinary temperatures (m. pt. 14°), and is distinguished from palmitic and stearic acids by the fact that it is unsaturated. It decolourizes bromine and reduces alkaline permanganate (*cf.* allyl alcohol, p. 59).

Preparation of Stearic Acid, $C_{17}H_{35}COOH$. — The common fats are generally mixtures of esters, in which the alcohol is glycerol, and the acid either stearic, palmitic, or oleic; the more oily the fat, the more glyceryl oleate is present, since this ester is liquid, while the glyceryl esters of stearic and palmitic acids are solids.

Mutton suet consists chiefly of glyceryl stearate with smaller quantities of the other two esters. The process of hydrolysis can be performed in the usual way by boiling with a solution of caustic alkali, when the trihydric alcohol—glycerol—is liberated and the sodium salts of the acids remain in solution. The sodium salts can be made to separate from the solution by the addition of common salt, the presence of which lowers their solubility; the sodium salts of the above acids prepared in this way constitute ordinary soap, and so the process of hydrolysis is frequently spoken of as “saponification.”



To obtain pure stearic acid from the impure acid resulting when the soap is treated with a mineral acid, the mixture of free acids is extracted with hot alcohol to remove any oleic acid, and is then further purified by fractional recrystallization of the free acid, or by fractional precipitation as the magnesium salt. In both cases the stearic acid is less soluble than the impurities, which therefore, for the most part, remain behind in the mother liquors.

Method.—Cut up half a pound of suet into small pieces, tie them in a piece of muslin, and put into a beaker containing 500 c.c. of boiling water; the fat soon melts, and on pressing, passes through the muslin, leaving the animal membrane behind. Pour the fat and water into a clean iron water-bath, and then add a solution of 50 grams of caustic soda in 500 c.c. of water; boil gently, with frequent stirring, for two or three hours, replenishing the water as fast as it boils away, till at last all the fat has been decomposed.

Pour the liquid into a beaker, allow to cool somewhat, and stir well into it 150 grams of finely powdered common salt; the soap will separate and rise to the surface; when quite cold it should be filtered off and washed with a little water.

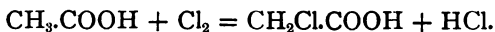
Take 100 grams of the above soap, dissolve in hot water, filter if necessary, and then to the solution add an excess of a mixture of concentrated hydrochloric acid with an equal bulk of water. The liberated fatty acid rises to the surface as an oil, and solidifies on cooling. The mass of fatty acid is separated from the water, boiled for a short time with 100 c.c. of alcohol, allowed to cool, and filtered. It is then dried by absorbent paper, and weighed. If the melting point of the acid be now determined, it will be found to be much below 69° , showing that the stearic acid is still far from pure.

The weighed mass of acid is dissolved in an excess of hot alcohol, and one-fifth its weight of magnesium acetate is added in hot alcoholic solution; the precipitate should consist of practically pure magnesium stearate. When cold, the solid is filtered off and well drained on the pump. It is then boiled with excess of dilute hydrochloric acid till the magnesium salt is decomposed, and after cooling, the stearic acid is filtered off. Finally, it is recrystallized from alcohol, and after careful drying, its melting point is taken. Pure stearic acid melts at 69° , and so the purity of the sample will be thereby tested.

If the acid is not pure, and a pure sample be required, repeated recrystallizations of the acid from alcohol, or further fractional precipitation of the acid as magnesium stearate, should be performed.

Monochloroacetic Acid, ClCH_2COOH .

Chlorine acts on acetic acid only in the presence of a "chlorine carrier," such as sulphur or iodine; sunlight also has a catalytic accelerating effect. The first product of the action is the monosubstituted acid—



If an excess of chlorine is used, the substitution of the second and even of the third atom of hydrogen occurs.

The equation shows that 60 grams of acetic acid yield 94.5 grams of monochloroacetic acid; consequently, in the preparation, chlorine gas is passed into hot glacial acetic acid, containing about 10 per cent. of sulphur, till the proper increase in weight has occurred.

Place in a small flask a mixture of 100 grams of glacial acetic acid with 10 grams of sulphur, and weigh; place the flask on a boiling water-bath, fit the neck with a doubly-bored cork, one hole of which is fitted with an adapter attached to a reflux condenser, while the other is fitted with a glass tube reaching down into the liquid. Pass chlorine gas steadily into the mixture through the glass tube.¹ The whole apparatus should be situated so as to be exposed to as bright sunlight as possible. The absorption of the correct quantity of chlorine will probably require at least six hours. The flask should be weighed occasionally to see how far the reaction has proceeded. When the increase in weight is 50 grams, the liquid should be decanted from the sulphur into a distilling flask, and distilled over wire gauze through an air condenser. The first part of the distillate contains acetyl chloride, sulphur chloride, and unchanged acetic acid. The fraction distilling from 150° to 190° is collected separately in a beaker, and should solidify on cooling. The liquid is drained off from the solid, the latter is redistilled, and the fraction between 180° and 190° collected; this consists of

¹ The chlorine gas can be most conveniently made by allowing concentrated hydrochloric acid to drip slowly from a dropping funnel on to potassium permanganate crystals, contained in a flask, and bubbling the evolved gas through a bottle containing a little strong sulphuric acid.

practically pure chloracetic acid. The yield varies from 75 to 100 grams.

Monochloracetic acid is a colourless crystalline solid ; it boils at 185–187°.

CHLORACETIC ACIDS

Monochloracetic Acid, $\text{CH}_2\text{Cl.COOH}$, forms colourless crystals, which are deliquescent, soluble in water, and melt at 62°. If the molten substance is heated for a short time above its melting point, and then allowed to solidify, an *unstable (metastable)* modification is formed, which melts at 52°,¹ and which is readily transformed to the stable modification by contact with a crystal of the ordinary acid. The strong acid blisters the skin.

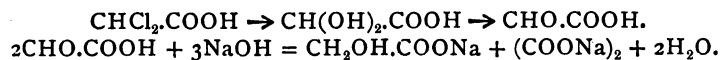
Dichloracetic Acid, CHCl_2COOH , is a liquid at ordinary temperatures, boiling at 190°. It is soluble in water.

Trichloracetic Acid, CCl_3COOH , forms deliquescent rhombohedral colourless crystals, which are very soluble in water. The melting point is 52°. It blisters the skin.

The three acids and their salts react very similarly to acetic acid and its salts, *e.g.* the neutral solutions give a red coloration with ferric chloride, and, on boiling, a basic acetate is precipitated out. They are distinguished from acetic acid by the fact that they contain chlorine, which may be easily detected by (1) Beilstein's test, (2) boiling with *alcoholic potash* (it is best to do this in a small flask, fitted with an air condenser) ; potassium chloride is formed, and may be tested for after acidifying with nitric acid.

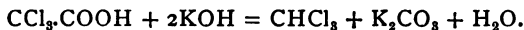
In the case of dichlor- and trichloracetic acids, other reactions take place under the influence of the alcoholic potash.

Dichloracetic Acid.—Glyoxylic acid is first formed, and this is then converted by the alkali into glycollic and oxalic acids. On acidifying with acetic acid and adding calcium chloride a white precipitate of calcium oxalate is obtained.



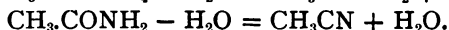
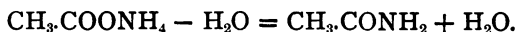
¹ It is important for the student to bear in mind that if a substance has once been melted and allowed to solidify again, the melting point of the solidified product is *not necessarily* the same as that of the original substance. This may be due to the formation of a metastable modification, as in the present case, or to the formation of a dynamic isomeride ; *e.g.* Thio-urea $[\text{CS}(\text{NH}_2)_2]$ on being melted is partially transformed into ammonium thiocyanate (NH_4SCN) , and *vice versa*. Re-determinations of the melting point should, therefore, always be made with fresh quantities of the original substance.

Trichloroacetic Acid.—Chloroform is produced and may be detected by the odour.



Acetamide, CH_3CONH_2 .

The dehydration of ammonium salts of fatty acids gives rise successively to the corresponding amides and nitriles. For the first dehydration mere heating is often sufficient, but the dehydration of the amide into the nitrile generally requires the use of phosphorus pentoxide.



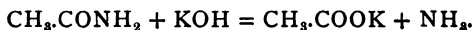
The conversion of ammonium acetate into acetamide takes place even if the salt is merely distilled, but the yield is very poor, and it is far more satisfactory to perform the heating in a sealed tube. The ammonium acetate can be prepared by adding powdered ammonium carbonate (roughly 20 grams) to 25 grams of glacial acetic acid; the mixture is heated on the water-bath, till a sample, on dilution, is neutral to litmus.

A thick walled glass tube is prepared in the usual way;¹ it is gently warmed, and then about two-fifths filled with molten ammonium acetate; the tube is then sealed, and heated in a bomb furnace for six hours at about 230°. The tube is allowed to cool, and while the body of the tube is still in the iron case the narrow tip is melted by means of a bunsen flame in order to release any excessive pressure in the interior of the tube; the latter is then opened by applying a red-hot glass rod to a file-mark made on the tube, and the contents are poured into a distilling flask. The oily liquid is distilled, using a glass tube (2 cms. diameter) as condenser, and the distillate which passes over above 180° is collected in a beaker. On standing, this fraction should solidify to a crystalline mass; it is dried on a porous plate and purified by redistillation, when the fraction distilling at a constant temperature should be collected separately. Yield about 50 per cent. of the ammonium acetate taken.

Pure acetamide is a colourless crystalline solid, melting at 82° and boiling at 223°.

¹ The preparation and sealing of thick walled tubes for use in a bomb furnace is much better understood from a demonstration by the teacher than from a written description.

Hydrolysis.—Boil a few grams of acetamide with caustic potash solution for a quarter of an hour in an open flask; ammonia is given off and can be detected in the escaping steam. Add excess of dilute sulphuric acid to the liquid in flask and distil through a condenser; the distillate is a weak solution of acetic acid, and can be tested in the usual way.



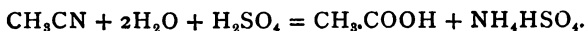
Acetonitrile, CH_3CN .

Acetonitrile, or methyl cyanide, is an interesting substance, since it provides the most important step in the synthesis of ethyl alcohol from methyl alcohol. By reduction it forms ethylamine, which easily gives ethyl alcohol on treatment with nitrous acid. It may be prepared by the distillation of a mixture of methyl hydrogen sulphate with potassium cyanide, but the method of preparation given below is preferable.

Introduce quickly into a distilling flask approximately 20 grams of phosphorus pentoxide, measuring the amount of the pentoxide by weighing the (corked) flask before and after its introduction. Then add 10 grams of powdered acetamide and shake the mixture together; attach a condenser to the flask, and heat the latter carefully over a smoky flame, distributing the heat as evenly as possible. When nothing more distils, add to the distillate about half its volume of water, and then more than sufficient anhydrous potassium carbonate to saturate the water present. Allow to stand an hour, with occasional shaking, in order to remove traces of acetic acid from the nitrile. Then separate the nitrile from the lower aqueous layer, pour into a distilling flask, add a few grams of phosphorus pentoxide, and distil. The acetonitrile distils over at about 80° . Yield c. 5 grams.

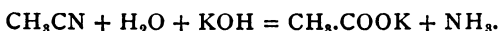
The pure liquid boils at 81.6° , and has a specific gravity of 0.789 at 15° . It is miscible with water, but is separated out on the addition of salts soluble in water, such as potassium carbonate.

Hydrolysis.—Boil a few c.c. of acetonitrile with 50 c.c. of dilute sulphuric acid for half an hour, using a reflux condenser; alter the position of the condenser, distil half the liquid through it, and test the distillate for acetic acid. Add potash to the residue in the flask till alkaline, and again distil; the distillate this time will be a dilute solution of ammonia.

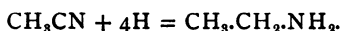


Caustic potash solution can also be used for the hydrolysis of

acetonitrile ; in this case the first distillate is the ammonia solution, then, after acidifying with dilute sulphuric acid, the acetic acid can be distilled off.

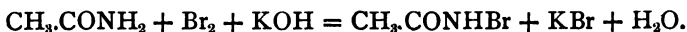


Reduction of Acetonitrile.—Nitriles are easily reducible to the corresponding amines ; the reduction is most suitably performed in alcoholic solution by the action of metallic sodium. Dissolve a few drops of acetonitrile in 10 c.c. of alcohol in a test-tube and heat till the solution boils. To the hot solution add one or two small fragments of sodium ; when the sodium has dissolved, heat the tube once more till the liquid begins to boil, when the ammoniacal odour of the ethylamine formed is apparent.

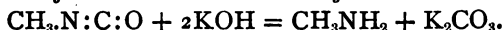


Methylamine Hydrochloride, $\text{CH}_3\text{NH}_2\text{HCl}$.

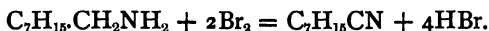
This substance is conveniently prepared from acetamide by means of Hofmann's reaction. If an acid amide be heated with bromine and potash, the first product is a bromamide.



The bromamide, on treatment with excess of hot caustic potash solution, gives first an isocyanate, which then hydrolyzes to an amine.



With the lower fatty acids, the action stops here ; but with the higher ones the action of more bromine and caustic potash gives rise to the nitrile of the acid containing one carbon atom less than the acid whose amide was originally taken.



Details of Procedure—Mix together 20 grams of acetamide with 54 grams (18 c.c.) of bromine (*i.e.* equimolecular proportions) in a half-litre flask ; cool by immersion in water, while a 10 per cent. solution of caustic potash is carefully added till the colour of the liquid changes to a deep yellow. The action represented by the first equation above then takes place, with formation of acetic bromamide.

A distilling flask is fitted with a cork, through which pass the stem of a dropping funnel and a thermometer, the latter reaching nearly to the bottom of the flask. A solution of 56 grams of

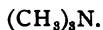
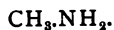
caustic potash in 100 c.c. of water (*i.e.* three molecules of caustic potash for each molecule of bromamide) is placed in the flask and heated to 60–70°. The solution of acetic bromamide is poured into the dropping funnel and allowed to run slowly into the flask. Care must be taken to keep the temperature from rising above 70°. After all the solution has been run in, the mixture is allowed to stand at the same temperature till completely de-colourized (about 10 to 15 minutes).

A few fragments of porous tile are dropped into the flask; the latter is then closed by a cork, and the liquid is distilled through an ordinary condenser. The condensed liquid is passed into 100 c.c. of dilute hydrochloric acid in a beaker, through a funnel attached to the end of the condenser; the funnel is so arranged that its lip just touches the surface of the acid; this prevents the acid sucking back into the flask.

When a little of the distillate, on testing, proves to be no longer alkaline, evaporate the hydrochloric acid solution to dryness on water-bath. The residue consists of methylamine hydrochloride mixed with a little ammonium chloride; it should be placed in a flask and extracted several times under a reflux condenser with small quantities of absolute alcohol. The combined alcoholic extracts, on cooling, deposit crystals of methylamine hydrochloride. Collect and dry in the usual way. The yield is variable.

Add caustic soda to a little methylamine hydrochloride in a test-tube, and warm; the strong ammoniacal odour of methylamine is at once apparent.

METHYLAMINE AND TRIMETHYLAMINE,



These two substances are gases at ordinary temperatures (methylamine boils at -6.7° and trimethylamine at $+3.5^\circ$), possessing a fishy odour, which, at the same time, reminds one of ammonia. They resemble ammonia in that they form white fumes with the vapours of volatile acids, and are alkaline to moist litmus-paper; they dissolve in water, giving alkaline liquids which probably contain the hydrates of the bases, *viz.* $\text{CH}_3\text{NH}_2\text{OH}$ and $(\text{CH}_3)_3\text{NHOH}$. They are distinguished from ammonia by their inflammability. With the mineral and organic acids they form salts. The hydrochlorides are soluble in water, and *also* in alcohol (distinction from ammonium chloride).

With chlor-platinic and chlor-auric acids they form crystalline salts, *e.g.* $(\text{CH}_3\text{NH}_2)_2\text{H}_2\text{PtCl}_6$, and $(\text{CH}_3\text{NH}_2)\text{HAuCl}_4$.

The solutions of the bases in water act very similarly to a solution of ammonium hydroxide; they precipitate many of the metals from solution as hydroxides [*e.g.* $\text{Fe}(\text{OH})_3$], and unite with oxides and salts, *e.g.* of silver, zinc, and cadmium, to form complex compounds.

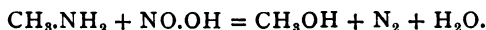
Methylamine and Salts.—The free base resembles ammonia very much in its odour, but at the same time it smells somewhat fishy. The solution in water dissolves aluminium hydroxide (distinction from ammonia).

The hydrochloride (methyl ammonium chloride) melts at 225–226°. A solution of this salt may be used for the following tests.

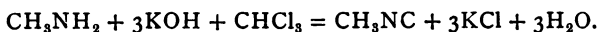
1. On warming with *caustic soda*, the free base is liberated as a gas, and may be recognized by its odour, alkaline reaction, and inflammability.



2. Acidify the solution with *dilute hydrochloric acid* and add a solution of *sodium nitrite*. Nitrogen is rapidly evolved. (Characteristic of a **primary amine**.)



3. When heated with *alcoholic potash* and *chloroform*, the very unpleasant odour of methyl isonitrile] is perceived (*cf.* tests for chloroform).



This test is also characteristic of a primary amine.

Trimethylamine and Salts.—In the concentrated form the free base is said to possess an odour very similar to that of ammonia, but generally it is diluted with air, and then it has an extremely unpleasant fish-like odour.

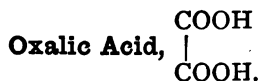
For the following tests a solution of the hydrochloride [trimethyl ammonium chloride, $(\text{CH}_3)_3\text{NHCl}$] may be used.

1. On warming with *caustic soda*, the free base is liberated as a gas, and may be recognized by its odour, alkaline reaction, and inflammability.

2. There is no action with dilute hydrochloric acid and sodium nitrite solution. (Distinction from methylamine.)

3. Isonitriles are *not* formed by the action of alcoholic potash and chloroform. (Distinction from methylamine.)

NOTE.—Primary amines and tertiary amines may be distinguished from each other by tests 2 and 3. Secondary amines give a nitroso-compound with nitrous acid, but these will be considered later, when dealing with the aromatic amines (see p. 122).



When cane sugar is oxidized by moderately strong nitric acid, oxalic acid is formed as the chief product.

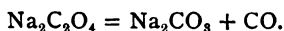
Place 250 c.c. of concentrated nitric acid in a large flask, and heat in a bath of boiling water. When the acid is hot, transfer flask to a fume chamber and add 50 grams of cane sugar. Brown fumes are evolved in abundance; when the action has ceased, pour the contents of the flask into a porcelain dish and evaporate on the water-bath to one quarter of the original bulk. On allowing to cool, the oxalic acid separates in large crystals. Pour off the liquid and drain the crystals as thoroughly as possible without the use of a filter-paper. Recrystallize from a little hot water. Yield *c.* 15 grams.

Oxalic acid forms colourless crystals, containing two molecules of water of crystallization. Readily soluble in water and alcohol. The crystals melt at 100° ; on further careful heating, the water of crystallization is driven off and the acid sublimes. If heated rapidly, decomposition also takes place.



The oxalates of Na, K, and NH_4 are soluble in water; the others are mostly insoluble in water, but soluble in hydrochloric acid.

1. All oxalates are decomposed on heating, *no blackening* taking place. The oxalates of the alkali metals and of the alkaline earths leave a residue consisting of carbonates, and carbon monoxide is liberated. Silver oxalate explodes on heating.



If the residue is strongly heated, the carbonates of the alkaline earths will be further decomposed, leaving the oxides; this takes place fairly readily with calcium carbonate, but a very high temperature is necessary to decompose barium carbonate.

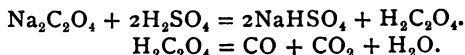
Oxalates of the heavy metals (*e.g.* Cu) produce an oxide, and oxalates of metals whose oxides decompose on heating (*e.g.* silver) leave the metal.

If acid oxalates are carefully ignited they first give off oxalic acid, leaving the normal salt, which is then decomposed as above.

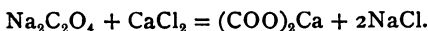
2. Oxalates and oxalic acid are decomposed by heating with *strong sulphuric acid*, carbon monoxide and carbon dioxide being evolved. The former gas may be detected by applying a light to the

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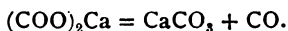
mouth of the test-tube, and the latter by passing the gases through lime-water, or by decanting them into a test-tube containing lime-water, and then shaking. The gases are evolved with effervescence, and no blackening takes place.



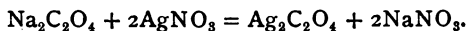
3. *Calcium chloride*, with neutral or alkaline solutions of oxalates, gives a white crystalline precipitate of calcium oxalate, insoluble in acetic acid, but soluble in hydrochloric or nitric acid.



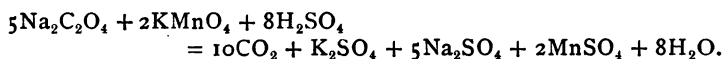
If the precipitate is washed, dried, and then ignited gently in a crucible, carbon monoxide is evolved, and a residue of calcium carbonate is left, which effervesces on the addition of hydrochloric acid.



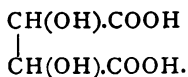
4. *Silver nitrate* gives a white crystalline precipitate of silver oxalate with neutral solutions of oxalates. The precipitate is soluble in ammonia and in nitric acid.



5. Add *potassium permanganate*, drop by drop, to the warm solution of an oxalate, acidified with *dilute sulphuric acid*. The permanganate is decolorized, and carbon dioxide is evolved.



TARTARIC ACID,



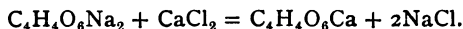
Forms large colourless crystals, which are soluble in water and alcohol. The ordinary acid of commerce is dextro-rotatory. The normal salts of the alkali metals are soluble in water, most others being insoluble. All tartrates are soluble in dilute hydrochloric acid. It is noteworthy that the acid salts of potassium and ammonium are only very slightly soluble in water.

1. Tartaric acid and tartrates blacken (due to charring) when heated in the dry state; the mass swells up and an odour of burnt sugar is given off.

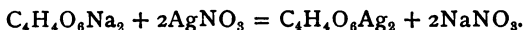
2. When heated with *strong sulphuric acid*, tartrates, or tartaric acid, almost immediately blacken ; carbon monoxide, carbon dioxide, and sulphur dioxide are evolved.¹ The carbon monoxide may be ignited at the mouth of the test-tube, and the sulphur dioxide is recognized by its smell. At the same time there is an odour of burnt sugar.

3. *Calcium chloride* gives, with neutral tartrate solutions, a white crystalline precipitate of calcium tartrate, which is soluble in cold, strong (20 per cent.) caustic potash or soda, and in acetic acid. Calcium tartrate readily gives supersaturated solutions, so that unless the tartrate solution is concentrated, the precipitate is only obtained after standing for some time, or on vigorous shaking. (It may be necessary to concentrate the solution.)

The crystalline particles are heavy and comparatively large, and rapidly sink to the bottom.



4. *Silver nitrate* added to the neutral solution of a tartrate gives a white precipitate of silver tartrate, which is soluble in ammonia and nitric acid, and also in excess of the tartrate.



Allow the precipitate to settle, pour off the supernatant liquid, and add water and just enough ammonia to dissolve the precipitate. Drop in a crystal of silver nitrate, and heat the test-tube in a beaker of water ; the silver salt is reduced, and the silver is deposited as a *bright mirror* on the sides of the tube.³

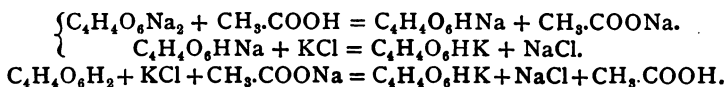
5. *Potassium salts*, when added to solutions of tartrates or of tartaric acid, give, under certain conditions, a white precipitate of potassium hydrogen tartrate. To obtain the precipitate from solutions of normal tartrates, it is necessary to add acetic acid ; if free tartaric acid is used, sodium acetate must be added to take away the free mineral acid which is set free when the precipitate is formed.³ (These difficulties may be obviated by using a solution obtained by dissolving

¹ The carbon dioxide may be detected in the presence of sulphur dioxide by first passing the evolved gases through a strong solution of potassium bichromate, and then through lime-water. This test, however, does not possess any analytical importance.

² The conditions for obtaining a good mirror are given under the tests for formaldehyde, p. 20.

³ For an explanation of this, reference should be made to modern textbooks of inorganic chemistry, such as Findlay's translation of Ostwald's "Outlines of Inorganic Chemistry." The reaction depends on the presence of hydrogen tartrate ions, $\text{H.H}_4\text{C}_4\text{O}_6'$, these being necessary for the formation of $\text{KH.H}_4\text{C}_4\text{O}_6$.

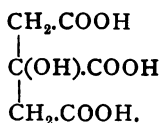
potassium carbonate in acetic acid.) In all cases the precipitation is accelerated by vigorous shaking.



6. Add a little of the solid tartrate to *strong sulphuric acid* containing 1 per cent. of *resorcin*, and heat very gently. A violet-red colour is produced. (Distinction from a citrate.) The test may be conveniently carried out on the lid of a porcelain crucible.

7. Free tartaric acid and alkaline tartrates prevent the precipitation by alkalis of certain metallic oxides, *e.g.* the oxides of copper, iron, etc. This property is made use of in the preparation of Fehling's solution (*cf.* p. 233). In order to remove the heavy metal from such solutions it is necessary to proceed as given on p. 84.

CITRIC ACID,



Crystallizes in rhombic prisms containing one molecule of water of crystallization. Very soluble in water and alcohol. The alkaline citrates are soluble in water, most of the others being insoluble or only sparingly soluble; all citrates are soluble in hydrochloric acid.

The reactions of citrates should be carefully compared with those of tartrates.

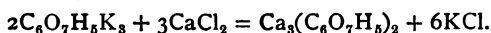
1. Citric acid melts on being heated and afterwards slowly darkens, pungent and irritating fumes of aconitic acid being given off—the odour may readily be distinguished from that obtained when tartaric acid is decomposed by heat. On continued heating, further decomposition takes place, and a black residue is left. Citrates behave in a similar manner.

2. When heated with *strong sulphuric acid* citrates, or citric acid, evolve carbon monoxide and carbon dioxide. It is only after prolonged heating that blackening takes place and sulphur dioxide is evolved (*cf.* tartrates).

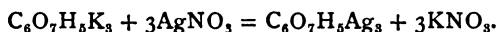
3. *Calcium chloride* gives, with neutral solutions of citrates, *no* precipitate in the *cold*, except after standing for some hours; if the solution is boiled for a short time a *crystalline* precipitate of calcium citrate is obtained. If the solution is too dilute, it will require concentrating before any precipitate forms. The formation of this precipitate is rendered more certain by the addition of a little

ammonia.¹ The crystalline precipitate is insoluble in caustic soda or potash, and also in ammonium chloride.

If *caustic soda* or *potash* is added to the cold solution of the citrate containing calcium chloride, there is an immediate white precipitate of *amorphous* calcium citrate, which is soluble in ammonium chloride; from this solution the crystalline compound separates out on boiling, and is then no longer soluble in ammonium chloride.²



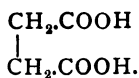
4. *Silver nitrate*, with neutral solutions of citrates, gives a white precipitate of silver citrate, which is soluble in ammonia. On heating this solution for some time there is a reduction of the silver compound, but no mirror is formed.



5. Citrates resemble tartrates in that they prevent the precipitation by alkalis of certain metallic oxides.

6. Add *caustic potash* in excess to the solution of a citrate, and a few drops of *potassium permanganate*. The solution becomes green on boiling. Tartrates under like conditions give a brown precipitate of hydrated peroxide of manganese.

SUCCINIC ACID,



Crystallizes in prisms, which melt at 185° , and boil at 235° with the formation of succinic anhydride. Soluble in water and alcohol. Most succinates are soluble in water.

1. The acid, on heating in a test-tube, melts, and then boils, giving a very irritating vapour, which, when inhaled, induces violent coughing; a sublimate forms in the cool part of the tube. Very little, if any, charring takes place.

Most succinates show a similar behaviour.

If a little of the acid is heated on platinum foil it burns with a non-luminous blue flame, leaving no residue of carbon. (Distinction from benzoic acid.)

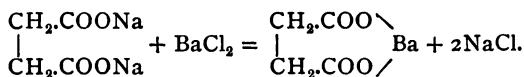
2. Succinates, or succinic acid, on being heated with *strong sulphuric acid*, give off the irritating vapour of the unchanged acid,

¹ Too much ammonia must not be added, otherwise an *amorphous* precipitate will be formed in the *cold*.

² This is a good example of the fact that the unstable form of a compound is more soluble than the stable. In this case the amorphous form is unstable; on standing for a long time, or more quickly on boiling, it changes to the stable crystalline form.

which may form a sublimate on the cool sides of the tube. If the heating is prolonged, sulphur dioxide is evolved and slight blackening takes place.

3. *Barium chloride* gives a white precipitate of barium succinate with neutral succinates. This precipitate forms fairly readily from concentrated solutions; from dilute solutions the precipitate is readily obtained by the addition of excess of ammonium hydroxide. The precipitation is more certain if alcohol is also added (*cf.* benzoic acid).

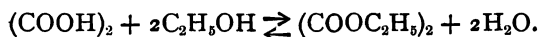


4. With neutral succinate solutions *ferric chloride* gives a pale brownish-red precipitate of basic ferric succinate. Filter off the precipitate, heat with *ammonium hydroxide*, and again filter. The filtrate will contain most of the succinic acid as the ammonium salt, the iron remaining on the filter as a more basic succinate. With *barium chloride* and *alcohol* the filtrate gives a white precipitate of barium succinate, but no precipitate with *hydrochloric acid* (*cf.* benzoic acid).

5. The precipitates obtained with *silver nitrate* and *calcium chloride* are not important.



Since oxalic acid is a stronger acid than acetic, it forms esters much more easily, but there is still a tendency for the water formed to stop the action before it is nearly complete, by giving rise to the reverse reaction. In the following preparation this tendency is checked to a large extent by removing the water from the mixture by a stream of alcohol vapour.



Dehydrate 50 grams of crystallized oxalic acid: the dehydration may be carried out by heating the powdered acid in a steam oven, or preferably in a flask heated in a water-bath, a constant stream of air being drawn through the flask till the acid is anhydrous. If great care be taken, the dehydration may be performed by heating the acid in a porcelain dish over a small bunsen flame, *with continual stirring*. The dehydration in each case is complete when the weight has decreased by 14 grams, leaving 36 grams of anhydrous acid. Place this acid in a distilling flask (A, Fig. 15) and add 35 c.c. of absolute alcohol. Fit the neck of the flask with a two-holed bung carrying a glass tube and

a thermometer,¹ both of which reach down into the mixture; attach the side tube of the flask to a condenser, and slowly heat the flask over a wire gauze till the temperature reaches 100° . The amount of liquid distilling at this temperature will be inappreciable, and the liquid should be maintained at this temperature for twenty minutes. Pour 60 c.c. of absolute alcohol into a small flask, B, fit the flask with a bung carrying a glass tube bent at right angles, and also a straight glass safety-tube; connect with flask A, as shown in the diagram. Boil the alcohol gently over a wire gauze, and pass the vapour into the hot mixture in A, at the same time slowly raising the temperature of the mixture to 130° . When all the alcohol has been vaporized,

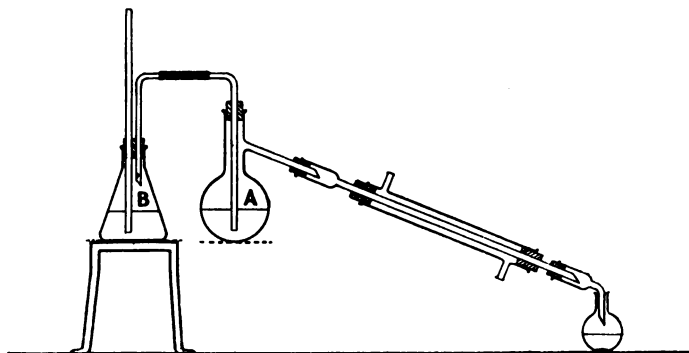


FIG. 15.

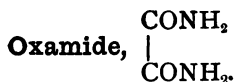
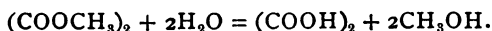
the thermometer bulb should be withdrawn from the liquid into the neck, and the residue in the flask should be fractionated with an air condenser. Collect three separate fractions: 100° – 160° , 160° – 180° , 180° – 186° . The distillate from 100° – 160° is reserved for the preparation of oxamide. The distillate from 180° – 186° is practically pure ethyl oxalate. The distillate from 160° – 180° consists chiefly of ethyl oxalate and alcohol; it is shaken with twice its volume of water to remove the alcohol, and the lower layer of ester separated off and dried overnight over calcium chloride. The dry ester is then redistilled, and the fraction distilling from 180° – 186° added to the pure fraction previously obtained. Total yield c. 30 grams.

Pure diethyl oxalate is a colourless liquid boiling at 186° . It is almost insoluble in water.

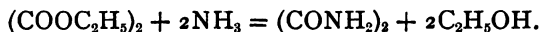
¹ The thermometer is not shown in the figure.

Dimethyl Oxalate can be prepared in the same manner as the ethyl ester. Unlike the latter, it is a solid substance, melting at 54° and boiling at 163° ; it is soluble in water, alcohol, and ether. In the preparation the distillate should be collected in three fractions, from 100° – 140° , 140° – 158° , and 158° – 163° . The last fraction, on the addition of a crystal of previously prepared methyl oxalate, will set to a solid mass of practically pure ester. The middle fraction, on the addition of a crystal, will also deposit crystals, and the solid should be separated from any mother liquor by pressing on a porous plate. The combined solid fractions can then, if necessary, be recrystallized from a little alcohol.

Hydrolysis.—Both diethyl and dimethyl oxalates are readily hydrolyzed; if either be shaken with water for a short time, the water becomes acid to litmus, and, after neutralizing, gives the tests for oxalic acid.



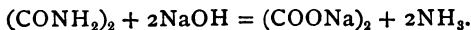
Add concentrated ammonia in excess to an alcoholic solution of ethyl or methyl oxalate; a white crystalline precipitate of oxamide immediately forms.



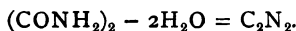
To obtain a fair quantity of this substance, the mixture of alcohol and ester which, in the above preparation of ethyl oxalate, distils off below 160° , should be treated with concentrated ammonia. The precipitate is filtered off, washed with a little alcohol, and dried.

Oxamide is a crystalline powder, almost insoluble in water, alcohol, and ether; on heating, it sublimes without melting, undergoing partial decomposition.

If it be boiled with caustic soda solution, hydrolysis ensues with liberation of ammonia, and formation of a solution of ammonium oxalate.



On heating a mixture of oxamide and phosphorus pentoxide, the former is dehydrated with formation of cyanogen (*cf.* preparation of acetonitrile from acetamide).



Formic Acid, H.COOH.

When oxalic acid is heated alone it decomposes partly into carbon dioxide and formic acid, but mainly into carbon dioxide, carbon monoxide, and water. If the oxalic acid is heated with glycerol to about 120°, the decomposition proceeds almost entirely according to the first method—



The mechanism of the process is supposed to be as follows: The glycerol and oxalic acid first give an ester, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{O}.\text{CO}.\text{COOH}$, which almost immediately decomposes with evolution of carbon dioxide, giving glyceryl monoformate, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{O}.\text{CHO}$. The glyceryl monoformate is then hydrolyzed by the water present (from $\text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O}$), forming glycerol and formic acid, the latter distilling off. The glycerol is then free to once more undergo the same changes and form a second quantity of formic acid; theoretically the action might go on indefinitely.

Details of Procedure.—Heat some glycerol in a porcelain dish slowly to 175° in order to expel water. Place 50 c.c. of anhydrous glycerol together with 40 grams of crystallized oxalic acid in a distilling flask, connect with a condenser, and heat carefully, the thermometer bulb being in the liquid. At 90° a vigorous evolution of carbon dioxide commences; the temperature should be allowed to rise to 110°, and remain there till the evolution of gas slackens. The mixture is then allowed to cool to 80°, a second lot of 40 grams of oxalic acid is added, and the previous treatment repeated. This is performed a third time with a third addition of 40 grams of acid. The distillate consists of aqueous formic acid.

The residue in the flask still contains formic acid as the glyceryl ester. It is therefore poured into a large round flask, diluted with 250 c.c. of water, heated on a sand-bath, and steam passed in (see Fig. 16). This steam distillation hydrolyzes the ester and carries over the formic acid, which collects together with water as the distillate; the distillation is stopped when the distillate is no longer acid.

To obtain the lead salt the combined solutions of formic acid are then placed in a porcelain dish, heated on a water-bath, and lead carbonate is added in small quantities and well stirred in each time, till a further addition gives no more effervescence.

The liquid is then filtered, and the solution of lead formate evaporated on the water-bath till it begins to crystallize; it is

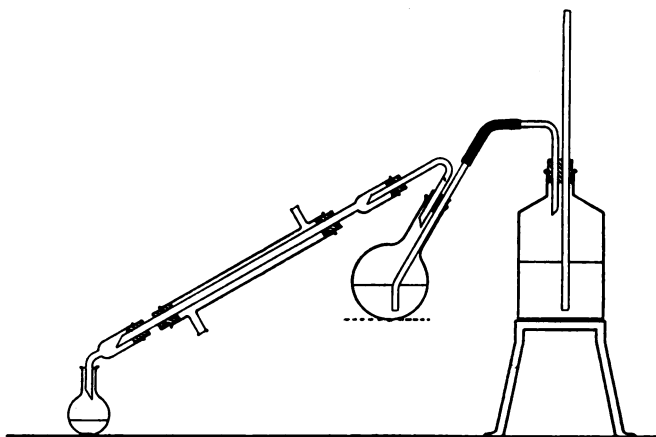


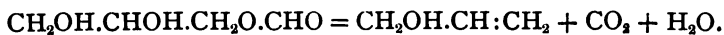
FIG. 16.

then set aside to cool. The white needle-shaped crystals are filtered off and dried. Yield *c.* 50 grams.

If anhydrous formic acid be required, the most convenient procedure is to dehydrate the weak acid by the action of anhydrous oxalic acid. The weak acid prepared by the above method is fractionated (see p. 86) until a 75 per cent. solution of formic acid is obtained; in this solution, anhydrous oxalic acid is dissolved by warming. When the solution is cooled, crystals of hydrated oxalic acid separate out, leaving the formic acid above practically anhydrous; on distillation, the latter is obtained pure.

Allyl Alcohol, $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$.

When excess of glycerol is heated with oxalic acid to 200° , the action is quite different from that obtaining when glycerol is heated with excess of oxalic acid to a lower temperature (see preparation of formic acid). In the former case, the glyceryl monoformate first formed decomposes, giving carbon dioxide, water, and allyl alcohol.



Mix 50 grams of oxalic acid with 200 grams of dried glycerol (see formic acid preparation) in a retort, and add 0.5 gram of

ammonium chloride;¹ fit a thermometer, by means of a cork, into the tubulure of the retort so that the bulb is in the mixture, and attach the beak of the retort to a condenser. Heat carefully over wire gauze; the temperature rises to 130° , and then remains constant for some time, while a brisk evolution of carbon dioxide takes place; the evolution then begins to slacken, and the temperature again rises slowly till 195° is reached. The collecting flask is then changed and the heating continued; at 205° – 210° the evolution of gas recommences, owing to the decomposition represented in the above equation; the retort is then heated carefully so that a temperature of 220° – 230° is maintained as long as possible; finally, when the temperature reaches 260° , the heating is stopped. The residue in the flask contains an excess of glycerol, which can be made to react with a further quantity of oxalic acid. Add 30 more grams of oxalic acid and repeat the above process.

The distillate contains allyl alcohol and water, with some allyl formate, acrolein, and glycerol; it is again distilled till a portion of the distillate gives no separation of allyl alcohol as oily drops, when solid potassium carbonate is added. The whole distillate is then shaken with solid potassium carbonate, and the allyl alcohol thus salted out is separated off and redistilled, when it comes over at 92° – 96° .²

Further purification of the distillate need not be carried out. Yield c. 15 grams.

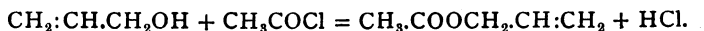
Allyl alcohol is a pungent, colourless liquid, with a burning taste (boiling point 96°). It is soluble in water in all proportions, and can be "salted out" from such solutions by the addition of potassium carbonate. It is typical of the *unsaturated* compounds, and, as such, answers to the following tests:—

1. *Bromine water* is instantly decolourized when added drop by drop to allyl alcohol.
2. Reduces cold *alkaline permanganate*. (Dilute a solution of potassium permanganate until transparent, and then make alkaline with a little sodium carbonate solution.)

¹ The ammonium chloride is added to decompose any traces of potassium oxalate which may be present in the commercial oxalic acid.

² The allyl alcohol so prepared still contains a small quantity of acrolein and water; the first of these is removed by allowing to stand over solid potash and redistilling; the water is removed from this distillate by treatment with anhydrous baryta.

As an alcohol it forms esters. Add *acetyl chloride* in excess to a little of the alcohol, and then add water to destroy the excess of acetyl chloride. The fragrant odour of allyl acetate will be noticed.



GLYCEROL (GLYCERINE),

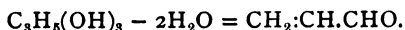


Glycerol is a colourless, inodorous, syrupy liquid, with a sweet taste. It is miscible with water and alcohol in all proportions, but is insoluble in ether. The anhydrous liquid boils, without decomposition, at 290° , but since glycerol is very hygroscopic it generally contains water, and then boils with decomposition. It is combustible, burning with a luminous flame and leaving no residue.

NOTE.—A solution of glycerol should be concentrated on the water-bath before carrying out tests 1–3.

1. On being heated alone, no blackening takes place if the glycerol is pure ; irritating fumes are evolved.

2. When mixed with cold, *strong sulphuric acid* there is no apparent change. On heating the mixture, blackening takes place, and irritating fumes of acrolein are evolved.



3. When heated with powdered *potassium hydrogen sulphate*, acrolein is evolved, and a slight darkening in colour takes place.

4. On soaking a *borax bead* in a solution of glycerol, and then heating in the bunsen flame, a green coloration is produced.

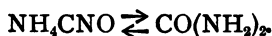
5. A solution of *borax* is alkaline, because of hydrolysis, and consequently gives a pink colour with phenol phthalein. On carefully adding a solution of glycerol—which should be neutral—to a one per cent. solution of borax, which has been coloured pink by the addition of phenol phthalein, the pink colour of the latter is destroyed. The pink colour reappears on warming, but disappears again on cooling.

NOTE.—Ammonium salts also cause the disappearance of the colour, but it does not reappear on warming. Polyhydric alcohols also behave in the same way as glycerol.

Urea or Carbamide, $\text{CO}(\text{NH}_2)_2$.

When ammonium cyanate is dissolved in water, it undergoes isomeric change into urea, the process going on until equilibrium is reached (see p. 62). However, if the solution is evaporated, the less soluble urea begins to separate out first, thus causing the remaining mixture in solution to contain a lower percentage

of urea than previously. Consequently, the equilibrium is disturbed and more cyanate changes to urea. The urea continues to separate, and so the action proceeds, till, finally, all the solvent has disappeared and only urea remains.



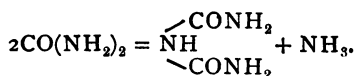
Method.—The usual method is to mix aqueous solutions of potassium cyanate and ammonium sulphate and evaporate to dryness. The urea is then extracted by alcohol.

Place in a steam oven 115 grams of finely powdered potassium ferrocyanide, and leave there till all the water of crystallization has been driven off and 100 grams of anhydrous solid remain. Mix this intimately with 75 grams of finely powdered potassium bichromate by grinding well in a mortar. Drop about 5 grams of this mixture into an iron tray, and heat carefully till the mixture first glows and forms a porous black mass; then add the remainder of the mixture in quantities of about 5 grams, allowing each instalment to char before adding the next. When all has been treated in this way, allow to cool, and extract the potassium cyanate from the mixture by boiling several times with 80 per cent. alcohol under reflux condenser; the combined alcoholic solutions, on cooling, deposit crystals of potassium cyanate, which should be dried between filter-paper.

Dissolve 25 grams of the potassium cyanate in 100 c.c. of water, and add a concentrated solution of 25 grams of ammonium sulphate; evaporate the mixture to dryness on a water-bath, breaking any crust that forms on the surface. Powder the residue, and extract it several times with boiling alcohol (using a reflux condenser), till a drop of the extract, on evaporation on a watch-glass, leaves very little residue. Then take the combined alcoholic extracts, boil off most of the alcohol, and pour the remainder into a small beaker to crystallize. The urea separates in long, colourless prisms. Yield c. 20 grams.

Urea is readily soluble in water or alcohol, but nearly insoluble in ether; melting point 132°.

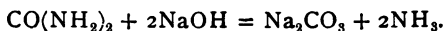
1. Heat urea carefully in a test-tube until it melts and ammonia can be readily detected at the mouth of the tube. Biuret is formed, together with a slight sublimate.



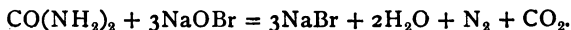
Allow to cool, dissolve the residue in a little water, and add *caustic soda* solution. Then add a dilute solution of *copper sulphate*, drop by drop, to the contents of the test-tube, which first turn red, then violet, and finally purple in colour. (*Biuret reaction*.)

If urea is strongly heated it is converted into cyanuric acid, which forms a sublimate on the sides of the test-tube. The final residue is inappreciable and there is no blackening.

2. *Caustic soda*, or *soda-lime*, liberates ammonia from urea, on heating.

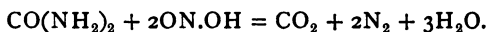


3. To a solution of urea add a solution of *sodium hypobromite* (freshly prepared from bromine and excess of caustic soda solution); nitrogen is evolved with effervescence.



The carbon dioxide is absorbed by the excess of caustic soda.

4. Acidify a solution of urea with *dilute sulphuric acid* and add *sodium nitrite*. There is a vigorous effervescence, due to the liberation of nitrogen and carbon dioxide.

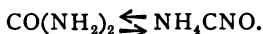


NOTE.—This is only a particular case of the action of nitrous acid on the $-\text{NH}_2$ group.

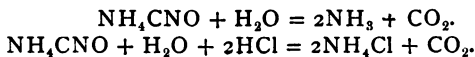
5. Urea is a mon-acid base. The nitrate and oxalate are readily produced by mixing a concentrated solution of urea with strong nitric acid and a strong solution of oxalic acid respectively. The salts are deposited as crystalline precipitates; they have the composition $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ and $2\text{CO}(\text{NH}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ respectively.

6. Aqueous solutions of urea are decomposed on boiling for some time; the decomposition is accelerated by the presence of dilute mineral acids.

A solution of urea really consists of urea and ammonium cyanate in equilibrium. (A tenth normal solution at 100° contains about 5 per cent. of cyanate.)



On boiling, the ammonium cyanate is gradually decomposed, thus disturbing the equilibrium, to restore which more urea transforms into cyanate, and so on. Finally all the urea disappears.



CHAPTER V

HYDROCYANIC ACID (PRUSSIC ACID)

HCN

THE anhydrous acid is a colourless liquid which boils at 26° . It is generally met with in aqueous solution, which smells of bitter almonds, and is only feebly acid. On exposure to light the solution decomposes, with the formation of ammonium formate (among other soluble compounds) and a brown deposit.

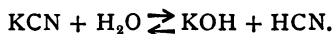
The cyanides of the alkalis, alkaline earths, and mercury are soluble in water; other cyanides are insoluble in water, but many of them are soluble in a solution of potassium cyanide, with the formation of complex cyanides.

The alkali cyanides, if dry, are not decomposed by heat; when moist, partial decomposition takes place, with evolution of ammonia and hydrocyanic acid. All others are decomposed, but no blackening takes place. The cyanides of silver and mercury yield cyanogen, $(\text{CN})_2$, which burns with a peach-blossom coloured flame.

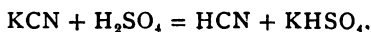
1. All cyanides, on being ignited with a *caustic alkali* or *soda-lime*, evolve their nitrogen as ammonia.

2. *Dilute sulphuric* (or *hydrochloric*) *acid* liberates hydrocyanic acid from cyanides, which may be recognized by the smell of bitter almonds.

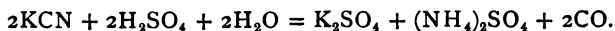
NOTE.—*Hydrocyanic acid is very poisonous*, so that this test should be carried out very cautiously. The student may safely learn what the smell of the free acid is like by smelling a solution of potassium cyanide in water. Hydrocyanic acid is such a weak acid that its salts are hydrolyzed in aqueous solution, with the consequent formation of a small amount of the free acid.



Cyanides nearly always contain carbonate (due to the action of the carbon dioxide and moisture of the air on the salt), so that the addition of the dilute acid generally causes effervescence at first, due to the escape of carbon dioxide.

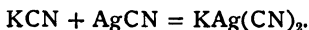


3. On warming a cyanide with *strong sulphuric acid* the nitrogen is all converted into ammonium sulphate, and carbon monoxide is evolved.

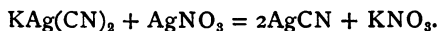


4. *Silver nitrate*, when added in excess to the solution of a cyanide, gives a white, curdy precipitate of silver cyanide, which is soluble in ammonia and potassium cyanide, but insoluble in nitric acid.

Add silver nitrate, drop by drop, to a solution of potassium cyanide. Each drop gives rise to a white precipitate, which dissolves on shaking up the contents of the test-tube. This is because of the formation of a soluble complex cyanide of potassium and silver.



When the formation of this compound is complete, the further addition of silver nitrate causes the precipitation of silver cyanide, according to the equation—

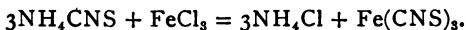


Silver cyanide resembles silver chloride very closely in appearance, but can be distinguished from it by the action of heat: cyanogen is evolved and metallic silver left. (Dissolve the residue after ignition in nitric acid, and add hydrochloric acid: precipitate of chloride indicates a cyanide.) It is also decomposed by prolonged boiling with concentrated nitric acid.

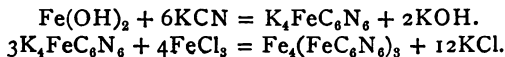
5. Place a small piece of the solid cyanide (or a little of the solution) in a small beaker or evaporating dish, and add a few drops of dilute *hydrochloric* or *sulphuric acid*. Rinse out another slightly larger evaporating dish with a solution of *yellow ammonium sulphide*, and invert it over the dish containing the cyanide. Allow to stand for a few minutes, warming very gently. The hydrocyanic acid evolved from the cyanide is absorbed, and transforms the yellow ammonium sulphide into ammonium thiocyanate.



Remove the upper evaporating dish, add a few drops of *dilute hydrochloric acid* and one drop of *ferric chloride* solution. A blood-red colour is produced, because of the thiocyanate formed.



6. Add *sodium* or *potassium hydroxide* and *ferrous sulphate* to the cyanide solution, and boil. Then add *ferric chloride*, and acidify with hydrochloric acid. Prussian blue is produced.



If you are at all doubtful whether Prussian blue has been formed, filter the contents of the test-tube. The least trace of Prussian blue will show itself on the filter-paper.

SPECIAL NOTE.—Mercuric cyanide does not respond to the ordinary tests for cyanides. The mercury must first be got rid of by means of sulphuretted hydrogen.

HYDROFERROCYANIC ACID,

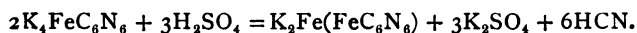


The free acid is obtained as a white precipitate by the addition of strong hydrochloric acid to a concentrated solution of potassium ferrocyanide. It is not very stable, rapidly oxidizing in the air, with the formation of Prussian blue. The most important salt is ferrocyanide of potassium, which is also known as yellow prussiate of potash, because of its yellow colour. It crystallizes with three molecules of water of crystallization. It is noteworthy that the iron in the ferrocyanogen radicle (or anion) is not precipitated by the ordinary reagents for ferrous salts, *e.g.* by ammonium hydroxide. The reason for this is that the ferrocyanogen anion ($\text{FeC}_6\text{N}_6^{4-}$) is a typical complex ion; it is very stable in solution, with the result that no ferrous ions (Fe^{2+}) are formed from it, and since the ordinary wet tests for ferrous salts are tests for ferrous ions, it follows that ferrocyanides do not respond to such tests.¹

The ferrocyanides of the alkali metals are soluble in water; those of the heavy metals are insoluble in water and dilute acids.

1. All ferrocyanides are decomposed by heat; no blackening takes place. The gases evolved depend on whether the solid is anhydrous or not; when not quite anhydrous, the smell of ammonia and hydrocyanic acid may be noticed.

2. On heating with *dilute sulphuric acid*, hydrocyanic acid is evolved.



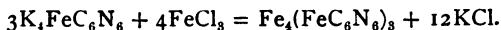
3. *Concentrated sulphuric acid*, under the action of heat, liberates carbon monoxide from ferrocyanides. All the nitrogen is transformed into ammonium sulphate.



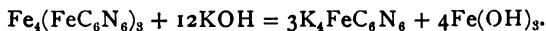
4. *Ferric chloride* gives a precipitate of Prussian blue with solutions of ferrocyanides. If the solutions, both of the ferric salt and of the

¹ For further information on the application of the theory of electrolytic dissociation to qualitative analysis the student is referred to any good modern text-book on inorganic chemistry.

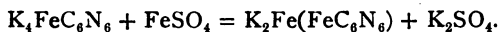
ferrocyanide, are very dilute, the Prussian blue will not be precipitated, but will remain in colloidal solution.



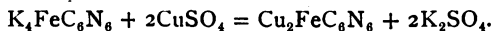
The precipitate is insoluble in dilute mineral acids, but it dissolves in *oxalic acid*, with the formation of a dark blue solution. It is decomposed by *caustic alkalis*, ferric hydroxide being precipitated, and potassium ferrocyanide (if caustic potash is used) remaining in solution.



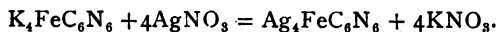
5. *Ferrous sulphate*, if quite free from ferric compounds, gives a white precipitate of potassium ferrous ferrocyanide, which rapidly oxidizes and turns blue. Usually the precipitate is light blue when first obtained, but it rapidly darkens.



6. *Copper sulphate* gives a chocolate brown precipitate of copper ferrocyanide, which is insoluble in dilute acids and decomposed by alkalis.



7. *Silver nitrate* gives a white precipitate of silver ferrocyanide, which is insoluble in ammonia and in nitric acid.



HYDROFERRICYANIC ACID,



The commonest salt is potassium ferricyanide, $K_3FeC_6N_6$, or red prussiate of potash. The alkali ferricyanides are soluble in water; those of the heavy metals are insoluble in water and dilute acids. The ferricyanides, like the ferrocyanides, are stable complex salts, and do not respond to the ordinary tests for ferric salts.

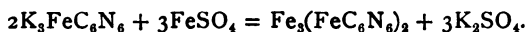
For the tests, make a fresh solution of potassium ferricyanide since the solution is slowly decomposed on exposure to light. The crystals used should first be washed, to free them from any superficial decomposition products.

1. All ferricyanides are decomposed by heat (*vide* test 1 for hydroferricyanic acid).

2. *Concentrated sulphuric acid*, on heating, liberates carbon monoxide from ferricyanides, the action being similar to that with ferrocyanides.

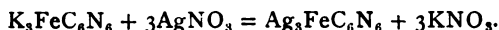
3. *Ferric chloride* produces a brown coloration but no precipitate, since the ferric ferricyanide formed is soluble in water.

4. *Ferrous sulphate* gives a dark blue precipitate of ferrous ferricyanide, or Turnbull's blue, which resembles Prussian blue in appearance. It is insoluble in dilute acids, including oxalic, but is decomposed by caustic alkalies.



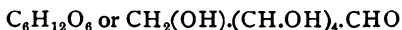
5. *Copper sulphate* gives a dirty greenish-yellow precipitate of copper ferricyanide, insoluble in hydrochloric acid.

6. *Silver nitrate* gives an orange-coloured precipitate of silver ferricyanide, which is insoluble in nitric acid, but readily soluble in ammonia.



CHAPTER VI

GRAPE SUGAR, GLUCOSE, OR DEXTROSE



DEXTROSE is readily soluble in water, crystallizing from the solution in granular masses which contain one molecule of water of crystallization. The solution possesses a sweet taste, but not so sweet as that of cane sugar. It is dextro-rotatory.

1. Heated in a dry test-tube, ordinary dextrose (containing one molecule of water of crystallization) melts at 86° , gives off water, and gradually blackens because of the liberation of carbon. A pungent odour of burnt sugar is emitted.

NOTE.—The anhydrous compound, which is obtained by crystallization from absolute alcohol, melts at 146° .

2. On adding *strong sulphuric acid* to dextrose there is no charring in the cold. On heating, a yellow colour is produced, which gradually darkens if the heating is prolonged. If the dextrose is impure (ordinary commercial), charring takes place.

3. On heating with *caustic soda* or *potash* the solution becomes dark brown (*cf.* cane sugar).

4. To a solution of dextrose add a little *copper sulphate* solution, and then excess of *caustic soda*. A deep blue solution results, copper hydrate not being precipitated. On warming the solution the glucose reduces the cupric salt and a precipitate of cuprous oxide is obtained. This precipitate generally comes down first as the *unstable yellow* modification, but it afterwards changes into the *stable red* form.

Similar results are obtained if *Fehling's solution* is added to a solution of dextrose, and the mixture warmed. (Distinction from cane sugar.)

5. Add *copper acetate* and a few drops of *acetic acid* (Barfoed's solution) to a solution of dextrose, and warm. Cuprous oxide is precipitated. (Distinction from cane sugar.)

6. *Ammoniacal silver nitrate* is reduced by dextrose, with the formation of a silver mirror. The test must be carried out in the same way as indicated under tartaric acid.

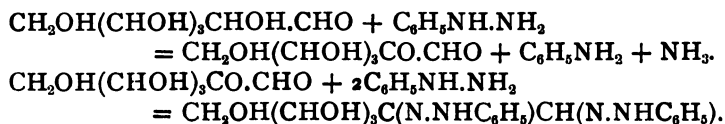
7. Dextrose yields an osazone, melting at 204° – 205° . (Distinction from cane sugar.)

Glucosazone, $C_6H_5(OH)_4.C(N.NHC_6H_5).CH(N.NHC_6H_5)$.

Aldehydes and ketones react with phenylhydrazine, giving phenylhydrazones, *e.g.* acetaldehyde gives acetaldehyde phenylhydrazone.



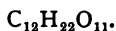
The six carbon atom sugars, *i.e.* the hexoses, which are either aldehydes or ketones, also form phenylhydrazones (easily soluble in water), but the action very easily proceeds further. The phenylhydrazine oxidizes the alcoholic group next to the carbonyl to a second carbonyl group, and so a body is formed containing two adjacent $-CO$ groups at the end of the chain; this so-called "osone" immediately condenses with two molecules of phenylhydrazine, giving an "osazone." These osazones give very valuable aid in the identification of the sugars, since they are crystalline bodies, and easily purified.



From the above equations it is evident that one molecule of a hexose requires three molecules of phenylhydrazine; therefore the relative weights of hexose and phenylhydrazine are 5 : 9.

Dissolve 2 grams of glucose in 10 c.c. of water, and add a solution of 4 grams of phenylhydrazine + 4 grams of glacial acetic acid in another 10 c.c. of water.¹ Heat the mixture in a wide test-tube on the water-bath for $1\frac{1}{2}$ hours, when the osazone slowly separates out. Filter off the precipitate, wash with water, then with a little alcohol, and drain well; recrystallize from alcohol. The glucosazone should be obtained in golden yellow needles, of melting point 204° . (The heating for the melting point determination should be performed rather rapidly, as the osazone decomposes near its melting point.) Yield *c.* 2 grams.

CANE SUGAR, SACCHAROSE, OR SUCROSE,



Cane sugar is very soluble in water, and crystallizes from the solution in large monoclinic prisms; it is only slightly soluble in

¹ If phenylhydrazine hydrochloride has to be used, proceed as above, but for the second solution take 4 grams of phenylhydrazine hydrochloride + 6 grams of sodium acetate in 15 c.c. of water.

alcohol. It melts at 160° , and on cooling gives a non-crystalline mass of "barley sugar." If heated to 200° it is converted into a dark mass, which is soluble in water, and known as "caramel." It is dextro-rotatory.

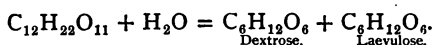
1. When heated in the dry state, cane sugar melts, blackens, and emits the characteristic odour of burnt sugar; a mass of charcoal is left behind.

2. *Strong sulphuric acid* rapidly chars cane sugar in the cold, carbon and sulphur dioxides being evolved.

On adding *strong sulphuric acid* to a concentrated solution of cane sugar, charring rapidly takes place; the mixture swells up (it may pour over the sides of the test-tube), and steam, sulphur dioxide, and carbon dioxide are evolved.

3. Solutions of cane sugar are not turned brown on being heated with *caustic soda*.

4. Cane sugar does not reduce an *alkaline copper solution* or *Fehling's solution* (*cf.* the fourth test for dextrose), although it gives a deep blue solution. If, however, the solution of cane sugar is first boiled for a short time with *dilute hydrochloric* or *sulphuric acid*, it is converted into a mixture of dextrose and laevulose, and the solution so obtained, after neutralization, will reduce the alkaline copper solution, or Fehling's solution. The mixture of dextrose and laevulose is known as "invert sugar," since it is laevo-rotatory, having a rotation of opposite sign to that of cane sugar.



5. *Barfoed's solution* is not reduced by cane sugar.

6. Cane sugar does not yield an osazone.

MILK SUGAR OR LACTOSE,



Milk sugar is much less soluble in water than cane sugar, and crystallizes from solution in the form of hard white prisms with one molecule of water of crystallization. It is insoluble in alcohol. The solution is not very sweet, and is dextro-rotatory.

1. On being heated in a dry tube, milk sugar blackens, emits the odour of burnt sugar, and leaves a mass of charcoal behind.

2. On adding *concentrated sulphuric acid* to milk sugar there is very little action in the cold. On warming, the solution becomes yellow, and then darkens in colour till it is finally black. Carbon dioxide and sulphur dioxide are evolved.

3. Milk sugar reduces an *alkaline copper solution*, or *Fehling's solution*, on warming, with the formation of a precipitate of cuprous

oxide. The reducing power is not so great as that of dextrose, consequently the reduction takes place much more slowly.

4. *Barfoed's solution* is reduced by milk sugar.

5. Milk sugar yields an osazone (melting point 200°).

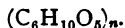
Distinction between Dextrose and Lactose.—It will be noticed that both dextrose and lactose respond to the tests which have so far been given, the only difference being that lactose is not such a strong reducing agent as dextrose. The solid sugars are readily distinguished from each other by their difference in solubility, dextrose being much more readily soluble than lactose. There is also a distinct difference in their taste, dextrose being decidedly sweet in comparison with lactose.

The following tests may also assist in their identification, but it should be pointed out that their reliability depends to a great extent on the concentrations of the sugar solutions used.

1. A solution of *bismuth nitrate*, to which *caustic soda* has been added until a precipitate has formed, gives a black precipitate of bismuth on boiling with *dextrose*, but with *lactose* there is only a slight darkening, and no precipitate, except after long heating.

2. To the sugar solution add a solution of *lead acetate*, and boil for a short time; then add *ammonium hydroxide* till a precipitate is just formed, and again boil. The white precipitate becomes a salmon-pink colour in the case of *dextrose*, and only a light yellowish-pink with *lactose*.

STARCH (*AMYLUM*),



Starch is a soft, white powder, which always contains a certain quantity of water. It is an organized body, as may be seen by examination under the microscope, which shows it to consist of round or oval granules, which have a peculiar striated appearance. The shape of the granules varies with the kind of starch. The smallest starch grains are those of rice; they are further characterized by being angular. Starch is insoluble in cold water, but on being boiled with water the granules burst, and their contents (the granulose) dissolve, giving a mucilaginous liquid, while the cell walls remain undissolved.

1. On being heated in a dry tube, starch chars, giving off water and combustible gases, and emitting an odour somewhat resembling that of burnt sugar.

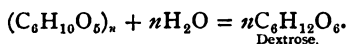
2. On being warmed with *strong sulphuric acid*, the mixture blackens, sulphur dioxide and carbon dioxide being evolved.

3. Mix a little starch into a paste with cold water. Pour boiling water on to this paste, and boil for a short time. Starch paste (the mucilaginous liquid referred to above) is thus produced. Add a little

iodine solution to some of the cold paste ; a deep blue coloration is produced (the so-called starch iodide). The colour is destroyed by boiling the liquid, but reappears on cooling.

4. If starch is boiled for a short time with *dilute sulphuric acid*, it is converted into dextrose. There are a number of intermediate products, the most important of which is dextrin, which gives a red colour with *iodine solution*. In order to detect the dextrin, the boiling with acid must only be continued for a very short time.

Both dextrin and dextrose reduce Fehling's solution, but dextrin will *not* reduce Barfoed's solution.



CHAPTER VII

Scheme for the Identification of a single substance contained in the following list (Stage I. Board of Education)¹:—

Methyl alcohol, ethyl alcohol, allyl alcohol, chloroform, iodoform, ethyl iodide, ethyl bromide, ethyl acetate, methyl oxalate, ethyl sulphuric acid, acetaldehyde, formaldehyde, acetone, acetic acid, chloracetic acids, formic acid, succinic acid, oxalic acid, tartaric acid, hydrocyanic acid, palmitic acid, methylamine and trimethylamine, methylammonium salts, acetamide, oxamide, acetonitrile, chloral hydrate, glycerol, urea, cane sugar, dextrose, lactose, starch, ferro- and ferri-cyanides.

The substances may be in a pure state or in aqueous solution, or, in the case of acids and bases, in the form of salts.

The difficulty of organic qualitative analysis lies in the fact that the *majority* of organic compounds are non-electrolytes, and as such do not enter into reactions with the same ease as inorganic compounds. In inorganic qualitative analysis we can always distinguish between bases and acids, and test for each independently. Organic analysis admits of no such simplification, but we follow up the same lines in so far as we devise typical reactions for different radicles.

A systematic course of procedure should be adopted in all cases; the method of "proof by exhaustion," *i.e.* testing for each compound separately until the list has been exhausted, is not systematic, has no educational value, and should never be resorted to.

A scheme of analysis which should, sooner or later, lead to the classification and identification of any of the commoner organic compounds is given on pp. 211-227; but a simpler scheme, and yet at the same time following the main lines of the larger

¹ See note on p. vi.

scheme, may be given to include those substances given in the Board of Education syllabus, as detailed above.

Method of Procedure.—A number of preliminary tests are made for the purpose of a rough classification. These tests should be carried out very carefully, since a mistake in any one of them may throw the student completely off the track.

After the substance has been classified, a special method of treatment is adopted which should lead to an idea of what the compound really is; the characteristic reactions may then be applied in order to confirm the conclusions arrived at.

Among the properties which should be specially studied are—

1. *Physical.*—Odour, colour, crystalline form, solubility, boiling point, melting point.

2. *Chemical.*—Special colour and precipitation reactions. Formation of derivatives and their characterization by melting point and boiling point determinations (solid derivatives are preferable, since they are more easily obtained pure).

Preliminary Tests.—*Colour.*—The only coloured substances are: Iodoform, ferro- and ferri-cyanides (the ferrocyanides of Zn, Pb, Ag, and Hg are white), salts containing metals such as Cu, Fe, etc.

State of Aggregation.—*Liquid.*—May be an aqueous solution, or, in the case of pure compounds, it may consist of alcohols (including glycerol), aldehydes, acetone, formic and dichloroacetic acids, glacial acetic acid (if temperature above 17°), acetonitrile, ethyl iodide, ethyl bromide, esters (except methyl oxalate), chloroform. *Solid.*—Salts of acids or bases, acids not mentioned above, amides, sugars, starch, methyl oxalate, iodoform, chloral hydrate.

Odour.—*Liquids with characteristic odour.*—All liquids mentioned above, with the exception of glycerol. *Solids with characteristic odour.*—Iodoform, acetamide, chloral hydrate, glacial acetic acid, (potassium cyanide), mono and trichloroacetic acids (on warming).

EXAMINATION OF A LIQUID.

The liquid may be either the pure compound, or it may be an aqueous solution; it is necessary to decide which, straight away. *If the liquid has no odour it is probably an aqueous solution*, since nearly all organic liquids possess an odour.

A. Solubility in Water.—The solubility of a liquid in water is easily tested by shaking it up with an *equal bulk* of water. If a homogeneous mixture is obtained, *i.e.* if there is no formation of an emulsion, or no separation into two layers on standing, the liquid is soluble.

1. Insoluble Liquid.—Ethyl bromide, ethyl iodide, chloroform, ethyl acetate. The odour gives a valuable indication in each case. *Test for the elements*—

| | |
|--------------------|-------------------------|
| Chlorine indicates | <i>Chloroform.</i> |
| Bromine | „ <i>Ethyl bromide.</i> |
| Iodine | „ <i>Ethyl iodide.</i> |

Apply confirmatory tests in each case, and take the boiling point. Remember that chloroform is non-inflammable, and that all three liquids are heavier than water.

No halogen indicates *ethyl acetate*. Confirm by saponification. Ethyl acetate is lighter than water.

2. Soluble Liquid.—May be a pure compound or an aqueous solution. The following liquids are soluble: alcohols (including glycerol), aldehydes, acetone, acetonitrile, formic acid, dichloroacetic acid, ethyl sulphuric acid. Proceed as under.

B. Test with Litmus.—**1. Acid reaction.**—May be due to an acid, or to the hydrolysis of a salt of a weak base in solution.

(a) *Salt of weak base.*—These may be divided into three classes: (a) The salts of the metals which give insoluble hydroxides (*e.g.* aluminium) are distinctly acid in solution. (Silver salts form an exception.) (β) The salts of ammonium, methylamine, and trimethylamine have only a *very slight* acid reaction in solution; in fact, it is scarcely appreciable. (γ) Salts of urea are hydrolyzed to a great extent, and give strongly acid solutions. On the addition of caustic potash the compounds in class (a) will give a precipitate of the hydroxide of the metal, which may be soluble in excess. If no such precipitate is obtained, warm gently: the amines may be distinguished by their smell and inflammability; ammonia may come either from ammonium salts or from salts of urea, which may be readily distinguished from each other by adding a pinch of NaHCO_3 to the original liquid. CO_2 will be evolved with effervescence from the solution of the urea salt. This, however, would not distinguish the urea salt from a free acid; to do this, make alkaline with caustic soda, and add

a solution of sodium hypobromite; nitrogen will be evolved from the urea (also from the ammonium salts; but these have been distinguished by NaHCO_3).¹

(b) *An acid*.—If the substance is not included under (a) it must be a free acid. The smell of volatile acids such as formic and acetic disappears on neutralization.

Neutralize and evaporate to dryness as above. Examine solid residue as on p. 83.

2. Alkaline Reaction.—May be due to a free base or to the hydrolysis of the salt of a weak acid.

(a) *Free base* indicated by the smell. Ammonia, methylamine, and trimethylamine. Heat, and test inflammability of the vapour.

(b) *Salt of weak acid*.—Evaporate to dryness on a water-bath, and test residue as on p. 78 (Remember that the solution of a cyanide smells of HCN .)

C. If the liquid is **neutral**, to a portion of it add an equal bulk of *anhydrous potassium carbonate*, and shake well. The alcohols, acetone, ethyl acetate (soluble in 17 parts of water), and acetonitrile are “salted out” from aqueous solutions in this manner, and form a distinct layer on the surface of the carbonate solution. Separate off the liquid and apply the appropriate tests given under F, first testing for nitrogen to distinguish acetonitrile. Dry a little of the liquid with more potassium carbonate, and take the boiling point.

D. **Distil another portion of the liquid.** (At the same time commence E.) If the liquid is a pure compound it will distil over at a constant temperature² (note the boiling point); if it is an aqueous solution, the boiling point will gradually rise, and

¹ If the evidence points to a salt of urea, add an excess of solid K_2CO_3 and then absolute alcohol. Shake well. If the alcohol is not “salted out” add more carbonate. The alcoholic layer will contain some of the urea in solution. Separate, evaporate off the alcohol on a water bath, and carry out the biuret test for urea.

² It would be more correct to say that the *main portion* of the liquid will distil over at a constant temperature, since the temperatures at which the first and last portions distil will be affected by traces of impurities. Moreover, even if the liquid were quite pure, the first portion would appear to come over at a temperature lower than the true boiling point, owing to the heat used up in warming the thermometer (see p. 4).

from the temperatures at which the main portions come over, some indications of the substance may be obtained.

This test may be somewhat indefinite in the case of an aqueous solution of allyl alcohol, since allyl alcohol boils at 96° , but test C would already have indicated a solution in this case.

E. Evaporate a portion of the liquid down on the water-bath.

Solid residue.—Examine by methods given later, but remember that formaldehyde, which is recognizable by its odour, leaves a solid residue of paraformaldehyde. Test for formaldehyde as under F.

Syrupy residue: Neutral.—*Glycerol*. Apply the special tests. Acid.—*Dichloroacetic acid*; *sulphuric acid* from ethyl hydrogen sulphate. (*Acetic acid*; not syrupy, and distinguished by smell.) Test for acids, as given on p. 83.

Completely volatile.—Alcohols, acetaldehyde, acetone, acetonitrile, ethyl acetate, amines, formic acid, (acetic acid), hydrocyanic acid (not probable). In each case the smell gives a valuable indication.

F. Examination of completely volatile liquid.

(a) If acid, test for formic, acetic, and hydrocyanic acid as on pp. 17, 19, and 63.

NOTE.—A solution of hydrocyanic acid is practically neutral.

(β) **Methylamine** and **Trimethylamine** are immediately recognized by their odour. Distinguish between them, as given on p. 48.

Acetaldehyde (and Formaldehyde).—Apply Schiff's reaction; formation of a mirror with ammoniacal silver nitrate. Distinguish between formaldehyde and acetaldehyde by oxidation to formic and acetic acids respectively.

Acetone and Ethyl Alcohol.—Iodoform test. Then distinguish between the two, using ammonia and iodine instead of caustic soda and iodine; acetone! gives iodoform under these conditions. The odour is also distinctive. Other confirmatory tests as given on pp. 22 and 36.

Acetonitrile.—Digest with conc. HCl under reflux condenser until it disappears. Make alkaline with NaOH and warm— NH_3 evolved. Test residue in flask for acetate.

Reduced with Na in alcoholic solution, ethylamine is produced.

Ethyl Acetate.—Distil with caustic soda. Ethyl alcohol collects in the receiver and sodium acetate is left in the flask.

Allyl Alcohol.—Bromine water decolourized; also alkaline permanganate reduced. (Remember that aldehydes and acetone also decolourize alkaline permanganate, but these compounds have already been tested for.)

Methyl Alcohol.—Apply tests given on pp. 21–22. Also the formation of methyl salicylate on warming with salicylic acid and H_2SO_4 .

Examination of a Solid, or Solid Residue.

I. Ignite on Platinum foil until all carbon has been burnt off. Note odours evolved, and whether the substance chars with or without melting. A *residue* indicates the presence of—

(a) A salt of: a carboxylic acid, ethyl sulphuric acid, hydrocyanic acid, hydroferro- or hydroferri-cyanic acid.

Remember that ammonium salts are volatile, as also are mercury salts (after decomposition).

(b) A bisulphite compound of an aldehyde or acetone.

To the *residue* apply the following tests:—

(1) Flame test. Na, K, Ca, Sr, Ba.

(2) Action on litmus. Alkaline reaction from carbonates of alkali metals and oxides of alkaline earth metals.

(3) Test for a *sulphate*. Salt of ethyl sulphuric acid. N.B. Some sulphate may have been reduced to sulphite or sulphide.

(4) Test for a *sulphite*. If found, identify the aldehyde or ketone.¹ Set free the aldehyde or acetone by warming with Na_2CO_3 solution; note the odour. Try iodoform reaction for acetone and acetaldehyde, and distinguish between these two by distilling a little into a test-tube containing water, and testing with Schiff's reagent for aldehyde.

(5) Test for a *cyanide*. Cyanide, ferro- or ferri-cyanide. N.B. Certain cyanides are decomposed by heat.

¹ A sulphite may also result from the ignition of a salt of ethyl sulphuric acid (see (3)).

(6) Group tests for metals, if necessary.¹ Note if the residue is coloured or not.

In the case of negative evidence from (3) and (4), apply the tests for acids (p. 83), after doing the tests for elements (IV. A. and B.) in order to detect the chloracetic acids (halogen present), and cyanides, ferro- and ferri-cyanides (nitrogen and metal present).

II. Heat in a dry tube.

- | | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>(a) Charring and characteristic odour of burnt sugar.</p> <p>(b) Irritating vapours and sublimate. No, or only very slight, blackening.</p> <p>(c) Ammonia evolved.</p> <p>(d) Inflammable gas evolved, which burns with (1) a peach-blossom coloured flame, (2) a luminous flame.</p> <p>(e) Completely volatile.</p> | <p>Tartrates, sugars, starch.</p> <p>Succinate.</p> <p>Urea and cyanides. Oxamide.</p> <p>(1) Mercury and silver cyanides. (2) Salt of ethyl sulphuric acid; bisulphite compound of aldehydes or acetone.</p> <p>Excludes salts (except ammonium and mercury salts and salts of the amines).</p> |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

III. Heat with soda-lime.

- (a) Most nitrogen bodies evolve ammonia (see p. 8).
- (b) Carboxylic acids lose CO_2 and give the hydrocarbon, *e.g.* formates give hydrogen, acetates give methane, succinates give ethane.

IV. A. Test for the halogens with Cu wire test.

B. Test with sodium for the elements present.

Elements present (other than C, H, and O)—

Chlorine.—*Chloral hydrate.*—See VI. *d.* Then confirmatory tests, p. 39. *Hydrochloride of amine.*—See VI. and VII. *Chloroacetic acids.*—See acid tests, XII.

Iodine.—*Iodoform.*—Confirm (colour, odour, etc.).

Nitrogen.—Ammonium salts, amines, amides, cyanides, ferro-

¹ According to the syllabus, it is not necessary to detect the metallic radicles present.

and ferri-cyanides, nitrates (inorganic nitrates will not give NaCN). See VI. and VII.

Nitrogen and Halogen.—Halogen acid salt of an amine. See VI. and VII.

Sulphur.—Salt of ethyl sulphuric acid. Bisulphite compound of aldehyde or ketone (already found).

Nitrogen and Sulphur.—Sulphate or sulphite of an amine. See VI. and VII.

V. Test solubility in water.—The solubility of a solid is tested by shaking it up with water; if readily soluble it will pass into solution at ordinary temperatures. If it does not appear to dissolve, warm gently. If still in doubt, filter off from the solid (or decant), and evaporate a little of the clear liquid to dryness on the water-bath, using a watch glass to hold the liquid.

If the substance dissolves, test the solution with litmus, and proceed as on p. 75. It is easy to decide whether an acid reaction is due to the free acid, since salts, with the exception of ammonium and substituted ammonium salts, salts of mercury and urea, and methyl oxalate,² would leave a residue in test I. To test the reaction of a substance which is difficultly soluble, put a little of the solid on a strip of litmus-paper, moisten with water, and leave for a short time. Then wash off, and note the colour.

The *insoluble* bodies are : Iodoform (see IV. B); oxamide (see VII.); palmitic acid (melts on warming with water; *lighter* than water) (see VI. g); starch (gelatinizes on boiling); certain salts.

VI. Heat with concentrated caustic soda solution.

- | | |
|--------------------------------------------------------------------|------------------------------------------|
| (a) Ammonia evolved. | Ammonium salt, urea, acetamide, oxamide. |
| (b) Ammoniacal odour (very slightly fishy); inflammable gas. | Salt of methylamine. |
| (c) Fishy odour; inflammable gas. | Salt of trimethylamine. |

¹ Urea nitrate and oxalate are not very soluble; if their presence is inferred from the tests given on p. 79, the urea may be extracted from the suspension of the salt in water, without any difficulty, by the method given.

² Methyl oxalate is so readily hydrolyzed in aqueous solution that the solution reacts acid and gives the reactions of oxalic acid. The methyl alcohol may be detected by distillation with caustic soda.

- | | |
|-----------------------------------------------------------------------------------------------|------------------------------------------------------|
| (d) Odour of chloroform. | Chloral hydrate ; trichloro- acetic acid or salt. |
| (e) Alcoholic odour. | Methyl oxalate. ¹ |
| (f) Solution turns brown. | Glucose ; lactose. |
| (g) Dissolves without evolution of gas ; reprecipitated by the addition of hydrochloric acid. | Palmitic acid. |
| (h) Resin formed. | Aldehyde bisulphite compound. |

VII. Classification of compounds containing nitrogen.

—These are ammonium salts, salts of the amines, amides, and cyanides. The amines have already been detected by their odour, and the cyanides are distinguished by the fact that besides nitrogen they also contain a metal ; they have already been indicated in I. 5, II., III., IV. B. In this latter case, test straight away for cyanides, ferro- and ferri-cyanides, after doing VIII. and X., remembering that silver and mercury cyanides require special treatment, but indications of their presence have been obtained in II. d.

It only remains to distinguish between ammonium salts, and amides—oxamide, acetamide, and urea.

(a) *Urea* is tested for specially by means of the biuret reaction.

(b) Heat with a solution of caustic soda until all the ammonia has been driven off. Neutralize the excess of caustic soda and test the solution for—

Oxalic Acid.—Presence indicates *oxamide* or *ammonium oxalate*. The former is insoluble, the latter is soluble in water.

Acetic Acid.—Presence indicates *acetamide* or *ammonium acetate*. The former is distinguishable by its odour, and also by its melting point (82°).

If an ammonium salt is found, proceed with the acid tests.

VIII. Heat with dilute sulphuric acid.

- (a) The substance is
soluble in water, but

¹ One would expect a salt of ethyl sulphuric acid to act in the same manner, but in this connection see p. 24.

a precipitate is obtained on adding the acid. The precipitate melts on warming.

- | | |
|------------------------------|-----------------------------------------------|
| (b) Smell of vinegar. | Formate, acetate. |
| (c) Odour of bitter almonds. | Cyanide, ferro- and ferricyanides. |
| (d) Odour of an alcohol. | Methyl oxalate; salt of ethyl sulphuric acid. |

IX. Solid and concentrated sulphuric acid.—Grind with pestle in a mortar. Characteristic odours of *formic* and *acetic* acids.

X. Add cold conc. sulphuric acid, and warm.

| IN COLD. | | ON WARMING. | |
|------------------|---------------------|--------------------------------------------------------------------------------------------|---------------------------------------|
| No charring. | No charring. | Odour of vinegar. | Acetates and chloracetates. |
| | | CO evolved. | Formate. |
| | | CO evolved and liquid becomes turbid. | Ferrocyanide. |
| | | CO and CO ₂ evolved. | Oxalate. |
| | | HCN evolved. | Cyanide. |
| | | HCN and later CO and white ppt. | Ferricyanide. |
| No charring. | Slowly darkens. | Irritating acid fumes. | Succinate. |
| No charring. | Chars. | Fragrant smell, ethylene evolved (burns with a luminous flame), and then SO ₂ . | Ethyl sulphate. |
| Yellow solution. | Gradual charring. | CO ₂ and SO ₂ evolved. | Dextrose, lactose, starch, tartrates. |
| Chars. | Chars very rapidly. | CO ₂ and SO ₂ evolved. Odour of burnt sugar. | Cane sugar. |

It now remains for the student to distinguish between the acids and the sugars, together with starch and methyl oxalate.

Starch should have already been detected by the fact that it is

insoluble in cold water, but gelatinizes with hot water. It does not melt on Pt. foil. Confirm.

Methyl Oxalate.—Indications of the presence of this compound should have been found by V., VI. c, and VIII. d. The aqueous solution will give the ordinary tests for oxalic acid. Distil with caustic soda and test for methyl alcohol in the distillate. Confirm by melting point, and by formation of oxamide with concentrated ammonia.

XI. Sugars.

Cane Sugar is immediately distinguished from dextrose and lactose by the fact that it does not reduce Fehling's solution unless it has previously been inverted by acids.

Dextrose and Lactose are distinguished as given on p. 71.

XII. Acids.

Ethyl Sulphuric Acid has been detected by E, I. 3, II. d, IV. B, VIII. d, and X. Confirm by adding HCl and BaCl₂. There is no precipitate in the cold, but on boiling, a white precipitate of BaSO₄ is formed. Also digest with 10 per cent. NaOH under reflux and then distil one-third. Test distillate for alcohol and residue for sulphate.

Chloroacetic Acids already detected by E, IV., VIII., and X. Do confirmatory tests.

Cyanides, Ferro- and Ferri-cyanides.—Distinguished from the other acids by the fact that the salts contain nitrogen as well as a metal (p. 81). Indications of their presence have been obtained by I. 5, II. c, IV. B, VIII., and X.

In the case of soluble salts these acids are readily distinguished by the action of silver nitrate, ferric chloride, and ferrous sulphate. (Silver and mercury cyanides have to be tested for separately. See pp. 64-65.)

Silver Nitrate.

| | |
|-------------------------------------------|------------------------|
| White precipitate, insol. in nitric acid. | Cyanide, Ferrocyanide. |
|-------------------------------------------|------------------------|

| | |
|--------------------------------------------|---------------|
| Orange precipitate, insol. in nitric acid. | Ferricyanide. |
|--------------------------------------------|---------------|

Ferric Chloride.

| | |
|----------------|---------------|
| Prussian blue. | Ferrocyanide. |
|----------------|---------------|

Ferrous Sulphate.

| | |
|------------------|---------------|
| Turnbull's blue. | Ferricyanide. |
|------------------|---------------|

TREATMENT OF INSOLUBLE CYANIDES, FERRO- AND FERRI-CYANIDES.

All the simple cyanides are decomposed on boiling with concentrated HCl into metallic chlorides and hydrocyanic acid. (Silver cyanide gives AgCl on boiling with aqua regia.)

All insoluble ferro- and ferri-cyanides may be decomposed by boiling with a strong solution of caustic soda, then adding a little sodium carbonate and again boiling. The metals which give hydroxides insoluble in excess of alkali (Cu, Fe, etc.) will be precipitated as hydroxides, and sodium ferro- or ferri-cyanide will remain in solution. Filter, acidify the filtrate with hydrochloric acid, and test for ferro- and ferri-cyanides. Dissolve the hydroxide in hydrochloric acid and apply the usual group tests.

Ferro- and ferri-cyanides of Zn, Al, Pb, etc., will dissolve completely in the strong solution of caustic soda. To distinguish between ferro- and ferri-cyanide take some of this solution, add (1) ferric chloride, and acidify (a precipitate of Prussian blue indicates a ferrocyanide); (2) ferrous sulphate, and acidify (a precipitate of Turnbull's blue indicates a ferricyanide).

ACIDS CONTAINING ONLY C, H, AND O.

If the acids are present as salts of the alkali metals (including ammonium) the usual tests may be applied to the solutions. If present as free acids, first neutralize with sodium carbonate. In all other cases it is necessary to replace the metal by Na (or K) before the acid tests are carried out. In most cases this can be done by boiling the solution with excess of sodium carbonate and then filtering to remove the carbonate of the heavy metal. The filtrate is then made just acid to litmus-paper, by the addition of dilute nitric acid (boil to drive off CO₂), and then made neutral by the careful addition of dilute ammonia.

In some few cases, *e.g.* antimony in tartar emetic, sodium carbonate will not remove the metal. The method of procedure is then: dissolve the substance in HCl and pass in sulphuretted hydrogen. Filter off the sulphide of the metal, make the filtrate alkaline with ammonia, and again pass sulphuretted hydrogen. Filter from any precipitated sulphides, make filtrate acid with hydrochloric acid and boil to expel sulphuretted hydrogen. Then neutralize as above.¹

¹ Since the solution contains hydrochloric acid, the test with silver nitrate on p. 85 cannot be applied.

If the solution becomes too dilute during these processes it should be concentrated before carrying out the tests.

To the neutral solution add—

Calcium Chloride.

Immediate white precipitate, insoluble in acetic acid. Oxalate.

White precipitate, after shaking well; soluble in acetic acid. Tartrate.

Silver Nitrate.

White precipitate, turning black on warming. Formate.

White precipitate, soluble in nitric acid. Acetate, oxalate, tartrate.

Ferrie Chloride.

Red colour; brown precipitate of a basic salt, on warming. Formate, acetate.

Brown precipitate, partly soluble in ammonia. Filtrate gives a white precipitate with BaCl_2 and alcohol. Succinate.

In each case apply the usual confirmatory tests.

Palmitic Acid has already been detected by VI. *a*. Confirm by tests on p. 40.

PART II

CHAPTER VIII

PURIFICATION OF NINETY PER CENT. BENZENE BY REPEATED FRACTIONAL DISTILLATION

THE 50 per cent. and 90 per cent. benzene of commerce are mixtures of benzene with homologues, chiefly toluene, and also a little thiophene. The homologues all boil at a higher temperature than benzene; consequently, by repeated distillations performed in a proper manner, most of the benzene can be separated from the impurities, excepting thiophene. Fractionating columns (Fig. 17) are of great assistance in such distillations, because they cause an increased amount of condensation of the vapour, and so assist in keeping the higher boiling homologues behind in the flask while the benzene passes over. The fractionating column in its simplest form is a straight, wide glass tube, with obstacles at intervals to prevent the vapour making an unimpeded rush to the condenser.

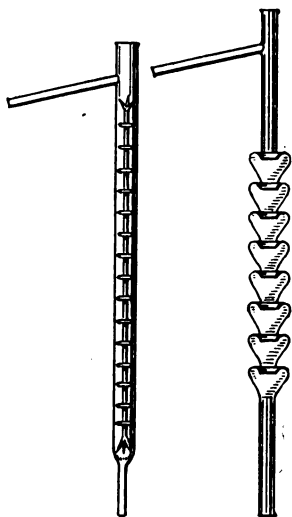


FIG. 17.

Place 200 c.c. of the 90 per cent. benzene in a flask (400 c.c.), fit the neck with a fractionating column, and attach to a double surface condenser. Boil the liquid in the flask over wire gauze at

such a rate that the distillate falls from the condenser in drops that can be easily counted. The thermometer reading should be noted continually, and the distillate coming over at different ranges of temperature should be collected in separate dry flasks or test-tubes; a suitable set of fractions to collect is: *a*, 79°–85°; *b*, 85°–90°; *c*, 90°–95°; *d*, 95°–100°; *e*, 100°–115°. The residue in the flask is rejected. By redistilling the above fractions it is intended to get as large a quantity as possible of fairly pure benzene, boiling at 79°–82°. To do this, place the first fraction *a* in the flask and redistil; the portion distilling below 79° can be discarded; as soon as the thermometer reading reaches 82°, add the second fraction *b* to the contents of the flask, and distil till the thermometer again reaches 82°; again add the fraction *c*, and distil till 82° is reached. Change the receiving vessel and label the distillate A. The remaining fractions contain so little benzene that practically nothing more will distil below 82°. To the residue in the flask add the fraction *d*, and boil till the temperature of the vapour reaches 100°, when the distillate obtained should be labelled B; add fraction *e* to the residue in the flask and distil, collecting separate fractions, 100°–108° (C) and 108°–113° (D).

The fraction A is redistilled; the part distilling between 80° and 81°, which should be collected separately, is almost pure benzene, but contains a trace of thiophene (C_4H_4S). To remove this thiophene, the benzene is mixed with one-tenth its volume of concentrated sulphuric acid, warmed in warm water, and shaken well; it is then separated off and shaken with a fresh quantity of sulphuric acid. After separating from the acid, the benzene is shaken with water to remove traces of acid, again separated, and then dried over fused calcium chloride. To obtain it quite pure it is frozen by placing it in a beaker and cooling by immersion in ice; any mother liquor remaining should be drained off, and the remaining crystals should be rapidly pressed between absorbent paper and then immediately returned to the beaker; the crystals are pure benzene, and the liquid obtained when they melt should be put in a stoppered bottle and labelled.

Pure benzene melts at 5·4°, and boils at 80·4°; it has a specific gravity of 0·883 at 15°.

The purity of the specimen obtained above should be tested by the boiling point and specific gravity. Also, when a crystal of isatine is

stirred into a mixture of a drop of the benzene with a drop of strong sulphuric acid on a glazed tile, no colour should be developed (showing absence of thiophene). Repeat this test with crude benzene, when a dark blue liquid is obtained (the "indophenin" test). A crystal of phenanthrenequinone mixed with crude benzene and sulphuric acid likewise gives a blue colour, which is not obtained with pure benzene.

Fractions B and C obtained above, consist of mixtures of benzene and toluene, which could be separated, if necessary, by still further repeated fractional distillations, but they may now be rejected. Fraction D consists chiefly of toluene. It is redistilled (still using the fractionating column), and the fraction from 109.5° – 110.5° collected separately; this is toluene containing a little methyl thiophene ($\text{CH}_3\text{C}_4\text{H}_3\text{S}$). The latter is removed by treatment with strong sulphuric acid, as with benzene, and after washing and drying, the pure toluene is redistilled. The boiling point of the pure liquid is 110.3° , and the specific gravity 0.870 at 15° .

Fractional Distillation under Reduced Pressure.—

In practical work substances often occur which could be conveniently purified by distillation, if it were not for the circumstance that they decompose to some extent at their normal boiling point. In such cases the distillation can frequently be successfully performed under reduced pressure, because then the temperature required is much lower. For such distillations the special apparatus necessary is a water-pump, thick-walled rubber tubing, a manometer, and a branched tube for collecting the fractions (see Fig. 18). For practice, a mixture of water with twice its volume of glycerol may be taken. Fill a distilling flask to about one-third with the mixture, fit the side tube into the neck of the branched tube, to each leg of which a small round flask is attached by means of a rubber bung, and attach the side arm of the branched tube to the pump and manometer by the rubber tubing. Fit the neck of the first distilling flask with a two-holed bung (N.B. As india-rubber bungs melt readily, corks must be used in cases where the temperature is likely to be high), carrying a thermometer which reaches just below the side tube, and a piece of ordinary glass tubing drawn to a capillary jet at the lower end, which reaches to the bottom of the flask. Start the pump working, and regulate the passage of air down the capillary tube by means of a short piece of rubber tube and a screw clip, so that a very fine stream of bubbles passes into the liquid; this stream of bubbles will greatly

facilitate the boiling and prevent bumping. For the distillation of liquids which are easily oxidized, it is obvious that the stream of air must be displaced by one of an inert gas. Place the flask in an oil-bath, and when the pressure reaches about 30 mm., begin to raise the temperature. The water begins to boil off at a very low temperature, and to some extent passes uncondensed straight to the pump, but most of it collects in one of the receiving flasks. When all the water has distilled, the temperature is further raised; a point is soon reached when distillation occurs at a

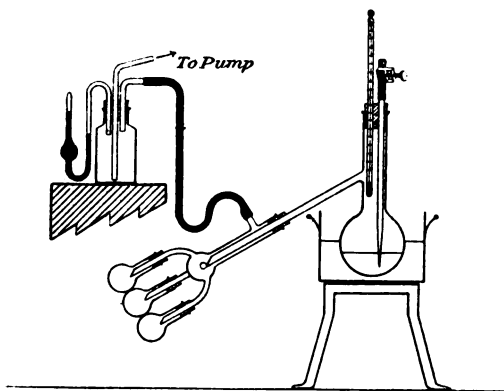


FIG. 18.

constant temperature.¹ The branched tube is then rotated so that a fresh flask receives the distillate, and the distillation is continued till the thermometer once more begins to rise in a marked manner. The constant boiling point and the pressure are both noted. Most of the liquid will now have distilled; the residue, on further heating, will give a third fraction, which should be collected in the third receiving flask. The middle fraction then contains pure glycerol; the other two contain more or less impurity, and should be rejected. The glycerol obtained should be colourless and have no pungent odour of acrolein.

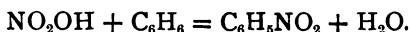
¹ In most vacuum distillations the boiling point of the main fraction of the distillate is so high that the side tube of the flask suffices for the condensation of the vapour, but if it is necessary, a small condenser jacket should be slipped over the side tube so that it may be continually cooled by a stream of cold water.

In all such distillations under reduced pressure the boiling point of the main fraction and the pressure registered by the manometer should be carefully noted.

Glycerol boils under 760 mm. at a temperature of 290° , at the same time undergoing a certain amount of decomposition; under a pressure of 12 mm. it boils without decomposition at 170° .

Nitrobenzene, $C_6H_5NO_2$.

The aromatic hydrocarbons differ in a very marked manner from the fatty hydrocarbons, in that they readily react with concentrated nitric acid giving nitro compounds; thus benzene gives nitrobenzene.



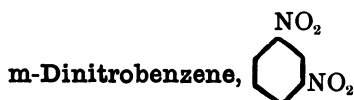
In the actual preparation of nitro compounds it has been found that the presence of sulphuric acid greatly aids the interaction, preventing side reactions, and increasing the yield very considerably, on account of its dehydrating action. In the preparation of nitrobenzene, the yield is also increased by using more than the theoretical quantity of nitric acid, but under these circumstances care has to be taken to prevent the temperature rising too high, or else comparatively large quantities of dinitrobenzene are also formed.

150 grams (80 c.c.) of concentrated sulphuric acid and 100 grams (70 c.c.) of concentrated nitric acid are carefully mixed in a flask and the mixture cooled by immersion in water. 50 grams (58 c.c.) of benzene are added to the cold mixture, in small portions at a time, shaking well after each addition. During this process a thermometer should be kept in the liquid, and the temperature kept constantly below 50° by judicious cooling in cold water. When all the benzene has been added, a vertical air condenser is fitted into the neck of the flask, and the latter is heated for an hour in a bath of water at 60° , shaking the flask from time to time.

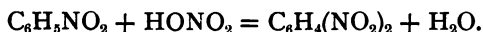
The contents of the flask are then poured into a large separating funnel, and water is added till the remaining acid mixture is so dilute that, on shaking, the nitrobenzene sinks to the bottom; the nitrobenzene is then separated from the acid mixture, and shaken in the funnel with an equal bulk of water; it is again

separated, and shaken with an equal bulk of dilute sodium carbonate solution; once more it is washed with water, then transferred to a flask, and dried by adding a few pieces of calcium chloride, and warming gently, till the liquid becomes clear. It is then carefully decanted into a distilling flask and distilled, using a straight glass tube as air condenser. The fraction distilling at 206° – 209° , which should constitute the chief part of the liquid, is the nitrobenzene. Yield *c.* 60 grams.

Pure nitrobenzene is a yellow liquid, of specific gravity 1.209 at 15° . It boils at 209° .



If benzene is allowed to react with a hot mixture of fuming nitric acid and concentrated sulphuric acid, meta dinitrobenzene is obtained, together with small quantities of the ortho and para dinitrobenzenes; the same result is obtained if nitrobenzene be treated in the same way, and in this case the product is purer.¹ To purify the crude product it is recrystallized from alcohol, in which the ortho and para bodies are more soluble than the meta, and so are removed.



A mixture of 44 grams (30 c.c.) of fuming nitric acid with 44 grams (24 c.c.) of concentrated sulphuric acid is taken in a flask, and 30 grams (25 c.c.) of nitrobenzene are added, and the whole well shaken; the flask and its contents are then heated on a boiling water-bath for half an hour, and then for the same time on a sand-bath, never allowing the mixture to reach its boiling point. At the end of this time a little of the liquid, on pouring into cold water, should set to a hard mass if the reaction is complete. When this is so, the contents of the flask are poured into a litre of water and stirred well. The separated dinitrobenzene is filtered off and dried. Yield *c.* 40 grams. One-third of the

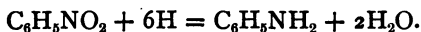
¹ It is useful to remember that the presence of any one of the groups NO_2 , CN , COOH , CHO in a benzene ring generally causes the next substituting group to enter in the meta position to the group originally present, while the presence of either Cl , Br , I , OH , or NH_2 causes the formation of a mixture of the ortho and para disubstituted derivatives in varying proportions.

product should be purified by recrystallization from alcohol; the remainder is reserved for the preparation of m-nitraniline.

m-Dinitrobenzene is solid, crystallizing in long yellow needles which melt at 90° and boil at 303° . It is insoluble in water.

Aniline, $C_6H_5NH_2$.

On reduction, nitro compounds yield amines; for the reduction of nitrobenzene as a laboratory experiment, the nascent hydrogen which is to act as reducing agent is usually obtained from tin or zinc and hydrochloric acid.



According to the equation, since 1 atomic weight of tin can produce 4 atomic weights of hydrogen (the tin forming first stannous and subsequently stannic chloride), 118 grams of tin will be capable of reducing 82 grams, or approximately two-thirds of its own weight, of nitrobenzene; a slight excess of tin, however, is generally used.

Into a 500 c.c. flask introduce 90 grams of granulated tin and add 50 grams (42 c.c.) of nitrobenzene. Fit the flask with a glass tube to act as a reflux condenser, pour in 20 c.c. of concentrated hydrochloric acid, and shake together till the mixture boils; the reaction should then be moderated by immersing the flask in cold water. When the boiling has ceased, add another 20 c.c. of hydrochloric acid, again shake, and when boiling occurs, again moderate the action. Proceed in this way till 200 c.c. of concentrated hydrochloric acid have been added. The air condenser is then removed and the flask is heated on a water-bath for an hour or so, till the odour of nitrobenzene has disappeared. Pour the liquid into a large flask (2 l. capacity), and rinse out the flask by the addition¹ of 100 c.c. of water. To the liquid in the large flask add gradually, shaking after each addition, a solution of 150 grams of caustic soda in 200 c.c. of water, cooling the flask if the mixture should begin to boil. Then steam-distil the contents of the flask through

¹ The mixture should not be allowed to cool down in the small flask as it crystallizes to a solid mass of a double salt of aniline hydrochloride and stannic chloride $(C_6H_5NH_2.HCl)_2SnCl_4$. If the experiment has to be interrupted this should be done immediately after the transference of the reaction product to the large flask; the addition of the caustic soda should be postponed till immediately before the steam distillation, so that the heat of neutralization may be utilized.

a condenser (see p. 58); the liberated aniline is carried over as vapour by the current of steam, and the distillate is a mixture of aniline with water. The distillate at first is milky and deposits aniline, but the later fractions are clear; since aniline is appreciably soluble in water the distillation is continued till approximately 200 c.c. of the clear distillate have been obtained. Transfer the whole of the distillate to a large separating funnel, add 20 grams of salt for each 100 c.c. of the distillate, and shake till the salt is dissolved (this lowers the solubility of the aniline in the water). Extract the aniline by shaking with ether, placing the ethereal extract in a clean flask; extract the residual aqueous liquid twice more with ether, and dry the combined extracts over a few fragments of caustic potash.

After drying several hours, decant the ethereal solution from the caustic potash into a small dropping funnel, fitted into the neck of a small distilling flask. Place the latter in a bath of warm water, run some of the ethereal solution into it, and distil off the ether through a double-surface condenser; as fast as the ether distils add more solution from the funnel, till all has been introduced; then slowly heat the water-bath to boiling. When nothing more distils, replace the water condenser by an air condenser, and fit a thermometer into the neck of the flask in place of the dropping funnel. Heat the flask over wire gauze, and collect separately that portion of the distillate which comes over at 180° – 184° . Yield c. 35 grams.

Aniline is a colourless liquid when pure, possessing a characteristic odour. It boils at 184° . The pure liquid becomes brown in colour on exposure to the air. It is only very slightly soluble in water, but readily soluble in alcohol and ether. It is volatile with steam. It is a mono-acid base, forming salts such as $C_6H_5NH_2 \cdot HCl$. These salts are decomposed by caustic soda, the free base separating as oily drops.

For the following tests, either the free base or its hydrochloride may be used.

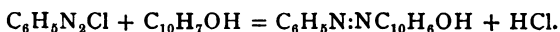
1. With dilute solutions (1 drop aniline to 30 c.c. water) of aniline or its salts, *bleaching powder* solution gives a violet coloration. (If a dirty violet precipitate is formed, the aniline solution was too strong.)

2. Add a solution of *sodium nitrite* to a cold solution of aniline in excess of *dilute hydrochloric acid*, until free nitrous acid is obtained (test with starch iodide paper), keeping the contents of the test-tube

cold by holding under the tap. A solution of diazo-benzene chloride is produced (*cf.* Chapter IX.).

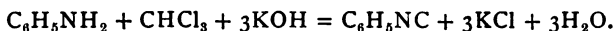


On pouring into *alkaline β-naphthol* (β-naphthol dissolved in caustic soda) a brilliant scarlet dye is produced, viz. benzene-azo-β-naphthol.



This reaction is generally spoken of as the *diazo-reaction*, and is always used for the detection of primary aromatic amines. The dyes produced are generally insoluble, unless they contain the sulphonic acid group, in which case a deep red solution is obtained.

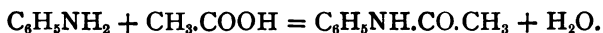
3. To an *alcoholic* solution of *caustic potash* add one or two drops of aniline and one drop of *chloroform*, and warm. The extremely unpleasant odour of phenyl isonitrile is produced (*cf.* chloroform).



4. To 5 drops of *concentrated sulphuric acid* (in a small porcelain dish) add 1 drop of aniline (by means of a glass rod). Remove the solid aniline sulphate from the rod by rubbing it on the sides of the dish. Then add 4 drops of an aqueous solution of *potassium bichromate*, and mix the contents of the dish by tilting it from side to side. After a short time the mixture becomes blue. If the colour does not appear, add two more drops of potassium bichromate, or gently warm the mixture for a very short time over a small flame.

Acetanilide, $\text{CH}_3\text{CO.NHC}_6\text{H}_5$.

Primary and secondary amines readily form acetyl derivatives on boiling with glacial acetic acid, acetic anhydride, or acetyl chloride (the two latter substances act more rapidly, but are more expensive). The reaction is of value in distinguishing primary and secondary from tertiary amines, which cannot be acetylated.



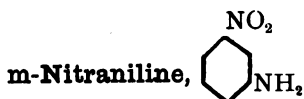
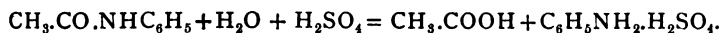
An excess of the acetylating agent is generally taken.

Mix 5 grams of aniline with 7 grams of glacial acetic acid, and boil gently in a small flask under reflux condenser for seven hours. Pour the hot liquid into 75 c.c. of cold water and stir, when acetanilide separates as a solid. Filter off the solid, transfer to a porcelain basin, add 200 c.c. of hot water, and heat to boiling with constant stirring; if the acetanilide does not completely dissolve, add a few c.c. of alcohol to aid the solution. Then filter the

solution while hot (see p. 11), and on cooling, the acetanilide crystallizes out in white plates. If the crystals are not quite colourless they should be re-dissolved in water, a little animal charcoal (approximately 1 gram) added, and the mixture boiled for half an hour. The charcoal should extract the colouring matter, and after filtering the hot solution, the acetanilide deposited should be pure white. The yield (c. 7 grams) is almost theoretical.

Acetanilide crystallizes in small white plates, melting at 112° ; it boils at 304° .

Hydrolysis.—Anilides are hydrolyzed by alkalies or acids (the latter, as a rule, acting more rapidly) into the corresponding aniline and acid. Take 2 grams of acetanilide and boil under a reflux condenser for half an hour with 50 c.c. of dilute sulphuric acid. The liquid will then have the odour of acetic acid, and if half of it be distilled off, the distillate will give the tests for the acid. The liquid remaining in the flask will contain aniline sulphate, and will therefore give the usual tests for aniline.



Reducing agents other than tin and hydrochloric acid are available for the reduction of nitro compounds, e.g. an alcoholic solution of ammonium sulphide is often used. This reducing agent has the special advantage that in substances containing more than one nitro group, only one group is, as a rule, reduced by it; thus the reduction of *m*-dinitrobenzene by this agent gives *m*-nitraniline.

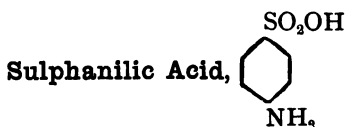


Mix together in a flask 20 grams of powdered *m*-dinitrobenzene, 75 grams (approx. 95 c.c.) of alcohol, and 13 grams (15 c.c.) of concentrated ammonia solution. Weigh the flask and contents. Pass a stream of sulphuretted hydrogen (washed with water) through the liquid in the flask till it is saturated with the gas; attach a reflux condenser, and boil the contents of the flask for a quarter of an hour on a water-bath. Allow the flask and contents to cool, again saturate with sulphuretted hydrogen, and reheat. Repeat this procedure till the weight of contents of the flask has increased

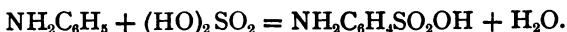
by 12 grams. Precipitate the nitraniline from the liquid by adding water as long as it causes the separation of any more solid ; filter off the precipitate. The solid obtained is a mixture of m-nitraniline and sulphur ; it is transferred to a flask and extracted several times by heating with small quantities (50 c.c.) of dilute hydrochloric acid ; the extract is each time decanted and filtered through a filter-paper, the residue being again extracted with more acid. When a small quantity of the filtrate no longer precipitates any solid on the addition of excess of dilute ammonia, the combined filtrates are evaporated down to approximately 100 c.c. The solution of nitraniline hydrochloride is cooled, and the nitraniline is precipitated by the addition of concentrated ammonia ; the precipitate is filtered off from the cold solution, and is purified by recrystallization from boiling water. Yield \approx 10 grams.

m-Nitraniline crystallizes in yellow needles, melting at 114° .

Acetyl Derivative.—Boil 2 grams of m-nitraniline with 5 c.c. of acetic anhydride for a quarter of an hour. Pour the liquid into cold water, and stir. Filter off the solid which separates out, and recrystallize it from water to which a little alcohol has been added ; m-nitroacetanilide, $C_6H_4NO_2.NH.CO.CH_3$, is obtained in prismatic crystals, melting at 150° .



The benzene hydrocarbons and many of their derivatives readily react with concentrated sulphuric acid, forming sulphonic acid compounds. Aniline can be substituted with a sulphonic acid group by heating with excess of concentrated sulphuric acid at 180° to 190° ; sulphanilic acid (p-amino benzene sulphonic acid) is slowly formed. Since this substance is soluble in caustic soda solution, the completion of the reaction may readily be determined.



Place 20 grams (20 c.c.) of freshly distilled aniline in a dry flask, and add gradually, with constant shaking, 70 c.c. of concentrated sulphuric acid ;¹ heat the flask in an oil-bath at 180° to

¹ The use of slightly fuming sulphuric acid (containing 8 to 10 per cent. of additional SO_3) will greatly diminish the time necessary for the heating.

190° for several hours (four or five), till, on withdrawing a little of the liquid, diluting and adding caustic soda solution, no separation of aniline occurs. Allow the mixture to cool, and pour it into 500 c.c. of cold water, stirring the liquids together. The sulphanilic acid separates out in crystals; it is filtered off, washed with water, and pressed. In order to purify the crystals and remove the dark colour from them, they are dissolved in as little hot water as possible, the solution boiled for a short time after the addition of a gram of animal charcoal, and then filtered through a funnel with a hot-water jacket. The crystals deposited on cooling should be colourless. The yield, after drying, should be about 20 grams.

Sulphanilic acid crystallizes with one or two molecules of water of crystallization, the crystalline form depending on the number of water molecules present. It is readily soluble in hot water, but only sparingly soluble in cold. It readily forms salts with the alkalis, but the presence of the sulphonic acid group so weakens the basicity of the amino group that no salts are known in which the substance acts as a base. On fusion with potash it does *not* yield an aminophenol, but aniline.

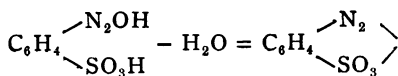
1. The tests for the elements show the presence of S. and N. The solution is acid.

2. On *diazotization* and coupling with *β-naphthol* it yields a soluble red dye (Orange II.).

Since sulphanilic acid does not dissolve in cold HCl, the usual method of diazotization has to be altered somewhat. Dissolve the sulphanilic acid in dilute caustic soda or sodium carbonate, add the sodium nitrite solution, and then dilute hydrochloric acid till free nitrous acid is present (indicated by starch iodide paper). Then pour a little into the alkaline solution of *β-naphthol*. This method of procedure should be adopted with all amino-sulphonic acids.

On coupling with *dimethylaniline*, methyl orange is produced. The diazotized solution is mixed with a small quantity of dimethyl aniline and the mixture well shaken. A red liquid is formed, from which methyl orange rapidly crystallizes out. A little of the product dissolves in acids to a red solution, which is turned yellow by alkalis.

3. Dissolve in *dilute soda*, mix the solution with a slight excess of *sodium nitrite*, and pour into well-cooled, *dilute sulphuric acid*. An internal salt of benzene-diazonium sulphonic acid is precipitated from the solution in colourless crystals.



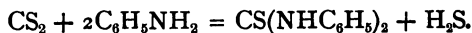
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On boiling with water these crystals give phenol-p-sulphonic acid, and nitrogen is evolved. They also readily react with dimethyl aniline, giving methyl orange.

4. With *chromic acid mixture* (p. 20) sulphanilic acid yields quinone, which may be recognized by its pungent and nutty odour. Hence proof of the para position of the sulphonic group.

Thiocarbanilide, Sulphocarbanilide, Diphenylthiourea, $\text{CS}(\text{NHC}_6\text{H}_5)_2$.

When carbon bisulphide is boiled with aniline in alcoholic solution, a reaction occurs with evolution of sulphuretted hydrogen and formation of thiocarbanilide.

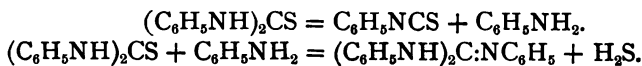


Mix 40 grams (40 c.c.) of aniline with 50 grams (40 c.c.) of carbon bisulphide, and 50 grams (60 c.c.) of alcohol in a flask; fit the flask with a reflux double-surface condenser, and heat for eight hours¹ on a water-bath in a fume chamber. The excess of carbon bisulphide and alcohol are then distilled off by heating on the water-bath; the residue is mixed with water, filtered, washed with a little dilute hydrochloric acid to remove unchanged aniline, and finally washed again with water. The major portion of the crude product is dried in a dish on the water-bath. A few grams may be purified by recrystallization from alcohol. Yield of crude product, *c.* 35 grams.

Thiocarbanilide crystallizes in colourless pearly plates, which melt at 151° . It is only slightly soluble in water, but is easily soluble in hot alcohol. Its behaviour on treatment with hot mineral acid is described in the next preparation.

Phenyl Isothiocyanate, Phenyl Mustard Oil, $\text{C}_6\text{H}_5\text{NCS}$.

On boiling with concentrated hydrochloric acid, thiocarbanilide is slowly decomposed into phenyl isothiocyanate and aniline; the aniline thus formed reacts, to some extent, with unchanged thiocarbanilide, giving sulphuretted hydrogen and triphenyl guanidine [guanidine is $(\text{NH}_2)_2\text{C}:\text{NH}$]; the latter substance, being basic, is obtained as the hydrochloride, and remains in solution, while the phenyl isothiocyanate separates out as an oil.

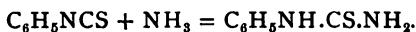


¹ The addition of 10 grams of powdered potassium hydroxide to the mixture facilitates the elimination of the sulphuretted hydrogen, accelerating the action to such an extent that three to four hours' heating is sufficient.

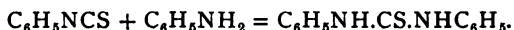
Boil 25 grams of thiocarbonyl chloride with 80 c.c. of concentrated hydrochloric acid, in a flask fitted with a reflux condenser, for half an hour; the phenyl isothiocyanate separates as an oil. Add 50 c.c. of water, and distil the mixture till about 20 c.c. remain in the flask. The phenyl mustard oil being volatile with steam, passes over in the distillate; this is therefore extracted with ether, the ethereal extract is dried over calcium chloride, decanted, and fractionated in the usual way, a short air condenser being used after the removal of the ether. The isothiocyanate distils at 197° – 222° . Yield c. 9 grams.

Phenyl isothiocyanate is a colourless liquid of pungent odour; it boils at 222° , and at 15° its specific gravity is 1.135. It is a very reactive substance as the following tests indicate.

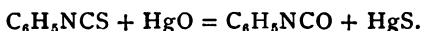
1. (a) To a few drops of the substance add twice the volume of concentrated ammonia, and then alcohol till a clear liquid is obtained. Boil off the alcohol; the residue, when cold, will set—it may be necessary to stir or shake it first—to a solid mass of mono-phenyl thiourea.



(b) Amines react similarly. Heat a mixture of equal volumes of the substance and aniline to boiling for a minute, and allow to cool; a solid mass of diphenyl thiourea is obtained.



2. Mix a little of the substance with alcohol and boil with a little yellow mercuric oxide. An irritating, tear-producing odour of phenyl isocyanate is obtained, and the mercuric oxide is converted into black mercuric sulphide.



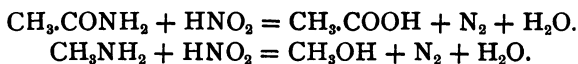
To the residue in the flask add 70 c.c. of water and allow to stand overnight. Crystals of the hydrochloride of triphenyl guanidine separate out; they should be filtered off, warmed for a short time with dilute caustic soda solution, and the liberated base filtered off and washed with water. Purify by recrystallization from alcohol.

Triphenyl guanidine consists of colourless needles which melt at 143° ; its nitrate is very difficultly soluble in water.

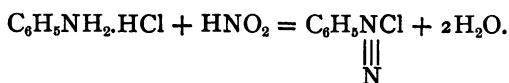
CHAPTER IX

THE DIAZONIUM SALTS AND THEIR REACTIONS

THE action of nitrous acid on most amino compounds is to cause the formation of the corresponding hydroxy body, with a simultaneous liberation of nitrogen. The usual method is to dissolve the amino compound in excess of acid, and to add a solution of an alkali nitrite. Treated in this way the amides and primary amines give rise to the corresponding acids and alcohols.

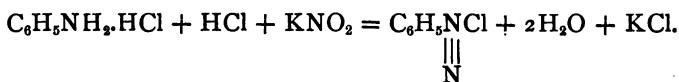


In the case of those substances in which the amino group is directly attached to one of the carbon atoms in a benzene ring, the use of hot solutions brings about a change similar to the above; but if cold solutions be used, no evolution of nitrogen occurs, but in the solution a substance is formed containing a group of two nitrogen atoms, and hence termed a diazo compound.



Since these bodies are salts they are often termed "diazonium" salts, from the similarity to ammonium salts.

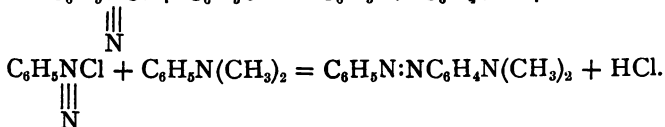
For the preparation of diazonium salts it is essential that there should be at least sufficient acid present to form a salt with the aniline, and also to liberate the nitrous acid from the nitrite.



The diazonium salts are, as a rule, very unstable, and in the solid state often explosive; hence, in synthetical chemistry, where

they are of extreme value, the diazonium salt is generally not isolated, but the solution, obtained in the manner indicated above, is used straight away.

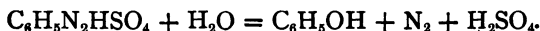
These substances will couple up with phenols and tertiary aromatic amines, giving rise to "azo" dyes, in which the group of two nitrogen atoms is still intact.



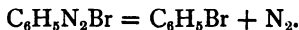
With primary and secondary aromatic amines, "diazoamino" compounds are obtained; these readily rearrange into "amino-azo" compounds.



The diazonium salts are also of immense value for the preparation of substituted derivatives of the aromatic hydrocarbons. Thus, if the solution be boiled, nitrogen is liberated, and the corresponding phenol is formed.



The solutions of the halogen salts also readily decompose, especially in the presence of certain catalytic agents such as cuprous salts, or copper, giving the halogen substituted hydrocarbon.



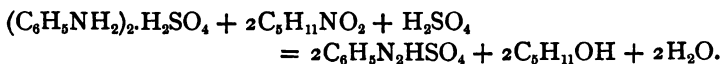
Examples of these actions will be seen in later preparations.

Preparation of Solid Benzene Diazonium Sulphate,
 $\text{C}_6\text{H}_5\text{NHSO}_4.$



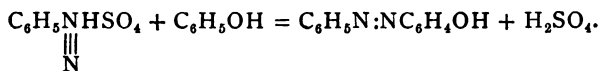
On account of the great solubility of the diazonium salts in water, an alcoholic solution of the aniline salt is taken for the preparation of the salts in the solid state, and the diazotization effected by amyl nitrite. The latter undergoes hydrolysis to amyl

alcohol and nitrous acid, and the nitrous acid acts in the usual way.

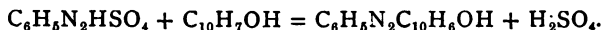


Dissolve 5 grams of aniline in 50 c.c. of absolute alcohol, and add slowly, with constant shaking, 10 grams of concentrated sulphuric acid. The aniline sulphate at first separates out, but dissolves up as the remainder of the acid is added. Cool the mixture thoroughly, and introduce $6\frac{1}{2}$ grams of amyl nitrite, drop by drop, shaking well after each addition. Then place the mixture in ice; on standing, the benzene diazonium sulphate separates out, and should be filtered off after half an hour; after washing with a little alcohol, a small quantity should be dissolved in water, and the following tests carried out with the solution.

1. Pour a few drops into a solution of a little *phenol* in *caustic potash* solution. An orange-yellow solution of p-hydroxyazo-benzene is obtained.



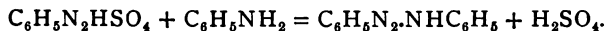
2. Pour a few drops into a solution of *β-naphthol* in *caustic potash*. A red precipitate is obtained.



3. Place a few drops of *dimethylaniline* in a test-tube, add a little of the diazo solution, and shake. A red solution of the hydrochloride of benzene azo p-dimethyl aniline is obtained; on adding caustic soda the free substance is liberated and the liquid turns yellow.

4. Primary and secondary aromatic amines couple with diazo salts, attaching themselves first by the amino nitrogen atom.

Add to a little of the solution a few drops of *aniline*, and shake. Diazoaminobenzene separates as a yellowish-brown crystalline solid.



5. Boil some of the solution for a short time till no more nitrogen is evolved. The formation of phenol in the solution is proved by the addition to the cooled solution of a little *bromine water*, which precipitates white tribromophenol.

The remainder of the solid benzene diazonium sulphate should be dissolved in water and thrown away, because, although it is much more stable than the nitrate, it is explosive when dry.

Iodobenzene, Chlorbenzene.

To obtain diazo salts for ordinary syntheses, the aniline is usually dissolved in excess of acid, and to the well-cooled solution, a solution of potassium nitrite is added; to tell when sufficient of the latter solution has been added, a drop of the mixed liquids is withdrawn on the end of a rod and tested with starch iodide paper; the presence of the least excess of nitrous acid is detected by a blue stain.

Since similar solutions of diazonium chloride are required for the preparation of iodobenzene and chlorbenzene, both preparations should be performed, if possible, on the same day, so that one diazotization may serve for both, a suitably larger quantity of aniline then being taken.

Iodobenzene.

Dissolve 9.5 grams of aniline in 50 c.c. of a mixture of equal volumes of concentrated hydrochloric acid and water, *and cool the solution in water containing ice.* Dissolve 12 grams of potassium nitrite in 20 c.c. of water, and add it to the aniline hydrochloride solution in small quantities (2 to 3 c.c.) about every two minutes, shaking well after each addition, till, after standing a short time, a little of the liquid, withdrawn on the end of a rod and diluted with a little water in a watch glass, stains starch iodide paper blue. The solution of the diazonium chloride is then ready for the preparation of iodobenzene or chlorbenzene.

To obtain iodobenzene it is merely necessary to add potassium iodide solution, when an immediate effervescence of nitrogen occurs and the iodobenzene separates out as a dark oil.

Dissolve 25 grams of potassium iodide in 50 c.c. of water, and add this solution to the cold diazo solution; a vigorous effervescence ensues; the mixture is allowed to stand a quarter of an hour, and is then heated on a water-bath till no further effervescence of nitrogen occurs; the iodobenzene sinks to the bottom as a black oil. The mixture is then made alkaline with caustic soda, poured into a half-litre flask, and steam distilled; the iodobenzene passes over as a brown oil. When no more oil comes over, the crude iodobenzene is placed in a separating funnel and shaken till colourless with a solution of sodium sulphite, in order to remove the dissolved iodine. Extract the iodobenzene with ether, and dry the solution over calcium chloride. The ether is distilled off on a water-bath; the residual liquid is then distilled

through an air condenser, the iodobenzene coming over at 186°–189°. Yield *c.* 16 grams.

Pure iodobenzene is a colourless liquid of specific gravity 1.838 at 15°; it boils at 188°. As in all similar simple substances, the halogen atom substituted in the benzene ring is unaffected by boiling with solutions of caustic alkalis.

Chlorbenzene, by the Sandmeyer Reaction.

As we have just seen, benzene diazonium iodide decomposes very readily into iodobenzene and free nitrogen; the various diazonium chlorides, bromides, and cyanides do not undergo a similar decomposition satisfactorily except in the presence of certain catalytic agents. Sandmeyer's reaction is merely an application of the appropriate cuprous salts for this purpose; these first form unstable double salts with the diazonium salts, and these double salts decompose, giving the corresponding substituted hydrocarbon.



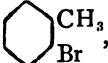
To prepare the cuprous chloride solution, weigh 4 grams of powdered black copper oxide into a tared flask, add 50 grams of concentrated hydrochloric acid and 6.5 grams of copper turnings. Loosely stopper the neck of the flask with a perforated cork, and boil till the liquid contents become colourless. Then add concentrated hydrochloric acid till the solution has a total weight of 102 grams. In this way, allowing for the weight of the undissolved copper, a 10 per cent. solution of cuprous chloride is obtained.

Prepare a solution of benzene diazonium chloride according to the directions for the preparation of iodobenzene, but take twice the quantities there mentioned, *i.e.* 19 grams of aniline, etc.

A flask containing 45 grams of the cuprous chloride solution is fitted with a reflux air condenser, and the liquid heated to just below boiling point. The cold solution of diazobenzene chloride is introduced slowly down the condenser, a few drops at a time, shaking well after each addition; each drop gives a momentary yellow precipitate which immediately decomposes with evolution of nitrogen. When all the diazo solution has been introduced, the chlorbenzene which has formed is distilled off with steam; it is then separated from the aqueous portion of the distillate, dried over calcium chloride, and fractionated.

The chlorbenzene distils over at about 130°. Yield *c.* 18 grams.

Chlorbenzene is a colourless liquid of pleasant odour; it boils at 132°, and at 15° has a specific gravity of 1.11.

***o*-Bromtoluene,** , **by Gattermann's Reaction.**

In the preparation of chlorbenzene it was seen that the presence of cuprous salts greatly assists the smooth decomposition of the corresponding diazonium salt into free nitrogen and a substituted hydrocarbon. It was discovered by Gattermann that finely divided copper has a similar effect, and so this substance is often used in place of cuprous salts.

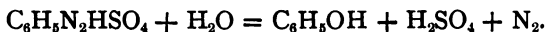
To prepare the copper powder, dissolve 40 grams of copper sulphate in 120 c.c. of water, cool the solution, and place it in a porcelain dish; dust into the solution, from a small muslin bag, about 10 grams of zinc dust, stirring the liquid vigorously all the time, till at last it is decolourized. Decant the solution of zinc sulphate from the deposited copper, and wash the copper by decantation several times with cold water. To remove any metallic zinc in the deposit, mix it with several times its volume of water, and add dilute hydrochloric acid with stirring, till no more hydrogen is evolved; then pour off the supernatant liquid, wash the residue with water, finally on the filter pump, till the washings are no longer acid. On account of its tendency to oxidize, the powder is not dried; if it is not required for immediate use it is preserved in a moist state in a well-stoppered bottle.

Dissolve 6 grams (approximately 6 c.c.) of *o*-toluidine in a mixture of 35 c.c. of hydrobromic acid of constant boiling point (see p. 114) with 40 c.c. of water. Cool the solution in ice, and diazotize as in the preparation of chlorbenzene. To the cold solution of the diazonium bromide add slowly the previously prepared copper powder, in small quantities, shaking after each addition; a vigorous effervescence ensues, but after half an hour the evolution of gas ceases, and a mixture of copper powder and bromtoluene sinks to the bottom of the liquid. The top aqueous layer is poured off and rejected; the residue in the flask is steam distilled. The distillate is extracted with ether, dried over calcium chloride, and fractionated. The yield is about 6 grams.

o-Bromtoluene is a colourless liquid of specific gravity 1.422 at 20°; it boils at 181°.

Phenol or Carbolic Acid, C_6H_5OH .

As has already been mentioned, diazonium salts in solution decompose on heating, liberating nitrogen and forming the corresponding phenol. The sulphate gives a purer product than the other salts. Although this action is of no commercial value for the preparation of ordinary phenol, it is often of great importance for the preparation of other phenolic substances.



Dissolve 20 grams of aniline in a hot mixture of 40 grams (23 c.c.) of concentrated sulphuric acid with 100 c.c. of water; pour the solution into 200 c.c. of water. Cool the diluted solution in ice till it becomes quite cold. Then diazotize the solution by the careful addition of 25 grams of potassium nitrite in 60 c.c. of water in the manner described under the preparation of iodo-benzene, till a slight excess of nitrous acid is present. Allow the still cooled solution of the diazonium sulphate to stand half an hour, and then warm for another half-hour in a water-bath at 60°. When the evolution of nitrogen has ceased, steam distil the contents of the flask, collecting about 500 c.c. of the liquid that comes over. Extract the cold distillate twice with ether, and dry the combined extracts over anhydrous potassium carbonate; decant the dry solution into a distilling flask, distil off the ether on a water-bath, and fractionate the residual phenol through an air condenser.

The fraction distilling from 178°–183° is practically pure phenol, and solidifies on cooling. Yield *c.* 12 grams.

Phenol forms colourless deliquescent crystals, which melt at 42.7° and boil at 181.5°. It is readily liquefied by the addition of a little water, and is miscible with water in all proportions above a temperature of 68.4°. Below this temperature two conjugate solutions¹—the one containing an excess of water and the other of phenol—are formed, unless either constituent is present in great excess, when a homogeneous solution results.

It is neutral to litmus, but is soluble in caustic soda (*not* sodium carbonate) with the formation of a phenate. Like nearly all phenates

¹ See "Findlay's Phase Rule," 2nd edit. p. 97.

it is decomposed by passing carbon dioxide into its solution in water ; phenols are often separated from solution in this way. It possesses a characteristic odour.

1. Heated in a dry tube phenol volatilizes, giving a characteristic odour.

2. *Ferric chloride* gives a violet coloration, which is destroyed by hydrochloric acid and by acetic acid ¹ (*cf.* salicylic acid).

3. *Bromine* water gives a precipitate of tri-bromphenol, even from very dilute solutions of phenol.

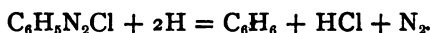


4. To an aqueous solution of phenol add a little *ammonium hydroxide* solution and then some clear *bleaching powder* solution. A blue colour is produced, which is turned red by the addition of acids.

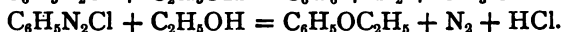
5. **Liebermann's nitroso-reaction.**—To 1 c.c. of *pure concentrated sulphuric acid* add about a gram of *phenol*, and shake till dissolved. Then add a "speck" of *sodium nitrite*, shake, and warm gently (if necessary). A blue-green colour is produced, which is changed to red on pouring the mixture into water ; excess of *alkali* then restores the blue-green colour.

Benzene, C_6H_6 .

If solutions of diazonium salts be reduced by treatment with alcohol or alkaline stannous chloride solution, the parent hydrocarbon can be obtained. In the first case, oxidation of the alcohol to aldehyde takes place ; in the latter, stannite is oxidized to stannate.



The alcohol, as a rule, however, does not give a pure product on account of a simultaneous reaction with the formation of an ether, *e.g.* of phenetol or phenyl ethyl ether in the case of diazotized solutions of aniline.



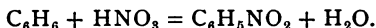
Dissolve 10 grams (approximately 10 c.c.) of aniline in a mixture of 30 c.c. of concentrated hydrochloric acid and 64 c.c. of water. Cool the mixture in ice, and diazotize the pasty liquid with a solution of 10 grams of sodium nitrite, till an excess of nitrous acid is present. Then pour into the diazotized solution, with constant shaking, an ice-cold solution of 26 grams of caustic soda in 80 c.c. of water. In a second flask place a solution of

¹ The colour is destroyed by almost anything else in the solution.

46 grams of stannous chloride in 110 c.c. of water, and add caustic soda solution (25 per cent. strength) till the original precipitate has practically redissolved. Fit this flask with a reflux water condenser, heat on a water-bath, and add *gradually* down the condenser the alkaline diazo solution. When the effervescence of nitrogen has ceased, distil the liquid in the flask, and when no more oily drops of benzene come over, separate the benzene from the water and dry over calcium chloride. Fractionate the dried liquid, heating on a water-bath; the benzene distils at 78° – 81° . Yield *c.* 6 grams.

Benzene is a colourless liquid with a characteristic odour, and boiling at 80.4° . It freezes at 5.4° . It is insoluble in water, but soluble in most organic solvents. It is inflammable, burning with a smoky flame. When pure it does not give any colour to concentrated sulphuric acid; the commercial article generally contains thiophene, however, and the sulphuric acid then becomes dark coloured on shaking up with the benzene and warming gently.

1. To 5 c.c. of a mixture of equal parts of *concentrated sulphuric* and *nitric acids* add 1 c.c. of benzene, drop by drop, shaking well after the addition of each drop, and cooling if the mixture becomes hot. Then warm gently and pour into a beaker of water. A yellow oil separates out and sinks to the bottom of the beaker; it is *nitrobenzene*, and possesses the characteristic odour of oil of bitter almonds.



2. In some cases it is advisable to reduce the nitro to the amino compound. The method of procedure in the case of benzene is then as follows: The yellow oil obtained in 1 is treated with zinc and hydrochloric acid (tin may be used instead of zinc) to reduce the nitrobenzene. The reduced solution is then poured off from the undissolved zinc, cooled, diazotized, and coupled with alkaline β -naphthol, as given on p. 94, with the formation of a red dye.

NOTE.—These tests can be readily carried out on much less than 1 c.c. of benzene. The reduction of a nitro to an amino compound, and then diazotization and the formation of a dye, is an exceedingly delicate test for the presence of a nitro group.

The above method of procedure is generally successful. In some cases, however, it may be necessary to liberate the amino compound from its salt by addition of caustic soda in excess, and then to extract with ether. The ethereal solution is separated, the ether evaporated off on a clock glass, and the amino compound diazotized as above.

It may be necessary to distinguish benzene from its homologues. This is readily done by oxidation of the side chains of the homologues,

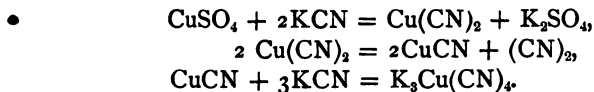
benzoic acid being produced. The oxidizing mixture used is the same as that given on p. 20 for the oxidation of alcohols and aldehydes. Heat in a flask connected with reflux condenser for a short time. On cooling, the benzoic acid may separate out; if not, the solution is extracted with ether, and the benzoic acid obtained from the ethereal extract. Apply the tests for benzoic acid given on p. 116.



This substance is prepared by Sandmeyer's reaction; p-toluene diazonium cyanide is caused to decompose in the presence of cuprous cyanide,



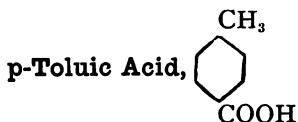
To prepare the solution of cuprous cyanide proceed as follows: Dissolve 50 grams of crystallized copper sulphate in 200 c.c. of water in a 2-litre flask. Heat the solution on a water-bath in a fume chamber, and add slowly a solution of 60 grams of potassium cyanide till the precipitate is just redissolved. A solution of the complex salt of cuprous cyanide and potassium cyanide is thus obtained. A good draught is necessary in the fume chamber during this operation because cyanogen is evolved—



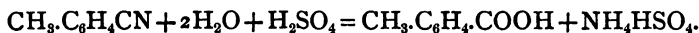
Dissolve 20 grams of p-toluidine in a warm mixture of 45 c.c. of concentrated hydrochloric acid and 150 c.c. of water. Cool in ice, stirring the solution vigorously meanwhile in order that the toluidine hydrochloride which separates may be in as small crystals as possible. To the cooled solution add, in small quantities at a time, a cold solution of 20 grams of potassium nitrite in 80 c.c. of water, stirring well after each addition; as the diazotization proceeds the crystals of the toluidine hydrochloride will disappear. When all the toluidine salt has been converted into diazonium salt, as shown by the presence of a slight excess of nitrous acid in the solution (the addition of the nitrite should be extended over a quarter of an hour), the solution is transferred to the fume

chamber, and is poured slowly, at intervals extending over a period of ten minutes, into the solution of cuprous cyanide (the latter at about 70°); the latter is frequently shaken, and after the addition of the whole of the diazonium solution, is heated for a quarter of an hour longer on the water-bath. The resulting mixture is then steam distilled in the fume chamber, when the p-toluy! nitrile passes over as an oil; when no more oil distils, the distillate is cooled, and the solidified nitrile is filtered off on the pump; it is then dried by exposure to the air on a porous plate. If required, it may be purified by distillation. Yield *c.* 12 grams.

p-Toluy! nitrile is a white crystalline solid melting at 29° and boiling at 218° ; on hydrolysis with mineral acids it forms p-toluic acid.



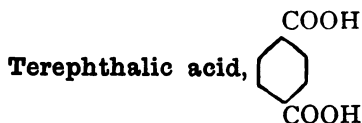
p-Toluy! nitrile behaves in a normal manner towards hydrolytic agents; for example, on boiling with sulphuric acid,¹ p-toluic acid and ammonium sulphate are obtained.



Place in a small flask 10 grams of p-toluy! nitrile, and add a mixture of 10 grams of water with 30 grams (17 c.c.) of concentrated sulphuric acid. Fit the flask with a reflux air condenser and boil gently till crystals of p-toluic acid appear in the condenser (about half an hour). Allow the contents of the flask to cool somewhat, pour into 500 c.c. of water, and when cold filter off the precipitated toluic acid. Dissolve the toluic acid in hot water (adding a little alcohol to aid the solution if necessary), and if the solid is discoloured, boil for a short time with a little animal charcoal. Filter the hot solution through a hot-water funnel and allow to crystallize. If necessary repeat the boiling with charcoal and the crystallization. Yield *c.* 9 grams.

p-Toluic acid is rather soluble in hot water, but almost insoluble in cold. It melts at 179° .

¹ Sulphuric acid has the advantage over hydrochloric acid that it is not volatile; however, it is not always as suitable as the latter substance, *e.g.* in the case of substances which easily form sulphonc acid derivatives.



The side chains of practically all aromatic substances are easily oxidized, leaving the benzene nucleus unaltered; all that is left of the group of carbon atoms is, as a rule, a carboxyl group. *p*-Toluic acid behaves in this way towards suitable oxidizing agents yielding *p*-dicarboxy benzene or terephthalic acid. In the following experiment an alkaline solution of permanganate is used for oxidizing purposes; under such conditions the permanganate is reduced to hydrated manganese dioxide, which separates out.



Dissolve 3 grams of caustic soda in 250 c.c. of water, add 5 grams of toluic acid, and heat in a porcelain dish on the water-bath. Make 250 c.c. of a 5 per cent. solution of potassium permanganate, and add this gradually to the hot solution of the toluic acid, waiting until reduction is complete after each addition. When the colour of the permanganate persists, even after heating for an hour, the oxidation is complete. A little alcohol is then added to remove the excess of permanganate, and the liquid is filtered from the precipitated manganese dioxide; the filtrate, while hot, is acidified with concentrated hydrochloric acid, and after cooling, the precipitated terephthalic acid is filtered off; the solid is then washed with water, pressed, and dried on the water-bath. Yield *c.* 5 grams.

Terephthalic acid obtained in this way is an amorphous powder, practically insoluble in water, alcohol, and ether. It sublimes at 300° without melting and without formation of an anhydride (*cf.* *o*-phthalic acid).

CHAPTER X .

Brombenzene, C_6H_5Br .

Chlorine and bromine (also iodine in the presence of iodic acid) will react with hydrocarbons (aliphatic or aromatic), replacing a hydrogen atom by a halogen atom.¹



The substitution is greatly accelerated by the presence of so-called halogen carriers (*cf.* preparation of chloracetic acid), iodine, iron, or iron chloride being the most commonly used; they are all substances which are capable of forming more than one compound with the halogens, and probably act by forming the more highly chlorinated or brominated compound, which then reacts with the hydrocarbon forming the substitution product, and is continually regenerated by the action of the free halogen. In the preparation of mono-substituted bodies, it is obviously important to avoid any large excess of halogen, because the substitution of a second hydrogen atom very easily takes place. For the preparation of monobrombenzene the theoretical quantities are 78 grams of benzene to 160 grams of bromine; generally an excess of benzene is taken.

Place 50 grams (approximately 56 c.c.) of benzene in a flask, and add 2 grams of iron filings. Immerse the flask in a bath of cold water, and fit it, by means of a cork (preferably soaked previously in paraffin wax) with a reflux condenser. Into the top of the condenser insert a small dropping funnel, and a bent glass tube leading down to the surface of 200 c.c. of water in a beaker, the actual contact with the water being made by a small inverted funnel (Fig. 19); the water is for the purpose of absorbing the large quantity of hydrobromic acid which will be evolved. Place 60 grams (20 c.c.) of bromine in the tap funnel and allow it to

¹ In sunlight benzene *adds on* chlorine and bromine giving crystalline solids, the hexachloride $C_6H_6Cl_6$ and the hexabromide $C_6H_6Br_6$ respectively.

drop slowly down the condenser into the benzene, extending the addition of the whole of the bromine over half an hour. The action is very vigorous, hence the necessity of adding the bromine slowly. After the addition of the bromine heat the water-bath to boiling, then remove the flask and allow it to cool. Decant the liquid contents into a separating funnel, shake with water, and then with dilute caustic soda solution to remove hydrobromic acid. Place the washed brombenzene in a litre flask and distil in a current of steam (see p. 58). The first part of the distillate contains the excess of benzene, which floats on the water and can be rejected. As soon as the oily drops sink below the liquid, change the receiver and distil till no more oily drops come over.¹

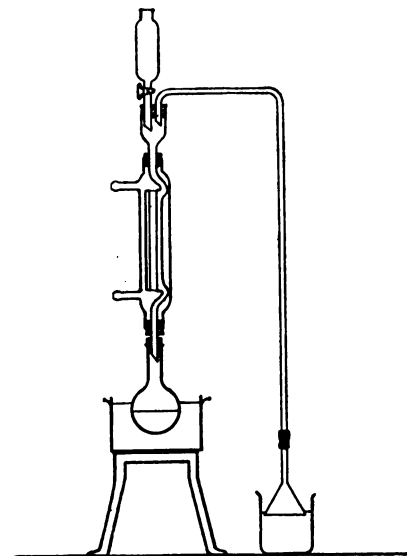


FIG. 19.

Separate the monobrombenzene from the water, and dry over calcium chloride; when the turbidity has completely disappeared, decant the liquid into a distilling-flask and distil. The fraction from 152° – 155° is practically pure. Yield \approx 35 grams.

Brombenzene is a colourless liquid boiling at 155° . Its specific gravity is 1.50 at 15° . It is insoluble in water, and is not affected by boiling with alkalis.

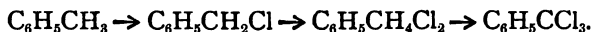
NOTE.—The solution of hydrobromic acid obtained in the above preparation should be concentrated by fractional distillation; the fraction coming over at a constant temperature of 126° contains 46

¹ Towards the end of the distillation, if a considerable amount of a white crystalline solid collects in the condenser, allow the water to run from the cooling jacket of the latter, and collect the distillate in a fresh receiver. The oil in this distillate, on cooling, solidifies to a white crystalline mass of p-dibrombenzene; this should be separated and recrystallized from alcohol. Melting point 89° .

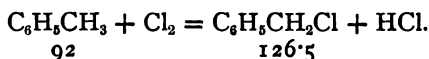
per cent. of hydrobromic acid ; it is a solution of this strength which is used in the preparation of o-bromtoluene (see p. 105).

Benzyl Chloride, $C_6H_5CH_2Cl$.

If chlorine or bromine be allowed to act on an aromatic hydrocarbon at a low temperature in the presence of a catalytic agent, the halogen atom substitutes itself in the benzene nucleus. If, however, the action of the halogen element on a homologue of benzene be allowed to occur at the boiling point of the hydrocarbon in the absence of any catalytic agent, substitution occurs in the side chain ; thus toluene, when chlorinated at its boiling point gives benzyl chloride, which by continued chlorination changes to benzal chloride and ultimately to benzo-trichloride.



To obtain benzyl chloride the chlorination is continued till the increase in weight corresponds with that calculated for the formation of this substance.

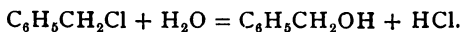


Into a wide-necked flask (150 c.c.) weigh 50 grams of toluene. Fit the flask to a condenser by means of a cork carrying an inlet tube and an adapter, just as in the preparation of chloracetic acid (*q.v.*). Place a sand or oil bath under the flask and keep the toluene boiling gently. Pass a steady stream of chlorine into the liquid.¹ Weigh the flask occasionally till an increase of 19 grams is observed. Transfer the contents to a distilling flask and distil. The fraction distilling below 165° is chiefly unchanged toluene, that from 165°–185° contains most of the benzyl chloride, while that above 185° consists chiefly of benzal chloride and benzo-trichloride, which boil at 204° and 214° respectively. The middle fraction is fractionated twice more, in the second distillation collecting from 170°–180°, and in the last from 175°–179°. Yield *c.* 40 grams.

Pure benzyl chloride is a colourless liquid, boiling at 178° ; at 15° its specific gravity is 1.113. Like all aromatic halogen compounds in which the halogen is in the side chain, the odour is irritating, and the substance behaves towards hydrolytic agents just

¹ As in the preparation of chloracetic acid, bright daylight greatly accelerates the absorption of the chlorine, completing the change in a few hours.

like an aliphatic halide. For example, by boiling with water, preferably containing a little added potassium carbonate, benzyl alcohol and hydrochloric acid are obtained (*cf.* ethyl bromide or iodide, and contrast with chlorbenzene).



Benzoic Acid ($\text{C}_6\text{H}_5\text{COOH}$) and Benzyl Alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), from Benzaldehyde.

The aromatic aldehydes behave in a characteristic way towards caustic alkalis, undergoing simultaneous oxidation and reduction, one molecule being oxidized to benzoic acid, while a second is reduced to benzyl alcohol.



In a bottle of 200 c.c. capacity place 20 grams of benzaldehyde, and add a cold solution of 18 grams of caustic potash in 12 c.c. of water; close the bottle by a cork (a glass stopper should not be used), and shake vigorously till the contents form a permanent emulsion. Allow the mixture to stand overnight, when it becomes pasty from the separation of potassium benzoate. Then add water to the mixture till, on shaking, a clear solution is obtained. Extract the benzyl alcohol by shaking several times with ether, and dry the ethereal solution over anhydrous potassium carbonate; decant the liquid into a distilling-flask, distil off the ether, and fractionate the residue through an air condenser; the benzyl alcohol comes over at 200° – 206° . Yield *c.* 8 grams.

The aqueous liquid remaining from the extraction is acidified with sufficient concentrated hydrochloric acid to completely precipitate the benzoic acid. After cooling, the benzoic acid is filtered off, washed with water, and pressed; it is then recrystallized from hot water. A little of the crude substance may be left for purification by sublimation as follows :—

Place a few grams in a porcelain dish, place over the dish a filter paper which has been perforated with small holes (*e.g.* pin holes), and keep the paper in position by placing over it an inverted funnel. On carefully warming the dish, the benzoic acid vaporizes and passes through the perforations in the paper, condensing in colourless needles on the paper and the walls of the funnel.

Benzyl alcohol is a colourless liquid of feeble aromatic odour. It boils at 206° and at 15° has a specific gravity 1.049.

At the ordinary temperature it dissolves in approximately 25 times its own weight of water. Towards oxidizing agents it behaves just like the aliphatic alcohols, forming first benzaldehyde, and then benzoic acid.

BENZOIC ACID,



Benzoic acid crystallizes in the form of white shining needles or plates, which melt at 121° , and sublime at somewhat higher temperatures. It is only very slightly soluble in cold water, but readily soluble in hot. It is volatile with steam. The salts are mostly soluble in water, but ferric benzoate is insoluble.

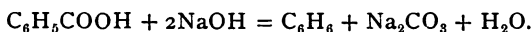
1. Heated in an ignition tube, benzoic acid melts and sublimes, condensing on the cool parts of the tube. At the same time a vapour is given off which has a pleasant aromatic odour, but which causes coughing. Charring does not take place.

When heated on platinum foil the acid burns with a blue smoky flame.

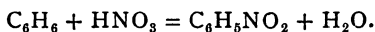
2. Benzoic acid and benzoates do not char when heated with *strong sulphuric acid*. The liberated acid forms a sublimate on the sides of the test-tube, and irritating fumes are evolved.

3. *Hydrochloric acid* precipitates benzoic acid from cold solutions of benzoates, in the form of a white crystalline precipitate.

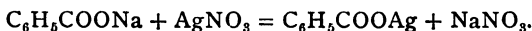
4. When heated with *soda-lime*, benzoic acid and benzoates yield benzene.



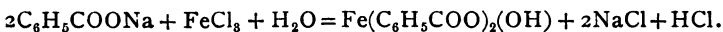
By fitting the tube in which the mixture is heated with a cork and delivery tube, the benzene may be collected in a test-tube cooled in a beaker of water. On warming the benzene with a few drops of *strong nitric and sulphuric acids*, the characteristic odour of nitrobenzene will be perceived.



5. *Silver nitrate* gives a white precipitate of silver benzoate from neutral solutions of benzoates. The precipitate is soluble in hot water and in *ammonia*.



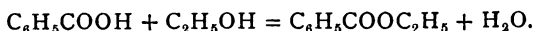
6. *Ferric chloride* produces a buff-coloured precipitate of basic ferric benzoate from neutral solutions of benzoates. The precipitate is soluble in *hydrochloric acid*, but at the same time benzoic acid crystallizes out (see test 3).



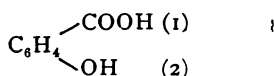
The precipitate, after being filtered off, may also be boiled up with ammonia and again filtered. The filtrate will contain ammonium benzoate, and the addition of *hydrochloric acid*, if the solution is not too dilute, will precipitate the benzoic acid.

If *barium chloride* and *alcohol* are added to part of the ammoniacal filtrate, no precipitate is formed (*cf.* succinates).

7. On heating with *strong sulphuric acid* and *alcohol*, benzoates and benzoic acid give the pleasant and characteristic odour of ethyl benzoate.

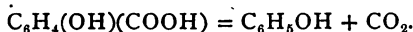


SALICYLIC ACID,



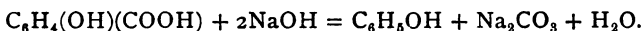
Salicylic acid forms colourless needle-shaped crystals, which melt at 155° . It is sparingly soluble in cold water, but more soluble in hot, and is volatile with steam. Most of the salicylates are soluble in water.

1. On being heated in a dry tube, salicylic acid melts and then sublimes, there being scarcely any blackening. If rapidly heated, it is decomposed, with the formation of phenol and carbon dioxide.



Salicylates char when heated alone, and phenol is evolved.

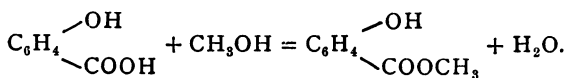
2. When heated with *soda-lime*, phenol is evolved, and may be recognized by its characteristic odour.



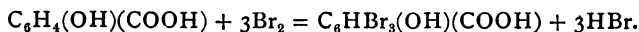
3. On being warmed with *concentrated sulphuric acid*, salicylates blacken, and carbon monoxide and sulphur dioxide are evolved.

4. *Ferric chloride* gives a violet coloration with salicylic acid or neutral solutions of salicylates. The colour is destroyed by mineral acids, but not by acetic acid (*cf.* phenol). The violet colour is restored by neutralization with ammonia.

5. Salicylic acid and salicylates when heated with *concentrated sulphuric acid* and *methyl alcohol* give the characteristic odour of methyl salicylate (oil of wintergreen).



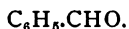
6. *Bromine water* gives a white precipitate of tribromosalicylic acid.



7. *Dilute hydrochloric acid*, on being added to the solution of a salicylate, causes a precipitate of salicylic acid, which is soluble in hot water, but crystallizes out again on cooling.

8. *Silver nitrate* gives a white precipitate of silver salicylate from strong neutral solutions of salicylates. The precipitate is soluble in hot water.

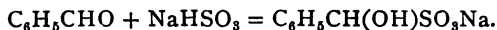
BENZALDEHYDE,



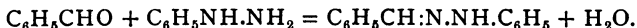
Benzaldehyde is a colourless liquid, with the pleasant and characteristic smell of oil of bitter almonds. It boils at 178.3° . On exposure to the air it rapidly oxidizes, with the formation of benzoic acid. It is only slightly soluble in water. It gives the characteristic reactions of aldehydes. (Schiff's reagent only reacts very slowly.)

1. *Ammoniacal silver nitrate* is reduced, with the formation of a silver mirror.

2. On shaking with a saturated solution of *sodium bisulphite*, the crystalline addition product separates out.



3. To a mixture of 5 drops of *phenylhydrazine* and 5 c.c. of water add 3 drops of *glacial acetic acid*. Then add 2 drops of benzaldehyde, and shake the mixture. The contents of the tube first go milky, and then a flocculent precipitate of benzaldehyde-phenylhydrazone separates out.



4. The formation of benzyl alcohol and benzoic acid by the action of very strong *caustic soda* (40 to 60 per cent.) (*cf.* preparation on p. 115) takes place quickly on warming. The benzoic acid may then be tested for in the usual manner.

Benzoyl Chloride, $\text{C}_6\text{H}_5\text{COCl}$.

The hydroxyl group of all carboxy acids can be replaced by chlorine, the most convenient agents for carrying out the replacement being the chlorides of phosphorus; for those acids, *e.g.* acetic acid, which form chlorides easily, the action of phosphorus trichloride or phosphorus oxychloride is sufficient, but the aromatic acids, which are less reactive, necessitate the use of phosphorus pentachloride.



Fit a dry half-litre flask with a reflux air condenser. Remove the condenser for a time and introduce into the flask 50 grams

of phosphorus pentachloride (do this in the fume chamber) ; then add 28 grams of benzoic acid. Attach the condenser, and shake together the contents of flask. The reaction soon commences, the mass becoming liquid, and abundance of hydrochloric acid fumes being evolved. After standing a short time the liquid is decanted into a dry distilling flask and distilled in the fume chamber. Three fractions should be collected ; that from 100° – 140° is chiefly phosphorus oxychloride, that from 140° – 190° is a mixture, while that from 190° – 200° is practically pure benzoyl chloride. The middle fraction is redistilled, and the part which distils between 190° and 200° is added to the previous fraction of benzoyl chloride. Total yield *c.* 25 grams.

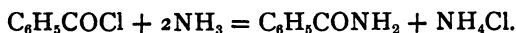
Benzoyl chloride is a colourless liquid with an extremely pungent odour which excites tears ; it is not miscible with water ; its boiling point is 198° , and its specific gravity at 15° is 1.21.

Hydrolysis.—Benzoyl chloride is only slowly hydrolyzed by water, but the action is more rapid with a dilute solution of an alkali. Heat a gram of benzoyl chloride with dilute caustic soda solution till the mixture becomes homogeneous. Allow the liquid to cool, and then pour a little into excess of dilute nitric acid and test for a chloride. Acidify the remainder with concentrated hydrochloric acid, and when cold filter off the precipitated benzoic acid ; resublime and take its melting point.



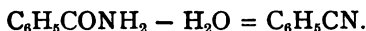
Benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$.

Benzoyl chloride is very reactive, and constitutes a very valuable agent for the preparation of derivatives of benzoic acid, *e.g.* the amide, anilide, or esters. For the preparation of benzamide it is merely necessary to grind together benzoyl chloride with ammonium carbonate.



Weigh 10 grams of finely powdered ammonium carbonate into a porcelain dish, add 5 grams of benzoyl chloride, and stir together with a glass rod. Heat the mixture on a water-bath till the smell of benzoyl chloride has disappeared (if the odour has not disappeared after ten minutes, add a few drops of concentrated ammonia). Add cold water, stir, and filter, washing the residue with a little cold water. Recrystallize the moist residue from hot water. Yield, theoretical.

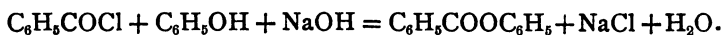
Benzamide crystallizes in colourless plates, which are very slightly soluble in cold water; it melts at 128° . Heated in a small tube with phosphorus pentoxide it becomes dehydrated, and the odour of benzonitrile becomes evident.



Hydrolysis.—Boil a gram of benzamide with caustic soda solution till a clear solution is obtained; ammonia is evolved, and the solution contains sodium benzoate. Precipitate the acid, and identify it by the tests given on p. 116.

Phenyl Benzoate, $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$, by the Schotten-Baumann Reaction.

The Schotten-Baumann reaction is of great value for the preparation of the benzoic esters of hydroxy compounds, *e.g.* phenols, sugars, glycerol, etc., and of the benzoyl derivatives of primary and secondary amines. The process is merely to bring the hydroxy compound or amine into contact with an excess of benzoyl chloride in the presence of an aqueous solution of an alkali; the alkali serves the purpose of removing the hydrochloric acid formed, and also at the end of the action of removing the excess of benzoyl chloride.



Dissolve 5 grams of phenol in 70 c.c. of a 10 per cent. solution of caustic soda contained in a small wide-mouthed bottle; add 10 grams of benzoyl chloride. Cork the bottle, and shake vigorously till the odour of benzoyl chloride has completely disappeared. The action may be hastened by slightly warming the mixture by immersion in a bath of warm water. At the end of the action the oil in the bottle should, on cooling, solidify to a crystalline mass; the crystals are filtered off, washed with water, and recrystallized from alcohol. Yield *c.* 9 grams.

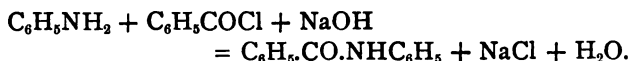
Phenyl benzoate is a white crystalline solid, melting at 69° . Its hydrolysis is best performed by caustic potash in alcoholic solution, when potassium phenate and benzoate are formed. These can be separated by passing carbon dioxide through the liquid; the phenol is then liberated, and, after dilution with water, can be extracted with

ether while the sodium benzoate is unaltered ; the benzoic acid can afterwards be liberated by mineral acids.



Benzanilide, $\text{C}_6\text{H}_5\text{CO.NHC}_6\text{H}_5$, by the Schotten-Baumann Reaction.

The formation of the benzoyl derivatives in a pure state is of importance for the identification of hydroxy compounds and amines. The method of procedure for hydroxy substances has just been described ; the action is the same for amino compounds, but, as a rule, they do not dissolve in the alkaline solution.



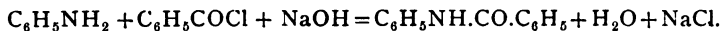
Mix 5 grams of aniline with 100 c.c. of water, containing 10 grams of caustic soda, in a small, wide-necked bottle, and add 14 grams of benzoyl chloride. Shake vigorously till the odour of benzoyl chloride disappears. Filter off the residue, wash with water, and recrystallize from a mixture of alcohol and water (add the water first, heat, and then add sufficient alcohol to dissolve the anilide).

Benzanilide is a white crystalline solid, melting at 163° .

THE SCHOTTEN-BAUMANN REACTION IN QUALITATIVE ANALYSIS.

The compounds formed by the interaction of benzoyl chloride with alcohols, phenols, primary and secondary amines are generally solid, and difficultly soluble in water, and the determination of their melting point helps in the characterization of the alcohol, phenol, or amine.

The following example will show how the reaction is carried out on a small scale, and, at the same time, how delicate it is, since the substance used, aniline (or o-toluidine), is so sparingly soluble in water. To a solution of aniline (or of o-toluidine) in water add a little benzoyl chloride (about $\frac{1}{2}$ c.c.), and then make distinctly alkaline with caustic soda. Warm gently for a short time, shaking the tube meanwhile. Benzanilide (resp. o-benzotoluide) crystallizes out, and may be identified by its melting point, 163° (resp. 131°), after recrystallization from dilute alcohol.

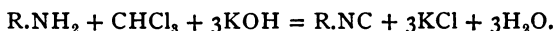


Other aromatic acid chlorides react similarly, and may be used instead of benzoyl chloride.

DISTINCTION BETWEEN PRIMARY, SECONDARY, AND TERTIARY AMINES,

Primary Amines may be distinguished from both secondary and tertiary amines by the following tests :—

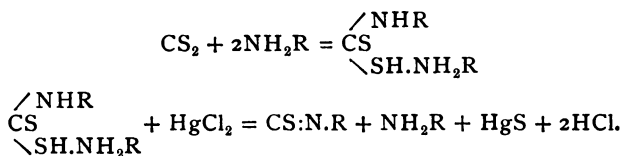
1. **Isonitrile or Carbylamine Reaction.**—To a very little of the substance add two or three drops of *chloroform*, and then a few c.c. of *alcoholic potash*. Warm gently. Obnoxious and disgusting odour of an isonitrile (*cf.* tests for chloroform and aniline).



NOTE.—All primary aromatic amines do not respond to this test, *e.g.* naphthylamine.

2. **Hofmann's Mustard Oil Reaction.**—Digest a little of the substance with *carbon bisulphide* and a solution of *mercuric chloride*. Characteristic and very pungent odour of a mustard oil.

An amine salt of an alkyl- or arylthiocarbamic acid is first formed, and this is then desulphurized by the mercuric chloride.



To distinguish between aliphatic and aromatic primary amines, use is made of the **diazo reaction**.

Dissolve the amine in an excess of *dilute hydrochloric acid*, and carefully add a dilute solution of *sodium nitrite* until free nitrous acid is obtained, as evidenced by its action on starch iodide paper. The contents of the tube must be kept cold by holding under the tap.

Divide into two parts—

1. Pour into a solution of *β-naphthol* in *caustic soda*. The production of a dye indicates a primary aromatic amine (*cf.* test for aniline).

2. Heat. Nitrogen is evolved. The odour of phenol indicates an aromatic primary amine, and that of an alcohol an aliphatic primary amine.

Secondary and Tertiary Amines.—Proceed as in the diazotization of a primary amine. The addition of *sodium nitrite* gives a yellow solution, or else an oily precipitate (solid in some cases) of a

nitrosamine. Extract with ether,¹ free from nitrous acid, by means of caustic soda, and carry out Liebermann's nitroso reaction (*cf.* phenol, p. 107).

NOTE.—Nitrosodimethylaniline does not respond to Liebermann's reaction. On adding sodium nitrite to the solution of the dimethylaniline in hydrochloric acid, a yellow solution results, and a green precipitate of the p-nitroso compound forms on the addition of caustic soda. Diphenylnitrosamine gives a deep blue colour with sulphuric acid alone.

The secondary and tertiary amines may be distinguished by the following tests :—

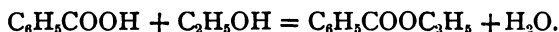
1. Schotten-Baumann's reaction (pp. 120–121) gives an anilide with a secondary (and primary) amine and benzoyl chloride.

2. Tertiary amines readily combine with methyl iodide to give a substituted ammonium iodide.²

Mix the amine with methyl iodide in approximately equal proportions, and warm gently. Crystals of the substituted ammonium iodide will be formed (after cooling, if necessary). The crystals are soluble in water, and AgNO_3 gives an immediate precipitate of silver iodide. They are not decomposed by caustic soda.

Ethyl Benzoate, $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$, by the Fischer and Speier method

Until the year 1895 it was supposed that to obtain the best results in an esterification it was necessary to add large quantities of sulphuric or hydrochloric acid to the mixture of the alcohol and organic acid; thus a common procedure was to saturate the mixture with hydrochloric acid gas. In 1895, Fischer and Speier (*Ber.* 28, 3252) proved that much smaller quantities of acid were sufficient, the most suitable amount being, approximately, 3 per cent.; the part played by the mineral acid is therefore not nearly so much dehydrating as catalytic.



In a 250 c.c. flask place 100 grams (125 c.c.) of absolute alcohol; weigh the flask, and pass into the alcohol a steady stream of dry hydrochloric acid gas till an increase in weight of

¹ If the nitrosamine separates out, it may be filtered off from the aqueous solution, and well washed with water while on the filter-paper to free it from nitrous acid. Wet the filter-paper before pouring the solution on to it.

² Primary and secondary amines also react with methyl iodide, but as a rule more slowly than do tertiary amines. Hence the tests for primary and secondary amines should be carried out before testing for a tertiary amine.

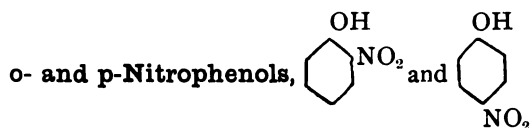
3 grams is observed. The hydrochloric acid gas is very conveniently made by fitting a flask with a tap funnel and delivery tube; concentrated hydrochloric acid solution is placed in the flask, and strong sulphuric acid is allowed to drip in from the funnel.¹ Hydrochloric acid gas is evolved; it should be dried by bubbling through concentrated sulphuric acid, and then passed through a large vertical pipette into the alcohol. Care should be taken that the alcohol does not suck back into the wash-bottle.

When the 3 per cent. solution of hydrogen chloride in alcohol is ready, 50 grams of benzoic acid are introduced into the flask, a reflux condenser fitted, and the mixture is boiled on a water-bath for two hours. The excess of alcohol is then distilled off on the water-bath, and the residue is poured into 300 c.c. of water; powdered sodium carbonate is then gradually added and carefully stirred in till the liquid is no longer acid to litmus. The oily ester is then removed from the mixture by extracting twice with ether; the combined extracts are dried over anhydrous calcium chloride, and after distilling off the ether the residue is fractionated, the ethyl benzoate distilling over between 205° and 211° . Yield c. 45 grams.

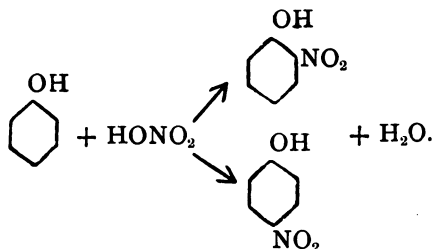
Ethyl benzoate is a colourless, oily liquid of specific gravity 1.050 at 15° . It has a pleasant aromatic odour, and boils at 213° . It can be hydrolyzed in the usual way, giving ethyl alcohol and benzoic acid.

¹ Although at first sight it may seem more satisfactory to drop the hydrochloric acid into the strong sulphuric acid, and so avoid the necessity of a drying-bottle, this procedure is unsuitable, because the hydrochloric acid tends to float on the sulphuric acid instead of mixing with it.

CHAPTER XI



When a nitro group is substituted into phenol, the substitution takes place, as would be expected, in the ortho and para positions to the hydroxyl group; the two isomeric nitrophenols are easily separated by making use of the volatility of the ortho compound with steam, the para compound being practically non-volatile at 100° . The nitrating agent is fairly dilute nitric acid.



In a small flask place 40 grams of phenol, add 5 c.c. of alcohol, and warm gently until a homogeneous liquid is obtained. Into a large flask (1 litre) measure 70 grams (50 c.c.) of concentrated nitric acid, and add 160 c.c. of water. Introduce the molten phenol in small quantities into the larger flask, shaking well after each addition; the temperature of the mixture should be kept throughout below 30° by immersion in cold water. The mixture of acid and phenol becomes dark coloured, and a dark oil separates; allow to stand several hours (preferably overnight), and then add twice its volume of water. After well shaking, the contents are allowed to settle, and as much as possible of the upper aqueous layer

is decanted off; the washing and decantation are again repeated. To the residue in the flask (chiefly *o*- and *p*-nitrophenols and some tarry matter) are added 300 c.c. of water, and the mixture is distilled with steam until the condensed liquid is practically colourless. Should the *o*-nitrophenol solidify in the condenser, run the water out of the cooling jacket for a short time. The steam soon melts the solid, and clears the tube of the condenser. Then run the water into the cooling jacket again; this must be done slowly, or else the hot condenser may be cracked by the cold water. The distillate, which should be collected in several fractions, on cooling deposits practically pure *o*-nitrophenol in the form of needles; the crystals are filtered off, pressed, and dried. If necessary, they may be recrystallized by dissolving in hot alcohol, carefully adding water till a slight turbidity is produced, and allowing to cool. Yield *c.* 15 grams.

To obtain the *p*-nitrophenol from the residue in the flask, boil several times with 200 c.c. of water; filter the extract each time through a fluted filter-paper. There still remains in the residue a certain amount of nitrophenol, to abstract which it is necessary to boil with a mixture of 35 c.c. of concentrated hydrochloric acid and 70 c.c. of water; this extract is filtered, combined with the previous ones, and the whole boiled for half an hour with 10 grams of animal charcoal in a large porcelain dish; the liquid is then filtered through a previously moistened paper to remove the charcoal. The clear solution is made just alkaline by the addition of caustic soda solution, and then evaporated down to a bulk of approximately 100 c.c.; on cooling, the sodium salt of the nitrophenol separates in the form of yellow crystals. These should be filtered off, dissolved in a little hot water, and a slight excess of concentrated hydrochloric acid added; after cooling, the crystals of *p*-nitrophenol are filtered off and recrystallized from hot water. Yield *c.* 7 grams.

o-Nitrophenol consists of yellow needles which melt at 45° , and boil at 214° ; it has a characteristic odour, is slightly soluble in water, and very soluble in alcohol and ether.

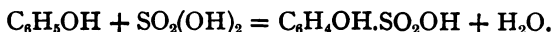
p-Nitrophenol consists of needles which are almost colourless; it melts at 114° , and has no odour; it is easily soluble in alcohol and hot water.

Both the above nitrophenols are soluble in solutions of the alkalis, the ortho compound giving salts with a dark red colour, while the salts of the para compound are a strong yellow; the solutions have

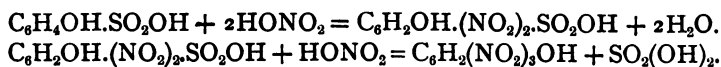
the same colour as the solid salts. On account of their decided acid character, they decompose sodium carbonate, giving salts, and consequently they cannot be separated from solutions of their salts by the action of carbon dioxide. Both substances, on warming with zinc and dilute sulphuric acid for a short time, are reduced to the corresponding aminophenols; the solution containing these can be decanted from the zinc, cooled, and diazotized; on pouring into an alkaline solution of β -naphthol, a red dye is obtained.



Only three nitro groups can be substituted into phenol, the final nitration product being trinitrophenol or picric acid. The method of nitration is to dissolve phenol in concentrated sulphuric acid, when phenol sulphonic acid is obtained.



This phenol sulphonic acid, on treatment with nitric acid, yields first a mono and then a dinitro substituted product, and the latter, on further action with nitric acid, undergoes a kind of double decomposition with formation of trinitrophenol and sulphuric acid.



Mix 12.5 grams of phenol with 12.5 grams (7 c.c.) of concentrated sulphuric acid in a small flask, and heat in a steam oven until a clear solution of phenol sulphonic acid is obtained; carefully add to the solution 10 c.c. of water, and cool well. Introduce the cold mixture, in small quantities at a time, into a fairly large flask containing 50 grams (35 c.c.) of concentrated nitric acid, shaking well after each addition. Brown fumes are evolved owing to part of the phenol being oxidized by the nitric acid. After the addition of all the phenol sulphonic acid, 13 grams of fuming nitric acid are added, and the mixture is heated for two hours on the water-bath. On cooling, the picric acid crystallizes out; the cold mixture is diluted with water, filtered, and the crystals washed with cold water. Recrystallize from hot water to which a little sulphuric acid has been added.

Picric acid crystallizes from aqueous solutions in the form of pale yellow laminae; from ethereal solutions as yellow prisms. It is slightly soluble in water, giving a yellow solution; very soluble in alcohol and ether. It melts at 122.5° , and sublimes if slowly heated, but if a few milligrams are dropped into a red-hot tube, violent detonation occurs; if heated on platinum foil it decomposes and burns quietly. The aqueous solutions are acid, and it forms salts which in most cases have an intense yellow colour, and explode when struck or when slowly heated. The potassium salt is only slightly soluble in water.

1. Mix a solution in benzene with a solution of (a) *naphthalene*, (b) *anthracene*, in benzene, and evaporate. Naphthalene picrate (yellow crystals) and anthracene picrate (ruby red crystals) separate out, which melt at 149° and 138° respectively.

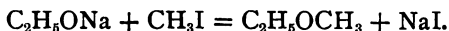
In the case of a salt of picric acid, hydrochloric acid is added to the aqueous solution, and the picric acid extracted with benzene. (The picric acid is precipitated by the HCl, but on shaking up with benzene most of it goes into solution in that solvent. The upper layer is pipetted off and used for the test.)

2. On warming an aqueous solution of picric acid with *potassium cyanide* an intense red colour is produced.

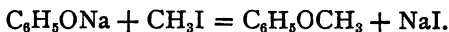
3. The nitro groups may be reduced to amino groups by *tin* and *hydrochloric acid*, and then the diazo reaction applied, as given on p. 122.

Anisol or Phenyl Methyl Ether, $C_6H_5OCH_3$.

The interaction of monohalogen derivatives of aliphatic hydrocarbons with the sodium salts of the alcohols provides a general method for preparing mixed ethers, *i.e.* ethers containing two different radicles linked together by the oxygen atom.



The sodium compounds of the phenols react in a similar manner with alkyl halides, even in the presence of water, giving mixed ethers containing a fatty and an aromatic radicle.



Place 30 c.c. of methyl alcohol in a small flask, add $1\frac{1}{2}$ grams of sodium cut into small slices, or pressed into wire by means of a sodium press, and attach the flask to a reflux water condenser; when the sodium has dissolved, allow the liquid to cool, and add 12 grams of methyl iodide and 6 grams of phenol. Heat the mixture on a water-bath under a reflux condenser for two to three

hours, till the liquid is no longer alkaline; distil off as much of the alcohol as possible on the water-bath, and mix the residue with cold water in a separating funnel, when an oily layer of anisol rises to the surface. Extract with ether, and dry the ethereal solution over calcium chloride; remove the ether on a water-bath, and finally distil the residue over wire gauze, using an air condenser. Collect from 150° – 154° .

Anisol is a colourless liquid of pleasant odour, and boils at 154° ; at 15° its specific gravity is 0.997. It is unaltered by boiling with solutions of caustic alkali.

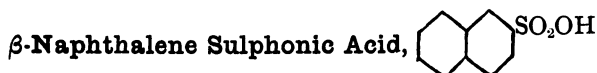
NAPHTHALENE,



Naphthalene crystallizes in white monoclinic tables, which melt at 80.1° and boil at 218.2° . It possesses a very characteristic odour. It sublimes very readily, and is volatile with steam. It is insoluble in water, but readily soluble in alcohol, benzene, ether, and glacial acetic acid.

Mix a solution of naphthalene in benzene with a solution of *picric acid* in benzene. On evaporation, yellow crystals of naphthalene picrate, $[\text{C}_{10}\text{H}_8.\text{C}_6\text{H}_2(\text{NO}_3)_3\text{OH}]$, separate out, which melt at 149° .

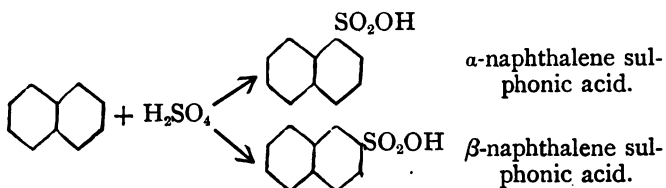
The above properties, *i.e.* very characteristic odour, melting point, and melting point of the picrate, are sufficient to characterize naphthalene. The oxidation to phthalic acid may be done with nitric acid (1 volume concentrated acid to 3 volumes water), but it takes a long time. The quickest way of preparing phthalic acid would be to carry out the preparation (p. 132) on a small scale. The phthalic acid could then be identified by the formation of fluorescein (*cf.* p. 136).



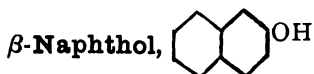
As has already been mentioned, the benzene hydrocarbons have the characteristic property of being readily attacked by sulphuric acid forming sulphonic acids, *e.g.* benzene gives benzene sulphonic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$. The action is rather slow with ordinary sulphuric acid, and consequently fuming sulphuric acid is sometimes used; with the use of this latter agent, however, some sulphone compound is often formed at the same time, *e.g.* benzene sulphone, $(\text{C}_6\text{H}_5)_2\text{SO}_2$. Naphthalene treated with sulphuric

K

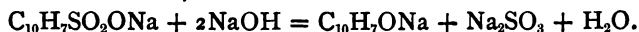
acid yields a mixture of two isomeric sulphonic acids, the relative amounts of each in the mixture depending to a great extent on the temperature at which the reaction proceeds; at 80° – 100° the α -acid is the chief constituent, while at 160° – 180° the product consists mainly of the β -acid.



Mix 50 grams of finely powdered naphthalene with an excess of concentrated sulphuric acid (35 c.c.) in a small flask, and heat in an oil-bath at 170° – 180° for four hours. Allow the liquid to cool somewhat, and then pour it carefully, with constant agitation, into a litre of water in a large porcelain dish. Heat the liquid to boiling, and neutralize it by adding a thick cream of precipitated chalk (*c.* 70 grams) and water, stirring thoroughly after each addition, till the addition of more calcium carbonate causes no further effervescence. Filter the hot liquid through a wet calico filter, wash the residue on the filter with boiling hot water, and finally squeeze as much of the liquid as possible from the pasty residue. If the latter portion of the filtrate is turbid, filter it again through a filter-paper. The clear solution of the calcium salt of the sulphonic acid is then evaporated over a small flame till a small quantity, when withdrawn on a glass rod, will crystallize on cooling. The solution is then allowed to cool, and the deposited salt is filtered off and well pressed; it is redissolved in hot water, and a concentrated solution of sodium carbonate is added, till, on filtering a small portion and adding a little more sodium carbonate solution, all the calcium is found to have been precipitated. The calcium carbonate is filtered off, and the filtrate is evaporated on a water-bath till it begins to crystallize. The liquid is then allowed to stand several hours at the ordinary temperature, and the sodium β -naphthalene sulphonate is filtered off; a second crop can be obtained by further evaporation of the mother liquor. The substance is then first dried by pressing, and subsequently by standing in the air or heating on a water-bath. Yield *c.* 60 grams.



On fusion with caustic alkali the sulphonic acid derivatives of the aromatic hydrocarbons yield the corresponding hydroxy derivatives. This is the method by which most phenols are prepared; *e.g.* phenol is obtained in this manner from potassium benzene sulphonate and the naphthols from the naphthalene sulphonates.



For this preparation a large nickel or iron crucible (capacity $\frac{1}{2}$ to 1 litre) is required, and also a metal stirrer consisting of a hollow iron tube closed at one end and fitted *into* a cork near the other end (the cork is for convenience in holding the stirrer when the latter gets hot during the experiment). A little mercury is placed in the tube, and a thermometer is introduced so that its bulb reaches down into the mercury.

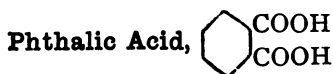
Break 90 grams of caustic soda into small pieces and place in the nickel crucible; add 3 c.c. of water and heat carefully, stirring with the iron tube, till the thermometer shows the fused mass to be at 280° . (N.B. It is advisable to wear an old glove during this fusion as the caustic soda may sputter on to the hand.) The temperature is then maintained constant while 30 grams of sodium β -naphthalene sulphonate are added in separate portions of, approximately, 5 grams; the molten mass is vigorously stirred after each addition, and the temperature is allowed to rise each time to 280° before introducing the next portion. When all the sulphonate has been added, the heating is increased; the liquid becomes more viscid and froths as the temperature rises, and at a temperature of 310° the reaction proper commences. This temperature is maintained for about ten minutes, when the reaction will be practically complete, as evidenced by the melt becoming more fluid and separating into two layers. The heating is then stopped, and the product is poured out on to a copper tray and allowed to solidify. It is then broken up, dissolved in 500 c.c. of water, and treated with a mixture of equal volumes of strong hydrochloric acid and water till it reacts acid to litmus. After cooling, the precipitated β -naphthol is filtered off and recrystallized from water. Yield *c.* 15 grams.

β -Naphthol crystallizes in small colourless plates which melt at 122° and boil at 286° .

With *ferric chloride* solution the aqueous solution of β -naphthol gives a green colour, which quickly disappears, and a white precipitate of dinaphthol, $C_{20}H_{14}O_2$, separates.

β -Naphthyl acetate, $C_{10}H_7OCOCH_3$, can be prepared by boiling together 3 grams of β -naphthol with 7 grams of acetic anhydride for a quarter of an hour, pouring the product into water and stirring. The crude solid which separates is recrystallized from a small quantity of alcohol or a mixture of alcohol and water. Melting point 70° .

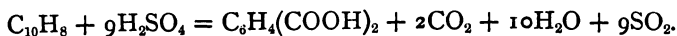
β -Naphthyl benzoate, $C_{10}H_7OCOC_6H_5$, can be prepared by the Schotten - Baumann reaction, as described for phenyl benzoate. Recrystallize the product from alcohol and water. Melting point 107° .



Phthalic acid, or more correctly ortho phthalic acid, is nearly always prepared by the oxidation of naphthalene; in recent years the oxidation has been carried out on a large scale, in the preparation of artificial indigo. The method of oxidation which has proved a commercial success, is to heat naphthalene with concentrated sulphuric acid and a little mercuric sulphate; the latter acts as a catalytic agent, being recovered unchanged at the end of the operation, when it can be used for the oxidation of a fresh quantity of naphthalene. As the oxidation takes place at about 300° , the substance which distils is phthalic anhydride, which fairly readily combines again with water giving phthalic acid.



Or—



In a fairly large retort (400 c.c.) place 20 grams of naphthalene, 10 grams of mercuric sulphate (or 7 grams of mercury), and add a mixture of 150 c.c. of concentrated sulphuric acid with 40 c.c. of water. Clamp the retort so that the beak will act as a reflux condenser, and heat the mixture carefully till the naphthalene has dissolved (this is the case when the layer of molten

naphthalene disappears from the surface). Now place the retort in a fume chamber, arranging it as in an ordinary distillation, fit over the end of its beak a glass tube about $1\frac{1}{2}$ feet long to act as an air condenser, and heat the retort strongly over a naked flame (during this distillation it is advisable to keep a tray of sand on the bench under the retort to absorb the acid if the retort should crack). The liquid darkens, and sulphur dioxide is copiously evolved. At first a little unchanged naphthalene may distil over, but afterwards crystals of phthalic anhydride appear in the condenser and receiver. The distillation is continued till the residue in the flask has become viscous or even solid; the residue contains the mercuric sulphate, and can be used for the oxidation of another lot of naphthalene. The distillate is a mixture of sulphuric acid, phthalic anhydride, and a little phthalic acid; it is poured into twice its bulk of water, and, after cooling, the solid is filtered off, washed, and dried. Yield \approx 9 grams. A small quantity of this solid is then dissolved in hot dilute caustic soda solution; on acidifying the solution with dilute hydrochloric acid, the phthalic acid separates out on cooling.

Phthalic acid crystallizes from water in small white tables. It possesses no definite melting point, because when heated it becomes dehydrated to a greater or less extent into the anhydride; as usually determined, the melting point varies between 180° and 200° . The acid is only very slightly soluble in water; at 14° , 5 parts in 1000.

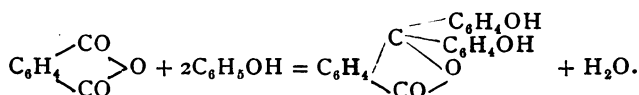
Phthalic anhydride is easily obtained by subliming a little phthalic acid in the manner described previously for benzoic acid.



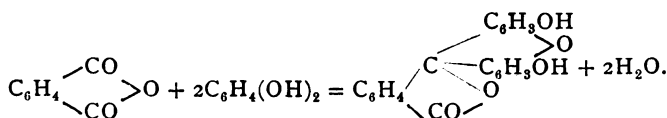
The substance forms beautiful needle-shaped crystals, which melt at 128° ; it boils at 284° . On dissolving in hot water, boiling for some time, and then allowing to crystallize, phthalic acid is again obtained.

Take half the remaining crude phthalic anhydride, add half its bulk of phenol and an equal bulk of sulphuric acid, and boil the mixture for a minute or so. On pouring the red liquid into water an almost colourless solid is obtained. If a little of this be dissolved in dilute caustic soda, a red solution is obtained, which is decolourized by the

addition of dilute acid. The colour change is due to the phenolphthalein formed.



Mix the other half of the crude anhydride with, approximately, half its weight of resorcinol, and heat the mixture in a test-tube for a few minutes till the liquid becomes red. Dissolve a little of the cold product in caustic soda solution and pour into a beaker of cold water, when a beautiful green fluorescence will be observed when the liquids mix; this is due to the fluorescein formed.



ANTHRACENE,

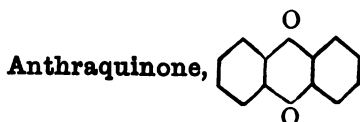


Anthracene crystallizes in four- or six-sided monoclinic white tables, which melt at 216.5° . When quite pure it shows a violet fluorescence. The ordinary purified anthracene is distinctly yellow in colour. It is insoluble in water, but sparingly soluble in alcohol, glacial acetic acid, ether, and benzene, the last liquid being the best solvent.

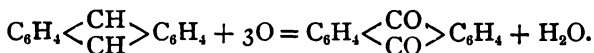
1. Mix a solution of anthracene in benzene with a solution of *picric acid* in benzene. On evaporation, ruby-red crystals of anthracene picrate, $\text{C}_{14}\text{H}_{10} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, separate out. Melting point 138° .

2. Dissolve a little anthracene in a small quantity of hot *glacial acetic acid*. Add roughly twice the weight (of the anthracene) of *chromium trioxide*, and heat to boiling. On pouring the contents of the test-tube into water, anthraquinone separates out. Wash with a little dilute sulphuric acid, and then with water, and recrystallize from glacial acetic acid. Anthraquinone forms yellow rhombic crystals, which melt at 284.6° ; on sublimation it gives yellow needles.

The crude anthraquinone may be tested for as follows. On warming with *caustic soda* and a little *zinc dust*, a red coloration is produced (oxanthranol). If the red liquid is poured off from the zinc dust and shaken up in a test-tube, the colour gradually disappears, owing to oxidation by the air, anthraquinone being again formed.



Anthracene is oxidized by suitable oxidizing agents, forming anthraquinone, a substance which is an important step in the manufacture of the colouring matter alizarin. For the preparation of anthraquinone on a large scale the usual oxidizing agent is a mixture of potassium bichromate with concentrated sulphuric acid; for the preparation of comparatively small quantities in the laboratory, a solution of chromic acid in glacial acetic acid is used. In both cases the oxidizing agent is taken in excess.



Into a $\frac{1}{2}$ -litre flask, fitted with a reflux air condenser, introduce a mixture of 10 grams of anthracene with 100 c.c. of glacial acetic acid; heat the mixture over wire gauze till it boils and till the anthracene has dissolved. Dissolve 20 grams of chromic acid, (CrO_3), in 15 c.c. of distilled water, and add 50 c.c. of glacial acetic acid; place this solution in a tap funnel, and allow the mixture to drip from the funnel down the condenser into the boiling solution of anthracene. The addition of the chromic acid solution should take about three-quarters of an hour; the liquid in the flask is then boiled for a quarter of an hour more, and then, on placing a drop of the liquid on a silver coin, a brown stain should be produced, showing an excess of chromic acid. The mixture is allowed to cool, and is poured into 500 c.c. of water. After standing for a short time the precipitated anthraquinone is filtered off, washed well with hot water, then with a little warm dilute caustic soda solution, and finally again with water. Yield, almost theoretical, *c.* 10 grams.

The substance may be purified by sublimation. The melting point of the purified specimen should be taken; the melting point of pure anthraquinone is 285° , and the boiling point 382° .

SCHEME FOR THE CLASSIFICATION AND IDENTIFICATION OF AN ORGANIC COMPOUND.

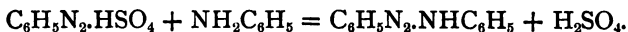
A full scheme is given on pp. 211-227. The student should leave out of consideration substances or classes of compounds which are not mentioned in the Stage II. Syllabus.

PART III

CHAPTER XII

Diazoaminobenzene $\text{C}_6\text{H}_5\text{N}_2\cdot\text{NHC}_6\text{H}_5$.

As has been previously mentioned under the preparation of diazonium compounds, diazonium salts condense with primary anilines, yielding diazoamino compounds. These, however, are more easily obtained by diazotizing the aniline in the presence of insufficient acid for complete conversion into the diazonium salt; the diazonium salt formed then reacts with the unchanged aniline, thus giving diazoaminobenzene in one operation.



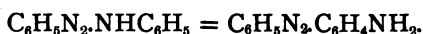
Pour a mixture of 6 grams of sulphuric acid and 600 c.c. of water into a large beaker (1 litre) and add 20 grams of aniline. Warm the mixture to 30° , add slowly 7.5 grams of sodium nitrite dissolved in a little water, and stir thoroughly; maintain the temperature constant for a quarter of an hour. The diazoaminobenzene soon begins to separate. The mixture is allowed to stand at the ordinary temperature for half an hour; the diazoaminobenzene is then filtered off, washed with cold water, and pressed on a porous plate. Yield *c.* 19 grams. A little may be recrystallized from ligroin; this should be done as expeditiously as possible because the substance decomposes if its solution is boiled for any length of time. Shake the crude product with hot ligroin of B.Pt. about 60° – 70° , filter (away from flames), and cool quickly.

Diazoaminobenzene crystallizes in golden-yellow plates, which melt at 98° ; the substance explodes at a slightly higher temperature. The hydrogen atom attached to nitrogen is replaceable by metals; *e.g.* if

alcoholic solutions of the substance and of silver nitrate be mixed, a red crystalline precipitate of $C_6H_5N_2 \cdot NaAgC_6H_5$ is obtained.

Aminoazobenzene, $C_6H_5N_2 \cdot C_6H_4NH_2$.

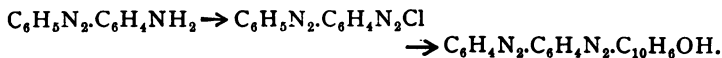
Diazoamino compounds, if suspended in dilute hydrochloric acid, or if kept in alcoholic solution mixed with aniline hydrochloride, slowly undergo rearrangement into para-aminoazo compounds; if the para position is already substituted an ortho-aminoazo compound is obtained. The action is especially favoured by dissolving the diazoamino compound together with some of the hydrochloride of the corresponding aromatic amine in the amine itself. Diazoaminobenzene treated in this way yields p-aminoazobenzene.



Mix together 10 grams of powdered diazoaminobenzene, 5 grams of aniline hydrochloride and 20 grams of aniline, and warm to 40° for an hour. Allow the mixture to stand overnight. Treat the reaction mixture with dilute acetic acid, when the aniline will dissolve, and the aminoazobenzene separate as a friable crystalline mass. Filter and purify by recrystallization from dilute alcohol.

p-Aminoazobenzene forms brownish-yellow needles which melt at 126° ; it is a very stable substance, which can be boiled at a temperature above 360° without decomposing. It is a weak base, which does not form salts with weak acids, *e.g.* acetic, but will do so with mineral acids; *e.g.* it gives a hydrochloride which crystallizes in bluish-violet needles, which dissolve in water with a red colour.

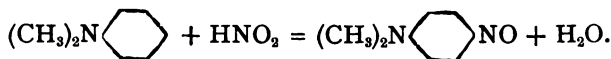
On account of the presence of the amino group, the hydrochloride can be diazotized, forming a diazonium salt which gives a coloured dye a so-called "disazo" compound, with β -naphthol.



On reduction with stannous chloride (*vide* helianthine, p. 149) it forms aniline and p-phenylene diamine. The latter substance gives a violet colour (Lauth's violet) when treated in dilute acid solution with sulphuretted hydrogen and dilute ferric chloride (*cf.* p-amino dimethylaniline). Therefore, after the reduction, make alkaline, extract with ether, and, after evaporating off the latter, test the remaining mixture of aniline and p-phenylene diamine in the manner described.

p-Nitrosodimethylaniline, $\text{NOC}_6\text{H}_4\text{N}(\text{CH}_3)_2$.

Primary aromatic amines on treatment with nitrous acid in acid solution yield diazonium compounds, containing the $\begin{array}{c} \text{—N—} \\ ||| \\ \text{N} \end{array}$ group; secondary amines yield nitrosamines containing the $=\text{N.NO}$ group. Many tertiary aromatic amines have no action with nitrous acid, but those which are dialkyl anilines, containing an unsubstituted hydrogen in the para position, form substances with a nitroso group substituted in the para position, *i.e.* para-nitrosodialkyl anilines.



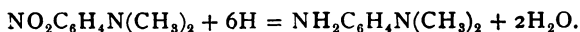
Dissolve 20 grams of dimethylaniline in a mixture of 70 c.c. of concentrated hydrochloric acid with 50 c.c. of water; cool the solution in a freezing mixture, and add slowly, in small portions, with continual shaking, a solution of 12 grams of sodium nitrite in 20 c.c. of water. Allow the mixture to stand in the cold for about an hour, and then filter off the yellow nitrosodimethylaniline hydrochloride which has separated, and wash the precipitate with a little dilute hydrochloric acid. Yield *c.* 23 grams. Three-fourths of the hydrochloride may be purified by recrystallization from hot water containing a few drops of hydrochloric acid.

To obtain the free base, take the remaining crude hydrochloride, mix into a thin cream with water, and treat in the cold with caustic soda solution till the liquid becomes alkaline; the green free base is liberated. The base is extracted with ether, the ethereal solution dried over potash, and after decanting from the latter, most of the ether is distilled off; the residual solution is poured into a beaker, and allowed to crystallize.

Para-nitrosodimethylaniline crystallizes in large green leaves, which melt at 85° ; its hydrochloride crystallizes in small yellow needles.

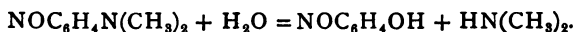
Reactions.—Although a nitroso compound, this substance does not respond to Liebermann's "nitroso" reaction.

On reduction in dilute hydrochloric acid solution by granulated zinc, the nitroso group is transformed into an amino group, an almost colourless solution of p-amino dimethylaniline being obtained.



A little of this solution, on diluting with water and treating with a little sulphuretted hydrogen and ferric chloride solutions, gives the methylene blue test (*cf.* p. 150).

Add 5 grams of nitrosodimethylaniline hydrochloride in small quantities to a boiling solution of 5 grams of caustic soda in 200 c.c. of water, waiting for each portion to dissolve before adding the next. The odour of dimethylamine will be observed in the steam. When the green colour has been replaced by a reddish-brown, allow the liquid to cool, acidify with hydrochloric acid, and extract with ether. After removal of the ether in the usual way, a dark crystalline residue of *p*-nitrosophenol (quinone oxime) is obtained; if required, this can be recrystallized from benzene, but for the following two tests it is unnecessary.



1. As a nitroso compound, nitrosophenol gives the Liebermann's reaction (*q.v.*).

2. It dissolves in caustic soda solution with a reddish-brown colour, and is reprecipitated as a colourless solid on adding acid.

Benzoin, $\text{C}_6\text{H}_5\text{CO}.\text{CHOH}.\text{C}_6\text{H}_5$.

When an alcoholic solution of benzaldehyde is heated with a small quantity of potassium cyanide, the benzaldehyde polymerizes, forming benzoin.



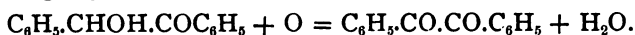
This action is not restricted to benzaldehyde, but is common to many aromatic aldehydes.

Dissolve 5 grams of potassium cyanide in 50 c.c. of alcohol and add 25 grams of freshly distilled benzaldehyde. Heat the mixture on a water-bath for half an hour, in a small flask fitted with a reflux condenser. Allow to cool; filter off the separated benzoin, and recrystallize a portion from a little alcohol. Yield *c.* 20 grams.

Benzoin crystallizes in colourless prisms, which melt at 137° . It is slightly soluble in hot water, very soluble in hot alcohol, but only slightly in cold. When dissolved in concentrated sulphuric acid it gives a violet colour. It reduces Fehling's solution, itself becoming oxidized to benzil.

Benzil, or **Dibenzoyl**, $\text{C}_6\text{H}_5\text{CO}.\text{CO}.\text{C}_6\text{H}_5$.

The $-\text{CHOH}$ group of benzoin can easily be oxidized to a ketone group in the usual manner of secondary alcohols.



Place 15 grams of benzoin in a small flask, add 35 c.c. of strong nitric acid, attach an air condenser, and heat on a water-bath for about two hours. At the end of the action the benzoin crystals will have disappeared completely, and a clear oil will remain in its place. Pour into cold water, when the oil will solidify to a yellow solid. Filter off this solid, wash with water, and recrystallize from alcohol. Yield *c.* 12 grams.

Benzil crystallizes in pale yellow needles, which melt at 95°. It forms three distinct dioximes, whose existence is accounted for by stereoisomeric differences, as explained under the Beckmann rearrangement (p. 142). On boiling with alcoholic potash a violet colour is obtained.

Benzilic Acid, or Diphenylglycollic Acid,
 $(C_6H_5)_2COH.COOH$.

When benzil is heated with fused caustic potash, a reagent which often causes the disruption of the molecule of an organic substance, not only is the benzil not disrupted but a remarkable rearrangement occurs, in which two phenyl groups become attached to the same carbon atom. The product of the action is the potassium salt of benzilic acid.

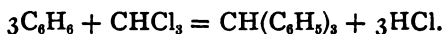


Place 50 grams of caustic potash and 5 c.c. of water in a nickel crucible, and fuse the mixture. Regulate the temperature to 150°, and add ten grams of finely powdered benzil. Stir the mixture with a stout iron wire (holding the latter by means of a cork), when the mixture soon sets to a solid mass on account of the formation of potassium benzilate. Allow to cool, dissolve in water, and precipitate the benzilic acid by acidifying with hydrochloric acid. When cold, filter off the precipitate, dissolve in hot water, and boil for a quarter of an hour, when traces of benzoic acid which have been formed will pass off in the steam; again allow to cool. The benzilic acid separates in small colourless needles.

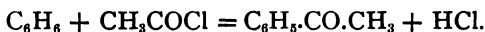
Benzilic acid melts at 150°. It is readily soluble in alcohol and ether and boiling water, but is only slightly soluble in cold water. It is dissolved by concentrated sulphuric acid, with formation of a red colour, which disappears on dilution.

Acetophenone, $\text{CH}_3\text{CO}\cdot\text{C}_6\text{H}_5$, by the Friedel and Crafts Reaction.

The Friedel and Crafts reaction, which is applicable to the preparation of aromatic hydrocarbons and ketones, depends on the catalytic effect of anhydrous aluminium chloride in the elimination of hydrochloric acid from a mixture of two substances, one of which is a hydrocarbon and the other a chloro-compound. Thus triphenyl methane can be made by the interaction of benzene and chloroform in the presence of anhydrous aluminium chloride.



For the preparation of aromatic ketones the process is similar, except that the chlorine compound taken is an acid chloride; in this way benzoyl chloride and benzene yield benzophenone, while acetyl chloride and benzene yield acetophenone. The aluminium chloride acts by forming an addition compound with the acid chloride; the addition compound then reacts with the hydrocarbon to form the ketone, while the aluminium chloride is regenerated. The action is so vigorous that generally a suitable solvent, *e.g.* carbon bisulphide, or a large excess of the hydrocarbon reagent, is taken in order to moderate it.



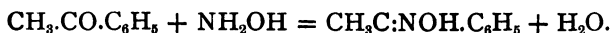
Acetophenone Preparation.—Weigh into a dry flask ($\frac{1}{2}$ -litre) 30 grams of powdered anhydrous aluminium chloride and add 200 grams of benzene; fit the flask with a reflux condenser, and stand in a bath of cold water. Place 20 grams of acetyl chloride in a tap funnel, insert the latter loosely into the top of the condenser, and allow the acetyl chloride to drop slowly into the mixture in the flask, shaking the latter frequently in order to ensure a good intermixing of the liquids. When the addition of the acetyl chloride is complete, the flask should be immersed for an hour in a bath of water at 50° . When cold, the contents of the flask are poured into an equal bulk of cold water in a large flask, and after shaking well, the benzene layer is separated by means of a tap funnel; the acetophenone is in solution in the benzene. The benzene solution is shaken with dilute caustic soda to remove free acid, and is then dried over calcium chloride. Finally, the liquid (after filtration, if necessary) is distilled on a water-bath in order to remove most of the benzene; the residue is distilled with an air condenser, and the fraction from 196° – 202°

collected separately. This fraction, which consists of an almost colourless oil, solidifies completely on standing. Yield c. 15 grams.

Acetophenone consists of colourless crystalline plates, which melt at 20° and boil at 202° ; it has a faint characteristic odour. It is insoluble in water. Like all ketones in which the carbonyl group is directly attached to the benzene ring, it gives no sodium bisulphite compound; it reacts with hydroxylamine, however, in the usual way. By gentle oxidizing agents, *e.g.* alkaline permanganate, it is oxidized to benzoyl formic acid, $\text{C}_6\text{H}_5\text{CO}\cdot\text{COOH}$; stronger oxidizers, *e.g.* chromic acid, give benzoic acid and carbon dioxide.

Acetophenoneoxime, $\text{CH}_3\text{C:NOH}\cdot\text{C}_6\text{H}_5$.

This is prepared in the usual way by the interaction of the ketone with hydroxylamine, the latter being obtained by mixing the hydrochloride with the theoretical quantity of potassium hydroxide.



Dissolve 6 grams of hydroxylamine hydrochloride in 10 c.c. of water, add 9 grams of molten acetophenone, and then add a solution of 5 grams of caustic potash in 5 c.c. of water (care must be taken to avoid an excess of potash, else the potassium salt of the oxime, which is soluble in water, will be obtained). Add boiling alcohol, shaking continuously, till the mixture becomes clear; heat the solution on a water-bath for two or three hours, and then pour into 100 c.c. of water. The oxime separates out and is extracted with ether; after removal of the ether, the residue is recrystallized from a little petroleum ether. Yield 9 grams.

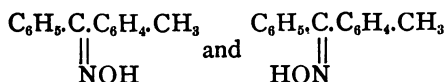
Acetophenoneoxime forms colourless needles, which melt at 59° . It is extremely soluble in alcohol and ether; it is also soluble in acids and in alkalis, although only slightly soluble in water.

Beckmann's Rearrangement.—Under the influence of certain substances, the most important of which is phosphorus pentachloride, the oximes of aromatic ketones, even at comparatively low temperatures, undergo a remarkable intramolecular rearrangement. The rearrangement occurs in such a way that the $-\text{OH}$ of the oxime group exchanges positions with one of the hydrocarbon radicles. The substance thus primarily obtained is, as a rule, not stable, but is the tautomeric form of a

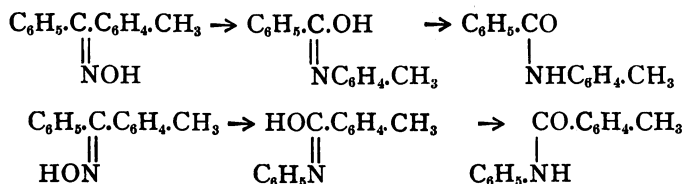
stable amide or anilide into which it immediately changes by the movement of a hydrogen atom. For example, acetophenone-oxime yields acetanilide.



This "Beckmann" rearrangement, so named after its discoverer, is of extreme value in the case of stereoisomeric ketoximes. Certain aromatic ketones yield more than one oxime, *e.g.* phenyltolylketone yields two oximes whose constitutions seem to be identical. The isomerism is supposed to be due to the nitrogen atom, of which the third valency, when two are attached as a double bond to one other atom, does not project in the same plane as the other two bonds, but sticks out at an angle. In phenyltolylketoxime the third valency carrying the $-\text{OH}$ group may project in the direction of the phenyl group, or in the direction of the tolyl group, and in this way the possibility of the existence of the two stereoisomers is explained; the two formulæ can be expressed—



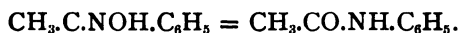
If these two formulæ are correct, we should expect that in the Beckmann rearrangement one oxime would allow the OH group to interchange positions more readily with the adjacent phenyl group, while the other would allow the OH to interchange with the tolyl group. This is completely in accord with the experimental results, for the one oxime yields benzoyl toluidide, while the other yields toluidyl anilide—



The Beckmann rearrangement is therefore of great value in investigating the constitution of such stereoisomeric ketoximes. Acetophenone yields only one oxime, in which, from the behaviour

in the Beckmann rearrangement, the OH of the oxime group must be adjacent to the phenyl group.

To perform such a rearrangement with acetophenoneoxime, 4 grams are dissolved in 50 c.c. of dry ether (free from water and alcohol, see p. 147), and 6 grams of powdered phosphorus pentachloride are slowly added in small quantities at a time. The ether is then distilled off, and the flask containing the residue is cooled by immersion in cold water, while 20 c.c. of water are slowly added. The cold mixture is then filtered, and the solid (acetanilide) is recrystallized from water. The melting point (112°) of the dried product should be taken.



Preparation of Ethyl Benzene, $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$, by Fittig's Synthesis.

The action of sodium on mixtures of the halogen compounds of the hydrocarbons provides a general method of synthesizing hydrocarbons; when applied to the aliphatic compounds the process is generally known as Wurtz' synthesis, while with aromatic compounds it is termed Fittig's synthesis. For the lower and more reactive compounds the action is best allowed to proceed in ethereal solution, while with halogen derivatives of higher hydrocarbons the sodium is allowed to act directly on the mixture of the liquids; a little ethyl acetate is often added because it has a catalytic effect.

To prepare ethyl benzene, a mixture of ethyl bromide and brombenzene is taken in ethereal solution.



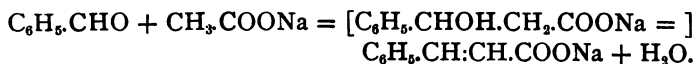
Take 200 c.c. of ether and shake with half its volume of water three times in a separating funnel to extract the alcohol. Allow the moist ether to stand for at least two hours over calcium chloride, and then either filter through a fluted filter or distil. Place 100 c.c. of this alcohol-free ether in a dry $\frac{1}{2}$ -litre flask, containing 27 grams of sodium, cut into thin slices or pressed into wire. Fit the flask with a reflux condenser (double surface) and stand it on a cork ring. Allow to stand an hour or so, and when the evolution of hydrogen (due to the presence of traces of water) has ceased, add 60 grams of ethyl bromide and 60 grams of brombenzene; if the liquid begins to boil, it should

be cooled by immersing the flask for a short time in cold water. It is then allowed to stand overnight. The liquid is then poured off from the blue powder which has formed, the powder is shaken with a little fresh ether, and after settling, the extract is poured off into the main quantity of liquid, and the ether distilled off from the latter on a water-bath. The residue is distilled, using a fractionating column; the fraction from 127° to 137° should be redistilled, and the portion which distils at a constant temperature collected. Yield *c.* 24 grams.

Ethyl benzene is a colourless liquid which boils at 136° ; its specific gravity is 0.872 at 15° .

Preparation of Cinnamic Acid, $C_6H_5CH:CH.CO_2H$, by the Perkin Reaction.

Aromatic aldehydes, on heating with the sodium salt of a fatty acid in the presence of the corresponding acid anhydride, condense with the sodium salt, giving as final product the sodium salt of an unsaturated acid. This method of preparing unsaturated acids is known as the Perkin reaction. It is probable that the aldehyde and sodium salt first form an addition compound, which, under the influence of the high temperature and of the dehydrating action of the acid anhydride, loses water, giving the salt of an unsaturated acid. Benzaldehyde and sodium acetate treated in this way give the sodium salt of cinnamic acid.



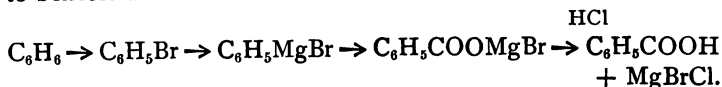
Weigh into a small flask 20 grams of freshly distilled benzaldehyde, 30 grams of acetic anhydride, and 10 grams of anhydrous sodium acetate. Fit the flask with a long air condenser, and heat for eight hours in an oil-bath at 180° – 190° . Pour the reaction mixture while still warm into a round-bottomed litre flask containing 100 c.c. of warm water, rinse the walls of the small flask with a little water, and add the rinsings to the contents of the large flask. Add powdered sodium carbonate in small quantities to the large flask till the contents are alkaline, and then steam distil off the residual benzaldehyde. Filter the liquid remaining in the flask to remove any tarry matter, and precipitate the cinnamic acid from the clear solution by the addition of concentrated hydrochloric acid. When the mixture is cold, filter

off the cinnamic acid and recrystallize from hot water. Yield, 17 to 20 grams.

Cinnamic acid crystallizes in pearly plates; it melts at 133° , and, if quickly heated, boils at 300° . It is practically insoluble in cold water, but dissolves readily in ether, alcohol, and hot water. As an aromatic acid containing an unsaturated side-chain, it is easily oxidizable, *e.g.* it turns alkaline permanganate green almost immediately. Also in carbon bisulphide solution, bromine is added, forming dibromcinnamic acid, $C_6H_5.CHBr.CHBr.COOH$, whilst in alkaline solution it is reduced by sodium amalgam to hydrocinnamic acid or β -phenyl propionic acid, $C_6H_5.CH_2.CH_2.COOH$.

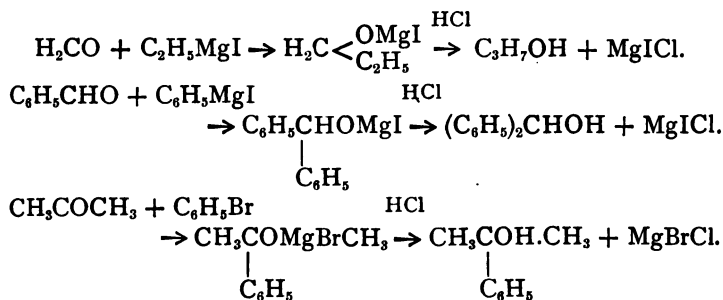
Diphenyl Carbinol (Benzhydrol), $(C_6H_5)_2CHOH$, by use of a Grignard Reagent.

When magnesium is warmed with organic halogen compounds (preferably the iodides or bromides) in the presence of ether, an organo-magnesium compound of the type $R.Mg.Hal$ is obtained, where R represents an organic radicle, and Hal a halogen atom. The ether which is used acts as a catalytic agent. The probable mechanism of the action is the primary formation of an oxonium compound, $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O < \begin{matrix} R \\ Hal \end{matrix}$, with which the magnesium can enter into reaction, since only in exceptional cases will magnesium and organic halides react directly without the intervention of a third substance. The organo-magnesium halides (Grignard compounds) formed are extremely reactive substances which have proved themselves of great value for synthetic work. If carbon dioxide be passed through their ethereal solution it is absorbed with formation of a compound, which yields the corresponding carboxy-acid derivative on treatment with dilute mineral acid; *e.g.* phenyl magnesium bromide gives benzoic acid, and we thus have a simple method of passing from benzene to benzoic acid.

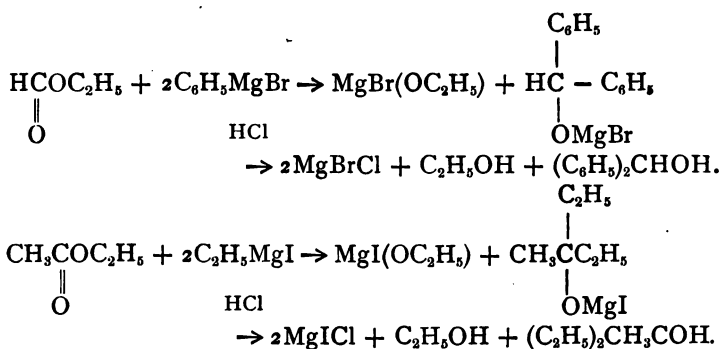


Substances containing a double linkage are acted on in such a way that the double bond is changed to two single ones; *e.g.* when a carbonyl group is acted on, the $MgHal$ group attaches itself to the oxygen, while the hydrocarbon radicle attaches itself to the carbon. In this way paraformaldehyde yields primary,

other aldehydes yield secondary, and ketones yield tertiary alcohols.



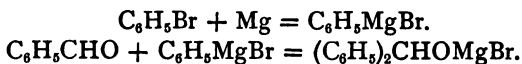
If the carbonyl group be part of a carboxy ester group, *e.g.* $-\text{COOC}_2\text{H}_5$, not only does the above action take place at the carbonyl group, but the OC_2H_5 group is removed and replaced by a hydrocarbon radicle; in this way formic esters yield secondary, and other esters tertiary, alcohols.



As will be seen from the above statements, with phenyl magnesium bromide, benzaldehyde yields diphenylcarbinol $(\text{C}_6\text{H}_5)_2\text{CHOH}$. For the successful performance of such a preparation, clean magnesium is allowed to act on the correct quantity of brombenzene dissolved in *dry* ether¹ (free from

¹ The ether should be prepared by extracting ordinary ether three times with one-third its bulk of water in order to remove as much of the alcohol as possible; the ether is then dried for at least a day over calcium chloride, poured into a bottle containing finely divided sodium (wire or shavings), and allowed to stand till no more bubbles of hydrogen are seen to rise from the metal; the ether is then distilled off and preserved for use.

water and alcohol), and the solution of the organo-magnesium compound is then allowed to act on rather less than the theoretical quantity of pure benzaldehyde, also in dry ether solution; since the organo-magnesium compounds are decomposed by water, great care should be taken throughout the experiment to exclude moisture as completely as possible. It is convenient to take one-tenth of the quantities expressed in the equations—



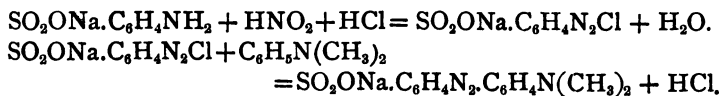
Clean several lengths of magnesium ribbon by drawing them through emery-paper, and then through a clean duster or through folded filter-paper. Cut the magnesium into lengths of about 2 centimetres. Weigh out into a dry 250 c.c. flask 16 grams of freshly distilled dry brombenzene, add 30 grams of dry ether, introduce 2.4 grams of the cleaned magnesium, and fit the flask with a reflux condenser (double surface). On warming for a short time on the water-bath, reaction soon sets in, when the flask should be removed from the bath and allowed to stand on a cork ring (a dry duster will also serve the purpose) until the action almost ceases; the reaction is then completed by boiling on the water-bath for twenty minutes, when the magnesium will have passed almost completely into solution. (If the action is slow in starting, the addition of a minute crystal of iodine will often expedite it.) Place in a dry flask 10 grams of freshly distilled benzaldehyde, add 25 grams of dry ether, and cool the mixture in ice and water; to the cold solution of benzaldehyde add slowly, with continual shaking, the solution of phenyl magnesium bromide. A vigorous action takes place and a precipitate separates out. After the addition of all the reagent, and while the flask is still in the cooling bath, the mixture is carefully treated with a few lumps of clean ice, or with 25 c.c. of cold water; a mixture of equal volumes of concentrated hydrochloric acid and water is then added, till, on shaking, the precipitate of magnesium hydroxide is dissolved, and the aqueous layer becomes clear. Extract with ordinary ether, shake the ethereal extract with dilute sodium bisulphite solution to remove any unchanged benzaldehyde, and dry over anhydrous potassium carbonate. Evaporate off the ether on a water-bath, pour the oily residue into a porcelain dish, and stir well with a glass rod to make it crystallize; the liquid will then almost

completely solidify, and the crystals should be pressed on a porous plate. Yield \approx 13 grams. The benzhydrol can be further purified by recrystallization from petroleum ether.

Benzhydrol consists of white colourless needles which melt at 68° ; at 298° it boils with partial dehydration into its ether, $(C_6H_5)_2CH.O.CH(C_6H_5)_2$. As a secondary alcohol it is oxidized by suitable agents (e.g. chromic acid) to a ketone, benzophenone, $C_6H_5COC_6H_5$. The benzoyl derivative of benzhydrol (benzhydrol benzoate), which can be prepared by the Schotten-Baumann reaction, melts at 89° .

Methyl Orange (Helianthine), $SO_2ONa.C_6H_4N_2.C_6H_4.N(CH_3)_2$.

The preparation of this substance depends merely on the coupling of a diazo compound with a tertiary amine. The substance to be diazotized, sulphanilic acid, is dissolved in the theoretical quantity of sodium carbonate, the theoretical quantity of sodium nitrite is then added, and the nitrous acid for the diazotization is slowly liberated by the cautious addition of the correct quantity of hydrochloric acid. A solution of dimethylaniline hydrochloride is then added to the diazo solution, when the coupling ensues.



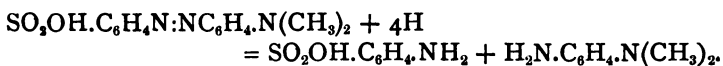
Dissolve 12 grams of sulphanilic acid (containing 2 molecules of water of crystallization) in 100 c.c. of water containing 3 grams of anhydrous sodium carbonate, and add a solution of 4 grams of pure sodium nitrite in 20 c.c. of water. Cool the mixed solutions in ice, and very gradually add a cold mixture of 7 c.c. of concentrated hydrochloric acid and 10 c.c. of water. Dissolve 7 grams of dimethylaniline in a mixture of 7 c.c. of concentrated hydrochloric acid and 20 c.c. of water, and pour this cold solution slowly into the diazo solution.

Make the mixture slightly alkaline with caustic soda solution, when the methyl orange will begin to separate out. Add 20 grams of finely powdered common salt, and dissolve by shaking, in order to salt out the methyl orange more completely. When the precipitation is complete, the solid is filtered off, pressed on a porous tile, and recrystallized from hot water. Yield \approx 16 grams.

Methyl orange is the sodium salt of a complex sulphonic acid,

and the colour of its ion is yellow; the un-ionized free acid is red when in solution, and the use of the substance as an indicator depends on this colour change.

Reduction of Methyl Orange.—The constitution of most azo compounds, of which obviously methyl orange is one, is usually most easily proved by means of reduction with a solution of stannous chloride in hydrochloric acid. The azo molecule then undergoes disruption at the double bond of the azo group, and two simpler amino compounds are formed; one of these is the substance which was originally diazotized, but the other product contains an $-\text{NH}_2$ group more than the other original reagent; for example, methyl orange yields sulphanilic acid and p-aminodimethylaniline.



Dissolve 3 grams of methyl orange in as little hot water as possible, add a solution of 12 grams of stannous chloride in 30 grams of concentrated hydrochloric acid, and heat till the mixture loses its colour. Pour the colourless mixture into a strong beaker, cool well, and rub the walls with a glass rod; sulphanilic acid separates, and should be filtered off through a little asbestos. Add 30 c.c. of water to the filtrate, and then caustic soda solution, till the precipitate of stannic hydroxide, which first forms, has completely redissolved. Extract three times with a little ether, dry the ethereal extract over caustic potash, and decant into a small distilling flask; evaporate off the ether on a water-bath, when p-aminodimethylaniline remains as an oil. On cooling and stirring, it will solidify. When pure it is a white crystalline solid, which melts at 41° and boils at 257° .

Reactions of p-aminodimethylaniline.—1. On oxidation by a mixture of *potassium bichromate* and *sulphuric acid*, quinone is formed, as is the case with most p-disubstituted bodies. The quinone is easily detected by its odour.

2. Dissolve a little of the substance in the least possible quantity of dilute *sulphuric acid*. Add a few drops of this solution to, approximately, 100 c.c. of a dilute solution of *sulphuretted hydrogen*, to which has been added 2 c.c. of concentrated *hydrochloric acid*. On adding to this mixture a few drops of a dilute solution of *ferric chloride*, an intense blue colour is obtained (methylene blue). This can be used as a delicate test for sulphuretted hydrogen. The mechanism of the

Fuse about 30 grams of anhydrous zinc chloride in a porcelain dish, and pour the fused mass on to a stone slab to solidify. Weigh 10 grams of the powdered chloride into a clean porcelain dish, and add 25 grams of dimethylaniline and 10 grams of benzaldehyde, both freshly distilled. Heat on a water-bath for four hours, with frequent stirring. Add warm water to the hot product, stir together, and pour into a flask ($\frac{1}{2}$ -litre). Distil off any residual dimethylaniline by steam. Allow the contents of the flask to cool, decant the water, and wash the residue in the flask several times with water, decanting each time. Then add alcohol to the residue, and warm on a water-bath till dissolved; filter the hot solution, and allow to stand overnight in a cold place. Filter off the colourless crystals, and dry in the air between several sheets of filter-paper.¹ A further crop may be obtained by evaporating the mother liquor to a smaller bulk.

Leuco malachite green crystallizes from alcohol in small plates, which melt at 93° – 94° , and from benzene in needles which melt at 102° .

Oxidation of the Leuco Base.—For the oxidation, freshly precipitated lead peroxide is used. Take 12 grams of lead acetate dissolved in 60 c.c. of water in a porcelain dish, add excess of a filtered bleaching-powder solution (about 25 grams in 400 c.c. of water), and keep the mixture just below its boiling point till the precipitate, which was originally yellow, becomes deep brown. Decant the mother liquor from the precipitate, and wash the latter by decantation several times with water.

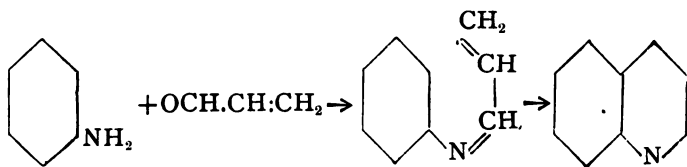
Take 8 grams of the leuco base, dissolve by warming in a mixture of 10 c.c. of concentrated hydrochloric acid and 20 c.c. of water, and mix with 500 c.c. of water in a large flask (1 litre). Add 10 c.c. of water containing 4 c.c. of glacial acetic acid, and introduce several pieces of ice to cool the mixture. Mix the lead peroxide, prepared as above, with water to obtain a thin paste, and pour this slowly into the contents of the large flask, extending the addition over five minutes. Allow the mixture to stand five minutes more, with frequent shaking, then add a solution of 10 grams of sodium sulphate in 50 c.c. of water, and filter through a fluted filter-paper to remove the lead sulphate and chloride. Add to the filtrate a solution of 8 grams of zinc chloride in as little water as possible, then add 300 c.c. of saturated salt solution to aid the separation

¹ If the substance separates as an oil, it must be redissolved in more hot alcohol and allowed to separate once more.

of the dye. The complete separation of the dye is indicated by a drop of the liquid, when placed on filter-paper, giving practically no stain where it spreads itself round the little patch of solid in the centre. Filter off the dye on the pump, wash with a little salt solution, and dry on a porous tile. To further purify it, it may be dissolved in hot water and again salted out. The product is a double salt with zinc chloride, $(C_{23}H_{25}N_2Cl)_3 \cdot 2ZnCl_2 \cdot 2H_2O$. It is used largely as a dye.

Quinoline, C_9H_7N , by the Skraup Reaction.

The Skraup reaction is of value for the preparation of quinoline and its derivatives; it depends on the condensation of aniline and glycerol in the presence of sulphuric acid, when quinoline is formed; by replacing aniline by its homologues, homologous quinolines are obtained. For the preparation of quinoline, a mixture of aniline, glycerol, nitrobenzene, and sulphuric acid is allowed to react. The mechanism of the action is probably that the glycerol is first dehydrated to acrolein, which condenses with the aniline, forming a body with a tertiary amine group in the side chain; the end of this side chain then attaches itself to the benzene nucleus under the oxidizing influence of the nitrobenzene.



Weigh into a large round flask (2 litre) 24 grams of nitrobenzene, 36 grams of aniline, 100 grams of glycerol, and 100 grams of concentrated sulphuric acid. Fit the flask with as wide a condenser as possible (because of the vigour of the action), and warm the flask very carefully on a sand-bath. As soon as the action commences (indicated by white fumes forming above the liquid) the hot sand-bath should be removed and the flask supported on a duster. When the first vigorous action has subsided, replace the sand-bath and boil the mixture for three hours. Add 200 c.c. of water to the dark-coloured product, and steam distil to remove the residual nitrobenzene. Make the contents of the flask alkaline by the addition of solid caustic soda, and again distil with steam. The distillate contains the quinoline mixed with some aniline.

To remove the aniline, acidify with sulphuric acid, and add sodium nitrite solution till a drop of the liquid, withdrawn on the end of a glass rod and diluted with water in a watch glass, stains starch iodide paper blue. The aniline is thus converted into benzene diazonium sulphate. The liquid is then boiled, when the diazonium salt is decomposed, forming phenol. Make the liquid alkaline once more with caustic soda, and again distil with steam. Pure quinoline then passes over, and is extracted from the distillate with ether. The extract is dried over solid caustic potash, and, after decanting the liquid, the ether is evaporated off. The residue is distilled, and the quinoline comes over between 234° and 239° . Yield *c.* 40 grams.

Quinoline is a colourless, highly refractive liquid. It boils at 239° , and at 15° has a specific gravity 1.098.

CHAPTER XIII

QUANTITATIVE DETERMINATION OF THE ELEMENTS

Carbon and Hydrogen.

The elements carbon and hydrogen are always estimated simultaneously. A little of the substance (usually contained in a platinum or porcelain boat) is placed in a long tube of hard glass filled with copper oxide, and a current of air or oxygen is passed through the tube ; on heating (in a special "combustion furnace"), the substance is oxidized, partly by free oxygen and partly by the copper oxide, to water and carbon dioxide. The water is collected in a U-tube containing pumice soaked with concentrated sulphuric acid, whilst the carbon dioxide is absorbed in a suitable piece of apparatus containing potassium hydroxide solution (sodium hydroxide is not used, because on absorbing carbon dioxide it readily gives a precipitate of sodium carbonate which would choke the apparatus). U-tubes of soda-lime are also sometimes used for the absorption of the carbon dioxide, but this substance is hardly as satisfactory as caustic potash solution.

The air and oxygen are stored in separate gas holders so that the gases are under a slight pressure. Each holder is connected to two large U-tubes (see Fig. 20), one filled with beads wetted with strong caustic potash solution, and the other with beads wetted with strong sulphuric acid ; each tube is fitted by a bung into the neck of a bottle (A and A') containing a store of the corresponding liquid. Before an experiment, the glass plug (B and B') should be withdrawn from the neck of each bottle, and air should be forced into the space above the liquid so as to drive the latter up on to the beads ; the liquid is then allowed to fall back again, and the plug is replaced. In this way the beads are wetted with fresh liquid each time. Both the sulphuric acid tubes are connected to a T-tube attached to a small bulb containing a little strong sulphuric acid, which serves to show the rate at which either gas is passing.

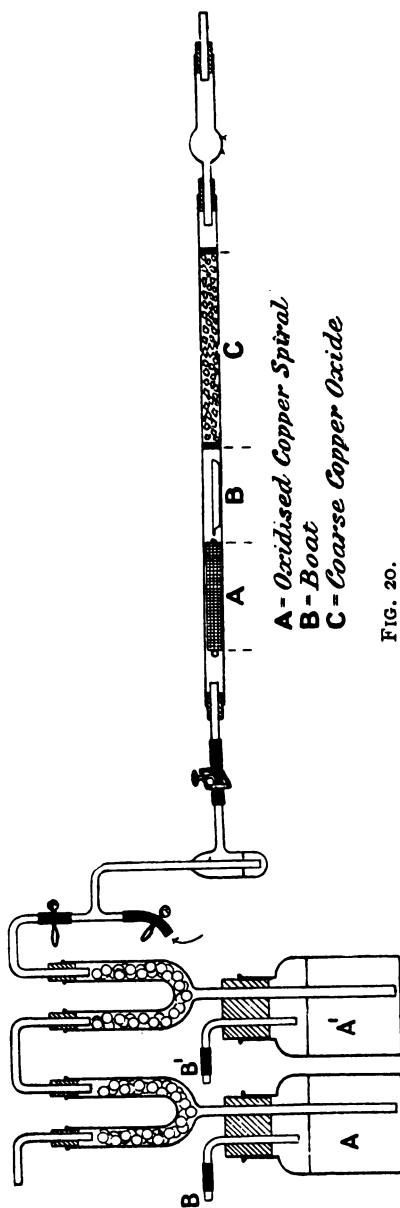


FIG. 20.

The U-tube for the absorption of the water formed in the combustion is usually of the shape shown in Fig. 21. To fit it up, small fragments of pumice are heated in a dish with a little concentrated sulphuric acid till they become saturated; when cold, the pumice is introduced into the tube, and the top of each vertical limb should be sealed off carefully in a blow-pipe flame (the tube should *not* be closed by bungs). The tube is then fitted with a small wire loop (platinum) so that it may be easily suspended for weighing. The small bulb serves to collect a great deal of the water by mere condensation, any moisture not condensed in the bulb being absorbed by the sulphuric acid on the pumice; in this way, unnecessary dilution of the acid is avoided. If the tube has been used previously, the water should be shaken from the small bulb, a piece of rubber tubing attached, and fresh sulphuric acid drawn into the tube, the excess being afterwards allowed to drain out again; the sulphuric acid should be removed from the interior of the

narrow side tube by means of a narrow roll of filter-paper. The acid, when the tube has been allowed to stand a short time, must not nearly fill the bore of the tube at the bend. A tube prepared in this way, if the condensed water is ejected from the bulb after the completion of each combustion, can be used for several experiments without requiring fresh acid. When not in use, the U-tube should be kept closed by small pieces of rubber tubing plugged with glass rod.

There are two common forms of carbon dioxide absorption apparatus, the Geissler potash bulbs (Fig. 22), and the Arnold potash bulb (Fig. 23). Geissler's apparatus is so arranged that the gas bubbles, laden with carbon dioxide, pass successively through three small bulbs containing caustic potash, and then through a small straight tube, half filled with soda-lime, and half with porous

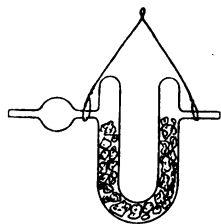


FIG. 21.

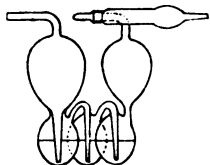


FIG. 22.

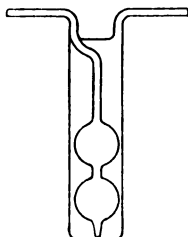


FIG. 23.

anhydrous calcium chloride. The last substance absorbs any moisture that may be taken up by the gas from the potash solution, or that may be liberated by the action of carbon dioxide on the soda-lime. To fill the bulbs the calcium chloride tube is removed and as much strong caustic potash solution (1 gram of potash to 2 of water) is drawn in through the side tube (the left-hand one in figure) as will, approximately, half fill the small bulbs without any potash remaining in the larger bulbs. The potash solution is then carefully wiped from the side tube, and the calcium chloride tube is attached once more. For the Arnold apparatus, a caustic potash solution of similar strength should be introduced, so that when the bulbs are empty the level of the solution is just above the higher bulb; a short calcium chloride tube should again be attached to absorb any moisture taken up from the bulb. To both pieces of apparatus a platinum loop should be attached in order to facilitate suspension; the potash apparatus and calcium

chloride tube should always be weighed together. As with the sulphuric acid tube, the apparatus should be kept closed by plugged pieces of rubber tubing when out of use.

To prepare the combustion tube, take hard glass tubing, about 1 cm. internal diameter, and cut a piece about 1 dm. longer than the furnace; round off the sharp edges by heating in a blow-pipe flame. The tube is then loosely stopped, at about 5 cms. from one end, by a plug of asbestos or an oxidized coil of copper gauze (5 cms. long). Granular copper oxide (which has been previously heated to a dull red heat on a copper tray to remove moisture and organic matter, and when cold has been preserved in a stoppered bottle) is then introduced by means of a copper funnel till it fills the tube to within 25 to 30 cms. of the other end.

Another short oxidized copper spiral, or a small loose asbestos plug, is introduced to keep the layer of copper oxide in position; finally, a long oxidized spiral of copper gauze (10 to 12 cms.) is introduced so that it is 5 cms. from the open end of the tube. The tube is then placed in the combustion furnace so that it projects equally at each end, with the long copper oxide spiral towards the air and oxygen holders; this end of the tube (which for convenience may be called the back) is attached to the small "bubbling" tube by means of a piece of rubber tubing, a short piece of glass tubing, and a one-holed bung. A slow current of air is then passed through the tube, while the latter is raised throughout its length to a dull red heat; any moisture that condenses at the open end should be removed by a roll of filter-paper. After about half an hour, the tube is fitted at the open end with a bung carrying a calcium chloride tube, the burners under the tube from the back to the centre are turned off, and the tiles are opened above the same length of tube. While the hinder part of the tube is cooling, about 0.15 to 0.2 gram of the substance is weighed accurately in a small recently heated porcelain or platinum boat, and the boat placed in a desiccator. The sulphuric acid U-tube and the potash apparatus with its attendant calcium chloride tube are then weighed¹ (the rubber-tubing caps being removed for the purpose), and carried to the combustion tube.

The calcium chloride tube is removed from the combustion tube, and the sulphuric acid U-tube is fitted directly into the

¹ The absorption apparatus should always be allowed to stand in the balance room for twenty minutes before weighing.

tube by means of a suitable bung, the bulb being next to the tube; the potash bulbs are then attached to the sulphuric acid U-tube by a short piece of stout walled rubber tubing,¹ care being taken that the apparatus is attached the right way round. Finally, a guard tube of soda-lime is attached to prevent any absorption of moisture or carbon dioxide from the air. It will be found very convenient to suspend all these tubes and bulbs from a long glass rod clamped in a horizontal position. When all the tubes are in place, the rubber joints are made tight by binding with wire. The hinder part of the tube is then opened, the long copper oxide spiral is withdrawn by a long copper wire, with a hook at the end, and placed on a clean clock glass; the boat containing the substance is then pushed into the tube till it can go no further, care being taken not to upset it; the long copper oxide spiral is then replaced, and the tube is rebunged. A screw clip is placed on the rubber tubing between the small bulb of acid and the combustion tube. While the slow current of air is still passing at such a rate that two bubbles pass through the potash bulbs every second, the burners are very gradually turned on one by one, working from the front of the tube towards the boat. When the flames get within 1 dm. of the boat, a small flame is lit under the spiral, as far behind the boat as possible, and gradually turned up. In this way the tube, excepting for about 2 dm. where the boat lies, is raised to a dull red heat (care must be taken not to overheat). Small flames are then started nearer the boat, when the combustion of the substance soon commences; this is indicated by an increased rate of bubbling through the potash absorption apparatus, which should be moderated by cutting off the air supply to some extent by the screw clip; the stage of the combustion is also indicated, with Geissler's bulbs, by the relative rates of bubbling in the first and last bulb. When the rate of bubbling decreases, the heating is increased slowly, with cautious regulating, till the tube near the boat gets hotter and hotter, and the boat itself is finally directly heated by a flame.² Any moisture that condenses in the end of the tube near the sulphuric acid U-tube should be driven over

¹ Wherever two glass tubes are joined by a short piece of rubber tubing, they should be in actual contact under the surface of the rubber.

² Great care must be taken that the moisture does not work *backwards* in the tube to behind the long copper spiral and into the rubber tube, because this would be fatal to the experiment.

into the latter by gently warming with a hot tile, or a small spirit lamp flame. When the combustion, as judged by the rate of bubbling, seems to be complete, the tiles over the boat are closed, and the whole tube is kept at a dull red heat, while a current of oxygen is slowly passed through until a glowing splint can be ignited at the exit of the soda-lime guard tube. The flames are then slowly turned down, and a current of air is passed through the tube for half an hour to sweep the oxygen from the absorption bulbs and U-tubes. When the tube is cold, the absorption bulbs and tubes are disconnected, closed with rubber caps, and allowed to stand in the weighing room for half an hour; the caps are then removed, and the bulbs and tubes weighed. The increase in the weight of the sulphuric acid tube gives the weight of water from the complete oxidation of the hydrogen in the substance, while that of the potash bulbs gives the weight of carbon dioxide from the carbon in the substance. A simple calculation gives the percentage of carbon and hydrogen.¹

It is very necessary in such combustions not to be hasty; the process should take at least two hours. Great care should be taken to avoid heating too rapidly, or too strongly; a tube, with proper care, can be used repeatedly for many combustions.

Specimen Calculation—

0.1800 gram of succinic acid taken.

Weight of water formed 0.0841 gram.

„ „ carbon dioxide 0.2672 „

Weight of hydrogen in 0.0841 gram of water = $\frac{0.0841}{9}$ gram.

\therefore percentage of hydrogen = $\frac{0.0841 \times 100}{9 \times 0.1800} = 5.19$.

Weight of carbon in 0.2672 gram
of carbon dioxide } = $\frac{0.2672 \times 12}{44}$ gram.

\therefore percentage of carbon = $\frac{0.2672 \times 12 \times 100}{44 \times 0.1800} = 40.5$ per cent.

$(\text{CH}_2\text{COOH})_2$ requires hydrogen 5.08 per cent., carbon 40.7 per cent.

The results are, as a rule, a little too high for the hydrogen,

¹ In the case of salts of the alkali metals it must be remembered that the boat will contain the carbonate as residue; this should be weighed, and its carbon must be taken into consideration in the calculation.

probably on account of traces of moisture from the gases and from the tube ; the carbon results are usually a little below the theoretical, probably due to a trace of the carbon dioxide escaping absorption and to the evaporation of a small quantity of water from the solution in the bulbs.

For the combustion of liquids the only modification necessary is that the substance is weighed in a small bulb with a capillary neck, the porcelain boat being used for holding the bulb ; the boat containing the bulb is slipped into the combustion tube, and the subsequent procedure is the same as usual.

There is no good method for the direct determination of oxygen ; this element can only be estimated by difference.

SPECIAL PRECAUTIONS NECESSARY FOR SUBSTANCES CONTAINING NITROGEN, HALOGEN, OR SULPHUR.

The presence of nitrogen in an organic substance, especially if present as a nitro group, often introduces error into the result of a combustion; there is a tendency for the nitrogen to form nitrogen peroxide, and this is dissolved by the potash, causing the carbon to be too high. To avoid this error a little of the copper oxide at the front of the combustion tube is replaced by a long spiral of reduced copper gauze (10 to 15 cms.),¹ so that there still remains the clear space of 5 cms. at the extreme end. The coil of reduced copper is then kept cool during the experiment till the actual combustion of the substance is about to begin ; it is then raised to a dull red heat, and any nitrogen peroxide passing over it is reduced to nitrogen, which passes through the bulbs unabsorbed. In other respects the process is the same as that previously described.

The presence of halogens and sulphur causes errors which are more difficult to obviate. The halogens may pass as free gas into the potash bulbs, and also would form the volatile copper halide,

¹ The spiral of copper gauze should be reduced before the experiment by heating it in a blowpipe flame and dropping it while hot into about 0.5 c.c. of methyl alcohol in a glass tube. The alcohol burns, and as soon as the flame languishes the tube should be loosely plugged. When cold, the reduced spiral is withdrawn, and heated in a clean glass tube in a current of carbon dioxide to remove traces of alcohol, a current of dry air afterwards being drawn through when the tube is only just warm, to remove the carbon dioxide. It is then kept in a desiccator till required.

which may pass into the sulphuric acid tube; sulphur gives rise to sulphur dioxide, which is absorbed by the caustic potash apparatus. To avoid the errors due to chlorine, a coil of thin silver sheet is sometimes placed at the front of the tube, in place of the reduced copper spiral, to decompose any copper halide and absorb any free chlorine. Another method which can be applied to either halogen or sulphur compounds is to replace the copper oxide by granulated fused lead chromate. For further particulars a larger text-book must be consulted.

Nitrogen.

Nitrogen can be estimated by several methods, of which the best are the Kjeldahl method, in which the nitrogen is converted into ammonia, and the "absolute" method in which the nitrogen is obtained and measured in the free state. The former method is quicker, but is not applicable to all substances; while the latter is universally applicable to carbon compounds containing nitrogen. The latter method is applied in two different ways.

ABSOLUTE METHODS FOR THE ESTIMATION OF NITROGEN.

I. *Dumas Method*.—Take a hard glass tube 1 dm. longer than the combustion furnace, and at 5 cms. from one end fix a loose plug of asbestos. Tilt the tube slightly, and introduce coarse copper oxide (recently heated on a copper tray and allowed to cool) to form a column 1 dm. long. Weigh into a small porcelain dish from a small weighing tube, about 0.2 gram of the nitrogenous substance; mix this, using a steel spatula, with powdered copper oxide (also recently heated), and introduce the mixture, by means of a copper funnel, into the tube; rinse out the dish into the tube with a little more fine copper oxide, so that the layer of fine oxide is 1.5 to 2 dms. long. Then rinse out the dish into the tube repeatedly with coarse copper oxide, till the layer reaches to within approximately 20 cms. of the end. Then introduce a reduced copper spiral (dried by placing on a clean clock glass in a steam oven for a few minutes), and place the tube in the furnace.

The additional apparatus required is a source of dry carbon dioxide and a suitable vessel for collecting the nitrogen.

The most convenient carbon dioxide apparatus is that illustrated in the diagram (Fig. 24). The Woulff's bottle contains a mixture of

equal volumes of concentrated sulphuric acid and water (the mixture should be made in a flask and introduced when cold). Concentrated potassium carbonate solution (80 grams to 100 c.c. of water) is introduced into the bulb of the dropping funnel F,¹ and, on turning the tap, flows through the small hole A in the trap into the acid. Once the stem of the funnel and the mercury trap are filled

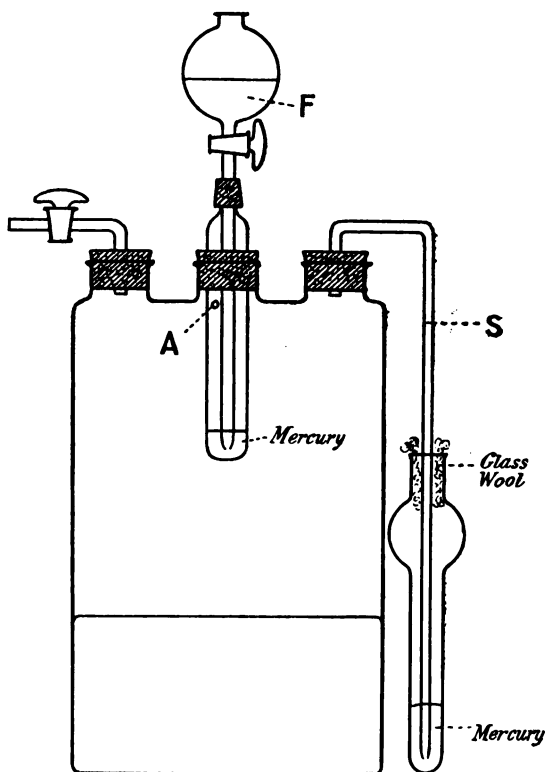


FIG. 24.

with the solution, the flow of the potassium carbonate is regulated as desired. The safety tube S on the right serves as a valve should the evolution of gas become too violent. The air is completely expelled from the apparatus by running about 100 c.c. of the carbonate solution into the acid. The gas then obtained

¹ It is advisable to boil the solutions before use.

contains less than 0.1 c.c. of air in 5 litres, and only needs to be passed through one wash-bottle of sulphuric acid to remove its moisture. It is convenient to have the Woulff's bottle as large as possible (2 to 3 litres), and charged with 800 to 1200 c.c. of the diluted acid ; it then requires refilling only at long intervals.

The most suitable collecting vessel for the nitrogen is Schiff's azotometer (Fig. 25). A little mercury is introduced so that it rises to about 5 mm. above the lower side tube ; caustic potash solution (80 grams in 240 c.c. of water) is poured into the bulb and allowed to fill the graduated tube by turning on the tap for a short time. The mercury in the lower portion of the tube should just be sufficient to prevent the alkali from passing into the lower side tube.

The lower side tube of the azotometer is then attached by a short piece of stout-walled rubber tubing, to a suitably bent glass tube fitted into a bung at the end of the combustion tube containing the spiral (the two glass tubes should meet under the rubber tube) ; the joints are then made fast with wire. The other end of the combustion tube is fitted to the carbon dioxide apparatus, a sulphuric acid wash-bottle intervening between the two. A rapid current of carbon dioxide is passed through the tube till all the air is swept out. During this process it is advisable to open the tap of the azotometer and lower the reservoir, so that the potash falls from the tube ; after fifteen minutes the air should have been almost completely removed. Raise the potash reservoir at intervals (every five minutes), and when the gas issuing from the tube is completely absorbed by the potash, only a fine foam of inappreciable bulk being left, completely fill the azotometer tube with potash, close the tap, and again lower the reservoir as far as possible. When this is done, great care must be taken that there is sufficient mercury in the trap of the carbon dioxide generator to prevent air being drawn through it into the apparatus. The current of carbon dioxide is almost completely stopped, and the heating of the tube is commenced, beginning at the end containing the spiral. When the front half of the tube is at a dull red heat, the flames are slowly approached to the neighbourhood of the substance, the same precautions being taken to heat the substance carefully as in the ordinary combustion previously described. The rate of the combustion should never be allowed to become so rapid that the bubbles pass into the azotometer at the rate of more than two or three to the second.

When the whole tube is at a dull red heat, the current of carbon dioxide is again hastened somewhat, and the gas passed until

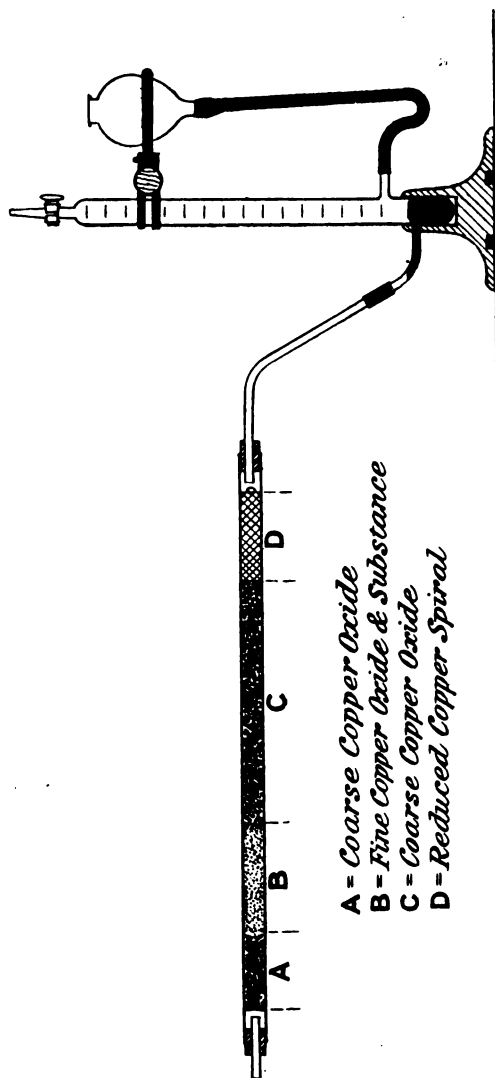


FIG. 25.

A = Coarse Copper Oxide
 B = Fine Copper Oxide & Substance
 C = Coarse Copper Oxide
 D = Reduced Copper Spiral

the bubbles are once more completely absorbed, and the level of the liquid in the azotometer is constant. The burners may be

extinguished just before this point. Disconnect the azotometer by removing the bung from the combustion tube, and transfer the gas carefully, by means of the arrangement shown in Fig. 26, into a measuring tube over water (the funnel arrangement is readily made by breaking the bottom from a bottle). Allow the tube to stand completely immersed in a cylinder of water for half an hour; raise the tube by a pair of crucible tongs, so that the water-level is the same inside and out, and read the volume of the gas; at the same time read the temperature of the water and the barometric pressure. Correct the volume of gas to N.T.P. (remembering to allow for the vapour pressure of the water), and from the fact that the molecular weight in grams occupies 22.4 l. at N.T.P., calculate the weight of the gas and hence the percentage of nitrogen in the original compound.



FIG. 26.

Specimen calculation—

0.1650 gram dinitrobenzene gave 23.70 c.c. nitrogen at 763 mm. and 16°.

Vapour pressure of water at 16° = 13.5 mm.

∴ actual pressure on gas = 763 - 13.5 = 749.5 mm.

Volume of gas at N.T.P. = $\frac{23.70 \times 749.5 \times 273}{760 \times 289}$ c.c.

22.4 l. of nitrogen at N.T.P. weigh 28 grams

∴ weight of gas obtained = $\frac{23.70 \times 749.5 \times 273 \times 28}{760 \times 289 \times 22.4}$ grams

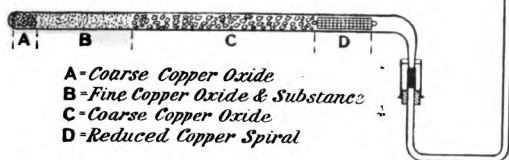
Hence percentage of nitrogen = $\frac{23.70 \times 749.5 \times 273 \times 28 \times 100}{760 \times 289 \times 22.4 \times 0.1650}$
= 16.73 per cent.

Theoretical for $C_6H_4(NO_2)_2$ = 16.67.

II. *Vacuum Method.*—In this method the combustion is performed in a hard glass tube sealed at one end; the air is withdrawn by a Sprengel pump at the beginning, and the nitrogen and carbon dioxide are withdrawn in a similar way at the end of the experiment.

Seal a long piece of hard glass tubing at one end, and, when cold, clean it out with chromic acid mixture and then with water;

finally dry it by warming while a current of air is drawn through it by inserting a long narrow tube attached to a water-pump. A short layer (5 cms.) of freshly heated copper oxide is introduced, and then the solid mixed with fine copper oxide; above this is placed a layer of coarse copper oxide, and finally a reduced copper spiral. The tube is then heated in a blowpipe flame at a distance of 1 dm. above the spiral, and when softened is drawn out to a width of approximately 0.5 cm., and at the same time bent to a right angle. The



wide part of the tube beyond the narrow portion is then carefully cut off, and the tube with the narrow bend at the end, after tapping gently to ensure a free passage throughout its length, is transferred to the furnace and attached to the Sprengel pump by means of a piece of stout-walled pressure tubing. The joint is made quite air-tight by pushing up over the joint the cup of water or glycerine which is fitted over the pump tube (Fig. 27).

The pump is then set working till all the air is removed, this being indicated by the mercury falling in the pump with a sharp click; allow the mercury to click for ten minutes and then stop the pump. A gas-measuring tube, which has been filled one-third full of strong caustic potash (2 parts of potash to 3 of water) and the rest with mercury, is carefully inverted over the exit tube of the pump under the mercury in the receiving vessel, and the combustion is allowed to proceed in the usual way. The copper

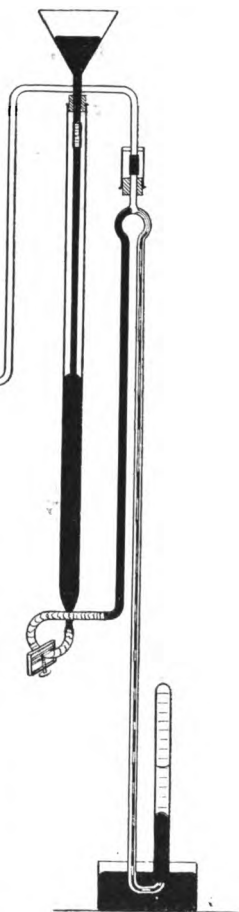


FIG. 27.

spiral and coarse copper oxide are first heated, and the flames are slowly approached to that part of the tube containing the substance. The bubbles of gas should not come off more rapidly than one every two seconds. When no more gas comes off, and all the tube is at a dull red heat, the pump is again set working, and the burners are slowly turned down; when the pump has again clicked for ten minutes, indicating the complete removal of the gas, the tube containing the gas is transferred (by means of a small crucible) to a cylinder of water, and is allowed to stand completely immersed for half an hour. The measurement of the gas and the calculation are performed in exactly the same manner as in the previous method.

KJELDAHL PROCESS FOR THE ESTIMATION OF NITROGEN.

Kjeldahl's method for the determination of nitrogen in organic compounds¹ consists in heating the substance with concentrated sulphuric acid until all the nitrogen has been converted into ammonia. The ammonium sulphate thus formed is then decomposed by means of caustic soda, and the ammonia liberated is estimated by absorption in standard acid. If sulphuric acid alone is used it sometimes happens that the nitrogen is not completely converted into ammonia; this is because the temperature of boiling sulphuric acid is not high enough to bring about complete conversion of the nitrogen. The acid is therefore mixed with potassium sulphate, whereby the temperature to which it may be raised without boiling is considerably increased.

The sulphuric acid used in the process must be free from ammonium sulphate and oxides of nitrogen. It can be tested by carrying out a blank experiment with some substance which does not contain nitrogen, *e.g.* sugar.

Kjeldahl's process is especially useful in the estimation of nitrogen in food stuffs, manures, etc., and in order to show the method of introducing the substance into the flask without loss, the estimation of nitrogen in Mellin's food will be described.

Clean and dry a round-bottomed Jena flask of about 500 c.c. capacity. Weigh out about 10 grams of powered potassium

¹ The method is not applicable to every compound containing nitrogen. For further details see any of the larger works on organic chemistry.

sulphate on a rough balance, and then weigh out accurately about 2.5 grams of Mellin's food on to a watch glass. Transfer the food to a small sheet of glazed paper and, using this as a chute, let the food slide into the flask. Remove the last traces of the food from the watch glass by bringing some of the potassium sulphate on to the glass and then transferring it by means of the paper to the flask. If all the sulphate is transferred in this way it will carry with it any small traces of the food which may have adhered to the glass or the paper in the first instance.¹ Then pour 20 c.c. of strong pure sulphuric acid into the flask, slowly rotating the flask meanwhile so that the acid washes down any powder adhering to the neck. Now support the flask on wire gauze in an inclined position, and heat it with a small flame until all the violent frothing has ceased, and then with a larger flame so that the acid boils vigorously, condensing for the most part, however, on the upper part of the flask and flowing back. This heating must be continued until the liquid is pale yellow (generally from one to three hours). When cold, the contents of the flask are diluted with water. Meanwhile make up a solution of caustic soda containing 25 grams of sodium hydroxide to about 50 c.c. of water; cool this solution.

Fit up the distilling apparatus as shown in the diagram (Fig. 28), which does not require further explanation. The flask A is the one which has been used for digesting with sulphuric acid. Into the conical flask C, which is kept cool by a bath of cold water, place 25 c.c. of semi-normal acid (sulphuric or hydrochloric).

Disconnect the flask A, and holding it in a slanting position, pour the solution of sodium hydroxide gently down the neck, so

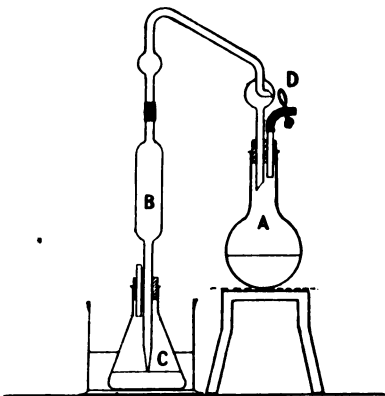


FIG. 28.

¹ In most cases the use of paper may be avoided, and the substance transferred directly to the flask, using a wide funnel with a short leg. "Wash" down with potassium sulphate, as usual.

that it forms a heavy layer at the bottom of the flask. Do not let the two liquids mix, or some ammonia will be given off and lost. Add one or two fragments of granulated zinc; the object of this is to evolve hydrogen and cause the liquid to boil gently instead of bumping. Now connect up the whole apparatus as shown in the figure. Shake the contents of the large flask so as to mix the two liquids, and commence to heat. The distillation of the ammonia will take from half to three-quarters of an hour. The large pipette B acts as a safety trap, and prevents the acid in the conical flask being sucked back into the distilling flask. If at any time it seems probable that sucking back will take place to such an extent that some of the liquid may be carried back into the distilling flask, the clip D may be momentarily opened. When the distillation is complete, the burner is not removed from under the flask, or turned out, until the clip D has been opened.

The apparatus is then disconnected, the pipette washed down into the conical flask, the sides of the flask also washed down, and then the contents titrated with semi-normal caustic soda, using methyl orange as an indicator.

Knowing how much acid has been neutralized by the ammonia, the percentage of nitrogen in the food can be calculated.

Urea or acetanilide (0.2 to 0.3 gram) may be taken instead of a food, for practice in the estimation of nitrogen by this method.

Estimation of Halogens, Sulphur, and Phosphorus by the Carius Method.

The most convenient methods for the estimation of all these elements are the same in principle. For the halogens, the substance is heated in a sealed tube with fuming nitric acid and silver nitrate, when the halogen element is completely converted into the corresponding silver halide. For sulphur and phosphorus, the substance and nitric acid are heated alone, and the sulphuric or phosphoric acid formed determined by the usual methods. It is obvious that the nitric acid must be pure and free from sulphur, chlorine, and phosphorus. The heating of the sealed tubes is performed in a special "bomb" furnace.

Halogens.—Weigh carefully into a small narrow test-tube (6 to 8 cms. long) about 0.2 gram of the substance. Take a

thick-walled wide glass tube (Carius tubing or "bomb" tubing) about 6 dms. long, and clean it by pulling through it several times a pad of cotton wool by means of a string. Seal¹ the tubing at one end, and carefully anneal the hot portion; when cold, introduce into it about half a gram of silver nitrate in crystals and about 7 c.c. of fuming nitric acid; the acid should be introduced down a long thistle funnel in order to avoid wetting the sides. Tilt the tube, and allow the small tube containing the substance to slip gently down to the bottom; then, without allowing the acid to wet the substance, close up the end of the tube, pulling it out into the form of a sealed capillary with very thick walls.¹ When the tube is sealed it should not be left lying about, but should immediately be placed in the bomb furnace with the capillary end near the opening. The tube is then heated for several hours; different substances require different lengths of time, but as a rule, it is sufficient if the temperature is maintained at 170° – 200° for four hours, and then at 200° – 230° for another four hours. When the furnace is *quite cold* the tube is carefully pulled out (by the hand protected with a duster) so far that the capillary projects a few centimetres from the iron jacket; the capillary is then warmed carefully by a flame till it gets so soft that the pressure inside the tube blows a small hole in the glass and the pent-up gases escape² (the tube must *never* be opened directly by the use of a file, else an explosion may result). Not till the internal pressure has been released is the tube removed from the iron jacket. A file mark is then made on the tube just below the point where it has been drawn out and the narrow portion is cracked off by the application of a piece of hot glass rod, care being taken that no glass splinters fall inside the tube. The contents of the tube and also of the part broken off, if it contains any precipitate, are then rinsed out into a beaker, the silver halide is collected, washed, and weighed in the usual way. From the weight of silver halide a simple calculation gives the percentage of halogen.

Sulphur and Phosphorus.—To estimate sulphur or phosphorus, the substance and fuming nitric acid are introduced into the Carius tube, and the heating performed as above. For sulphur,

¹ The preparation of tubes for Carius estimations is best learnt from a demonstration by the teacher.

² Take care that no silver halide is blown out when the pent-up gases escape.

the contents of the tube, after the addition of excess of strong hydrochloric acid and 1-2 grams of sodium chloride, are evaporated down almost to dryness, then diluted and precipitated with barium chloride; the precipitated barium sulphate is washed, dried, ignited in the usual manner, and weighed. For phosphorus, the contents of the tube are neutralized with ammonia, the phosphate precipitated as ammonium magnesium phosphate, and weighed as magnesium pyrophosphate. The method of calculation is obvious.

CHAPTER XIV

DETERMINATION OF THE MOLECULAR WEIGHT OF AN ORGANIC COMPOUND

THE chemist has the choice of a large number of different methods for determining the molecular weight of an organic compound. These methods may be divided into two classes, viz. chemical and physical.

CHEMICAL METHODS.

Chemical methods are usually applied to substances which are acid or basic in character. A salt of the acid or base is prepared, and by analysis the proportion of the metal to the acid radicle or to the base is found. This proportion may then be used to calculate the molecular weight of the acid or base, it being assumed that the basicity of the acid, or the acid equivalent of the base, is known. If the acid is fairly soluble in water, its equivalent may often be determined by titration with standard alkali.

Molecular Weight of an Acid.—The salt which is used should admit of easy purification, and be readily prepared. In practice, either the silver or the barium salt is taken; the former yields metallic silver on ignition, and the latter gives barium sulphate on treatment with strong sulphuric acid.

Silver Salt Method.—The method of carrying out the determination is best explained by taking a particular example, as, for instance, benzoic acid. This acid can be shown to be monobasic by the usual methods, *e.g.* it gives only *one* silver benzoate.

The silver salts of organic acids are generally precipitated from neutral solutions, and in preparing the neutral solution it is best to use ammonium hydroxide, since ammonium salts are most easily got rid of in the subsequent operations. The acid is

dissolved in ammonia, and the excess of the latter is driven off by boiling until a neutral solution remains; a fairly concentrated solution should be prepared. The addition of silver nitrate to this solution, which should be cold, gives a white precipitate of silver benzoate, which is filtered off and well washed with cold water in order to remove all soluble salts. The salt is then carefully dried in the steam oven, and afterwards stored in a dry bottle in a desiccator ready for analysis. It should be protected from the light as much as possible.

In carrying out the analysis, about 1 gram of the dry silver benzoate is accurately weighed into a porcelain crucible, which is then covered with the lid and carefully ignited. The heating must be carried out *very gently* at first, in order to avoid loss by too rapid decomposition; the crucible is finally raised to a red heat, and heated until all the carbon is burnt off. It is then cooled and weighed, and then heated again, etc., till the weight is constant.

Suppose 1 gram of the silver benzoate was weighed out, and that the weight of silver obtained was g gram. Then the weight of C, H, and O combined with 107.93 grams of silver, *i.e.* with one gram-atom, is $\frac{107.93(1-g)}{g}$ grams. But 107.93 grams of silver in the molecule of the silver salt are combined with the same weight of C, H, and O as is 1 gram of hydrogen in the acid,

$$\therefore \text{molecular weight of benzoic acid} = \frac{107.93(1-g)}{g} + 1.$$

Barium Salt Method.—The method of procedure in the case of barium salts may be illustrated by reference to the determination of the molecular weight of succinic acid. The barium succinate is prepared by adding barium chloride to a concentrated solution of the free acid, and making just alkaline with ammonia. The precipitate so obtained is well washed with water containing ammonia, in which the barium succinate is less soluble than in pure water, and dried in the steam oven.

Weigh out 0.5 to 0.75 gram of barium succinate into a platinum crucible, and add 0.5 c.c. concentrated sulphuric acid. The crucible and lid are then arranged as in the determination of sodium or potassium as sulphate,¹ and one side of the lid very carefully heated; or the crucible may be put to stand on asbestos

¹ See any text-book on Quantitative Analysis.

in a larger nickel crucible, which is then gently heated. In either case, after the excess of sulphuric acid has been driven off, the crucible and its contents are raised to a red heat for a short time, and then cooled and weighed. The process of heating, etc., is carried out again until the weight is constant. The residue of barium sulphate should be pure white, showing that all the carbon has been burnt off; it should not react alkaline (due to BaO), as such a reaction would indicate that enough sulphuric acid had not been used to transform all the barium into sulphate.

The calculation may then be carried out by making use of the following proportion :—

$$\begin{aligned} \text{Molec. wt. of the barium succinate} &: \text{molec. wt. of BaSO}_4 (233.46) \\ &= \text{wt. of barium succinate taken} : \text{wt. of BaSO}_4 \text{ found.} \end{aligned}$$

The molecular weight of barium succinate having been calculated, the molecular weight of succinic acid is found by subtracting the atomic weight of barium (137.4) and adding 2.02 (twice the atomic weight of hydrogen).

If the acid is monobasic the result obtained will be twice the required molecular weight, since barium is divalent. Corresponding corrections will have to be made for acids of other basicity.

Titration Method.—By this method the equivalent of the acid is determined by titration with standard alkali. If the basicity of the acid is known, the molecular weight can be calculated. Since organic acids are generally classed among the “weak” acids, a strong alkali (caustic soda or potash free from carbonate; or baryta¹) must be used for the titration, with phenol phthalein as indicator.

Example.—Weigh accurately about 1.5 grams of succinic acid. Dissolve in water and make up to 250 c.c. Take 25 c.c. of the solution and titrate with $\frac{N}{10}$ baryta. From the results of the titrations calculate the weight of succinic acid equivalent to 85.8 grams $\left(= \frac{\text{Ba(OH)}_2}{2}\right)$ of baryta. This gives the equivalent of the acid, which is half of the required molecular weight.

¹ Baryta solutions are free from carbonate, and are the most convenient to use if the Ba salt of the acid is fairly soluble.

Molecular Weight of a Base.

I. Gravimetric Method.—Use is made of the fact that organic bases generally form salts with chlorplatinic acid, and these salts are readily decomposed by heat, giving a residue of pure platinum. The salts are of the same type as ammonium platinichloride, $(\text{NH}_4)_2\text{PtCl}_6$, NH_3 being replaced by a molecule of the base; e.g. the aniline salt is $(\text{C}_6\text{H}_5\text{NH}_2\cdot\text{H})_2\text{PtCl}_6$. Thus each molecule of the complex salt contains 2 molecules of the base, and if the molecular weight of the complex salt can be found, the molecular weight of the base can also be determined.

As an example, we will take the determination of the molecular weight of the alkaloid cinchonine, which acts as a monacid base.

Dissolve some pure cinchonine in hydrochloric acid (50 per cent. by volume), and to the warm solution add an excess of chlorplatinic acid. Allow to cool, and filter off the complex salt; wash first with 50 per cent. HCl , and then several times with alcohol. Dry carefully in the steam oven, or in vacuo over strong sulphuric acid.

Weigh out accurately about 1 gram (0.5 to 1 gram) of the dry platinichloride into a porcelain crucible; cover with the lid and heat very gently at first, finally more strongly, until all the carbon has been burnt away. (It may be necessary to stir the contents of the crucible from time to time with a clean platinum wire, in order to promote the combustion of the carbon.) Heat till the weight is constant.

The calculation is as follows:—

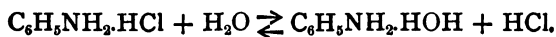
$$\begin{aligned} \text{Molec. wt. of the platinichloride : atomic wt. of Pt (194.8)} \\ = \text{weight of complex salt taken : weight of Pt found.} \end{aligned}$$

From the molecular weight of the platinichloride thus calculated, subtract the weight represented by H_2PtCl_6 ($= 409.52$), and divide the remainder by two. This gives the required molecular weight of the base.

II. Volumetric Methods.—These may be used when the salts of the bases are fairly soluble in water, the hydrochloride of the base being chosen for preference.

The amount of hydrochloric acid may be found in the usual way by titration with standard alkali. The method depends upon the fact that the hydrochloride is strongly hydrolyzed in solution; titration of the free acid destroys the equilibrium, and the process

goes on until all the hydrochloric acid has been hydrolyzed away from the base, *e.g.*—



The molecular weight of aniline may be determined by these methods. Freshly distil some aniline and dissolve a little of it in a small quantity of warm hydrochloric acid, made by mixing equal volumes of concentrated acid and water. On cooling, the hydrochloride separates out. Filter and wash with hydrochloric acid (1 : 1), and recrystallize from dilute hydrochloric acid ; dry between filter-paper. When dry, weigh out accurately 0.3 to 0.4 gram, dissolve in water, and titrate the solution with tenth-normal alkali, using phenol phthalein as indicator. From the results of the titrations, calculate the weight of hydrochloric acid in the weight of salt weighed out, and then the molecular weight as follows :—

Molec. wt. of the hydrochloride : molec. wt. of HCl (36.46)
= wt. of hydrochloride taken : wt. of hydrochloric acid found.

From the molecular weight of the hydrochloride thus calculated, subtract the weight represented by HCl (36.46), and this gives the required molecular weight of the base.

PHYSICAL METHODS.

The physical methods which can be used for determining the molecular weight of an organic compound are of two kinds. If the substance is readily volatile its vapour density may be determined, and hence its molecular weight ; if it is not readily volatile its molecular weight in solution is measured by one of the methods which depend on the osmotic pressure of a dissolved substance.

Of the vapour density methods we shall only consider two, *viz.* Dumas' and Victor Meyer's. The latter is the one which is most convenient to use in chemical laboratories, but as the former is also very often used it will be described.

Dumas' Method.—A light glass bulb of 100–300 c.c. capacity, and with a tube drawn out to a fine point, as shown in the diagram, is dried and weighed. A few cubic centimetres of the liquid under examination are then introduced

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into the bulb by warming the latter and then allowing the liquid to be sucked into it as it cools. The bulb is then placed in a bath of water or oil so that the fine point is just above the surface of the heating liquid, and is held in position by means of an appropriate holder (*vide* Fig. 29). The temperature of the bath should be at least 20° above the boiling point of the liquid. The liquid in the bulb boils, and its vapour escapes through the fine jet, forcing the air before it. As soon as all the liquid has

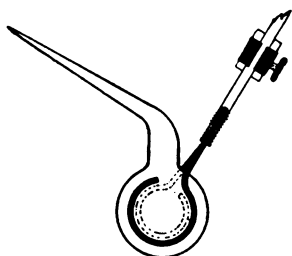


FIG. 29.

vaporized, which is indicated by no more vapour issuing from the jet (hold the flame of a bunsen near; it will not be blown away unless vapour is issuing), the jet is sealed by means of a blowpipe, and at the same time the temperature of the bath is noted, as well as the height of the barometer. The bulb is then removed from the bath, cooled, and carefully dried; after standing in the balance case for at least fifteen minutes to acquire the

temperature of the case, it is weighed. The temperature of the balance and the barometric height are noted at the time of weighing.

The narrow tube is then immersed in air-free water (or mercury), and the fine point broken off; the bulb then becomes filled with water (or mercury), if all the air had been expelled from it. The bulb full of water (or mercury) is again weighed.

The molecular weight may be calculated as follows, omitting corrections for the expansion of glass and water, or for the loss of weight of the bulb full of water due to the buoyancy of the air.

Let W_a = weight of the bulb full of air,

W_v = apparent weight of the bulb full of vapour,

W = weight of the bulb full of water (or mercury),

t and p = temperature and pressure respectively at the time of sealing,

t' and p' = temperature and pressure respectively at the time of weighing,

and 0.001293 gram = weight of 1 c.c. of air at 0° and 760 mm.

Then volume of bulb = $W - W_a = V$ c.c. [If filled with mercury the volume is $\frac{(W - W_a)}{13.596}$.]

Apparent weight of vapour = $W_v - W_a$.

During the weighing of the bulb full of vapour it was buoyed up by its own bulk of air at the temperature and pressure of the balance-room.

The weight of this air (not taking into account the water vapour contained in it) is approximately $V \times 0.001293 \times \frac{p'}{760} \times \frac{273}{273 + t'}$ gram.

Therefore true weight of vapour = $W_v - W_a + V \left(0.001293 \times \frac{p'}{760} \times \frac{273}{273 + t'} \right)$ gram.

But this weight of vapour filled the bulb at the time of sealing, *i.e.* at t° and p mm.

Therefore V c.c. of the vapour at t° and p mm. weigh $W_v - W_a + V \left(0.001293 \times \frac{p'}{760} \times \frac{273}{273 + t'} \right)$ gram.

Therefore 22400 c.c. of the vapour at 0° and 760 mm. weigh $\left\{ (W_v - W_a) + V \left(0.001293 \times \frac{p'}{760} \times \frac{273}{273 + t'} \right) \right\} \frac{22400}{V} \times \frac{273 + t}{273} \times \frac{760}{p}$ grams, and this is the molecular weight required.

If the bulb does not completely fill with water when the point is broken under the surface of that liquid, all the air has not been completely expelled by the vapour. Generally, the amount of air left in is not very large and there is no need to correct for it in ordinary work; the bulb is then filled with water from a wash-bottle before being weighed, and the calculation carried out as usual. In other cases a correction can be applied, but it is better to repeat the experiment.

There are many sources of error in Dumas' method, and the results are only accurate after numerous corrections have been applied. Consequently, it is always better to use the following simpler method, which is due to Victor Meyer.

Victor Meyer's Method.—In this method the gaseous volume of a weighed quantity of the liquid is determined by

the air expelled from the apparatus when the liquid is quickly evaporated.

The best form of apparatus is shown in the diagram (Fig. 30). The side tube D is closed by a tightly fitting indiarubber stopper,

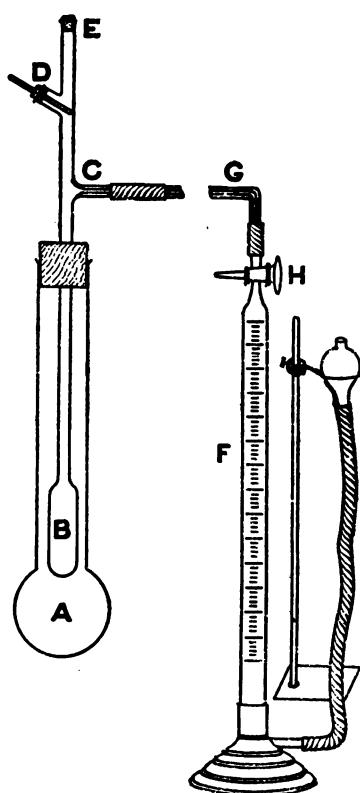


FIG. 30.

through which a glass rod, with flattened end, passes air-tight; it should be lubricated with graphite. The horizontal portion of the capillary tube G, connecting the side tube C, with the Hempel gas burette F, may be $1\frac{1}{2}$ to 2 feet long. All the rubber connections should be of thick-walled indiarubber tubing, and the ends of the two glass tubes should be brought close together.

The tube B (capacity of the bulb about 200 c.c.), the upper end of which is closed by a rubber stopper, is placed in the wider tube A, which contains a liquid, the boiling point of which is at least 20° to 30° above the boiling point of the liquid to be vaporized.¹

The mouth of A is closed by a slit cork. To prevent bumping, a few pieces of porous tile, or similar material, are placed in A, and the liquid is boiled, the three-way cock

H being meanwhile open to the air to allow the expanded gas to escape. After the liquid in A has been boiling vigorously for ten minutes, it is ascertained whether the temperature in B has become constant, by turning the tap H, so as to make connection between B and the burette. If the temperature has become constant, the level of the water in the burette will remain

¹ Suitable heating liquids are water (100°), amyl alcohol (131°), aniline (184°), nitrobenzene (209°), α -bromonaphthalene (279°)

unchanged. When constant temperature has been attained, the tap H is again opened to the air, the stopper E removed, and a weighed quantity of the liquid to be vaporized, contained in a small stoppered weighing bottle, is dropped on to the flat end of the glass rod passing through D. The stopper E is then replaced, communication between B and the burette made through H, and the bottle with the liquid allowed to drop to the bottom of B by rotating, or slightly withdrawing, the glass rod. On reaching the bottom of the tube, the liquid is vaporized, and expels a volume of air equal to the volume of the vapour at the particular temperature. As the air passes over into the burette, the reservoir must be lowered so that the level of the water in the reservoir and burette remain about the same. This diminishes the danger of leakage. So soon as the volume of air in the burette becomes constant, the water-levels are adjusted, and the cock H is closed. The burette is then detached, moved away from the remainder of the apparatus, and allowed to stand till the temperature becomes constant. The water-levels are again adjusted, and the volume of expelled air read off. At the same time the temperature is read from a thermometer hung up beside the burette, and the height of the barometer is also noted.

Instead of the gas burette for collecting the expelled air, the following arrangement may be used. Attached to the side tube C is a bent capillary tube, the end of which dips under water contained in a pneumatic trough. After the temperature of the apparatus has become constant, as indicated by no more bubbles issuing from the end of the capillary, a graduated measuring tube, filled with water, is inverted over the mouth of the capillary. The experiment is then carried out as previously described, the expelled air being collected in the measuring tube. When all the air has been expelled, the measuring tube is closed with the thumb, and transferred to, and completely immersed in, a deep cylinder of water. After the tube and its contents have assumed the temperature of the water, the water-levels are adjusted and the volume of the enclosed air read off. At the same time the temperature of the water and the barometric height are noted.

Details.—The process of vaporization should take place as rapidly as possible; otherwise diffusion and condensation of the vapour on the upper cool parts of the tube may take place, with

the result that the volume of air expelled will be too small. For the same reason, when using the Hempel gas burette, the stop-cock H should be closed, after adjusting the water-levels, as soon as the volume becomes constant (the volume should not diminish).

Sometimes the stopper of the weighing bottle becomes fixed, so that vaporization is prevented, or only takes place very slowly. To obviate this, the stopper should be loosened, or removed altogether (if the liquid is not too volatile), before the weighing bottle is dropped on to the glass rod at D. In this case, care must be taken that the weighing bottle is not filled so full that the liquid wets the stopper. Instead of the weighing bottle, a small, thin glass bulb, drawn out to a fine point, may be used for holding the liquid. After it has been partially filled with the liquid, the point is sealed, before it is weighed. It is so placed on the glass rod at D that the point is downwards; when it falls to the bottom the point is then broken. If the liquid is not too volatile the point may be broken off before it is dropped on to the glass rod; in this case, of course, it is placed point upwards. To prevent vaporization as far as possible while the weighing bottle and liquid rest on the rod at D, the upper end of the tube B should be protected from the heat of the flame and of the bath A, by means of a sheet of asbestos board, placed on the top of the cork closing the mouth of A.

To prevent the bottom of the tube B being broken by the fall of the weighing bottle, it is covered with asbestos or sand, which has previously been strongly ignited. Mercury may also be used if the temperature employed is not much above 150° , and if the substance has no action on mercury.

After each experiment, all vapour must be removed from the tube by blowing air through it.

Calculation.

Let w = weight in grams of the substance taken,

v = volume of air expelled in cubic centimetres,

t = temperature,

p = pressure,

f = vapour pressure of water at temperature t° .

Then the volume of air expelled, reduced to N.T.P., is—

$$v_0 = v \times \frac{p - f}{760} \times \frac{273}{273 + t};$$

i.e. at N.T.P. v_0 c.c. of the vapour of the substance weigh w gram,

$\therefore 22,400$ c.c. of the vapour of the substance weigh $\frac{22,400}{v_0} w$ gram.

$$\begin{aligned} \text{i.e. the molecular weight} &= \frac{22,400 w}{v_0} \\ &= \frac{22,400 w (273 + t) 760}{v (p - f) 273} \end{aligned}$$

The error in the determination should be within 5 per cent.

The molecular weight of a substance in solution is most conveniently determined either by the freezing point or by the boiling point method.

Freezing Point or Cryoscopic Method.—In this method it is necessary to determine the freezing point of the pure solvent, and also the freezing points of solutions of known strengths. The most convenient apparatus (*vide* Fig. 31) is that devised by Beckmann. The freezing-point tube C, which is furnished with the side tube D, is supported by means of a cork in the neck of a wider tube, B, so that the freezing-point tube is surrounded by an air mantle. The tube B passes through the centre of the brass lid, L, of a large glass vessel, A, being fixed in its place by means of a cork, or by metal springs. Through another opening in the lid there passes a stirrer, E, by means of which the freezing mixture contained in A can be stirred and the temperature kept more uniform. A third opening in the lid allows of the passage of a thermometer.

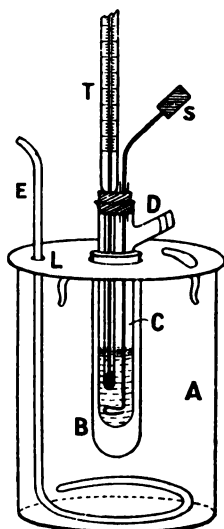


FIG. 31.

The freezing-point tube C is fitted with a cork through which pass a Beckmann thermometer, T, and a stirrer, S, and to the upper end of the latter a non-conducting handle of cork or wood is attached. The stirrer is made entirely of platinum, or else of glass with a horizontal ring of thick platinum fastened at the bottom; in order to ensure freedom of movement it is made to pass through a short piece of glass tubing inserted in the cork of the freezing-

point tube. Care must be taken that the stirrer does not scrape against the thermometer bulb.

In order to keep the temperature of the cooling bath more uniform, it is generally surrounded with thick felt, and the lid is also covered with the same material.

In carrying out the determinations it is necessary to observe the following precautions :—¹

1. The temperature of the cooling bath must be so regulated that it is not more than 3° below the freezing point of the liquid in C.

2. The amount of supercooling of the liquid before freezing is allowed to take place should not exceed 0.3° to 0.5° , otherwise so much of the solid solvent separates out that the concentration of the solution is thereby considerably altered.

3. The stirring should be uniform, and at the rate of about once per second. Too rapid stirring would generate too much heat by friction.

4. Always tap the thermometer before making a reading, as the mercury is likely to stick in the bore of the capillary.

The method of carrying out a determination will now be described.

Determination of the molecular weight of naphthalene in benzene solution.—The freezing-point tube is cleaned and dried, and fitted with two unbored corks. It is weighed, and then after the introduction of 15 to 20 grams of pure benzene weighed again, in order to obtain the weight of the benzene; the weighings need only be carried out to the nearest centigram. The Beckmann thermometer is then set (*vide infra*) so that at the temperature of 5.5° (melting point of benzene) the mercury stands not lower than the middle of the scale; after drying thoroughly it is inserted, along with the stirrer, in the freezing-point tube, so that the bulb of the thermometer is completely immersed in the benzene. Fill the vessel A with water and ice, so that a temperature of 2° – 3° is obtained. This can be regulated by varying the amount of water and ice.

An approximate determination of the freezing point of the benzene is first made by placing the freezing-point tube directly in the cooling bath,² so that the temperature falls comparatively rapidly; the liquid should be slowly stirred all the time. When solid begins to separate, which will be denoted by the fact that the

¹ These precautions are fully discussed in Findlay's "Practical Physical Chemistry," which the student should consult.

² The lid is supplied with a hole for this express purpose.

temperature begins to rise, quickly dry the tube, and place it in the air mantle in the cooling bath; stir slowly, and read the temperature when it becomes constant. Now withdraw the tube from the mantle, and melt the solid benzene by means of the hand. If in this operation the temperature of the liquid is raised more than about 1° above the freezing point, place the tube again directly in the cooling bath, and allow the temperature to fall to within about half a degree of the freezing point as determined above; quickly dry the tube and place it in the air mantle, and allow the temperature to fall, stirring slowly meanwhile. When the temperature has fallen to from 0.2° to 0.5° below the approximate freezing point found above, stir more vigorously. This will generally cause freezing to take place, and the temperature will now begin to rise.¹ Stir slowly again, and with the help of a lens, read the temperature every few seconds, tapping the thermometer before each reading. The temperature rises quickly at first, then much more slowly, and finally remains constant at the freezing point of benzene. Repeat the observation several times, not fewer than three concordant readings being taken; the mean of the readings gives the freezing point of the benzene. The deviations of the separate readings from the mean value should not exceed 0.002° .

The freezing point of the solvent having been determined, a weighed amount of naphthalene, in the form of a fine powder, is introduced into the benzene through the side tube D. The naphthalene is contained in a long narrow ignition tube, from which it can be shaken without any of it falling into the side tube D. The ignition tube is weighed before and after the experiment, and so the amount of naphthalene introduced is known. Pastilles of the substance are not convenient to use, as they dissolve so very slowly. The amount taken should be such that a depression of the freezing point of 0.2° – 0.5° is caused; generally about 0.2 gram of the substance is enough for this.

After the naphthalene has dissolved, the freezing point of the solution is determined in exactly the same manner as described for the pure solvent, except that in the case of a solution the

¹ Sometimes the liquid remains persistently supercooled, even on stirring vigorously. In such cases, freezing is started by the introduction of a small crystal of the solid solvent through the side tube D, the stirrer being raised and touched by the crystal. The crystals are held in reserve in a small tube immersed in the cooling bath.

temperature does not finally remain constant, but rises to a *maximum* and then falls slowly, owing to the freezing-out of the solvent causing an increase in concentration of the solution, and therefore a fall in the freezing point. The maximum reading is taken as the freezing point of the solution. A number of determinations should be made and the mean taken. The difference between the freezing point of the pure solvent and of the solution is the observed depression of the freezing point.

Two further additions of the naphthalene should then be made, and the freezing point determined after each addition.

In the case of the determination of the molecular weight of liquids, the latter are introduced into the freezing-point tube by

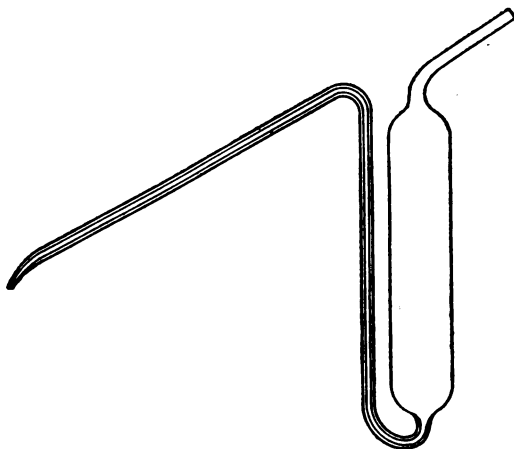


FIG. 32.

means of a pipette with a long tube (Fig. 32). The pipette is weighed before and after the liquid has been run out of it.

The Beckmann Thermometer.—In order that the determinations should be sufficiently accurate, the thermometer should be graduated to, at least, hundredths of a degree, and the temperature may then be estimated to thousandths with sufficient accuracy. Such a thermometer, if made in the ordinary way, would have only a very short range, unless its length were inconveniently great; and it would therefore be necessary to have a number of thermometers for use at different temperatures. In order to use one and the same thermometer for different temperatures, Beckmann has designed one in which the amount of mercury in

the bulb, and therefore the temperature at which the thermometer can be used, can be altered. The lower the temperature, the greater must be the quantity of mercury in the bulb. This regulation of the amount of mercury in the bulb is rendered possible by having at the upper end of the capillary a small reservoir, R (Fig. 33), into which the excess of mercury can be driven, or from which a larger supply of mercury can be introduced into the bulb. The thermometer does not allow of the absolute temperature being measured, but it enables one to determine differences of temperature at any desired absolute temperature. It usually has a range of only five or six degrees.

In order to use the thermometer it is necessary to "set" it, *i.e.* to arrange that the top of the mercury column shall be on the scale. The thermometer is inverted and gently tapped so as to collect the mercury at the upper end of the reservoir. Return the thermometer carefully to the upright position, and warm the bulb in a beaker of water until the thread of mercury unites with the mercury in the reservoir. Then cool slowly in a water-bath to a temperature which is 2° – 3° higher than the freezing point of the solvent. This higher temperature is necessary because the scale does not extend upwards to the end of the capillary. The temperature of the beaker of water should be read by means of an ordinary thermometer, preferably graduated in tenths of a degree. After a few minutes, when the thermometer will have taken the temperature of the bath, strike the upper end of the thermometer against the palm of the hand so as to cause the excess of mercury to break off from the end of the capillary. Make sure, now, that the amount of mercury has been properly regulated, by placing the thermometer in a bath of the temperature of which is equal to the highest that will occur in the experiment, and see that the mercury stands on the scale. If it does not, the operation must be repeated till the correct adjustment has been obtained.

Calculation of the Molecular Weight.—The molecular weight (m) of the solute is calculated by means of the formula—

$$m = k \frac{w}{\Delta W}$$



FIG. 33.

where w is the weight in grams of the solute dissolved in W grams of the solvent, Δ is the observed depression of the freezing point, and k is a constant depending on the solvent. The values of k for the commonest solvents are given in the following table :—

| Solvent. | Freezing point. | k |
|----------------------------------|-----------------|------|
| Water | 0.0° | 1850 |
| Benzene | 5.4 | 5000 |
| Glacial acetic acid ¹ | 17.7 | 3900 |
| Nitrobenzene . . | 3.6 | 7000 |

The error in the determination of molecular weights by this method should not exceed 3–5 per cent. The student should bear in mind, however, that many substances possess abnormal molecular weights when in solution, *e.g.* electrolytes when dissolved in water are dissociated, whereas such substances as acetic and benzoic acids are associated in benzene solution.

Boiling Point or Ebullioscopic Method.—In this method the boiling point of the pure solvent, and also the boiling points of solutions of known strength, are determined. Beckmann has devised an apparatus which may be used for very accurate work,² but for ordinary chemical purposes, when it is only desired to decide what multiple of the empirical formula of a compound represents the molecular formula, where, therefore, an accuracy of 5–10 per cent. is sufficient, the Landsberger method, as modified by Walker and Lumsden, is conveniently employed. The advantage which this method possesses is that several determinations of the molecular weight can be carried out with one and the same sample of material, so that only one weighing is necessary. Instead, also, of determining the amount of the solvent by weight, its amount by volume is measured.

Landsberger-Walker Apparatus.—The apparatus (Fig. 34) consists of a boiling flask, F , and a graduated tube, N , surrounded by the wider tube E , which is connected at the bottom with a condenser. The graduated tube is fitted with a cork

¹ Glacial acetic acid is very hygroscopic, so that when using this substance as a solvent, special precautions have to be taken to keep moisture away. For details, the student is referred to books on Practical Physical Chemistry.

² For details see Findlay's "Physical Chemistry."

carrying a thermometer, T, graduated in tenths of a degree, and a tube, R, by means of which vapour can be led into the tube N from the boiling flask. Excess of the vapour passes out through the hole H, near the top of N, forms a hot mantle for the graduated tube, and is then condensed, and can be used over again in the flask F. S is a safety tube.

The apparatus is fitted together as shown in the figure, the boiling flask containing a quantity of the pure solvent. About

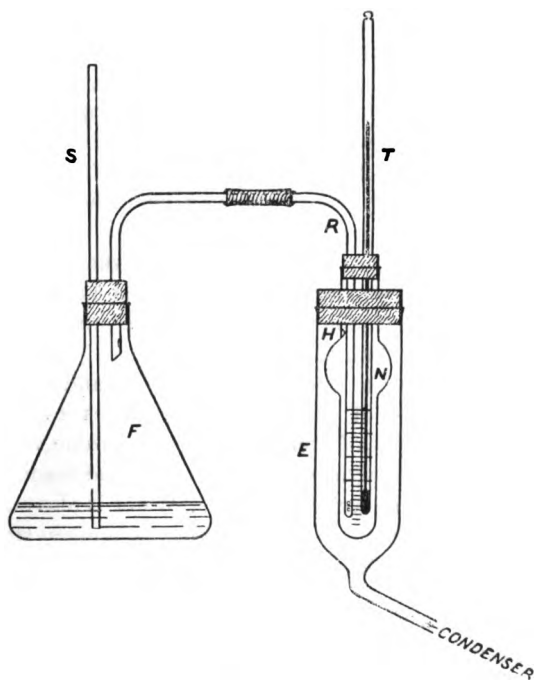


FIG. 34.

10 to 12 c.c. of the solvent are also placed in the graduated tube, and the vapour is then passed through it from the flask F, until the drops fall regularly from the condenser at the rate of one a second, or one every two seconds. The temperature is then read on the thermometer with the help of a lens, the hundredths of a degree being estimated.

The boiling point of the pure solvent having thus been determined, most of the liquid is poured out of the graduated tube,

only 5–7 c.c. being left. In this, a weighed quantity of the substance to be investigated is dissolved, and the apparatus again fitted together. Vapour is then passed through the solution until the liquid drops from the condenser at the same rate as before. The temperature is now read, and the boiling flask *immediately* disconnected from the graduated tube. If the solvent is inflammable, the flame must first be removed or extinguished. Remove the thermometer and the inlet tube,¹ place the graduated tube in a perpendicular position, and read the volume of the liquid, the tenths of a cubic centimetre being estimated.

After having determined the volume of the solution, put the different parts of the apparatus together again, and again pass vapour through the solution, until the liquid drops from the condenser at the same rate as before. Read the thermometer, and measure the volume of the liquid as above. Three readings of the temperature and the corresponding volume should, if possible, be made.

To ensure the uniform ebullition of the solvent in the flask F, a fresh piece of porous tile should be placed in the flask each time the apparatus is disconnected, and before proceeding to pass the vapour into the solution.

The best solvents to employ are alcohol and ether. With benzene the volume of the solution increases so rapidly on account of the low heat of condensation of benzene vapour, that not more than two, sometimes not more than one reading can be obtained with the same weight of solute. Water is also not a good solvent to use, on account of the fact that for a given strength of solution, only a comparatively small elevation of the boiling point is obtained.

Calculation of the Molecular Weight.—The molecular weight (m) of the solute is calculated by means of the expression—

$$m = k \frac{w}{\Delta v},$$

where w is the weight in grams of the solute contained in v c.c. of the solution, Δ is the observed elevation of the boiling point, and

¹ A little of the solution will remain clinging to the thermometer and inlet tube; they should therefore be hung up so that the solution cannot drain away, or otherwise some of the solute would be lost for the remainder of the experiment. The solvent lost by evaporation does not matter in the least.

k is a constant depending on the solvent. The values of k for some solvents are as follows :—

| | k |
|-------------------|------|
| Alcohol | 1560 |
| Ether | 3030 |
| Acetone | 2220 |

The same remarks apply with respect to abnormal molecular weights as those given in connection with the freezing-point method (see p. 188).

CHAPTER XV

SPECIAL QUANTITATIVE WORK

IN a number of cases, after carrying out the preparation of an organic compound, the student has submitted the compound to the process of saponification, and the resulting products were tested for qualitatively. In the determination (*vide infra*) of certain radicles which occur in organic compound, it is very often necessary to carry out a quantitative saponification; the method of doing this will now be described.

Quantitative Saponification of Ethyl Benzoate.—

Into a Jena flask of about 150 c.c. capacity weigh out accurately about 2 grams (not more) of ethyl benzoate. Add 50 c.c. of $\frac{N}{2}$ alcoholic potash,¹ connect the flask with a reflux condenser, and gently boil the contents of the flask for half an hour, after which time the saponification should be complete.

The contents of the flask are allowed to cool, phenol phthalein is added, and the excess of alkali is determined by titration with standard acid.² From the quantity of alkali which was used up in the saponification the purity of the ethyl benzoate can be calculated.

Applications.—In many cases it is necessary to determine the “hydroxyl radicle” in organic compounds. The method used depends on the preparation of derivatives, the most common of which are the acetyl and benzoyl compounds. A weighed quantity of the pure derivative is then submitted to the action of alcoholic potash, and the amount of acetic acid or benzoic

¹ This solution should be made up of approximate strength, as required, and then standardized with semi-normal acid.

² An alternative method is to acidify the contents of the flask with a non-volatile acid, and steam-distil over the benzoic acid, which is then estimated in the distillate. This method takes much longer than the one given.

acid formed is determined as given above, *i.e.* a quantitative saponification is carried out. The number of acetyl or benzoyl groups in the derivative may then be calculated, and hence the number of hydroxyl groups in the original compound.

The *acetylation* is most conveniently carried out by means of a mixture of anhydrous sodium acetate and acetic anhydride. About equal weights of sodium acetate and the substance are taken, and 3-4 parts by weight of acetic anhydride. The mixture is boiled for a short time in a flask attached to a reflux condenser, and the acetyl derivative isolated by pouring the products of reaction into water. If the acetyl derivative is soluble in water it must either be "salted out" or else extracted with benzene. Liquid compounds must be purified by distillation, any acetic anhydride remaining being removed by distillation under reduced pressure, and solid compounds must be purified by recrystallization. Ethyl acetate is very often convenient to use as a solvent in the latter case.

The *benzoyl derivatives* are generally prepared by the Schotten-Baumann reaction (see p. 121). A 10 per cent. solution, or in some cases, even a 20 per cent. solution, of sodium hydroxide should be used, together with excess of benzoyl chloride. The mixture is well shaken until the smell of benzoyl chloride disappears. The benzoyl derivatives are usually solid, and are purified by recrystallization.

As an exercise, the student may show that there is only one hydroxyl group in β -naphthol by the preparation and saponification of the acetyl derivative (see p. 132).

Determination of the $-\text{NH}_2$ and $=\text{NH}$ Groups.—

The $-\text{NH}_2$ group may be determined by the preparation of the acetyl derivative, and then quantitative saponification, as described for the $-\text{OH}$ group. In many cases, however, it may be determined directly as follows:—

Weigh out accurately about 1 gram of aniline into a small flask fitted with a reflux condenser. The aniline is introduced into the flask by means of the small pipette shown in Fig. 32; from the weight of the pipette before and after running the aniline into the flask, the weight of aniline used is determined. Then add about 2 grams of acetic anhydride. This may be done either by making use of a sealed bulb containing a weighed quantity of the anhydride, and then breaking the bulb so as

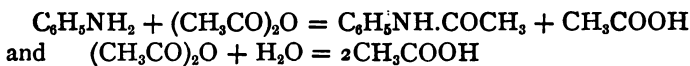
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to mix its contents with the aniline ; or, more conveniently, 2 c.c. may be measured by means of a pipette fitted with rubber tubing and soda-lime tube in order to prevent the vapour of the anhydride coming into the mouth. In either case it will be necessary to perform a blank experiment, so that it is immaterial whether the anhydride be weighed or measured.

Attach a reflux condenser, shake up the mixture, and digest on the water-bath for about half an hour. Then add 50 c.c. of water, and digest for a further forty-five minutes. Cool, wash down the condenser and flask, and make up to 250 c.c. After well mixing, titrate 25 c.c. of the solution with $\frac{N}{10}$ barium hydroxide, using phenol phthalein as the indicator.

It is necessary to perform a blank experiment, using no aniline, in order to find out the strength of the acetic anhydride used. The experiment is carried out exactly as above, and the same method must be used for measuring the anhydride in both cases.

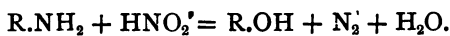
From the equations



the purity of the aniline, or the number of amino groups, may be calculated.

The *imino group* ($=\text{NH}$) may be determined by acetylation in an exactly similar manner. Monomethylaniline, $\text{C}_6\text{H}_5\text{NHCH}_3$, may be taken by the student as an example, and having done this he may proceed to determine the composition of a mixture of monomethyl- and dimethyl-aniline, since the latter compound does not form an acetyl derivative.

The *aliphatic amino group* may very often be conveniently estimated by measuring the nitrogen evolved by the action of nitrous acid.



For further details the student must consult a more advanced text-book.

Determination of Methoxyl and Ethoxyl.—The method used depends on the decomposition of the methoxy compound by means of hydriodic acid, methyl iodide being

liberated. The methyl iodide is decomposed by silver nitrate, and the silver iodide formed is weighed. The method to be described is Perkin's modification of Zeisel's method.¹

The apparatus used is shown in the diagram (Fig. 35). The neck of the distilling flask should be about 20 cms. long (between the side tube and the bulb of the flask). The beaker contains glycerol, and the two flasks which are connected by a siphon tube contain an alcoholic solution of silver nitrate. The end of the siphon tube in the first flask comes down close to the silver solution, whilst that in the second flask passes into it, so that any methyl iodide vapour carried over from the first flask has to bubble through the solution in the second flask, and, in this way, is perfectly absorbed. If any sucking back takes place, a little

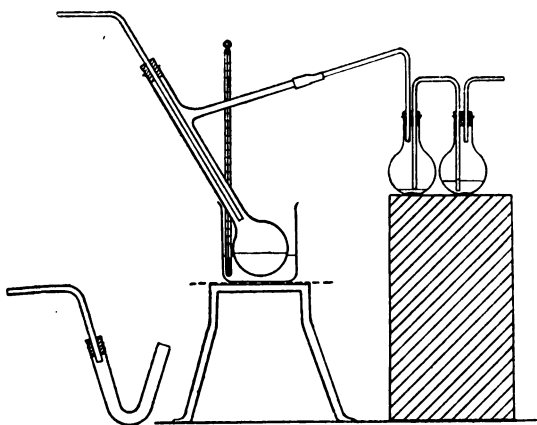


FIG. 35.

of the silver solution is drawn through the siphon tube into the first flask, and afterwards forced back again into the second.

During the experiment a current of carbon dioxide, which must be washed with water and also with silver nitrate or copper sulphate solution, to remove any hydrogen sulphide arising from impurities in the marble, is passed through the apparatus by means of the tube in the neck of the distilling flask.

¹ Another modification is that due to Hewitt and Moore. See *Journ. Chem. Soc.*, 1902, 81, 318.

The solution of hydriodic acid used must have been prepared by means of phosphorus, and not by means of sulphuretted hydrogen. Its specific gravity should be 1.68–1.72, and the boiling point about 126°; it is the solution of maximum boiling point. Stronger acid *cannot* be used.

The silver nitrate solution is prepared by dissolving 2 parts of the fused salt in 5 parts of water, and adding 45 parts of absolute alcohol; it is kept in the dark, and the quantity required for each determination filtered into the absorption flasks.

The method of carrying out the experiment is as follows: 15 c.c. of the hydriodic acid are put into the distilling flask. 0.3 to 0.5 gram of the substance (*e.g.* quinine, brucine, vanillin) is weighed in a portion of an ignition tube, which is then placed in the neck of the distilling flask, and pushed down into the bulb by means of the carbon dioxide tube; the indiarubber stopper carrying the latter is then firmly fixed in the neck. The two flasks, containing about 20 c.c. of the alcoholic solution of silver nitrate in the first, and 15 c.c. in the second, are then connected with the distilling flask by means of vulcanized tubing. The glycerol bath is heated to 130°–140°, a constant current of carbon dioxide being passed through the apparatus at the rate of about three or four bubbles in two seconds. In a very short time, the turbidity due to silver iodide appears in the silver solution contained in the first flask, the amount formed in the second flask being very small. After a time, the temperature of the glycerol may be raised until it causes the hydriodic acid to boil gently, and the neck of the distilling flask to become heated almost up to the delivery tube, but so that there is no actual distillation into the silver solution. The operation is often complete in about three-quarters of an hour, but this is not always so, and, as the time varies with different substances, it is best to heat for an hour; the flasks are then disconnected, and a V-tube (*vide* Fig. 35) containing a few cubic centimetres of silver solution substituted. The heating is then continued for about twenty minutes, and, if no appreciable quantity of crystalline precipitate forms, the operation may be considered complete; but otherwise the solution should be poured into the bulk in the flasks, a fresh quantity put into the tube, and the process allowed to continue another twenty minutes, and so on until the formation of the precipitate ceases. In some cases, where the substance is

attacked with difficulty, the decomposition is greatly facilitated by the addition of acetic anhydride.

When the action is complete the contents of the flasks are gradually added to 50 c.c. of boiling water acidified with nitric acid, and contained in a beaker of about 250 c.c. capacity, a small piece of porous porcelain being added to prevent bumping. The boiling is continued until nearly all the alcohol has been driven off, and the solution allowed to remain for one hour at the ordinary temperature; the precipitate is then collected and weighed in the usual manner.

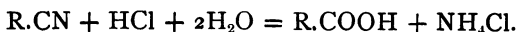
Before carrying out the actual determination it is always advisable to do a blank experiment, in order to be sure that no hydriodic acid distils over into the silver nitrate. If there should be any difficulty in preventing this, a set of potash bulbs containing 0.25 to 0.5 gram red phosphorus suspended in water may be inserted between the distilling flask and the silver nitrate; the bulbs are kept warm by immersion in water heated to 50°.

The method is only suitable for non-volatile compounds; it has to be modified for use with compounds which are volatile.

Ethoxyl determinations may also be made in a similar manner, but the results are usually somewhat low, a small amount of the ethyl iodide being probably reduced by the hydriodic acid.

Substances which are volatile with steam sometimes give low numbers owing to oily globules sticking to the glass and not being washed down by the condensed water or acid; this is obviated to some extent if the mixture of hydriodic acid and acetic anhydride is employed, as the acetic acid present dissolves the volatilized substance and carries it back into the hydriodic acid.

Determination of the Nitrile (—CN) Group.—The nitrile is digested with hydrochloric or sulphuric acid, in a flask fitted with a reflux condenser, until it has been completely hydrolyzed. As most nitriles are insoluble in water, the completion of the hydrolysis is indicated by the disappearance of the layer of nitrile.



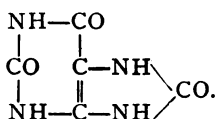
The product is then treated with alkali in excess, and the ammonia distilled over into standard acid, as in the estimation of nitrogen according to Kjeldahl (see p. 168).

Determination of the Amido ($-\text{CO.NH}_2$) Group.—

This may be carried out similarly to the determination of the nitrile group. Or the amido compound may be decomposed by heating with a known amount of standard alkali, and titration of the excess of alkali after all the ammonia has been driven off.

CHAPTER XVI

URIC ACID,



URIC acid is a white crystalline powder, which is not appreciably soluble in cold, and only very slightly soluble in hot, water. It is insoluble in alcohol and ether. It possesses acid properties, and is soluble in alkaline liquids. Acids precipitate uric acid from solutions of its salts.

1. Heated in a dry tube, uric acid is decomposed without fusion, but charring takes place. A sublimate containing cyanuric acid and other products is formed, and ammonia and hydrocyanic acid are evolved.

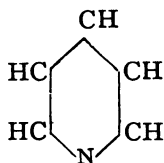
2. Uric acid is soluble in cold concentrated *sulphuric acid*, and is precipitated again on the addition of water. On heating the solution, decomposition takes place after a time, carbon monoxide, carbon dioxide, and sulphur dioxide being evolved.

3. **Murexide Reaction.**—Add a few drops of strong *nitric acid* to a little uric acid and evaporate to dryness on the water-bath. An orange or reddish-coloured residue is obtained, which, when cold, is coloured violet-red by *ammonia*, and violet or blue by *sodium hydroxide*.

4. Dissolve a little uric acid in *sodium carbonate*, and put a few drops of this solution on to a filter-paper moistened with *silver nitrate*. A dark brown stain of reduced silver is formed.

5. Uric acid reduces *Fehling's solution* on warming for some time. A white precipitate of cuprous urate is first formed.

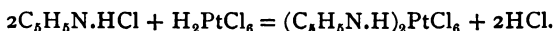
PYRIDINE,



Pyridine is a colourless liquid, with a penetrating and characteristic odour. Boiling point, 116°; volatile with steam. It is miscible with

water in all proportions, and also with alcohol and ether. It fumes with HCl. It acts as a base, forming salts with acids. The aqueous solution is alkaline, and precipitates the hydroxides of metals such as iron, aluminium, and chromium from solutions of their salts. With copper sulphate it gives a pale blue precipitate, which dissolves in excess of pyridine, forming a deep blue liquid. Pyridine is **not** attacked by boiling nitric acid or chromic acid.

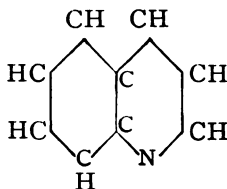
1. Pyridine dissolves in hydrochloric acid with the formation of the hydrochloride. This solution, since it contains a substituted ammonium compound, gives, with *chlorplatinic acid*, an orange precipitate of pyridine platinichloride.



This precipitate is soluble in hot water, and the aqueous solution, on long boiling, gives a yellow insoluble salt, $(\text{C}_5\text{H}_5\text{N})_2\text{PtCl}_4$.

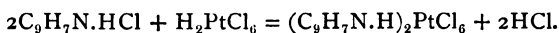
2. As a tertiary base it combines readily with *methyl iodide*. The reaction is brought about by gently warming a mixture of equal volumes of the two substances; once the action has started it goes on vigorously. On cooling, the yellow crystalline methiodide separates out. When the reaction is completed, add *alcoholic potash*, and warm very gently (the tube should just feel warm to the hand). A brown resin forms. Pour off the liquid and dissolve the resin in alcohol. A deep red solution is obtained, which is turned bright red by *hydrochloric acid*, and orange-red by *acetic acid*.

QUINOLINE,



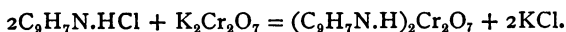
Quinoline is a colourless liquid with a peculiar and characteristic odour. Boiling point, 239° ; volatile with steam. The liquid slowly becomes yellow on standing. It is only slightly soluble in water, but is miscible with alcohol and ether. Very hygroscopic. It acts as a base and forms salts. It will precipitate the hydroxides of metals such as iron or aluminium from solutions of their salts. Quinoline is oxidized by boiling nitric acid or chromic acid.

1. *Chlorplatinic acid* gives a yellow precipitate of quinoline platinichloride with solutions of quinoline in hydrochloric acid. The precipitate is soluble in hot water.



2. Combines readily with *methyl iodide*. Potash does not form a resin (*cf.* pyridine).

3. The bichromate is the least soluble salt of quinoline. It is formed by adding *potassium bichromate* to an *acetic acid* solution of quinoline, and shaking. A yellow crystalline precipitate is produced, which is soluble in hot water.



Pyridine bichromate is too soluble to give a precipitate under these conditions.

ALKALOIDS.

The alkaloids comprise a large number of compounds which are basic in character, and since they are obtained from plants they are known as "vegetable bases." This latter term is synonymous with the term "vegetable alkaloid." Only a few, such as *piperidine*, *coniine*, and *nicotine* are liquids, and these have unpleasant odours; most of them are colourless, inodorous, crystalline solids. They have an alkaline reaction and a bitter taste. Most of them are insoluble, a few are sparingly soluble, in water, but they are more or less soluble in ether and readily soluble in alcohol.

With acids they form salts which are readily soluble in water; solutions of such salts are precipitated by alkalies; in some cases the alkaloid dissolves in excess of the precipitant, *e.g.* morphine in excess of caustic soda or potash.

Most of the alkaloids are tertiary amines, so that they yield addition products with methyl iodide; some of them are secondary amines, but no one of them is a primary amine.

There are a number of *general reagents* for the alkaloids; the precipitates obtained are characteristic of the alkaloids as a class, but do not serve the purpose of identifying them individually.

Some of these reagents are as follows:—

1. *Chlorplatinic acid*. Yellow precipitates of varying shades; some crystalline and some flocculent. Some of the compounds are sparingly soluble in water, and some are rather easily soluble. They are not so readily obtained as the precipitates with the following reagents.

2. A solution of *iodine* in *potassium iodide*. Reddish-brown or brown precipitates of the periodides.

3. A solution of *phosphomolybdic acid* in nitric acid gives light yellow or brownish-yellow precipitates.

4. *Potassium mercury iodide*. White or yellowish-white precipitates.

5. *Picric acid*. Yellow crystalline precipitates.

Besides the general reagents there are a number of *special reagents*, which give characteristic reactions with the individual alkaloids. They

are colour reactions, so that they are most conveniently carried out on a white glazed tile, or in a porcelain dish, a very little of the alkaloid being taken, and only a drop or two of the reagent.

Erdmann's reagent.—Six drops of nitric acid of 1.25 sp. gr. are mixed with 100 c.c. of water, and 10 drops of this solution are added to 20 grams of pure concentrated sulphuric acid.

Fröhde's reagent.—One gram of ammonium molybdate in 100 c.c. of concentrated sulphuric acid. (This reagent gradually decomposes.)

Mandelin's reagent.—One gram of vanadate of ammonium in 100 c.c. of concentrated sulphuric acid.

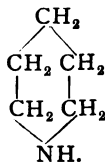
For carrying out a number of the reactions the free alkaloid is necessary. If a salt is given, the alkaloid may be precipitated by caustic soda or sodium carbonate. MORPHINE, however, dissolves in excess of caustic soda, so that ammonia should then be used as the precipitant. PIPERINE generally occurs as the free alkaloid, since salts such as the hydrochloride are decomposed by water.

The reactions for the following alkaloids will be given :—

Volatile alkaloids, possessing a characteristic odour, and containing no oxygen. PIPERIDINE, CONIINE.

Fixed alkaloids, containing oxygen. As a rule they are white crystalline powders, having a bitter taste (in most cases **very poisonous**) and no smell. MORPHINE, QUININE, CINCHONINE, STRYCHNINE, BRUCINE, PIPERINE, CAFFEINE, THEOBROMINE.

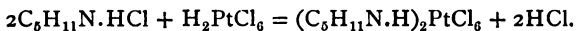
PIPERIDINE,



Piperidine is a colourless liquid, with an ammoniacal and peppery odour. Boiling point, 105°. It is miscible with water, alcohol, ether, and benzene in all proportions. It possesses an alkaline reaction, and absorbs carbon dioxide from the air. It is a secondary base, and forms salts with acids.

1. Piperidine precipitates salts of *zinc* and *copper*, but does not redissolve the precipitated hydroxides.

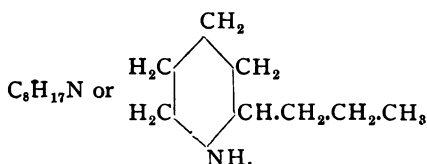
2. Dissolves in *hydrochloric acid* with the formation of a hydrochloride, and the solution gives a yellowish-red crystalline precipitate with *chlorplatinic acid*. The mixture may need concentrating on the water-bath before the crystals (needles) appear.



3. As a secondary base it forms a nitrosamine with *nitrous acid*. The nitrosamine is a pale yellow liquid, and responds to Liebermann's nitroso reaction. Carry out the test according to the method given on p. 123; the nitrosamine remains in solution, since it is slightly soluble in water, and must be extracted with ether.

4. When *methyl iodide* is added to piperidine the reaction is very violent (as violent as adding water to sulphuric acid), and the yellow solid methiodide separates out at once.

CONIINE,



Coniine is a colourless oily liquid, with a disagreeable, mouse-like odour; it is very poisonous. Boiling point, 166° . Volatile to some extent at the ordinary temperature, and also volatile with steam. It is only slightly soluble in cold water (1 part in 100), but is still less soluble in hot water, so that a cold saturated solution becomes turbid on warming. It is miscible with alcohol in all proportions, and is readily soluble in ether. It is a very strong base, forming salts with acids, and precipitating most metals as hydroxides from their aqueous solutions. The aqueous and alcoholic solutions are alkaline. With the volatile acids coniine forms dense white fumes; the smallest quantity of the base brought into contact with a trace of hydrochloric acid gives almost immediately non-deliquescent crystals of the hydrochloride.

1. A cold saturated aqueous solution of coniine becomes turbid on warming. The saturated solution is easily obtained by shaking up a little coniine with water and filtering.

2. To a solution of a coniine salt in water add *caustic soda* solution. The solution becomes milky owing to the liberation of the free base, and at the same time the odour of coniine becomes very pronounced. The base may be extracted with ether and obtained as oily drops by evaporating a little of the ethereal solution on a watch-glass.

3. *Mercuric chloride* gives a white precipitate, which is soluble in hydrochloric acid.

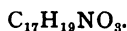
4. *Chlorine water* gives a white precipitate, or produces a milkiness, with aqueous solutions of coniine.

5. Coniine and its salts are oxidized on warming with *potassium*

dichromate and *sulphuric acid*, and the smell of butyric acid is observed.

6. If coniine is added to a solution of *alloxan*, an intense purple-red colour is developed on standing, and white needles separate out which dissolve in cold *potash*, giving a purple solution.

MORPHINE,



Morphine crystallizes from dilute alcohol in the form of colourless transparent prisms, which contain one molecule of water of crystallization. It melts at 247° with decomposition. It is only very sparingly soluble in water, ether, benzene, and chloroform, but more readily soluble in alcohol; hot amyl alcohol is the best solvent. The solutions in alcohol, or in hot water, are distinctly alkaline. Morphine is a tertiary base, and as such, forms salts with acids, which are soluble in water and alcohol, but insoluble in ether. It is also a phenol, so that it dissolves in caustic alkali with the formation of salts, which contain one atom of the metal, and are decomposed by carbonic acid; it is only slightly soluble in ammonium hydroxide. Morphine is very readily oxidized.

1. If *caustic alkali* is carefully added to the solution of a morphine salt, the morphine is precipitated as a white crystalline powder, which is very readily soluble in excess of the precipitant.

Ammonia produces the same precipitate, but it is only soluble in a large excess of the precipitant.

Sodium carbonate also gives the same precipitate, but does not redissolve it when in excess. The solid alkaloid may thus be separated, and used for the following tests.

2. Cold concentrated *sulphuric acid* dissolves morphine, giving a colourless solution. On warming, a reddish or brown colour develops, which deepens on continued heating.

If the solution in sulphuric acid is gently warmed for a short time, and then cooled, the addition of a drop of *nitric acid* or a trace of *potassium nitrate* produces a rich red colour, sometimes inclining to purple.

3. Strong *nitric acid* dissolves morphine, giving a yellowish-red colour. In dilute solutions the colour only appears on warming. *Stannous chloride* destroys the colour.

4. A few drops (excess must be avoided) of neutral *ferric chloride* give a deep-blue coloration with solid morphine, or with concentrated solutions of morphine salts. The colour is destroyed by *hydrochloric acid*.

The ferric chloride is reduced to the ferrous state in this reaction,

so that the addition of *potassium ferricyanide* gives a dark blue precipitate of Turnbull's blue.

5. Morphine liberates iodine from a solution of *iodic acid*. In very dilute solutions the iodine may be detected with starch.

6. Intimately mix 1 part of morphine with 6 to 8 parts of *cane sugar*. Place a little of the mixture on a white tile, and add a drop of concentrated *sulphuric acid*. A deep red colour is produced.

When solutions of morphine salts are used, a little of the solution is saturated with cane sugar, and a drop of the solution placed near a drop of sulphuric acid on a white tile ; on tilting the tile the two drops mix and the colour is produced.

7. The yellow precipitate produced by *phosphomolybdic acid* is dissolved by *ammonia*, giving a deep blue solution.

8. *Fröhde's reagent* gives a violet-red or purple coloration, which becomes green under the action of the air.

QUININE,



Quinine is precipitated by alkali from aqueous solutions of its salts as an amorphous and anhydrous mass, which, however, soon changes to the crystalline condition, forming a hydrate with three molecules of water of crystallization. Anhydrous quinine may also be obtained crystallized in the form of small needles. The trihydrate melts at 57° and the anhydrous substance at 173° . Quinine is only sparingly soluble in water, but fairly soluble in alcohol, ether, benzene, and chloroform. The solutions react alkaline, have an intensely bitter taste, and are lævorotatory.

Quinine is a tertiary base, and forms salts with acids (the sulphate is the most common). Most of these salts are crystalline solids, sparingly soluble in cold, more easily in hot, water. The solutions of salts of oxygen acids, especially sulphuric acid, have a blue fluorescence.

1. From solutions of quinine salts, *caustic soda*, *ammonia*, and normal *carbonates* give a white amorphous precipitate of the free alkaloid. On heating and cooling, the amorphous mass is changed to crystalline needles.

2. Cold concentrated *sulphuric acid* dissolves quinine, giving a colourless solution. On warming, the solution gradually turns yellow, and then brown. If the cold colourless solution is diluted by pouring into water, or, better, if quinine is dissolved in dilute sulphuric acid, a blue fluorescence is observed.

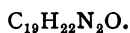
3. Strong *nitric acid* dissolves quinine, giving a colourless solution, which is turned yellow on warming.

4. To the solution of a quinine salt add about one-fifth of its volume of good *chlorine water*, and then *ammonia* in excess. An intense green colour is produced.

If, after the addition of the chlorine water, a few drops of freshly prepared *potassium ferricyanide* solution are added, and then a few drops of *ammonia*, a rich red colour is produced, which rapidly changes to a dirty brown.

5. *Mandelin's reagent* gives no colour until a drop of *nitric acid* is added, when a violet coloration is obtained.

CINCHONINE,



Cinchonine crystallizes from alcohol in anhydrous prisms, which melt at 255° . It is almost insoluble in water and the alkalies, slightly soluble in ether, chloroform, and benzene, and fairly soluble in hot alcohol. The best solvent is a mixture of alcohol and chloroform, in the proportion of 1 : 6 by volume. The solutions taste bitter, and have an alkaline reaction.

Cinchonine is a tertiary base, and its salts are generally more soluble than those of quinine. It is distinguished from quinine by the fact that it gives no colour reactions with chlorine and ammonia, and, moreover, it is dextrorotatory.

1. *Caustic soda, ammonia*, and *sodium carbonate* precipitate cinchonine as a white precipitate from solutions of its salts. The precipitate does not show a distinctly crystalline character, even when magnified two hundred times.

2. Concentrated *sulphuric acid* dissolves cinchonine, forming a colourless solution in the cold. On warming, it becomes yellow, then brown, and finally black. The diluted colourless solution shows hardly any fluorescence.

3. Strong *nitric acid* gives no characteristic reaction.

4. *Chlorine water* and *ammonia* give no green coloration, but a white, or yellowish-white, precipitate.

5. *Potassium ferrocyanide*, with solutions of cinchonine salts which contain little or no free acid, gives a flocculent precipitate of cinchonine ferrocyanide. On adding a slight excess of the ferrocyanide, and warming gently (do not boil), the precipitate dissolves, but deposits out again on cooling in the form of golden-yellow crystals. (This is a characteristic and delicate reaction.) The precipitate obtained with quinine under the same conditions is also soluble in excess of the precipitant, but does not crystallize out again on cooling.

6. *Mandelin's reagent* gives no colour until a drop of *nitric acid* is added, when a violet colour is obtained.

STRYCHNINE,



Strychnine crystallizes from alcohol in the form of prisms which melt, with decomposition, at 269°. It is almost insoluble in water, absolute alcohol, and ether; sparingly soluble in dilute alcohol, and readily soluble in chloroform.

It is a tertiary base, giving an alkaline reaction, and the salts are soluble in water and alcohol.

1. *Caustic soda* and *sodium carbonate* give a white precipitate of strychnine from solutions of its salts; the precipitate is insoluble in excess.

Ammonium hydroxide also precipitates strychnine, but the precipitate is soluble in excess of the precipitant; after a short time, however, the strychnine crystallizes out from the solution in the form of silky needles.

2. Dissolve a crystal of strychnine in a few drops of concentrated *sulphuric acid* in a porcelain dish. No colour is produced. Now rub into the solution a crystal of *potassium bichromate*; a blue or violet colour is produced, which quickly changes to red, and then reddish-brown. Other oxidizing agents, such as *potassium ferricyanide* and *lead peroxide*, produce similar colours, but the reaction is less rapid.

3. Concentrated *nitric acid* dissolves strychnine, giving a colourless solution; on warming, a yellow colour is produced.

4. *Mandelin's reagent* gives a fine blue coloration, which soon turns to violet, and lastly to red, or reddish-yellow. If a few drops of a solution of *caustic potash* or *soda* are added as soon as the red colour appears, a permanent rose-red colour is produced. (The presence of other alkaloids does not affect this reaction at all, or only to a slight extent.)

BRUCINE,



Brucine crystallizes in prisms containing four molecules of water of crystallization; the crystals melt at 178° when dry. It is sparingly soluble in cold, but more readily in hot, water; it is readily soluble in alcohol (both absolute and dilute), hot amyl alcohol, and chloroform, but is practically insoluble in ether.

It is a tertiary base, and forms salts, which are readily soluble in water.

1. *Caustic soda* and *sodium carbonate* give a white precipitate of

brucine from solutions of its salts, insoluble in excess. The precipitate is amorphous at first, but it suddenly changes to the crystalline form (needles).

Ammonium hydroxide gives a similar precipitate, but while it is in the amorphous condition it is soluble in excess of the precipitant ; after a short time the brucine crystallizes out from the solution in the form of needles.

2. Concentrated *sulphuric acid* dissolves brucine with the formation of a rose-red colour, which slowly turns yellow. If the sulphuric acid contains nitric acid (use *Erdmann's reagent*) a red colour is produced, which changes to yellow.

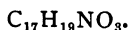
3. When treated with a little strong *nitric acid*, brucine gives an intense red colour, which turns yellow on warming. If the "yellow" solution is diluted with water, and then a few drops of *stannous chloride* added, an intense violet colour is produced.

4. *Mercurous nitrate* gives a colourless solution with brucine. If this solution is heated on the water-bath, a carmine colour gradually appears, which slowly increases in intensity.

5. *Mandelin's reagent* gives a yellowish-red colour, which quickly changes to orange, and finally disappears.

6. *Fröhde's reagent* gives a light red colour, which changes to a reddish-brown.

PIPERINE,



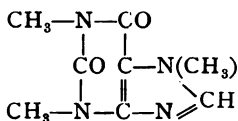
Piperine crystallizes in prisms, which melt at 128° – 129° . It possesses a pungent fragrant odour of pepper. It is almost insoluble in cold water, but fairly soluble in alcohol and ether. It is a very weak base, does not react alkaline, and is insoluble in dilute acids and alkalies. It is soluble in concentrated acids, forming salts, which are decomposed by water. The platinichloride, however, is not decomposed, even by hot water. On hydrolysis with alcoholic potash, piperine is split up into piperidine and piperic acid.

1. Concentrated *sulphuric acid* gives a blood-red solution ; the colour rapidly changes to brown, finally becoming black, especially on warming.

2. Concentrated *nitric acid* gives a greenish-yellow colour, changing to red.

3. *Erdmann's*, *Fröhde's*, and *Mandelin's reagents* each give the same reaction as with concentrated sulphuric acid alone. A yellowish-red colour is produced, which changes to red, then brown, and finally becomes practically black.

CAFFEINE, OR THEINE,



Caffeine crystallizes from hot water in long silky needles, with one molecule of water of crystallization. In the anhydrous condition it melts at 234° – 235° ; it sublimes and distils without decomposition. It is only slightly soluble in cold water, alcohol, and ether, but fairly soluble in hot water, chloroform, and benzene. It is a weak base, with neutral reaction, the salts being decomposed (hydrolyzed) by water.

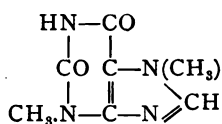
1. The long, silky needles are very characteristic.

2. Moisten with *chlorine* or *bromine water*, and evaporate to dryness on the water-bath; a yellow residue is left, which becomes red on further heating, and is turned purple by *ammonia*. (Murexide reaction. Cf. uric acid.)

3. Evaporate to dryness on the water-bath with dilute *hydrochloric acid* and a fragment of *potassium chlorate*; a pink residue is left, which turns violet on the addition of *ammonia*.

4. Caffeine gives a yellow precipitate with *phosphomolybdic acid*, but no precipitate with a solution of *iodine* in *potassium iodide*.

THEOBROMINE,



Theobromine crystallizes in microscopic needles, which are only slightly soluble in hot water and alcohol; it is almost insoluble in ether. It sublimes, without melting, at 290° – 295° . It is a weak base, and reacts neutral; its salts are decomposed by water. It possesses acid properties towards alkalis.

1. Theobromine gives the *murexide reaction* with *chlorine* or *bromine water* (cf. caffeine).

2. With cold saturated aqueous solutions of theobromine, *ammoniacal silver nitrate* gives a gelatinous precipitate, which dissolves on warming, and deposits on boiling, the crystalline silver salt ($\text{C}_7\text{H}_7\text{AgN}_4\text{O}_2$).

REACTIONS OF THE FIXED ALKALOIDS.¹

| | Conc. H_2SO_4 . | Conc. HNO_3 . | Erdmann's reagent. | Fröhde's reagent. | Mandelin's reagent. |
|----------------|--------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|-------------------------------|------------------------------------------|------------------------------------------------------------------------------------------|
| Morphine . . . | Colourless, cold; red-brown on warming | Yellowish-red. Destroyed by SnCl_2 | Rich red | Violet-red or purple \rightarrow green | — |
| Quinine. . . | Colourless, cold; yellow and then brown, on warming | Colourless; yellow, on warming | — | — | No colour, till drop of HNO_3 added; then violet |
| Cinchonine . . | Colourless, cold; yellow \rightarrow brown \rightarrow black, on warming | — | — | — | No colour, till drop of HNO_3 added; then violet |
| Strychnine . . | Colourless. With crystal of $\text{K}_2\text{Cr}_2\text{O}_7$, blue \rightarrow red \rightarrow reddish-brown | Colourless; yellow, on warming | — | — | Blue \rightarrow violet \rightarrow red \rightarrow reddish-brown. Red with alkali |
| Brucine . . . | Rose-red \rightarrow yellow | Intense red; turned purple by SnCl_2 | Red \rightarrow yellow | Light-red \rightarrow reddish-brown | Yellow-red \rightarrow orange |
| Piperine . . . | Blood-red \rightarrow brown \rightarrow black | Greenish yellow red | Red \rightarrow brown black | Red \rightarrow brown black | Red \rightarrow brown black |

¹ Caffeine and theobromine are not included.

CHAPTER XVII

SCHEME FOR THE IDENTIFICATION OF AN ORGANIC COMPOUND

THE compounds may be chosen from the list of substances given for Stage I. (p. 73), and also from the following: **Benzene, naphthalene, anthracene, phenol, aniline, benzoic acid, salicylic acid, benzaldehyde, and their most prominent chloro-, bromo-, and nitro- derivatives; uric acid, pyridine, quinoline, morphine, strychnine, quinine, cinchonine, coniine, piperine, piperidine, caffeine, and theobromine.**¹ The student may also be required to refer, without identification, unknown compounds to one or other of the following classes: (1) alcohols, (2) aldehydes, (3) acids, (4) ketones, (5) amides, (6) amines, (7) esters, (8) phenols.

In the following scheme it is assumed that the substance under examination is not a solution. If a solution is suspected, it must be tested for as given in the scheme for Stage I., p. 75. Only the more commonly occurring substances are considered, and since it is not possible, in the space at our disposal, to give the special tests for compounds not previously dealt with, *the student should always have a good text-book of organic chemistry at hand, for reference.*

I. The obvious properties of the substance should first be particularly noted.

A. Colour.—The chief classes of coloured compounds are: Nitro-compounds (generally pale yellow), azo-compounds (strongly coloured), quinones (generally yellow), p-nitroso dialkylanilines (green), ferro- and ferri-cyanides. (Remember that iodoform is yellow, and may be recognized by the smell.)

¹ The substances in italics belong to Stage III.

B. State of Aggregation.—

Liquid.—Lower hydrocarbons; most alcohols; ethers; esters; nitriles; mustard oils; aldehydes; ketones.

Solid.—Higher hydrocarbons, alcohols, etc.; most acids; sulphonic acids; salts; sugars; quinones; amides; anilides; phenols (except carvacrol).

C. Odour.—Most liquids have an odour; most solids are inodorous.

(1) *Liquids with no odour.*—Polyhydric alcohols (glycol, glycerol). Some esters—derived either from hydroxy acids or polyhydric alcohols, e.g. esters of glycerol and of tartaric acid. Such compounds are *viscous*.

As the number of inodorous liquids is limited, a liquid with no smell should be heated with KOH and tested as for esters (p. 226), then for glycerol, etc.

(2) *Liquids with more or less characteristic odours.*—Hydrocarbons, aliphatic and aromatic; haloid derivatives; nitriles; mustard oils; monohydric alcohols; ethers; aldehydes; ketones; acids; acid chlorides and anhydrides; most esters; nitro-compounds; amines; alkaloids.

In many cases the actual compound may be detected.

(3) *Solids possessing an odour.*—(NOTE.—The majority of solids are inodorous.) Some common solids possessing odours are: Naphthalene; chloral hydrate; quinone; β -naphthylamine; acetamide; iodoform; many phenols, and other simple substituted benzene derivatives.

II. If the substance is *solid*, **heat** a small portion **on platinum foil**. Note odours evolved, and whether the substance chars with or without melting; also whether the substance burns with a smoky flame.

Characteristic odours from tartrates, citrates, sugars, starch, alkaloids, etc.

Substances such as starch, uric acid, oxamide, succinamide, sulphonic acids, char without melting.

Smoky flame generally indicates an aromatic compound.

A *residue* indicates a metallic derivative (salts, bisulphite compounds of aldehydes and ketones, etc.). Test whether the residue is—

(a) *Carbonate, oxide, or metal*—from salts, including phenates and amido metallic derivatives.

(b) *Sulphate*—from *e.g.* salt of ethyl sulphuric acid. Some sulphate may be reduced to sulphite or sulphide.

(c) *Sulphite*—from bisulphite compound of an aldehyde or ketone; from sulphonates.

(d) *Cyanide*—from ferro- and ferri-cyanides, and cyanides of the alkali and alkaline earth metals.

III. Test the **solubility in water**, and at the same time the **reaction to litmus**, according to the method given in the scheme for Stage I. (p. 75); distinguish between acid and alkaline reactions due to the free acids and bases respectively, and those due to hydrolysis of salts.

Negatively substituted phenols react acid.

The salts of aromatic amines react strongly acid in solution; the free base is liberated when caustic potash is added, and separates out, since aromatic amines are insoluble, or only very sparingly soluble, in water. The salts of phenols are alkaline in solution.

Some acids, *e.g.* anthranilic acid, are practically neutral to litmus. Their acid character, however, is shown by the fact that they readily dissolve in NaOH, even when they are only sparingly soluble in water. They are also soluble in Na_2CO_3 , liberating CO_2 from warm solutions.

The majority of organic compounds are insoluble in water. Aliphatic compounds are, as a rule, more soluble than aromatic.

Soluble.—(If salts are excepted, solubility generally indicates the presence of $-\text{OH}$ groups.)

(1) *Aliphatic.*—Lower alcohols (n-butyl alcohol, 1:10); lower aldehydes; lower ketones (acetone); lower monobasic acids; polybasic acids; substituted acids; carbohydrates (except starch, cellulose); lower amines and amides; methyl and ethyl acetates (s.s.¹); methyl oxalate; urea and alkyl ureas; thiourea; glycerol; chloral and chloral hydrate.

(2) *Aromatic.*—Polyhydric phenols, the solubility increasing with the number of hydroxyl groups; amino-acids (some are very sparingly soluble, *e.g.* amino-benzoic acids); sulphonic acids (a number are only sparingly soluble, *e.g.* sulphanilic acid); nitrophenols (some are almost insoluble, but the aqueous solution is

¹ s.s. = sparingly soluble.

sometimes distinctly coloured); pyridine; coniine, piperidine, etc.

(3) *Salts*, either of acids with metals (including NH_4), or of bases with acids (HCl , H_2SO_4 , etc.).

These are all solid, and generally decompose without melting on heating.

NOTE.—Acid chlorides and acid anhydrides are decomposed more or less quickly by water, especially on warming. The acid formed may be soluble or insoluble.

IV. Solubility in Ether.—Most organic compounds are soluble in ether.

Insoluble.—Salts. Polyhydroxyl compounds, *e.g.* glycerol, starch, tartaric acid, etc. (Thus, glycerol is precipitated from alcohol by ether. This insolubility in ether is sometimes very useful, as the reactions of such substances as glycerol are often rather indefinite.)

V. Heat with an excess of soda-lime in an ignition tube.

- | | |
|-----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) Ammonia, or amines (inflammable) evolved. | Most N-compounds give off ammonia. Amines from salt of an amine. |
| (b) Hydrogen evolved . . . | Formate, oxalate. |
| (c) Hydrocarbon evolved . . . | From carboxy acid, or salt of acid (<i>e.g.</i> CH_4 from acetates, C_2H_6 from succinates, C_6H_6 from benzoic acid). |
| (d) Smell of a phenol . . . | From hydroxy acids (aromatic), such as salicylic acid and their salts. |
| (e) Smell of burnt sugar . . . | Carbohydrates; acids, such as tartaric, citric, etc. |

VI. Warm with concentrated NaOH . See table in scheme for Stage I., p. 80. In *addition* to this—

(a) *Aromatic amines* are liberated from their salts, and form an oily layer, or else precipitate out as a solid. (The aniline is only set free from anilides after very prolonged heating.) p-nitroso-dialkylanilines give off aliphatic amines. They are distinguished from salts of amines by their characteristic green colour.

(b) *Alkaloids* are precipitated from solutions of their salts. (Morphine is soluble in excess.)

(c) *Acids* and *phenols* dissolve, and are reprecipitated by the addition of HCl. (N.B.—In some cases the reprecipitation takes place only from concentrated solutions.) Some phenols are not reprecipitated by HCl (e.g. pyrogallol). Also, HCl does not precipitate soluble acids from solution.

(d) The characteristic smell of *esters* is removed after boiling for a time.

VII. Add cold concentrated H_2SO_4 , and warm. See table in scheme for Stage I, p. 82. Also note, in addition—

(a) Saturated and aromatic hydrocarbons and their halogen derivatives do not dissolve.

(b) Alkaloids, polyphenols, phenolic acids, etc., blacken.

VIII. Test for the Elements:—N, Halogens, S and P. (C and H are rarely tested for.)

NOTE.—Nitro-compounds—indicated by a yellow colour—must be carefully handled in carrying out the test with sodium. It is sometimes difficult to get the nitrogen test satisfactorily.

In carrying out the tests where sodium is used, some conclusions may often be drawn from the nature of the reaction.

No marked action.—Hydrocarbons, pure ethers, etc.

Vigorous action.—Acids, phenols, alcohols, etc.

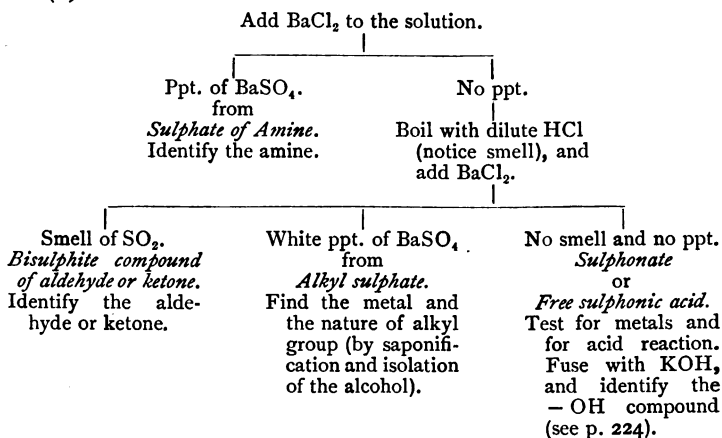
IX. Sulphur present.—We have the following possibilities: Mercaptans; thioethers; thiocyanates; mustard oils; thiourea and thiocarbanilide; sulphonic acids and salts; alkyl sulphates; sulphates of amines; bisulphite compounds of aldehydes or ketones.

A. Odour.—Mercaptans, thioethers, and mustard oils are immediately distinguished by their smell. The first two will not be dealt with (occurrence improbable).

Mustard Oils.—Also contain N. On heating with yellow HgO , formation of black HgS and disagreeable odour of isocyanate. On warming with aniline a thiourea is formed: recrystallize and take melting point for identification.

B. **No Odour.**—Treat with water.

(1) *Soluble.*



(2) *Insoluble.*—Test for *thiocarbanilide* (vide p. 98).

C. Apply special tests for *thiocyanates*. It is only necessary to test for inorganic salts; esters are not probable.

D. Test specially for *thiourea*. The melting point of the pure substance is 169° (see p. 2). Melt a little of the substance in a test-tube, and keep at the melting point for one minute. Cool, dissolve in water, acidify with HCl , and add FeCl_3 . Blood-red coloration, due to formation of ammonium thiocyanate.

NOTE.—This method of classification is used to determine the form in which the S is present. Other elements, in addition to C, H, and O, may have been indicated in the preliminary tests, in which case further tests, as given under X. and XI., must be applied.

X. **Halogens present.**—There may possibly be present: Haloid acid salts of amines; acid chlorides; halogen substituted acids; halogen combined with (a) an aliphatic radicle, (b) an aromatic radicle.

Note the odour carefully.

A. Pronounced odour.

(a) Pungent; an *acid chloride*. (Acetyl and benzoyl chlorides are the two common ones.) On treatment with water, HCl is liberated (test with

AgNO_3). Hydrolyze, and identify the organic acid formed. Also prepare the anilide with aniline, and take the melting point.

- (b) *Chloral* (liquid) or *chloral hydrate* (solid). Special tests p. 39.

B. Pungent odour of acetic acid, especially on warming. Soluble in water. *Chloroacetic acids*. Identify as on p. 43.

C. Liquid or solid, with a more or less characteristic smell. Insoluble in water.

- (1) Digest with alcoholic potash¹ (reflux) for some time. Acidify a portion with HNO_3 and add AgNO_3 .

(a) Precipitate of Halogen attached to aliphatic silver halide. radicle.

(b) No precipitate Halogen attached to benzene ring. Identify by boiling point or melting point.

- (2) If the substance responds to (1) (a), make special tests, as follows :—

(a) *Iodoform*. Yellow solid. Tests, p. 39.

(b) *Chloroform* and *bromoform* leave a *formate* in solution, after digesting with KOH . Test for CHCl_3 , p. 38.

(c) *Carbon tetrachloride*. Boiling point 77° . Gives the isonitrile test only after prolonged boiling. Is readily reduced to CHCl_3 by Zn and HCl , and then gives the isonitrile test immediately.

(d) Digest with aqueous KOH under reflux.

Methyl bromide and *iodide* give *methyl alcohol*.

Ethyl bromide and *iodide* give *ethyl alcohol*, etc.

Allyl derivatives give *allyl alcohol*. (Smell.)

Confirm by decolourization of solution of Br in CCl_4 .

(e) The substance may be an aromatic compound with the halogen in the side chain.

The only common ones are *benzyl* and *benzal chlorides*. The former boils at 178° and yields

¹ The solution of potash should be tested for chloride before being used. This also applies in D (b).

benzaldehyde only after very prolonged boiling with H_2O and $Pb(NO_3)_2$. It has an odour somewhat resembling mustard and cress, and is irritating to the eyes. The latter boils at 204° , and fumes in the air. Add one drop to a solution of potassium carbonate and boil; when the pungent odour has disappeared, the odour of benzaldehyde is apparent.

D. The substance is solid and has no odour. Soluble in water.

- (a) Solution gives an immediate precipitate of the silver halide. *Haloid acid salt* (probably hydrochloride) of a base.
- (b) Boil with KOH , acidify with HNO_3 , and add $AgNO_3$. Precipitate probably indicates the salt of a substituted fatty acid. The *chloracetic acids* are the only common ones. Apply special tests (p. 43).

XI. Nitrogen present.—We have the following possibilities: Ammonium salts, amides and nitriles of organic acids; free aromatic amines and salts of aliphatic and aromatic amines (primary, secondary, and tertiary); anilides; amino-acids; nitro-derivatives; (nitroso-derivatives); cyanides; mustard oils; azo-compounds; esters of nitrous and nitric acids; pyridine, quinoline, and the alkaloids; uric acid.

A. Odour.—Such substances as acetamide, nitrobenzene, mustard oils, pyridine, quinoline, coniine, and piperidine are indicated by their characteristic odours.

Acetamide.—Hydrolyze with KOH . Ammonia evolved and acetate formed. Melting point 82° .

Nitrobenzene.—Reduce with Sn and HCl , and test for aniline by isonitrile test and diazotization (p. 108).

Mustard oils.—Sulphur present besides nitrogen. See IX. A.

Pyridine, Quinoline, Coniine, and Piperidine are all liquids, and give the general tests for the alkaloids. Their smells are characteristic. Apply special tests.

B. Colour.—

(a) Red, orange, or yellow solid. *Azo-compounds.* Reduce with hot $SnCl_2$, and identify the amines.

(b) Green. *Nitroso-dialkylanilines.* Confirm by solubility in

HCl (yellow solution) and by action of hot NaOH, which gives a reddish-brown liquid, containing the Na salt of p-nitrosophenol, and a di-alkylamine is evolved (smell). The nitrosophenol may be confirmed by Liebermann's reaction.

(c) Colourless, or only pale yellow.

(α) **Shake with concentrated HCl**; filter if necessary, and add dilute NaOH to the filtrate.

(1) Original substance is reprecipitated (as liquid or solid). *Aromatic amine* (primary, secondary, or tertiary), *pyridine*, *quinoline*, or *alkaloids*, excepting caffeine¹ and theobromine. (Morphine is readily soluble in excess of NaOH. Repeat the test, using NH₄OH, to distinguish morphine.) Distinguish according to the following table (pyridine, quinoline, coniine, and piperidine have already been identified):—

| | Primary amine. | Secondary amine. | Tertiary amine. | Alkaloid. |
|-------------------------------------------------------|--------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|------------|
| Add dilute HCl | Dissolves | Dissolves | Dissolves | Dissolves |
| Dil. HCl + NaNO ₂ | No change (other than effervescence; unless very dilute and well cooled) | Oily ppt. (solid for some). Extract with ether; free from HNO ₂ by NaOH, and apply Liebermann's nitroso test | Dialkylanilines give a yellow solution. Cold NaOH gives a green ppt. of the para-nitroso base | No change |
| Pour the diazotized solution into alkaline β-naphthol | Red ppt. A red solution indicates an acid group in the aniline | — | — | No red dye |

Identify the amines by boiling point and melting point (if solid) and preparation of derivatives (Schotten-Baumann reaction for primary and secondary). Apply special tests for the alkaloids.

¹ If the solution is fairly concentrated, caffeine will also separate out.

- (2) No precipitate. Aromatic amines and alkaloids absent. (Make sure that morphine is absent by repeating the test, using NH_4OH , instead of NaOH .) Proceed as in (β).

(β) **Warm with concentrated NaOH .**

- (1) Ammonia evolved from ammonium salts, amides, nitriles, urea and its salts.

Ammonium salts give the smell of NH_3 in the cold with NaOH ; also NH_3 is readily evolved on heating with a solution of Na_2CO_3 . Identify the acid by special tests.

Amides.— NH_3 is only slowly evolved on heating with a solution of Na_2CO_3 . On boiling with a suspension of freshly precipitated mercuric oxide in water, a soluble Hg salt is formed. Filter, and test for Hg in the filtrate with H_2S . Confirm by taking the melting point of the original solid.

Nitriles.— NH_3 is only slowly evolved on warming with NaOH . Digest with concentrated HCl under reflux until the nitrile disappears. Make alkaline with NaOH , and warm; NH_3 evolved. Residue in the flask is tested for the acid.

On treatment with Na and absolute alcohol the amine is formed.

Urea and salts.—Apply special test for urea.

If a salt of urea is present, shake up with aqueous alcohol and excess of solid K_2CO_3 . Separate off alcoholic layer, evaporate on water-bath, and apply tests for urea to the residue.

- (2) Alkylamine (fishy odour) evolved from *salt of aliphatic amine* (the salt is soluble in water), or possibly from p-nitrosodialkylanilines (see p. 138). Test whether primary, secondary, or tertiary amine (p. 122), and identify by preparation of the platinichloride and determination of molecular weight. If

uncertain as to whether fatty or aromatic amine, try the diazo reaction.

- (3) Aromatic amine is liberated as solid or liquid from a *salt of aromatic amine*. (The salt is soluble in water.) Proceed as in (α) (1).
- (4) The substance is insoluble in water, but on boiling with KOH the odour of an alcohol is perceived. *Ester of nitrous acid*.¹ Proceed as with esters, XIII. G.
- (5) The substance is insoluble in water, and only after long boiling with KOH does an oily layer of aniline, or aniline derivative, form. *Anilide*. Hydrolyze with HCl (see p. 95), and identify the aniline and acid.
- (6) The substance is more or less yellow, and KOH has no action. Probably a *nitro-compound*.² Reduce with Sn and HCl, and test for primary amine.
- (7) Apply special tests for *phenylhydrazine*, e.g. reduction of Fehling's solution and the formation of benzaldehyde-phenylhydrazone (see p. 118).
- (8) *Amino-acids* do not evolve NH_3 on treatment with KOH, and must therefore be specially tested for. Owing to the fact that they contain both basic and acid groups, they are practically neutral to litmus. Nitrous acid converts the $-\text{NH}_2$ into the $-\text{OH}$ group, nitrogen being evolved. The acids thus formed may then be identified; e.g. aspartic acid and asparagine give malic acid; anthranilic acid gives salicylic acid, and so on.

Test specially for *glycine* (aminoacetic acid) and *hippuric acid* (benzoyl aminoacetic acid). *Glycine*, heated with soda-lime, gives methylamine. Freshly precipitated copper oxide

¹ Esters of *nitric acid* do not saponify in the normal way; the alcohol is always oxidized by the $-\text{NO}_2$ on hydrolysis.

² Trinitrobenzene, trinitrotoluene, etc., are readily soluble in KOH and precipitated by acid.

dissolves, giving a deep blue solution. Melts with decomposition at 232° .

Hippuric acid, on digestion with strong HCl (reflux), gives benzoic acid and glycocholl, which may be separately tested for. Melting point 187° .

(9) Apply special tests for *uric acid*, *caffeine*, and *theobromine*.

NOTES.—I. If the salt of an amine is found, test for chlorides, sulphates, nitrates, etc., in the ordinary manner.

II. The substance may belong to more than one class of compound; *e.g.* it may be a substituted acid (nitro or amino), a nitramine, etc. The groups must then be separately identified, *e.g.* in nitraniline the amino group is identified by diazotization, etc. It is then destroyed by warming with nitrous acid, giving a nitro-phenol, in which the nitro group may be detected by reduction with Sn and HCl, etc.

Nitro-phenols are characterized by their acid reaction and the deep colour of their salts, and must be specially tested for.

XII. Hydrocarbons.—These have been indicated by—(1) Unacted upon by NaOH, soda-lime, and Na (in testing for elements); (2) very stable towards concentrated H_2SO_4 ; (3) insoluble in water; (4) only C and H found among the elements (O cannot be tested for).

To distinguish between aliphatic and aromatic hydrocarbons try *nitration* with HNO_3 alone, or, if necessary, with HNO_3 and H_2SO_4 .

(a) **Nitration occurs.**—*Aromatic* hydrocarbon.

Confirm by isolation of the nitro compound, reduction with Sn and HCl and diazotization of the amine.

Identify benzene derivatives with side chains by oxidation to benzoic acid with dilute HNO_3 (see pp. 108, 109).

Test specially for benzene and homologues, naphthalene (p. 129), and anthracene (p. 134).

(b) **Nitration does not occur.**—*Aliphatic* hydrocarbon. Test whether saturated or unsaturated, by Br dissolved in CCl_4 . The only unsaturated aliphatic hydrocarbon likely to be met with is *amylenes*.

XIII. C, H, O present.

NOTE.—The presence of an $-\text{OH}$ is often indicated by the solubility of the substance in water, since hydrocarbons are insoluble.

The following classes of compounds are possible: Alcohols; aldehydes; ketones; acids; phenols; ethers; esters; acid anhydrides; carbohydrates.

A. Acids and Salts (including acid anhydrides).—These have already been indicated by II., III., and VI. (Sulphonic acids have been dealt with under IX. B; nitro-phenols have also been indicated.) The free phenols (unsubstituted) are just perceptibly acid to sensitive litmus, and in most cases are distinguished by their smell; the salts of most phenols are distinguished from acid salts by being decomposed by CO_2 .

Make use of the acid table given in scheme for Stage I. In addition, note the following:—

(a) If it is the free acid and is liquid, note the smell, especially on warming. *Propionic* and *butyric acids* may thus be detected.

(b) If a salt of an acid (only the Na, K, and NH_4 salts are taken into consideration; if the salt of a heavy metal, the Na salt must be prepared as on p. 84), dissolve in water, and add dilute H_2SO_4 in excess.

(1) *Oily precipitate*: *Butyric acid*, *valeric acid*, *oleic acid*, etc.

(2) *Precipitate* which melts in boiling water, forming an oily layer, which is lighter than water. *Palmitic*, *stearic*, and *oleic acids*.

(3) *Precipitate* consisting of an aromatic acid. *Benzoic*, *salicylic*, *cinnamic*, and *phthalic acids*.

(4) *No precipitate*, but smell of volatile acid on warming. *Formic*, *acetic*, and *propionic acids*.

(5) *No precipitate* and no smell on warming. Extract with ether and evaporate. Residue indicates: *Malonic*, *succinic*, or *gallic acid*.

(6) If (1)–(5) give no indications, try the action of CaCl_2 and FeCl_3 on the neutral solution, testing specially for *oxalic*, *tartaric*, *citric*, *malic*, *lactic*, and *tannic acids*.

Unsaturated Acids.—Of the acids which have been mentioned above, *oleic* and *cinnamic acids* are unsaturated, as may be shown by heating with bromine or alkaline permanganate. (The student should bear in mind, however, that these tests are not a sure sign of an unsaturated compound. Thus, bromine is instantly decolourized by amines, aldehydes, ketones, and phenols, in some

cases a precipitate being formed. Also alkaline permanganate is affected by a large number of substances, *e.g.* formic acid, aldehyde and benzaldehyde, phenols, glycerol, etc.)

Unsaturated acids may be identified by investigating the products of fusion with KOH. Melt a little potash in a crucible, and add half its weight of the acid in small portions at a time. Heat till action (effervescence) ceases, but do not char. Extract with water, and test extract for acids.

Oleic acid gives palmitic and acetic acids.

Cinnamic acid gives benzoic and acetic acids.

NOTE.—The individual acids (saturated or unsaturated) must be identified by appropriate tests. The preparation and analysis of the silver salt sometimes helps in the identification of the acid.

Acid anhydrides.—Three common ones are *acetic* (liquid), *benzoic*, and *phthalic* anhydrides. On boiling with NaOH the sodium salts of the corresponding acids are formed. For phthalic anhydride, see p. 133.

B. Phenols.—These are mostly insoluble, or very sparingly soluble, in water (an exception is *pyrogallol*), but readily soluble in NaOH. They have a characteristic phenolic odour.

(NOTE.—In the following tests substituted phenols are also referred to.)

(1) Most phenols are set free from their concentrated solution in NaOH by CO_2 . They separate out either as *oils* (phenol, cresols, salicylic esters, chlor-phenols, etc.) or as *solids* (resorcin, hydroquinone, amino-phenols, anisidin, α - and β -naphthol). *Exceptions* are pyrogallol, nitro-phenols, picric acid, trichlor-phenol, cyano-phenols, etc.

On dissolving in NaOH a change in colour often takes place; *e.g.* with p-nitrophenol and picric acid. In some cases the solution darkens rapidly in the air (pyrogallol, hydroquinone).

(2) *Ferric chloride reaction*.—Green, blue, violet, or purple coloration.

The reaction is very limited, the colour being destroyed by traces of acids or alkali, by alcohol, ether, many salts, etc. (and by warming). *Neutral* FeCl_3 must therefore be added to the pure phenol in water (not merely to a solution which may contain salts, etc.).

Colour with phenol, cresols (evanescent), p-nitrophenol (red), resorcin, orcin, salicylic ester, salicylic acid (stable towards acetic acid), hydroquinone (evanescent; oxidized to quinone), pyrogallol (reddish; turned purple by Na acetate).

No colour with o-nitrophenol, α - and β -naphthol (precipitate of dinaphthol), picric acid, nitroso-phenol, etc.

(3) *Prepare the benzoyl derivative* by the Schotten-Baumann reaction (p. 121), and identify by melting point.

C. Aldehydes.—Test for by means of *Schiff's* reagent. (Formic acid and ester do not respond to this reaction, although they contain the CHO group.)

Test specially for *formaldehyde* (p. 20); *acetaldehyde* (p. 21); *benzaldehyde* (p. 118); and *acrolein* (smell; unsaturated; boiling point 52°).

D. Ketones.—Give condensation products with hydroxylamine and phenylhydrazine, but do not affect Schiff's reagent. Test specially for *acetone* (p. 36), *acetophenone* (p. 142), and *benzophenone*.

E. Quinones.—Crystalline solids, generally yellow in colour, and possessing a peculiar odour.

Quinone.—Yellow. Pungent, nutty odour. Decolourized by SO_2 , giving hydroquinone.

Anthraquinone.—Yellow needles. Not decolourized by SO_2 . No quinone odour. Oxanthranol test with zinc dust and NaOH (see p. 134).

α -Naphthoquinone.—Yellow crystals. Quinone odour. Melting point 125° . Dissolved by alkalies and reprecipitated by acids.

β -Naphthoquinone.—Orange-coloured crystals (plates). Non-volatile and no quinone odour. Decomposes at 115° – 120° , with blackening.

Phenanthrenequinone.—Orange needles, melting at 200° . Mix 1 c.c. of *crude* toluene (containing thiotoluene) with 5 c.c. of a solution of 0.5 gm. phenanthrenequinone in 100 c.c. glacial acetic acid. Cool the mixture, and on adding 4 c.c. of concentrated H_2SO_4 , drop by drop, keeping cold all the time, a blue-green colour is produced. Allow to stand for a few minutes, pour into water, and extract with ether; the ethereal solution is coloured an intense reddish-violet.

F. **Alcohols.**—Indicated by the action of Na (H evolved) in the tests for elements (VIII.).

(a) Prepare the acetic or salicylic ester. Characteristic odours.

(b) Prepare the benzoyl derivative and take melting point or boiling point.

(c) Oxidize with chromic acid mixture, and identify the aldehyde or acid (from primary alcohols).

Test specially for the following alcohols: *methyl, ethyl, amyl, benzyl*. Also special tests for *glycerol* (p. 60).

G. **Esters.**—These are indicated chiefly by the smell, which is not removed at once by KOH, but disappears on boiling for a short time (see VI.)

NOTE.—Some esters, *e.g.* glycollic, glyceryl, and tartaric esters, have no smell. They are generally viscous liquids, or solids with low melting point.

Most esters are insoluble, and the common ones are nearly all liquids; some few are solids, *e.g.* *methyl oxalate* and *tartrate*; *phenyl benzoate* and *salicylate*.

A moderate quantity (since distillation will have to be carried out) is hydrolyzed by boiling under a reflux condenser with an excess of concentrated KOH (20 to 30 per cent.) until the ester disappears. Distil over about two-thirds of the liquid.

(a) *Distillate.*—Test for alcohol, as under F. Purify the alcohol by "salting out" and drying, with K_2CO_3 .

(b) *Residue.*—If no alcohol is found in (a), the ester was probably a phenyl one.¹ Separate the phenol with CO_2 . Extract with ether. Test according to B.

After separating the alcohol or phenol, the potassium salt of the acid is left (plus excess KOH or K_2CO_3). Add excess of dilute H_2SO_4 , and proceed as in A.

NOTE.—*Ethyl acetoacetate* on hydrolysis with aqueous KOH yields alcohol, acetone, an acetate and a carbonate; hydrolysis with

¹ It may also be a glyceryl ester (*e.g.* of palmitic, stearic, oleic, or acetic acid). The glycerol will remain in the distilling flask, unless the temperature has been raised very high. Make the residue just acid with sulphuric acid, add alcohol and excess of solid K_2CO_3 , and shake. The alcohol is salted out and takes some of the glycerol with it. Separate the alcoholic layer, and evaporate off the alcohol on the water-bath. A syrupy residue of glycerol is left.

sulphuric acid (1 : 2) yields almost exclusively acetone, carbon dioxide, and alcohol. The ester gives a violet coloration on shaking with ferric chloride.

H. Carbohydrates.—These have been indicated by VII. Test specially for *dextrose* (p. 68), *cane sugar* (p. 70), *lactose* (p. 70), *starch* (p. 71), *levulose*, *maltose*, and *dextrin*.

I. Ethers.—Have to be identified by boiling point. The decomposition with HI is troublesome. *Ordinary ether* is immediately identified by the smell.

APPENDIX

INTERNATIONAL ATOMIC WEIGHTS.

| O = 16. | | | O = 16. | | |
|--------------------|----|--------|---------------------|----|--------|
| Aluminium | Al | 27.1 | Neodymium | Nd | 143.6 |
| Antimony | Sb | 120.2 | Neon | Ne | 20 |
| Argon | A | 39.9 | Nickel | Ni | 58.7 |
| Arsenic | As | 75.0 | Nitrogen | N | 14.01 |
| Barium | Ba | 137.4 | Osmium | Os | 191 |
| Bismuth | Bi | 208.0 | Oxygen | O | 16.00 |
| Boron | B | 11.0 | Palladium | Pd | 106.5 |
| Bromine | Br | 79.96 | Phosphorus | P | 31.0 |
| Cadmium | Cd | 112.4 | Platinum | Pt | 194.8 |
| Cæsium | Cs | 132.9 | Potassium | K | 39.15 |
| Calcium | Ca | 40.1 | Praseodymium . . . | Pr | 140.5 |
| Carbon | C | 12.00 | Radium | Rd | 225 |
| Cerium | Ce | 140.25 | Rhodium | Rh | 103.0 |
| Chlorine | Cl | 35.45 | Rubidium | Rb | 85.5 |
| Chromium | Cr | 52.1 | Ruthenium | Ru | 101.7 |
| Cobalt | Co | 59.0 | Samarium | Sa | 150.3 |
| Columbium | Cb | 94 | Scandium | Sc | 44.1 |
| Copper | Cu | 63.6 | Selenium | Se | 79.2 |
| Erbium | Er | 166 | Silicon | Si | 28.4 |
| Europium | Eu | 152 | Silver | Ag | 107.93 |
| Fluorine | F | 19.0 | Sodium | Na | 23.05 |
| Gadolinium | Gd | 156 | Strontium | Sr | 87.6 |
| Gallium | Ga | 70 | Sulphur | S | 32.06 |
| Germanium | Ge | 72.5 | Tantalum | Ta | 181 |
| Glucinum | Gl | 9.1 | Tellurium | Te | 127.6 |
| Gold | Au | 197.2 | Terbium | Tb | 159.2 |
| Helium | He | 4.0 | Thallium | Tl | 204.1 |
| Hydrogen | H | 1.008 | Thorium | Th | 232.5 |
| Indium | In | 115 | Thulium | Tm | 171 |
| Iodine | I | 126.97 | Tin | Sn | 119.0 |
| Iridium | Ir | 193.0 | Titanium | Ti | 48.1 |
| Iron | Fe | 55.9 | Tungsten | W | 184 |
| Krypton | Kr | 81.8 | Uranium | U | 238.5 |
| Lanthanum | La | 138.9 | Vanadium | V | 51.2 |
| Lead | Pb | 206.9 | Xenon | Xe | 128 |
| Lithium | Li | 7.03 | Ytterbium | Yb | 173.0 |
| Magnesium | Mg | 24.36 | Yttrium | Yt | 89.0 |
| Manganese | Mn | 55.0 | Zinc | Zn | 65.4 |
| Mercury | Hg | 200.0 | Zirconium | Zr | 90.6 |
| Molybdenum . . . | Mo | 96.0 | | | |

Tension of Aqueous Vapour. Spirit-Gravity Table 229

TENSION OF AQUEOUS VAPOUR FOR EACH DEGREE CENTIGRADE
FROM 0° TO 30° C.

| Temp. C. | Tension in mm. of Mercury. | Temp. C. | Tension in mm. of Mercury. | Temp. C. | Tension in mm. of Mercury. | Temp. C. | Tension in mm. of Mercury. |
|----------|----------------------------------|----------|----------------------------------|----------|----------------------------------|----------|----------------------------------|
| 0° | 4·6 | 8° | 8·0 | 16° | 13·6 | 24° | 22·2 |
| 1° | 4·9 | 9° | 8·6 | 17° | 14·5 | 25° | 23·5 |
| 2° | 5·3 | 10° | 9·2 | 18° | 15·4 | 26° | 25·0 |
| 3° | 5·7 | 11° | 9·8 | 19° | 16·4 | 27° | 26·5 |
| 4° | 6·1 | 12° | 10·5 | 20° | 17·4 | 28° | 28·1 |
| 5° | 6·5 | 13° | 11·2 | 21° | 18·5 | 29° | 29·8 |
| 6° | 7·0 | 14° | 11·9 | 22° | 19·7 | 30° | 31·6 |
| 7° | 7·5 | 15° | 12·7 | 23° | 20·9 | | |

PERCENTAGE OF ABSOLUTE ALCOHOL, BY WEIGHT, CORRESPONDING TO
THE SPECIFIC GRAVITY TAKEN AT 60° F., OR 15·5° C. WATER = 1.

| Per Cent. | Specific Gravity. | Per Cent. | Specific Gravity. | Per Cent. | Specific Gravity. | Per Cent. | Specific Gravity. |
|--------------|----------------------|--------------|----------------------|--------------|----------------------|--------------|----------------------|
| 0 | 1·0000 | 25 | 0·9651 | 50 | 0·9183 | 75 | 0·8605 |
| 1 | 0·9981 | 26 | 0·9637 | 51 | 0·9160 | 76 | 0·8581 |
| 2 | 0·9963 | 27 | 0·9622 | 52 | 0·9138 | 77 | 0·8557 |
| 3 | 0·9944 | 28 | 0·9607 | 53 | 0·9116 | 78 | 0·8533 |
| 4 | 0·9928 | 29 | 0·9592 | 54 | 0·9094 | 79 | 0·8509 |
| 5 | 0·9912 | 30 | 0·9577 | 55 | 0·9072 | 80 | 0·8484 |
| 6 | 0·9896 | 31 | 0·9560 | 56 | 0·9049 | 81 | 0·8459 |
| 7 | 0·9880 | 32 | 0·9544 | 57 | 0·9027 | 82 | 0·8435 |
| 8 | 0·9866 | 33 | 0·9526 | 58 | 0·9004 | 83 | 0·8409 |
| 9 | 0·9852 | 34 | 0·9508 | 59 | 0·8981 | 84 | 0·8385 |
| 10 | 0·9839 | 35 | 0·9490 | 60 | 0·8958 | 85 | 0·8359 |
| 11 | 0·9826 | 36 | 0·9472 | 61 | 0·8935 | 86 | 0·8333 |
| 12 | 0·9813 | 37 | 0·9453 | 62 | 0·8911 | 87 | 0·8307 |
| 13 | 0·9800 | 38 | 0·9433 | 63 | 0·8888 | 88 | 0·8282 |
| 14 | 0·9788 | 39 | 0·9413 | 64 | 0·8865 | 89 | 0·8256 |
| 15 | 0·9775 | 40 | 0·9394 | 65 | 0·8842 | 90 | 0·8229 |
| 16 | 0·9763 | 41 | 0·9374 | 66 | 0·8818 | 91 | 0·8203 |
| 17 | 0·9751 | 42 | 0·9353 | 67 | 0·8795 | 92 | 0·8176 |
| 18 | 0·9739 | 43 | 0·9332 | 68 | 0·8772 | 93 | 0·8149 |
| 19 | 0·9727 | 44 | 0·9311 | 69 | 0·8748 | 94 | 0·8122 |
| 20 | 0·9714 | 45 | 0·9291 | 70 | 0·8724 | 95 | 0·8094 |
| 21 | 0·9702 | 46 | 0·9269 | 71 | 0·8700 | 96 | 0·8065 |
| 22 | 0·9690 | 47 | 0·9249 | 72 | 0·8676 | 97 | 0·8036 |
| 23 | 0·9677 | 48 | 0·9227 | 73 | 0·8652 | 98 | 0·8006 |
| 24 | 0·9664 | 49 | 0·9204 | 74 | 0·8629 | 99 | 0·7976 |
| 25 | 0·9651 | 50 | 0·9183 | 75 | 0·8605 | 100 | 0·7946 |

TABLE OF MELTING POINTS AND BOILING POINTS.¹

| | M.Pt. | B.Pt. | | M.Pt. | B.Pt. |
|------------------------------|-------|-------|------------------------------|-------|-------|
| <i>Hydrocarbons.</i> | | | <i>Ketones and Quinones—</i> | | |
| i-Amylene | | 21 | contd. | | |
| Benzene | 5 | 80 | Benzoin | 137 | |
| Toluene | | 110 | Benzoquinone | 116 | |
| Ethylbenzene | | 136 | α-Naphthoquinone . . | 125 | |
| Cumene | | 153 | Anthraquinone | 285 | 382 |
| o-Xylene | | 142 | Phenanthrenequinone | 200 | |
| m- „ | | 139 | | | |
| p- „ | 15 | 138 | <i>Acids.</i> | | |
| Cymene | | 175 | Formic | 9 | 101 |
| Mesitylene | | 164 | Acetic | 17 | 118 |
| Naphthalene | 80 | 218 | Propionic | | 140 |
| Anthracene | 217 | 351 | n-Butyric | | 163 |
| Phenanthrene | 99 | 340 | i-Butyric | | 155 |
| | | | i-Valeric | | 174 |
| <i>Alcohols.</i> | | | Palmitic | 62 | |
| Methyl | | 66 | Stearic | 69 | |
| Ethyl | | 78 | Acrylic | 7 | 140 |
| n-Propyl | | 97 | Oleic | 14 | |
| i- „ | | 83 | Chloracetic | 62 | 186 |
| n-Butyl | | 117 | Dichloroacetic | | 190 |
| i- „ | | 108 | Trichloroacetic | 52 | 195 |
| i-Amyl | | 131 | Bromacetic | 50 | 208 |
| Allyl | | 96 | Aminoacetic | 232 | |
| Glycol | | 197 | Oxalic (hydrated) . . . | 101 | |
| Glycerol | | 290 | „ (anhydrous) | 189 | |
| Benzyl | | 206 | Malonic | 132 | |
| | | | Succinic | 185 | |
| <i>Aldehydes.</i> | | | Glycollic | 80 | |
| Formaldehyde | | -21 | Lactic | 18 | |
| Trihydroxymethylene | 171 | | Tartaric | 167 | |
| Acetaldehyde | | 21 | Citric | 147 | |
| Paraldehyde | | 124 | Benzoic | 121 | 250 |
| Acrolein | | 52 | p-Bromobenzoic | 251 | |
| Chloral | | 97 | o-Hydroxybenzoic . . . | 155 | |
| Chloral hydrate . . . | 57 | 96 | m- „ | 200 | |
| Benzaldehyde | | 179 | p- „ | 210 | |
| Cinnamic Aldehyde . . | | 247 | o-Toluic | 102 | |
| Salicylic Aldehyde . . | | 196 | m- „ | 110 | 263 |
| Anisic „ | | 248 | p- „ | 179 | 275 |
| Vanillin | 80 | | o-Nitrobenzoic | 147 | |
| | | | m- „ | 141 | |
| <i>Ketones and Quinones.</i> | | | p- „ | 238 | |
| Acetone | | 56 | o-Aminobenzoic | 145 | |
| Acetophenone | 20 | 202 | m- „ | 173 | |
| Benzophenone | 46 | | p- „ | 186 | |
| Benzil | 95 | 347 | Gallic | 220 | |

¹ The temperatures are given to the nearest whole number of degrees.

| | M. Pt. | B. Pt. | | M. Pt. | B. Pt. |
|-------------------------------------------------------|---------|--------|------------------------------------------------------|--------|--------|
| <i>Acids—contd.</i> | | | <i>Esters and Hydrolysable Halogen Compounds</i> | | |
| Tannic | decomp. | | —contd. | | |
| Cinnamic | 133 | 300 | Methyl tartrate | 48 | 280 |
| Phthalic | 213 | | " benzoate | | 199 |
| Hippuric | 187 | | " salicylate | | 224 |
| Benzene sulphonic | 50 | | Ethyl iodide | | 72 |
| α -Naphthalene sulphonic | 90 | | " bromide | | 38 |
| β - " " " " | 161 | | " nitrate | | 86 |
| Sulphanilic | decomp. | | " chlorcarbonate | | 94 |
| <i>Acid Anhydrides.</i> | | | " formate | | 54 |
| Acetic | | 137 | " acetate | | 77 |
| Succinic | 120 | 261 | " acetoacetate | | 181 |
| Benzoic | 42 | 360 | " chloracetate | | 143 |
| Phthalic | 128 | 284 | " bromacetate | | 159 |
| <i>Acid Chlorides.</i> | | | " propionate | | 99 |
| Acetyl | | 55 | " butyrate | | 121 |
| Benzoyl | -1 | 198 | " valerate | | 135 |
| <i>Phenols.</i> | | | " oxalate | | 186 |
| Phenol | 43 | 181 | " malonate | | 198 |
| Quinol | 169 | | " succinate | | 216 |
| Resorcinol | 118 | 276 | " benzoate | | 213 |
| Catechol | 104 | 245 | " salicylate | | 227 |
| Pyrogallol | 132 | | n-Propyl chloride | | 44 |
| Orcinol (cryst.) | 56 | | " bromide | | 71 |
| " (anhydrous) | 107 | | " iodide | | 102 |
| o-Nitrophenol | 45 | 214 | " acetate | | 101 |
| p- " " " " | 114 | | " benzoate | | 229 |
| 1-2,4 Dinitrophenol | 114 | | n-Butyl chloride | | 77 |
| 1,2,6 " " " " | 64 | | t- " " " " | | 51 |
| p-Aminophenol | 184 | | i- " " " " | | 68 |
| o-Cresol | 31 | 188 | n- " bromide | | 100 |
| m- " " " " | 4 | 201 | t- " " " " | | 72 |
| p- " " " " | 36 | 198 | i- " " " " | | 92 |
| Picric acid | 122 | | n- " iodide | | 130 |
| Thymol | 44 | 230 | t- " " " " | | 103 |
| Carvacrol | 0 | 236 | i- " " " " | | 120 |
| α -Naphthol | 95 | 278 | i- " acetate | | 116 |
| β - " " " " | 122 | 286 | i- " valerate | | 169 |
| <i>Esters and Hydrolysable Halogen Compounds.</i> | | | i-Amyl chloride | | 100 |
| Methyl iodide | 43 | | " bromide | | 120 |
| " cyanide | 82 | | " iodide | | 148 |
| " formate | 32 | | " nitrate | | 147 |
| " acetate | 57 | | " nitrite | | 96 |
| " bromacetate | 144 | | " formate | | 123 |
| " chloracetate | 130 | | " acetate | | 139 |
| " propionate | 79 | | " benzoate | | 261 |
| " butyrate | 102 | | " salicylate | | 270 |
| " oxalate | 54 | 163 | Allyl bromide | | 71 |
| | | | " isothiocyanate | | 151 |
| | | | Glyceryl triacetate | | 258 |
| | | | " tripalmitate | 62 | |
| | | | " tristearate | 71 | |
| | | | " trioleate | -6 | |

| | M.Pt. | B.Pt. | | M.Pt. | B.Pt. |
|---------------------------------------------------------|-------|-------|-----------------------------------|-------|-------|
| <i>Esters and Hydrolysable Halogen Compounds—contd.</i> | | | <i>Bases—contd.</i> | | |
| Phenyl acetate . . . | | 195 | p-Toluidine . . . | 45 | 198 |
| „ benzoate . . . | 69 | 314 | α-Naphthylamine . . | 50 | 300 |
| „ salicylate . . . | 43 | | β- „ . . . | 112 | 294 |
| „ cyanide . . . | | 191 | 1.3.4. Xylidine . . . | | 215 |
| „ isothiocyanate . . | | 222 | Benzidine . . . | 122 | |
| Benzyl chloride . . . | | 178 | Diphenylamine . . . | 54 | 310 |
| „ acetate . . . | | 106 | Methylaniline . . . | | 192 |
| „ benzoate . . . | 20 | 323 | Ethylaniline . . . | | 206 |
| „ cyanide . . . | | 232 | Benzylaniline . . . | 33 | 298 |
| Methylene chloride . . | | 41 | Piperidine . . . | | 105 |
| Chloroform . . . | | 61 | Coniine . . . | | 166 |
| Bromoform . . . | 8 | 151 | Phenylhydrazine . . | 23 | 241 |
| Iodoform . . . | 120 | | Methyl diphenylamine | | 292 |
| Carbon tetrachloride . | | 76 | Dimethyl o-toluidine . | | 183 |
| Ethylidene chloride . . | | 58 | „ p- „ . . . | 0 | 208 |
| Ethylene dichloride . . | | 84 | Dimethylaniline . . . | | 192 |
| „ dibromide . . . | 8 | 131 | Diethylaniline . . . | | 213 |
| Benzal chloride . . . | | 204 | p-Nitrosodimethylaniline . . | 85 | |
| <i>Ethers.</i> | | | p-Nitrosodiethylaniline | 84 | |
| Diethyl ether . . . | | 35 | Pyridine . . . | | 116 |
| Anisol . . . | | 154 | Quinoline . . . | | 239 |
| Phenetol . . . | | 172 | Nicotine . . . | | 247 |
| <i>Carbohydrates.</i> | | | Quinine . . . | 173 | |
| Dextrose . . . | | 86 | Cinchonine . . . | 255 | |
| Galactose . . . | 160 | | Morphine . . . | 247 | |
| Lævulose . . . | | 95 | Strychnine . . . | 269 | |
| Sucrose . . . | | 160 | Brucine . . . | 178 | |
| Lactose . . . | | 205 | Caffeine . . . | 234 | |
| Maltose . . . | | | Theobromine . . . | subl. | |
| Dextrin . . . | | | <i>Amides and Anilides.</i> | | |
| Starch . . . | | | Formamide . . . | | 192 |
| Cellulose . . . | | | Acetamide . . . | 82 | 222 |
| <i>Bases.</i> | | | Urea . . . | 132 | |
| Methylamine . . . | | -6 | Thiourea . . . | 169 | |
| Trimethylamine . . . | | 4 | Benzamide . . . | 128 | 288 |
| Benzylamine . . . | | 187 | Salicylamide . . . | 138 | |
| Aniline . . . | | 184 | Formanilide . . . | 46 | 284 |
| o-Nitraniline . . . | 71 | | Acetanilide . . . | 112 | 304 |
| m- „ . . . | 114 | | Benzanilide . . . | 163 | |
| p- „ . . . | 147 | | Thiocarbanilide . . . | 151 | |
| o-Chloraniline . . . | | 207 | <i>Azo Compounds.</i> | | |
| m- „ . . . | | 230 | Azobenzene . . . | 68 | 293 |
| p- „ . . . | 70 | 230 | Diazoaminobenzene . . | 98 | |
| o-Bromaniline . . . | 31 | 229 | Aminoazobenzene . . | 126 | |
| m- „ . . . | 18 | 251 | <i>Ring Substituted Benzenes.</i> | | |
| p- „ . . . | 63 | — | Chlorbenzene . . . | | 132 |
| o-Toluidine . . . | | 197 | Brombenzene . . . | | 155 |
| m- „ . . . | | 199 | Iodobenzene . . . | | 188 |

| | M. Pt. | B. Pt. | | M. Pt. | B. Pt. |
|---------------------------------------------|--------|--------|-------------------------------------------------------|--------|--------|
| <i>Ring Substituted Benzenes</i> —contd. | | | <i>Ring Substituted Benzenes</i> —contd. | | |
| p-Dibrombenzene . | 89 | 219 | o-Nitrotoluene . . | 10 | 218 |
| Nitrobenzene . . . | 4 | 209 | m- " . . . | 16 | 230 |
| m-Dinitrobenzene . | 90 | 303 | p- " . . . | 54 | 230 |
| o-Chlornitrobenzene . | 32 | 243 | <i>Substituted Naphthalene</i> <i>Derivatives.</i> | | |
| m- " . . . | 44 | 236 | α-Chlornaphthalene . | | 263 |
| p- " . . . | 83 | 242 | β- " . . . | 56 | 265 |
| o-Bromnitrobenzene . | 41 | | α-Bromnaphthalene . | 5 | 279 |
| m- " . . . | 56 | | β- " . . . | 59 | 282 |
| p- " . . . | 126 | | α-Nitronaphthalene . | 61 | 304 |
| o-Chlortoluene . . . | | 156 | β- " . . . | 79 | |
| p- " . . . | 7 | 163 | | | |
| o-Bromtoluene . . . | | 181 | | | |
| p- " . . . | 28 | 184 | | | |

REAGENTS.

The following special reagents are required, in addition to those ordinarily used in qualitative inorganic chemistry.

Ferric Chloride.—54 grams of the crystallized salt to 1 litre. The solution should be made as nearly *neutral* as possible. This may be done in two ways: (1) Add dilute ammonium hydroxide until a precipitate just begins to form; (2) saturate with *freshly* precipitated and well-washed ferric hydroxide.

Fehling's Solution.—(1) Dissolve 69.28 grams of pure copper sulphate in water, and make up to 1 litre; if the solution is not clear, add a few drops of sulphuric acid.

(2) Dissolve 350 grams of Rochelle salt (potassium sodium tartrate) and 100 grams of caustic soda in water, and make up to 1 litre.

For use, equal volumes of (1) and (2) are mixed immediately before making a test. In qualitative work the volumes need only be approximate.

Solution of Iodine in Potassium Iodide.—5 grams iodine and 10 grams potassium iodide in 250 c.c.

Solution of Iodine in Ammonium Iodide.—5 grams iodine and 10 grams ammonium iodide in 100 c.c.

Barfoed's Solution.—10 grams copper acetate and 2 c.c. glacial acetic acid in 100 c.c.

Potassium Acetate Solution.—100 grams potassium acetate to the litre.

Solution of Resorcin in Strong Sulphuric Acid.—2 grams of resorcin in 100 c.c. concentrated sulphuric acid (dissolve in the cold).

Sodium Nitroprusside Solution.—Make *as required* by dissolving a few crystals in a little water.

Schiff's Reagent.—To a dilute solution of fuchsine (rosaniline hydrochloride) add sulphurous acid until the colour just disappears.

Oxidizing Mixture.—Dissolve 10 grams of sodium (or potassium) bichromate in 100 c.c. of 1 : 3 (by volume) sulphuric acid.

REAGENTS FOR ALKALOIDS.

Iodine in Potassium Iodide.—10 grams iodine and 15 grams potassium iodide in 1 litre.

Potassium Mercury Iodide.—13.5 grams mercuric chloride and 49.8 grams potassium iodide per litre.

Phosphomolybdic Acid.—10 grams of phosphomolybdic acid in 100 c.c. of nitric acid (1 : 3 by volume); filter if necessary.

Erdmann's Reagent.—6 drops of concentrated nitric acid are mixed with 100 c.c. of water, and 20 drops of this solution are added to 25 c.c. of strong sulphuric acid.

Fröhde's Reagent.—1 gram of ammonium molybdate in 100 c.c. of concentrated sulphuric acid. (A small quantity of this reagent should be made fresh each time it is required.)

Mandelin's Reagent.—1 gram of ammonium vanadate in 100 c.c. of concentrated sulphuric acid. (Instead of ammonium vanadate, vanadium chloride or oxide may be used.)

INDEX

A

Acetaldehyde, preparation, 33
 —, tests, 21
 Acetamide, preparation, 44
 —, hydrolysis, 45
 Acetanilide, preparation, 94
 —, hydrolysis, 95
 Acetic acid, tests, 19
 Acetone, tests, 36
 Acetonitrile, preparation, 45
 —, reduction, 46
 Acetophenone, preparation, 141
 Acetophenoneoxime, preparation, 142
 Acetoxime, preparation, 36
 —, hydrolysis, 37
 Acetylation, 28, 94
 Acid reaction, causes of, 75
 Acids, identification of, 223
 Alcohol from methylated spirit, 15
 —, determination in fermented liquor, 229
 —, specific gravity table, 229
 —, tests, 22
 Alkaline reaction, causes of, 76
 Alkaloids, 201
 —, table of reactions, 210
 Allyl alcohol, preparation, 58
 —, tests, 60
 Amido radicle, estimation, 198
 Amines, distinction between primary, secondary, and tertiary, 122, 219
 Amino radicle, estimation, 193
 Aminoazobenzene, preparation, 137
 p-Aminobenzene sulphonic acid, preparation, 96
 —, tests, 97
 p-Aminodimethylaniline, 138
 —, and tests, 150
 Amylum, tests, 71
 Aniline, preparation, 92
 —, tests, 93
 Anisol, preparation, 128
 Anthracene, tests, 134

Anthraquinone, preparation, 135
 —, test, 134
 Appendix, 228
 Aqueous vapour tension, table, 229
 Arnold's potash bulb, 157
 Atomic weights table, 228

B

Barfoed's solution, 233
 Barium salt method of molecular weight determination, 174
 Beckmann rearrangement, 142
 — thermometer, 186
 Beilstein's test for halogens, 9
 Benzaldehyde, tests, 118
 Benzamide, preparation, 119
 —, hydrolysis, 120
 Benzanilide, preparation, 121
 Benzene, preparation from aniline, 107
 —, tests, 108
 —, purification by fractional distillation, 86
 Benzenediazonium sulphate, preparation, 101
 Benzhydrol, preparation, 146
 Benzil, preparation, 139
 Benzoic acid, preparation, 140
 Benzoic acid, preparation, 115
 —, tests, 116
 Benzoin, preparation, 139
 o-Benzotoluide, 121
 Benzoyl chloride, preparation, 118
 —, hydrolysis, 119
 Benzyl chloride, preparation, 114
 Biuret reaction, 62
 Boiling point, determination, 3
 — method, for molecular weight, 188
 —, table, 230
 Bromobenzene, preparation, 112
 o-Bromtoluene, preparation, 105

Brucine, tests, 207
 Buchner funnel, 11

C

Caffeine, tests, 209
 Cane sugar, tests, 69
 —, —, oxidation of, 49
 Carbamide, preparation, 60
 —, tests, 61
 Carboic acid, preparation, 106
 —, tests, 107
 Carbon, tests, 7
 Carbylamine reaction, 38, 122
 Carius method for determination of
 halogens, sulphur, and phosphorus,
 170
 Chloracetic acid, preparation, 42
 — acids, tests, 43
 Chloral hydrate, tests, 39
 Chlorobenzene, preparation, 104
 Chloroform, preparation, 37
 —, tests, 38
 Cinchonine, tests, 206
 Cinnamic acid, preparation, 145
 Citric acid, tests, 52
 Combustion, estimation of carbon and
 hydrogen, 155
 —, of nitrogen, 162
 Coniine, tests, 203
 Corks, 10
 Cuprous chloride, preparation of
 solution, 104

D

Detection of carbon and hydrogen in
 an organic compound, 7
 — of a halogen element in an
 organic compound, 9
 — of hydroxyl groups in an organic
 compound, 28, 121
 — of nitrogen in an organic com-
 pound, 8
 — of phosphorus in an organic
 compound, 10
 — of sulphur in an organic com-
 pound, 9
 Determination of alcohol in fermented
 liquor, 16
 —, amido radicle, 198
 —, amino radicle, 193
 —, boiling point, 3
 —, elements, carbon, and hydro-
 gen, 155
 —, —, halogens, 170
 —, —, nitrogen, 162

Determination of elements, phos-
 phorus, 171
 —, —, sulphur, 171
 —, hydroxyl radicle, 192
 —, melting point, 1
 —, methoxyl and ethoxyl radicle,
 194
 —, nitrile radicle, 197
 —, molecular weight, Cryoscopic
 method, 183
 —, —, Dumas' method, 177
 —, —, ebullioscopic me-
 thod, 188
 —, —, V. Meyer's method,
 179
 —, — of an acid, barium
 salt method, 174
 —, —, silver salt
 method, 173
 —, —, titration me-
 thod, 175
 —, — of a base, gravimetric
 method, 176
 —, —, volumetric me-
 thod, 176
 —, specific gravity, 5
 Dextrose, tests, 68
 Diazo reaction, 94, 97, 100, 122, etc.
 Diazoaminobenzene, preparation, 136
 Diazonium salts, 100
 Dibenzoyl, preparation, 139
 Dichloroacetic acid, tests, 43
 Diethylether, preparation, 24
 —, purification, 147
 Diethyl oxalate, preparation, 54
 —, hydrolysis, 56
 Dimethylamine, 139
 Dimethyl oxalate, preparation, 56
 m-Dinitrobenzene, preparation, 91
 —, reduction, 95
 Diphenylcarbinol, preparation, 146
 Diphenylglycollic acid, preparation,
 140
 Diphenylnitrosamine, 123
 Diphenylthiourea, preparation, 98
 Drying agents, 13
 Dumas' method for estimation of
 nitrogen, 162
 — vapour density method, 177

E

Erdmann's reagent, 202, 234
 Esters, identification of, 226
 Ether, diethyl, preparation, 24
 —, purification of, 147
 —, methyl phenyl, preparation,
 128

Etherification of alcohol, mechanism of, 25

Ethyl acetate, preparation, 26

— —, hydrolysis, 27

— alcohol from methylated spirit, 15

— —, tests, 22

— benzoate, preparation, 123

— —, quantitative saponification, 192

— bromide, preparation, 30

— iodide, preparation, 29

— —, hydrolysis, 30

— oxalate, preparation, 54

— —, hydrolysis, 56

— potassium sulphate, preparation, 23

— — —, hydrolysis, 24

Ethylbenzene, preparation, 144

Ethylene, preparation, 31

— —, tests, 33

— dibromide, preparation, 31

Extraction with ether, 12

F

Fehling's solution, 52, 233

Filtration, 11

— —, under reduced pressure, 11

Fischer and Speier, method of esterification, 123

Fittig's synthesis, 144

Fluorescein, 134

Formaldehyde, tests, 20

Formalin, 20

Formic acid, tests, 17

— —, preparation, 57

Fractional distillation, 86

— — —, under reduced pressure, 87

Fractionating columns, 86

Friedel and Crafts' reaction, 141

Fröhde's reagent, 202, 234

G

Gattermann's reaction, 105

Geissler's potash bulbs, 157

Glucosazone, preparation, 69

Glucose, tests, 68

Glycerol, tests, 60

Grape sugar, tests, 68

Grignard's reagent, 146

H

Halogens, detection of, 9

Helianthine, preparation, 149

— —, reduction of, 150

Hofmann's mustard oil reaction, 122

Hydrocarbons, detection of, 222

Hydrocyanic acid, tests, 63

Hydroferricyanic acid, tests, 66

Hydroferrocyanic acid, tests, 65

Hydrogen, detection of, 7

Hydroxyl radicle, detection of, 28, 121

— — —, determination of, 192

Hydroxylamine, 36

I

Identification scheme, 211

— — —, for Stage I., 73

Indophenin test, 88

Invert sugar, 70

Iodobenzene, preparation, 103

Iodoform, tests, 39

— —, reaction, 22

Isatine, 89

Isonitrile reaction, 38, 122

K

Kjeldahl method for estimating nitrogen, 168

L

Lactose, tests, 70

Landsberger and Walker, ebullioscopic apparatus, 188

Lauth's violet, 137

Leuco malachite green, preparation, 152

Liebermann's nitroso reaction, 107, 123

M

Malachite green, preparation, 151

Mandelin's reagent, 202, 234

Marsh gas, preparation, 14

— — —, properties, 15

Melting point determination, 1

— — — table, 230

Methane, preparation, 14

— — —, properties, 15

Methoxyl group, determination, 194
 Methyl alcohol, tests, 21
 —, orange, preparation, 149
 —, —, reduction, 150
 — oxalate, preparation, 56
 — phenyl ether, preparation, 128
 — salicylate, 22, 117
 — thiophene in commercial benzene, 88
 Methylamine hydrochloride, preparation, 46
 —, tests, 48
 Methylated spirit, purification of, 15
 Methylene blue test, 139, 150
 Michler's ketone, 151
 Milk sugar, tests, 70
 Molecular weight determination, chemical methods, 173
 — — —, physical methods, 177
 Monochloroacetic acid, preparation, 42
 — — —, tests, 43
 Monophenyl thiourea, 99
 Morphine, tests, 204
 Murexide reaction, 199, 209
 Mustard oil reaction, 122

N

Naphthalene, tests, 129
 — oxidation, 129, 132
 β -Naphthalene sulphonie acid, preparation, 129
 β -Naphthol, preparation, 131
 β -Naphthyl acetate, 132
 — benzoate, 132
 m-Nitraniline, preparation, 95
 Nitration, 90
 Nitrile group, determination of, 197
 Nitrobenzene, preparation, 90
 —, reduction, 92
 o-Nitrophenol, preparation, 125
 p- —, preparation, 125
 Nitroso reaction, Liebermann's, 107, 123
 p-Nitrosodimethylaniline, preparation, 138
 p-Nitrosophenol, 139

O

Oil of wintergreen, 22, 117
 Oleic acid, tests, 40
 Oxalic acid, preparation and tests, 49
 Oxamide, preparation and hydrolysis, 56

P

Palmitic acid, tests, 40
 Paraformaldehyde, 20
 Perkin's synthesis, 145
 — modification of Zeisel apparatus, 195
 Phenanthrenequinone, 88
 Phenol, preparation, 106
 —, tests, 107
 Phenols, identification of, 224
 Phenolphthalein, 134
 Phenyl isocyanate, 99
 — isothiocyanate, preparation, 98
 — methyl ether, preparation, 128
 — mustard oil, preparation, 98
 p-Phenylenediamine, 137
 Phosphorus, detection of, 10
 —, estimation of, 171
 o-Phthalic acid, preparation, 132
 — anhydride, preparation, 133
 p- — acid, preparation, 111
 Picric acid, preparation, 127
 — — —, tests, 128
 Piperidine, tests, 202
 Piperine, tests, 208
 Potassium cyanate, 61
 — ethyl sulphate, preparation, 23
 — — —, hydrolysis, 24
 Prussian blue test for cyanides, 8, 64
 Prussic acid, tests, 63
 Pyknometer, 6
 Pyridine, tests, 199

Q

Quantitative determination of elements, carbon and hydrogen, 155
 — — — —, halogens, 170
 — — — —, nitrogen, 162
 — — — —, phosphorus, 171
 — — — —, sulphur, 171
 — saponification of ethyl benzoate, 192
 Quinine, tests, 205
 Quinoline, preparation, 153
 —, tests, 200
 Quinone oxime, 139
 Quinones, identification of, 225

R

Reagents, 233
 Recrystallization, 11

Reduction with ammonium sulphide,
95
—— sodium and alcohol, 46
—— tin and hydrochloric acid,
92

S

Saccharose, tests, 69
Salicylic acid, tests, 117
Salting out, 10, 41, 45, 93, etc.
Sandmeyer's reaction, 104, 109
Saponification, quantitative, 192
—— of beef suet, 40
Scheme for identification of an organic
compound, 211
—— ——— ———, Stage I.,
73
Schiff's reagent, 20, 234
Schotten-Baumann reaction, 120
Separating funnel, 12
Silowski's boiling point apparatus, 5
Silver salt method of molecular
weight determination, 173
Skraup's synthesis, 153
Soda-lime, 14
Sodium β -naphthalene sulphonate,
preparation, 130
—— nitroprusside, 9, 234
—— stearate, 40
Specific gravity, determination, 5
—— of alcohol, table, 229
Starch, tests, 71
Steam distillation, 57
Stearic acid, preparation, 40
Strychnine, tests, 207
Sublimation, 115
Succinic acid, tests, 53
Sucrose, tests, 69
Sulphanilic acid, preparation, 96
—— ———, tests, 97
Sulphocarbonyl, preparation, 98
Sulphonation, 96, 129
Sulphur, detection of, 9

T

Tartaric acid, tests, 50
Tension of aqueous vapour, table,
229
Terephthalic acid, preparation, 111
Tests for the elements, 7
Theine, tests, 209
Theobromine, tests, 209
Thiele's melting-point apparatus, 3
Thiocarbonyl, preparation, 97
Thiophene, removal from benzene,
87
p-Toluic acid, preparation, 110
p-Toluyll nitrile, preparation, 109
Trichloroacetic acid, tests, 43
Trimethylamine, tests, 48
Trinitrophenol, preparation, 127
——, tests, 128
Trioxymethylene, 20
Triphenyl guanidine, 98

U

Unsaturated acids, identification of,
223
Urea, preparation, 60
——, tests, 61
Uric acid, tests, 199

V

Vapour density, determination, 177
Victor Meyer's vapour density method,
179

Z

Zeisel apparatus, Perkin's modifica-
tion, 195

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