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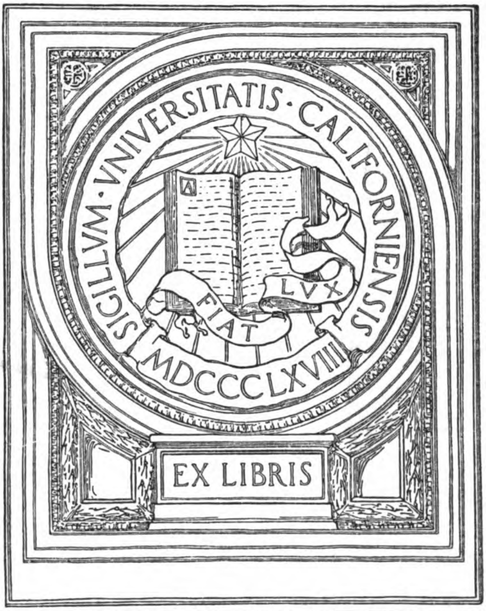
A laboratory manual of chemistry for beginners

Arnold Frederik Holleman, Andrew Jamieson Walker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A
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OF
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BY

A. F. HOLLEMAN, PH.D., F.R.A. AMST.

Professor Ordinarius in the University of Amsterdam.

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EDITED BY

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WITH THE CO-OPERATION OF THE AUTHOR.

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AUTHOR'S PREFACE TO THE THIRD EDITION.

THE whole of the manual has been carefully revised and some new experiments have been incorporated. Certain obsolete reactions, and others too difficult for the average student, have been omitted. I am again indebted to Dr. JAMIESON WALKER for the care bestowed by him on the revision.

A. F. HOLLEMAN.

AMSTERDAM, April, 1917.

AUTHOR'S PREFACE TO THE REVISED FIRST EDITION.

It is admitted universally that chemistry cannot be learnt by the study of text-books only, and that laboratory practice is essential. A student new to the science derives most benefit from a laboratory course of inorganic preparations, simple quantitative experiments, and qualitative inorganic analysis. He is brought thus into contact with work closely connected with the text-books and lectures on this division of chemistry, and is enabled to understand the subject much better than by any other method.

Formerly, a student beginning the study of organic chemistry usually had to content himself with text-books and lectures, and very seldom had the opportunity of handling the compounds about which he had to read. There was, therefore, an evident lack in the methods of teaching the elements of organic chemistry adopted in the Universities.

A number of years have elapsed since a course of practical work in organic chemistry was introduced into the Universities of the Netherlands, chiefly through the influence of Professor **Franchimont** of Leyden. This laboratory work is a complement to the lectures, and has proved very satisfactory.

At the suggestion of Dr. A. **Jamieson Walker**, the laboratory manual written by me in Dutch for this purpose is issued now in English. At his request, I have revised the whole text, and added some new experiments. In most instances I have indicated the weights or volumes suitable for the reactions, an experience of many years having taught me that students always employ much larger quantities than are necessary. The amounts prescribed are approximate, and, to ensure the success of the experiments, need not be weighed or measured with great accuracy.

It should be mentioned that this manual is related intimately to my text-book of organic chemistry, and constitutes an appendix to it. To obtain the maximum advantage from these experiments, I advise the student first to study them with the aid of the text-book, and afterwards to carry them out in the laboratory. This is the only method by which he can attain to a thorough comprehension of his laboratory work.

A. F. HOLLEMAN.

AMSTERDAM, January, 1908.

EDITOR'S PREFACE TO THE THIRD EDITION.

The first English edition of this manual was published in 1904, and a revision was issued in 1908. Owing to the very extensive alterations in the text and in the arrangement of the matter in Professor Holleman's "Text-book of Organic Chemistry" during the preparation of the last two editions, much revision was necessary for the second edition of this volume, published in 1913. For the present issue a certain amount of new matter has been added, and I have to thank Professor Holleman for the time and labour devoted by him to the work.

It should be noted that the references printed in Clarendon type in the text are to the paragraphs of the fourth edition of Professor Holleman's "Text-book of Organic Chemistry," and not to those of former editions.

A. JAMIESON WALKER.

REPTON, DERBY, May, 1917.

EDITOR'S PREFACE TO THE REVISED FIRST EDITION

During the time the English edition of Professor **Holleman's** "Text-book of Organic Chemistry" has been published, it has taken a foremost place among works on the science for students' use. This volume constitutes an appendix to the text-book, and forms an introductory guide to laboratory work in organic chemistry, as well as a compendium of experiments suitable for lecture-table illustration. Its mission is not to displace the standard works on organic preparations, but to supplement them by bridging a gap between theory and practice which they do not, and cannot, span. The text has been brought up to date for the present reprint.

The translation is from a completely revised and considerably extended copy of the Dutch edition, specially prepared by Professor **Holleman** for the purpose. To facilitate reference, I have added paragraph headings, and all the manuscript and proof-sheets have been corrected by the author, to whom I am much indebted for his careful revision.

References in the text printed in Clarendon type are to my translation of Professor **Holleman's** "Leerboek der Organische Chemie," and those to "Inorganic Chemistry" to Dr. **Cooper's** translation of his "Leerboek der Anorganische Chemie," published by Messrs. **John Wiley** and **Sons.**, Inc.

My thanks are due to the publishers for the care they have bestowed on the production of the work.

A. Jamieson Walker.

Derby, England, January, 1908.

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Light figures refer to pages; old-style figures to the author's "Text-book of Organic Chemistry."

A LABORATORY MANUAL OF ORGANIC CHEMISTRY.

I. QUALITATIVE ANALYSIS OF CARBON COMPOUNDS.

(3–5.)

DETECTION OF CARBON AND HYDROGEN (3).

1. **Carbonization.**—A small quantity of sugar is heated in a crucible covered with a lid. Inflammable gases are evolved, leaving a residue of charcoal. This is proved to be carbon by heating it in a hard-glass tube about 15 cm. long sealed at one end, and slightly inclined, the tube being first filled with oxygen, and closed with a loosely-fitting cork. Carbon dioxide is formed, part remaining in the tube. After cooling, lime-water is agitated with the gas, and becomes turbid owing to the formation of calcium carbonate, $CaCO_3$.

The presence of carbon in coal-gas is shown by the soot deposited when a cold surface, such as that of a porcelain crucible-lid, is introduced into a luminous flame.

2. **Oxidation with Copper Oxide.**—10 g. of finely-powdered copper oxide—a hygroscopic substance—are dried by heating in a dish or crucible. While still warm it is mixed carefully with a *small* quantity of sugar, and the mixture placed in a hard-glass tube sealed at one end; the open end of the tube is then closed with a cork, and a delivery-tube leading into lime-water. On heating, the sugar is oxidized by the

copper oxide; the carbon dioxide evolved makes the lime-water turbid, and the water formed condenses in drops on the cool part of the tube.

DETECTION OF NITROGEN (4).

3. *a*) **LASSAIGNE'S Method.**—A piece of dried albumin—a substance containing nitrogen—and a piece of sodium are placed in a narrow tube sealed at one end. The tube is then gradually heated to redness, and maintained at this temperature for a few minutes. The hot end of the tube is placed in 2–3 c.c. of water, whereupon it cracks, and the sodium cyanide formed dissolves. After filtering through a small filter-paper, and washing the residue with a few drops of water, a drop of a solution containing iron in the ferrous and ferric state is added to the filtrate, and the mixture acidified slightly with hydrochloric acid to dissolve the precipitated ferrous and ferric hydroxides. If sodium cyanide was present, there remains a blue precipitate, due to the formation of *Prussian blue.*

b) **WILL and VARRENTRAP'S Method.**—Small pieces of dry albumin are mixed with five times their bulk of soda-lime, and the mixture warmed in a test-tube. A strip of moist, red litmus-paper held at the open end of the tube is turned blue by the evolved ammonia, and the characteristic odour of the gas can also be detected.

c) **KJELDAHL'S Method.**—0·1 g. of acetamide is heated with 2 c.c. of concentrated sulphuric acid in a test-tube. After a short interval, the reaction-mixture is poured carefully into 25 c.c. of water, excess of sodium hydroxide added, and the beaker covered with a glass plate having a moistened strip of red litmus-paper adhering to its lower surface. In a few minutes the litmus is turned blue by the evolved ammonia.

DETECTION OF THE HALOGENS (5).

4. *a*) **BEILSTEIN'S Test.**—Copper oxide is introduced into a loop at the end of a piece of platinum-wire by dipping the moistened loop into finely-powdered copper oxide, heating in the flame, and repeating these operations several times. A piece of copper-oxide wire held by the platinum-wire can also be used. The copper oxide is then heated to redness until the flame is no longer coloured, cooled, moistened with a drop of chloroform, $CHCl_3$, by the aid of a capillary pipette, and again introduced into the flame. The vapour of the copper halide (chloride) formed imparts a fine green colour to the flame.

b) **Calcium-oxide Test.**—A lump of quicklime is heated in a test-tube to a high temperature, and, while still hot, two drops of chloroform are added. When cold, the contents of the tube are treated with water, and the lime dissolved by dilute nitric acid free from hydrochloric acid. On addition of silver nitrate to this solution, a precipitate of silver chloride is obtained, proving the presence of chlorine in the chloroform.

Chloroform is agitated with silver-nitrate solution, but no precipitate of silver chloride is formed.

DETECTION OF SULPHUR (6).

5. *a*) **CARIUS'S Test.**—0·1 g. of ammonium thiocyanate, NH_4CNS, is warmed with 5 c.c. of nitric acid of 1·2 specific gravity till the reaction begins; to prevent the oxidation becoming too violent, the heating is then discontinued. After dilution of the cold solution with 25 c.c. of water, barium chloride is added, the resulting white precipitate of barium sulphate indicating that the sulphur has been oxidized to sulphuric acid.

b) **Caustic-alkali Test.**—A small quantity of egg-albumin is warmed with a concentrated solution of sodium hydroxide (1 : 2), in which it dissolves, forming sodium sulphide among the products. This can be proved either by adding a few drops of lead acetate, resulting in the formation of black lead sulphide, PbS; or by bringing a drop of the liquid into contact with a bright silver coin, with production of a brownish-black stain of silver sulphide, Ag_2S; or by addition of two or three drops of a solution of sodium nitroprusside to the alkaline mixture, when a deep-violet coloration results, some minutes elapsing before the colour attains its maximum intensity. Traces of sulphur can be detected by this reaction.

c) **Ignition with Sodium.**—A piece of albumin is ignited with sodium as described in 3, *a*, and the hot tube placed in water. After filtration, the presence of sodium sulphide in the solution can be detected by means of lead acetate or sodium nitroprusside (5, *b*).

II. THE ALLOTROPIC MODIFICATIONS OF CARBON.

(16.)

1. **Graphite.**—0·1 g. of graphite is mixed with 5 g. of finely-powdered copper oxide, and heated to a high temperature in the apparatus described in I., 2. The evolved carbon dioxide renders the lime-water turbid.

2. **Wood-charcoal.**—A piece of wood-charcoal is gently heated in a test-tube; the water occluded in the pores of the charcoal evaporates, and condenses in drops on the cool parts of the tube.

A piece of wood-charcoal is placed in water, and the mixture warmed. The air present in the pores of the charcoal escapes, forming bubbles in the water.

3. **Bone-charcoal.**—Pieces of bone are placed in a crucible fitted with a lid, and heated in a fume-cupboard. Vapours of disagreeable odour are evolved, the residue in the crucible consisting of bone-charcoal and the mineral constituents of the bones. The bone-ash is freed from mineral matter by heating the residue with hydrochloric acid.

4. **Decolorization of Solutions by Bone-charcoal.**—20 c.c. of a very dilute solution of magenta—a red dye—are agitated

with a teaspoonful of bone-charcoal, and filtered. The filtrate is colourless (" Inorganic Chemistry," **176**).

5. Absorption of Lead Salts by Bone-charcoal.—20 c.c. of a very dilute solution of lead acetate are tested for lead by addition of an aqueous solution of hydrogen sulphide. The solution must be so dilute that it gives a brown turbidity, but no precipitate.

A like volume of the lead-acetate solution is agitated for a short time with a teaspoonful of bone-charcoal, and then filtered. On addition of hydrogen sulphide solution, no turbidity or brown coloration is developed in the filtrate (" Inorganic Chemistry," **176**).

6. Deodorizing Action of Bone-charcoal.—A dilute aqueous solution of hydrogen sulphide, having a perceptible odour of the gas, is agitated with bone-charcoal, and filtered. An odourless filtrate is obtained.

III. LABORATORY METHODS.

(17–26.)

1. Fractional Distillation.—50 c.c. of 90 per cent. alcohol diluted with 50 c.c. of water are placed in a 100 c.c. fractionating-flask fitted with a thermometer and connected with a condenser, and gently heated with a small flame. The liquid begins to boil about 78°, and the distillate is collected in two fractions, the first passing over below 88°, and the second above that temperature. After the distillation is complete the first fraction is returned to the flask, and slowly distilled till the thermometer again reaches 88°. The burner is then removed, the second fraction poured back into the flask, and the distillation continued without changing the receiver till the temperature has again risen to 88°. A different receiver is now employed, and the process continued till distillation is complete.

The first fraction contains most of the alcohol, and can be ignited; the second is chiefly water, and is incombustible.

2. Steam Distillation.—10 c.c. of petroleum are placed in a 200-c.c. flask *d* (**22**, Fig. 17) connected with a condenser. Water is boiled in the can *a*, which is fitted with a safety-tube *b* and a delivery-tube *c*, the evolved steam being passed into the flask *d* through a glass tube reaching to the bottom, and bent as in the illustration. The flask is inclined at an angle to prevent the petroleum being carried over mechanically. The distillate is a mixture of petroleum and water.

3. Extraction with Solvents.—10 c.c. of a five per cent. solution of urea and 10 c.c. of ether are introduced into a separating-funnel, and the mixture vigorously shaken. When the liquid has separated into two layers, these are removed, and each is evaporated to dryness in a porcelain dish on the water-bath. Only a trace of urea is obtained from the ether, this substance being very soluble in water, and almost insoluble in ether.

A saturated solution of salicylic acid is prepared by vigorously agitating 1 g. of the acid with 25 c.c. of water, and filtering. The filtrate is extracted with 10 c.c. of ether as described in the last paragraph. Almost all the salicylic acid dissolves in the ether, being very soluble in this solvent, and but slightly soluble in water.

4. Determination of the Melting-point.—A little naphthalene is placed in a narrow glass tube sealed at one end, several of these being obtained by drawing out a test-tube. The capillary tube is fastened with an india-rubber ring to the stem of a thermometer, so that the part containing the naphthalene is about half-way up the mercury bulb. The end of the thermometer carrying the tube is then immersed in a melting-point flask or beaker containing water, which is slowly heated with a small flame. When the substance melts, the temperature (80°) of the thermometer is observed.

5. Determination of the Boiling-point.—A small quantity of benzene is placed in a fractionating-flask having a high side-tube connected with a condenser. The flask is closed with a cork fitted with a thermometer, the bulb being placed several centimetres below the side-tube. The benzene is heated with a small flame to ebullition, and the temperature at which the mercury becomes stationary noted. This is the boiling-point.

6. **Crystallization.**—3 g. of crude oxalic acid are dissolved in 10 c.c. of hot water, and the impurities present in the acid removed by filtering the turbid solution. On standing, the clear filtrate deposits crystals of oxalic acid. The mother-liquor is poured off, the crystals are drained on a funnel, and dried on a porous plate or between sheets of filter-paper.

IV. SATURATED HYDROCARBONS.

(28–38.)

1. **Preparation of Methane,** CH_4.—5 g. of aluminium carbide are placed in a fractionating-flask, and covered with 100 c.c. of water. The mouth of the flask is then closed with a cork, and the methane evolved through the side-tube collected in thick-walled cylinders. One of these cylinders is closed with a glass plate, and turned mouth upwards. On removal of the cover, and ignition of the gas with a burner or taper, it burns with a flame of feeble luminosity. When combustion ceases, some lime-water is poured quickly into the cylinder, the cover replaced, and the contents agitated. The carbon dioxide formed by the combustion of the gas renders the lime-water turbid.

A thick-walled explosion-cylinder is filled about one-third full with methane, and the remainder with oxygen. On ignition, the mixture explodes with a loud report.

A cylinder is filled with chlorine by downward displacement, and over it is placed an inverted cylinder full of methane, closed with a glass plate. The plate is removed, and the gases mixed by inverting the cylinders several times, care being taken to prevent loss. After insertion of two glass plates between the cylinders, one is placed mouth downwards in a saturated solution of common salt, and the cover removed. In *diffused* daylight the liquid slowly rises, the colour of the chlorine disappears, and oily drops of the substitution-products—methylene chloride, CH_2Cl_2; chloroform, $CHCl_3$; and carbon tetrachloride, CCl_4—are deposited on the sides of the cylinder. The mixture must not be exposed to *direct* sunlight, or there is danger of an explosion. On ignition of the contents of the other cylinder, hydrochloric acid is produced, and soot deposited.

2. **Distillation of Petroleum.**—Petroleum is distilled slowly from a flask connected with a condenser and fitted with a thermometer. The boiling-point rises gradually, proving the liquid to be a mixture.

3. **Inflammability of Petroleum-vapour.**—5 c.c. of petroleum are poured into a porcelain dish. A lighted match plunged into the liquid is extinguished. If, however, the petroleum is carefully heated to 40° on a water-bath, the inflammable vapour evolved is ignited by the application of a burning match.

4. **Stability of the Saturated Hydrocarbons.**—Samples of petroleum and of paraffin-wax are agitated with concentrated sulphuric acid and with concentrated nitric acid. Being mixtures of saturated hydrocarbons, they are neither acted on nor dissolved.

V. ALCOHOLS, $C_nH_{2n+1}\cdot OH$.

(39–50.)

1. **Action of Sodium upon Alcohol.**—0·5 g. of sodium is introduced into a small fractionating-flask containing 10 c.c. of absolute alcohol, and fitted with a delivery-tube for collecting gas over water. The mouth of the flask is immediately closed

with a cork, and an energetic evolution of gas takes place. The gas is collected in a cylinder, and proved by ignition to be hydrogen.

2. **Fusel-oil.**—A small quantity of crude spirit is evaporated slowly on a water-bath. After the volatilization of the ethyl alcohol, the odour of fusel-oil is very marked. It is also perceptible when a few drops of the spirit are placed on the palm of the hand, and rubbed with the finger to promote the evaporation of the ethyl alcohol.

3. **Wine.**—25 c.c. of wine contained in a fractionating-flask connected with a condenser are heated on a water-bath. Alcohol distils, and can be recognized by its odour and inflammability.

4. **Heat Developed by Mixing Alcohol and Water.**—10 c.c. of absolute alcohol and 10 c.c. of water are poured into two small beakers, and these immersed in a large vessel of water to bring them to the same temperature. This is noted, and after removal of the beakers from the water their contents are mixed quickly and stirred with the thermometer. A rise in temperature is observed.

5. **Tests for Water in Alcohol.**—*a*) **Copper-sulphate Test.**—3 g. of blue crystallized copper sulphate, $CuSO_4,5H_2O$, are gently heated in a porcelain crucible till anhydrous, the salt being converted into a white powder. When cold, the residue is transferred to a test-tube or small flask containing 15 c.c. of aqueous alcohol; the copper sulphate soon regains its original blue colour, on account of the formation of the hydrated salt, $CuSO_4,5H_2O$.

b) **CRISMER'S Test.**—2 c.c. of petroleum are added to a like volume of alcohol of about 90 per cent. strength, and a thermometer is introduced into the liquid. At first, the two liquids do not mix completely, but the application of slight heat renders them wholly miscible. The liquid is allowed to cool, and the temperature is noted at the moment of appearance of turbidity. One drop of water is then added, and the liquid again heated until it becomes homogeneous. On cooling, turbidity reappears at a temperature some degrees higher than on the first occasion.

6. **Separation of Water from Alcohol.**—Alcohol of about 50 per cent. strength is agitated with solid potassium carbonate, and, if enough of the salt has been added, two layers are obtained. These are separated by means of a tap-funnel. The upper layer is strong alcohol, and burns on ignition; the lower layer is a concentrated, aqueous solution of potassium carbonate, containing only a trace of alcohol.

7. **Oxidation of Ethyl Alcohol.**—Ethyl alcohol is heated with an aqueous solution of potassium permanganate until the violet colour has disappeared and manganese dioxide has been precipitated. On acidifying the mixture with sulphuric acid and distilling, an acid distillate with an odour of acetic acid is obtained.

The iodoform-test for ethyl alcohol is given in **XIII.**, 6; the benzoate-test in **XXIX.**, 5.

VI. ALKYL HALIDES, ESTERS, ETHERS, AND MERCAPTANS.

(51–60.)

1. **Ethyl Chloride.**—A mixture of 10 c.c. of alcohol and 5 c.c. of concentrated sulphuric acid is added to 5 g. of common salt contained in a 50-c.c. fractionating-flask connected with a condenser in a fume-cupboard. On warming, gaseous ethyl chloride, C_2H_5Cl, is evolved, and dissolves in the condensed alcohol. When ignited, this distillate burns with a green-tinged flame—a phenomenon characteristic of many chlorine derivatives.

2. **Ethylsulphuric Acid.**—About 2 c.c. of concentrated sulphuric acid are poured carefully into an equal volume of absolute alcohol, the mixing being accompanied by rise of temperature.

The mixture is heated gently for a short time, cooled, and poured into 25 c.c. of water. This solution is stirred, and barium carbonate added till the liquid is no longer acid to litmus. Carbon dioxide is evolved, with formation of insoluble barium sulphate and soluble barium ethylsulphate, $Ba(C_2H_5SO_4)_2$. After filtering, dilute sulphuric acid is added to a portion of the filtrate; the precipitate of barium sulphate formed proves the presence of a barium salt in solution.

On warming the rest of the filtrate with dilute hydrochloric acid, barium sulphate is precipitated. This is due to the decomposition of the liberated ethylsulphuric acid into alcohol and sulphuric acid, followed by the interaction of the latter with the barium ions present in the solution.

3. **Diethyl Ether,** $(C_2H_5)_2O$.—A fractionating-flask is fitted with a cork carrying a tap-funnel and a thermometer, both arranged nearly to touch the bottom. After 50 c.c. of alcohol of ninety per cent. strength and 50 c.c. of concentrated sulphuric acid have been poured into the flask, 5 g. of anhydrous aluminium sulphate are added, and the flask is connected to a condenser with a rapid current of water flowing through its jacket. Heat is then applied till the thermometer indicates a temperature between 130° and 140°. As soon as the distillation of ether begins, alcohol is introduced slowly into the flask from the tap-funnel, and the distillation continued with a small flame so as to maintain the temperature constant. The distillate is agitated in a separating-funnel with a like volume of water, which dissolves most of the alcohol, leaving a layer of ether floating on the surface of the solution. After separation from the aqueous liquid, the ether is dried by agitation for a few minutes with fused and finely-powdered calcium chloride.

A small quantity of the ether is agitated with a large excess of water, in which it dissolves.

A mixture of 5 c.c. of ether and 5 c.c. of water is shaken in a separating-funnel, and the ethereal and aqueous layers separated carefully. Anhydrous copper sulphate added to this ether turns blue, proving that the ether has dissolved some of the water. On gently warming the aqueous layer in a porcelain dish, ether-vapour is evolved, and can be recognized by its odour and by its combustion with a bright, luminous flame. This proves that the water has dissolved some of the ether.

The absorption of heat caused by the evaporation of ether can be demonstrated by placing a small quantity in the palm of the hand, and blowing on it. A sensation of cold is felt immediately.

4. **Ethylmercaptan.**—On warming 2 c.c. of a saturated solution of potassium ethylsulphate with a like volume of a thirty-three per cent. solution of potassium hydrogen sulphide, KHS, the odour of ethylmercaptan at once becomes perceptible.

VII. AMINES AND NITRO-COMPOUNDS.

(61–70.)

AMINES (61–67).

1. **Methylamine.**—A thin paste of bleaching-powder is rendered strongly alkaline by addition of slaked lime, and mixed with an aqueous solution of 5 g. of acetamide, $CH_3 \cdot CONH_2$. On distillation, an aqueous solution of methylamine, $CH_3 \cdot NH_2$, is obtained (**259**).

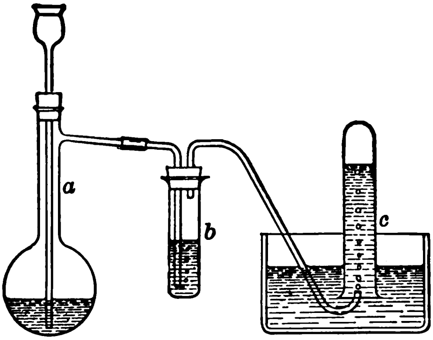
2. **Carbylamine-Reaction.**—A portion of the solution thus obtained is warmed gently with one or two drops of chloroform and a small quantity of alcoholic potash. Owing to the formation of methylcarbylamine, $CH_3 \cdot NC$, the odour characteristic of *iso*nitriles is perceived (**77**).

3. **Mustard-oil Reaction.**—A mixture of carbon disulphide and absolute alcohol in like proportions is added to another

portion of the distillate obtained in I, till solution is complete, and the liquid is warmed for a short time. On addition of ferric chloride, a black precipitate of sulphide of iron is formed; and, on further heating, the odour of methyl-mustard-oil, $CH_3 \cdot NCS$, becomes perceptible (**260**).

4. **Reaction with Copper Salts.**—The remainder of the distillate of I is added drop by drop to 1 c.c. of a dilute solution of copper sulphate. At first a precipitate of copper hydroxide is formed, and on further addition of the amine-solution redissolves, with production of a deep-blue colour. The reaction, therefore, is analogous to that between ammonium hydroxide and copper salts ("Inorganic Chemistry," **244**).

5. **Nitrous-acid Test.**—A concentrated aqueous solution of 1 g. of ethylamine hydrochloride, $C_2H_5NH_2,HCl$, and 1 g. of potassium or sodium nitrite is poured slowly through a thistle-funnel into a 50-c.c. fractionating-flask *a*, containing 20 c.c. of glacial acetic acid (Fig.). The evolved nitrogen is freed from ethyl nitrite by passing it through a small wash-bottle *b*, containing alcoholic potash. The gas is collected over water in a cylinder *c*, and proved to be nitrogen by its extinguishing a lighted wood-splint or taper. By means of the iodoform-



Nitrous Acid Test for Primary Amines.

test (**XIII.**, 6), the presence of alcohol in the fractionating-flask can be shown.

6. **Nitrosoamines.**—To a cold, saturated, aqueous solution of 1 g. of potassium or sodium nitrite is added 1 g. of solid diethylamine hydrochloride, $(C_2H_5)_2NH,HCl$, and one drop of dilute sulphuric acid. On gently heating the liquid, diethylnitrosoamine, $(C_2H_5)_2N \cdot NO$, collects on the surface as a yellow oil of characteristic odour.

7. **Dimethylamine and Trimethylamine.**—A small quantity of sodium-hydroxide solution is added to herring-brine contained in a distilling-flask connected with a condenser. On heating, a distillate is obtained; this is alkaline, owing to the presence of dimethylamine and trimethylamine. Like ammonium hydroxide, it precipitates ferric hydroxide, Fe_2O_3,nH_2O, from a solution of ferric chloride.

NITRO-COMPOUNDS (68–70.)

1. **Sodium Nitromethane.**—A solution of 3 drops of nitromethane in 1 c.c. of absolute alcohol is prepared. To this are added a few drops of a solution of sodium ethoxide, obtained by dissolving small pieces of sodium in 10 c.c. of absolute alcohol. The white precipitate of sodium nitromethane is filtered off, and, while still moist, is dissolved in a small quantity of water. *It must not be dried or a dangerous explosion may result.* When moist, it is innocuous.

2. **Nitrolic-acid Reaction.**—The liquid thus obtained is mixed with a few drops of a concentrated aqueous solution of sodium nitrite, and carefully acidified with dilute sulphuric acid. The blood-red colour of the sodium salt of methylnitrolic acid is produced. It is discharged by adding more acid, but returns on addition of a dilute solution of sodium hydroxide.

3. **Reduction of Nitro-compounds.**—3 drops of nitromethane are added to potassium-hydroxide solution and granulated

zinc contained in a test-tube. The characteristic odour of methylamine at once becomes perceptible, and a strip of red litmus-paper held in the vapour is turned blue.

VIII. NITRILES AND *iso*NITRILES.

(76–78.)

1. **Preparation.**—A mixture of 10 g. of potassium ethylsulphate and 10 g. of dried potassium ferrocyanide is submitted to dry distillation in a retort connected with a condenser. The distillate has the *iso*nitrile odour, due to the presence of ethylcarbylamine. Agitation with dilute sulphuric acid for a short time removes this smell, whereupon that of the nitrile—propionitrile—formed in the reaction becomes perceptible, although it was previously wholly masked by that of the *iso*nitrile, a by-product.

2. **Hydrolysis of Nitriles.**—The liquid of 1 is made alkaline with potassium hydroxide, and boiled in a test-tube. The evolution of alkaline vapours can be detected by means of a strip of moistened, red litmus-paper.

The reaction-mixture contains potassium propionate. On acidifying with dilute sulphuric acid and distilling, propionic acid passes over, the distillate turning blue litmus red.

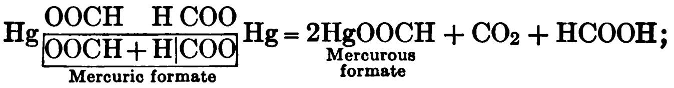
IX. SATURATED ACIDS, $C_nH_{2n}O_2$; AND ESTERS.

(79–88; 91–95.)

1. **Formic Acid.**—A mixture of 10 g. of glycerol and 10 g. of crystallized oxalic acid is heated in a fractionating-flask connected with a condenser. Carbon dioxide is evolved, as can be demonstrated by holding a test-tube containing lime-water at the outlet of the condenser so that the gas enters the tube. After an energetic evolution of gas has continued for some time,

5 g. of crystallized oxalic acid are added, and the heating renewed. Formic acid distils (**153**).

2. Decomposition of Mercuric Formate.—A portion of the distillate of 1 is agitated with a small quantity of finely-divided mercuric oxide, prepared by triturating the powder in a mortar with a little water. The resulting solution of mercuric formate is filtered from the excess of mercuric oxide, and heated. At first, carbon dioxide is evolved, and white mercurous formate precipitated. On further heating, the mercurous salt is decomposed with evolution of carbon dioxide, and precipitation of metallic mercury:



$$\underset{\text{Mercuric formate}}{\mathrm{Hg}\begin{matrix}\mathrm{OOCH}\quad\mathrm{H\,COO}\\ \boxed{\mathrm{OOCH+H|COO}}\end{matrix}\mathrm{Hg}} = \underset{\text{Mercurous formate}}{2\mathrm{HgOOCH}} + CO_2 + \mathrm{HCOOH};$$

$$\underset{\text{Mercurous formate}}{\mathrm{Hg}\boxed{\mathrm{OOCH+H|COO}}\mathrm{Hg}} = 2\mathrm{Hg} + CO_2 + \mathrm{HCOOH}.$$

The liquid now contains free formic acid, and, therefore, turns blue litmus red. It is filtered, and the filtrate is neutralized exactly with sodium or ammonium hydroxide; on addition of silver-nitrate solution, silver formate is precipitated. When this is heated, it decomposes with evolution of carbon dioxide, liberating half the formic acid and precipitating metallic silver, analogously to the mercury salt. The reaction of the liquid, therefore, again becomes acid.

3. Action of Concentrated Sulphuric Acid on Formic Acid.—Another portion of the distillate of 1 is placed in a small flask, and kept cool during the slow addition of twice its volume of sulphuric acid. The flask is closed with a cork and delivery-tube, the end of the latter dipping under water in a pneumatic trough. On the application of heat, a gas is evolved. It is collected in a cylinder, and, on ignition, burns with the blue flame characteristic of carbon monoxide. Agitation of the contents of the cylinder with lime-water produces turbidity, proving the formation of carbon dioxide by the combustion.

4. Oxidation of Formic Acid by Potassium Permanganate.—The remainder of the formic acid obtained in 1 is heated with a small quantity of potassium permanganate and dilute sulphuric acid in the apparatus employed in 3, the end of the delivery-tube being immersed in lime-water contained in a test-tube. The permanganate solution is decolorized, and the carbon dioxide produced by the oxidation of the formic acid renders the lime-water turbid.

5. Cacodyl-Test for Acetic Acid.—On distilling sour beer (200 c.c.), an acid distillate is obtained with an odour of acetic acid. The distillate is nearly neutralized with a few drops of sodium-hydroxide solution, a slightly acid reaction being maintained. It is then evaporated, the last traces of water being removed by heating over a free flame. A portion of the anhydrous sodium acetate thus obtained is mixed with arsenious oxide, and the mixture heated gently in a test-tube. The excessively disagreeable odour of cacodyl oxide, $(CH_3)_2As—O—As(CH_3)_2$, is soon perceived (**73**). *This substance being extremely poisonous, great care must be exercised in carrying out the experiment, and the heating should be discontinued as soon as the odour has been detected.*

6. Stability of Acetic Acid towards Oxidizing Agents.—Small quantities of dilute potassium-permanganate solution and dilute sulphuric acid are added to 5 drops of acetic acid. Unlike formic acid, the acetic acid does not decolorize the permanganate solution.

7. Silver Acetate.—1 g. of sodium acetate is dissolved in 10 c.c. of water, and a solution of silver nitrate added. The precipitate of silver acetate, which is only slightly soluble in water at the ordinary temperature, is collected on a filter, and sufficient to saturate the aqueous solution at the boiling-point transferred to a beaker containing 50 c.c. of boiling, distilled water. On cooling, the salt crystallizes in long, silky needles. These are filtered off, spread on a porous plate to remove as much of the mother-liquor as possible, and dried in a dish on the water-bath. On carefully heating the salt in a porcelain crucible, it decomposes, leaving a residue of metallic silver.

8. Test for Acetic Acid.—A few drops of ferric chloride are added to a *dilute* solution of sodium acetate. Owing to the formation of a complex aceto-ferric acetate, the liquid turns blood-red. On boiling this solution, a reddish-brown, flocculent precipitate of basic acetate of iron is formed. If allowed to stand for a short time, this sinks to the bottom of the test-tube, leaving the supernatant liquid colourless.

9. Oxidation of Ethyl Alcohol to Acetic Acid.—A mixture of 6 g. of potassium dichromate and 10 g. of concentrated sulphuric acid is introduced into a 100-c.c. distilling-flask connected with a condenser, and a solution of 2 c.c. of alcohol in 10 c.c. of water added drop by drop from a tap-funnel. On heating, acetic acid distils, and can be recognized by its odour, or, after careful neutralization with sodium carbonate, by the ferric-chloride test (8).

10. Action of Caustic Alkalis on Sodium Acetate.—One part by weight of sodium acetate, which has been fused and finely powdered, is thoroughly mixed with four parts by weight of soda-lime. The mixture is heated in a hard-glass retort of 100 c.c. capacity, fitted with a delivery-tube for collecting the gas in cylinders over water. The gas is collected in a thick-walled cylinder and ignited (**IV.**, 1).

Methane thus prepared always contains some hydrogen, and to obtain a product of maximum purity, it is best to keep the temperature as low as possible.

11. Saponification of Butter.—About 5 g. of butter are saponified by boiling in a porcelain dish with 20 c.c. of a solution of 1 part of sodium hydroxide in 2 parts of water, the mixture being constantly stirred. After a few minutes, it begins to foam. The heating is continued for twenty minutes, and the contents of the dish allowed to cool. The liquid separates into two layers—the lower an aqueous solution of glycerol and sodium hydroxide, and the upper the fused sodium salts of the fatty acids, which are insoluble in concentrated sodium-hydroxide solution. When cold, the upper layer is semi-solid. It is separated from the aqueous solution, and dissolved in water to free it from unsaponified fat. This can be almost completely removed by filtration through a moistened filter-paper.

12. **Calcium and Lead Salts of the Higher Fatty Acids.**—A part of the soap solution obtained by the method described in 11 is neutralized with dilute acetic acid, and calcium chloride and lead acetate respectively added to separate portions. Precipitates of the calcium and lead salts of the higher fatty acids are formed.

13. **Volatile Fatty Acids.**—The rest of the soap solution is poured into a 100-c.c. distilling-flask connected with a condenser, and excess of dilute sulphuric acid added. On heating, water and the *volatile fatty acids* of the butter distil, chief of the latter being *n*-butyric acid. They can be detected by their odour and acid reaction.

14. **Higher Fatty Acids.**—After the distillation of the volatile fatty acids, the residue in the flask consists of the solid *higher fatty acids.* It is transferred to a porcelain dish, allowed to cool, and the solid layer of fatty acids triturated with water several times to remove adhering sulphuric acid. To prove that the mixture has an acid reaction, it is dissolved in alcohol, and the solution added drop by drop to a very dilute solution of sodium hydroxide coloured red by a drop of phenolphthaleïn. The colour disappears, and the acids dissolve, proving that the alkali has been neutralized.

15. **Soap.**—A few drops of an alcoholic solution of phenolphthaleïn are added to a concentrated, neutral soap solution. On dilution with a large excess of water, the colourless liquid becomes red, owing to the liberation of free alkali by the hydrolytic dissociation of the salts of the fatty acids.

A solution of calcium sulphate is added to one of soap, whereupon the calcium salts of the higher fatty acids are precipitated.

16. Emulsifying Action of Soap.—About 2 g. of soap are dissolved in sufficient water to render the solution alkaline, a few drops of oil are added, and the solution vigorously agitated. An emulsion is produced. .

17. Cleansing Action of Soap.—A mixture of soot and water is decanted into a filter. The filter-paper is then removed from the funnel, refolded with the black surface outward, and replaced in the funnel. Water poured into the reversed filter remains clear during percolation; but filtration of a soap-solution renders it black, and cleanses the paper completely.

18. Ethyl Acetate.—Dry hydrochloric-acid gas is passed into a mixture of 10 c.c. of glacial acetic acid and 15 c.c. of 90 per cent alcohol. The gas can be prepared by gently heating dried common salt with concentrated sulphuric acid in a flask, or can be obtained from a Kipp generator charged with lump ammonium chloride and concentrated sulphuric acid. The mixture is heated for an hour under a reflux-condenser, and then poured into brine. Drops of ethyl acetate separate, a liquid characterized by its pleasant and refreshing odour.

19. Velocity of Saponification of Ethyl Acetate.—A small quantity of ethyl acetate is dissolved in water, and like volumes of the solution transferred to two test-tubes fitted with corks. One portion is agitated with a few drops of potassium or sodium hydroxide, and the other with a like volume of dilute sulphuric acid. Since the saponification is effected much more rapidly by the caustic alkali than by the acid, the odour of the ester vanishes from the first tube much sooner than from the second.

20. Solubility of Ethyl Acetate in Water.—An excess of ethyl acetate is vigorously agitated with 25 c.c. of water at the ordinary temperature till saturation is complete, and the aqueous solution is separated from the undissolved ester. When warmed, the solution becomes turbid from the separation of ethyl acetate, which is more soluble in cold than in hot water.

X. ALDEHYDES AND KETONES.

(98–111.)

ALDEHYDES (98–109).

1. **Acetaldehyde.**—A mixture of 60 g. of water, 20 g. of concentrated sulphuric acid, and 15 g. of ninety per cent. alcohol is added to 13 g. of potassium dichromate contained in a 200-c.c. fractionating-flask connected with a condenser. Sometimes the oxidation begins spontaneously; should it not, however, the flask is gently heated on a sand-bath, with a rapid current of cold water flowing through the condenser. A mixture of water, alcohol, acetaldehyde, and acetal distils, and can be used in carrying out the aldehyde-reactions described in 2, 3, and 4.

2. **Silver-mirror Test.**—A small portion of the distillate is diluted with water in a *clean* test-tube, and a few drops of an ammoniacal silver solution added. This is prepared by adding a small excess of a solution of sodium hydroxide to one of silver nitrate, and then ammonium hydroxide drop by drop in exactly sufficient quantity to redissolve the precipitate. After being shaken, the test-tube is immersed in water heated almost to its boiling-point. If the tube is thoroughly clean, the reduced silver is deposited on its sides as a mirror; if not, a black precipitate of the metal is obtained.

3. **Aldehyde-resin.**—Potassium hydroxide is added to another portion of the distillate, and the mixture warmed. A yellow coloration is produced at once, and, on further heating, a precipitate of aldehyde-resin is formed.

4. **SCHIFF'S Reaction.**—Another portion of the distillate is added to a solution of magenta decolorized with sulphurous acid—SCHIFF'S *reagent.* The red colour of the dye is restored.

5. Production of Formaldehyde.—A red-hot copper spiral is placed in a test-tube containing 1 c.c. of methyl alcohol, and a cork is loosely inserted in the mouth of the tube. When cold, the spiral is removed, and the presence of formaldehyde detected by the reduction of FEHLING's solution (**XVI.**, 6).

6. Action of Formalin on Proteïns.—The yolk of an egg is carefully placed in formalin. After the lapse of some time, it will be found to have acquired the consistency of an india-rubber ball.

7. Non-resinification of Formaldehyde.—A few drops of formalin are diluted with water, and a solution of sodium hydroxide added. Heating the liquid produces no resinification.

KETONES (98–103, 110 and 111).

8. Acetone.—About 50 g. of dried calcium acetate are heated to a high temperature in a retort connected with a condenser. Acetone is the principal constituent of the distillate, to which the by-products present impart an empyreumatic odour. On addition of water, most of the liquid dissolves; the insoluble tar-like products are separated by filtration through a moistened filter-paper.

9. Test for Acetone.—The filtrate obtained in 8 is added to a solution of mercuric nitrate made strongly alkaline by addition of alcoholic potash. On agitating the mixture, the acetone dissolves a part of the mercuric oxide suspended in the liquid. By repeated filtration, a *clear* filtrate is obtained. On addition of ammonium sulphide to this, a precipitate of mercuric sulphide is formed, proving the presence of mercury in the solution.

10. Addition-product of Acetone and Sodium Hydrogen Sulphite.—5 c.c. of acetone are agitated with a like volume of a very concentrated solution of sodium hydrogen sulphite; a crystalline addition-product is precipitated, being almost insoluble in the concentrated sulphite solution. On addition of water, it dissolves.

11. Separation of Acetone from Aqueous Solution.—5 c.c. of acetone are added to a like volume of water, with which the ketone is miscible in all proportions. On addition of solid potassium hydroxide to the mixture till saturation is complete, the liquid separates into two layers, the upper one being chiefly acetone, and the lower an aqueous solution of potassium hydroxide containing traces of acetone.

12. Oxidation of Acetone.—An aqueous solution of 2 c.c. of acetone is prepared, and a dilute solution of potassium permanganate added till the pink colour of the liquid persists. After removal of the manganese dioxide by filtration, the filtrate is acidified with dilute sulphuric acid and distilled. After careful neutralization with sodium carbonate, the presence of acetic acid in the distillate can be proved by the ferric-chloride test (**IX.**, 8).

XI. UNSATURATED HYDROCARBONS.

(112–127.)

OLEFINES (112–120).

1. Ethylene.—A mixture of 20 c.c. of alcohol of eighty per cent. strength and 120 c.c. of concentrated sulphuric acid is allowed to stand for some time. It is then heated in a large flask on a sand-bath, the tendency to foam being checked by the addition of 7 g. of anhydrous aluminium sulphate, or a quantity of sand. The ethylene evolved is collected over water in cylinders, being thereby freed from most of the carbon dioxide and sulphur dioxide generated along with it.

2. Luminosity of the Ethylene Flame.—One of the cylinders is turned mouth upwards, and its contents ignited; the ethylene burns with a luminous flame.

3. Action of Bromine on Ethylene.—A small quantity of bromine-water is added to another cylinder, the open end closed with a glass plate, and the contents agitated. The red colour is discharged, and oily drops of ethylene bromide, $C_2H_4Br_2$, collect on the sides of the cylinder, the characteristic odour of this compound also becoming perceptible.

4. **VON BAEYER'S Test for the Double Bond.**—The gas in a third cylinder is shaken up with mixed aqueous solutions of potassium permanganate and sodium carbonate. The violet colour of the solution is discharged, and a brown precipitate of hydrated manganese dioxide, MnO_2,nH_2O, formed.

5. **Explosive Mixture of Ethylene and Oxygen.**—A thick-walled cylinder one-quarter full of ethylene is filled up with oxygen, the contents mixed by shaking, and a light applied. The mixture explodes with a loud report.

6. **Unsaturated Hydrocarbons in Coal-gas.**—Two cylinders are filled with coal-gas by displacement of water. By the application of the tests described in 3 and 4, the gas can be shown to contain unsaturated compounds.

7. **Double Linking in Amylene.**—The presence of a double linking in amylene can be demonstrated by the reactions described in 3 and 4.

ACETYLENE (126).

8. **Preparation of Acetylene.**—A piece of calcium carbide is dropped into water contained in a 100-c.c. fractionating-flask fitted with a delivery-tube dipping under water, and the neck of the flask quickly closed with a cork. A vigorous evolution of acetylene ensues. The gas is collected in cylinders, and submitted to the tests described in 2, 3, and 4.

9. **Copper Acetylene and Silver Acetylene.**—An ammoniacal solution of cuprous chloride is prepared by adding ammonium hydroxide to a mixture of cuprous chloride and water till solution is complete. On addition of a portion of this liquid to a cylinder containing acetylene a red precipitate of copper acetylene is formed, readily soluble in hydrochloric acid with evolution of acetylene.

An ammoniacal silver solution—prepared by adding ammonium hydroxide carefully to a solution of silver nitrate till the precipitate first formed has *just* redissolved—gives with acetylene a white precipitate of silver acetylene.

XII. MONOBASIC UNSATURATED ACIDS.

(134–138.)

1. **Double Bond in Almond Oil.**—5 c.c. of almond oil, consisting principally of glyceryl oleate, are diluted with 10 c.c. of ether or carbon disulphide. A portion of the solution is agitated with bromine-water; the colour is discharged. To another portion is added a solution of potassium permanganate and sodium carbonate; a brown precipitate of hydrated manganese dioxide is obtained.

2. **Oleïc Acid from Almond Oil.**—5 c.c. of almond oil are saponified by the method described in **IX.**, 11, the heating with sodium hydroxide being continued for not less than an hour. Periodically, water is added to replace that lost by evaporation. The resulting sodium-soap is dissolved in water and the solution acidified with dilute sulphuric acid. The liberated oleïc acid forms a liquid layer on the surface of the aqueous solution, from which it is removed by the aid of a separating-funnel. The tests for double linkings described in **XI.**, 3 and 4, are carried out with portions of this acid.

3. **Elaïdic Transformation.**—Some of the liquid oleïc acid is poured into 2 or 3 c.c. of a concentrated solution of sodium nitrite, a small quantity of dilute sulphuric acid added, and the mixture allowed to stand for some time. Owing to its transformation into elaïdic acid, the liquid oleïc acid gradually becomes solid.

4. **Fusion of Oleïc Acid with Caustic Alkali.**—5 g. of sodium hydroxide are heated to fusion with a few drops of water in an iron crucible, and 2 c.c. of oleïc acid added. The mixture is stirred, and maintained for some time in the fused state.

After cooling, it is dissolved in water, and excess of dilute sulphuric acid added. On distillation from a fractionating-flask, an acid distillate is obtained, containing acetic acid.

5. **Lead Oleate.**—5 c.c. of almond oil, 25 c.c. of water, and 10 g. of lead monoxide are boiled in a porcelain dish, with constant stirring, until the red colour of the lead oxide has disappeared. The operation requires at least an hour. Water is added periodically to replace that lost by evaporation. After cooling, the water is poured off, and the plaster-like lead oleate (so-called "lead-plaster") formed is triturated thoroughly with ether by the aid of a pestle. After filtering, and distilling the ether, the lead oleate is left in the semi-solid state. Addition of hydrogen-sulphide solution proves the presence of lead, a black precipitate of lead sulphide being produced.

XIII. CHLOROFORM AND IODOFORM.

(144–146.)

1. **Preparation of Chloroform.**—25 g. of *fresh* bleaching-powder, 10 c.c. of alcohol of eighty-five per cent. strength, and 10 c.c. of water are heated gently in a litre flask on a sand-bath till the reaction begins; the flame is then removed. There is much foaming, and water and chloroform distil, the latter constituting the lower layer of the distillate.

2. **Formation of Chloroform from Trichloroacetic Acid.**—An aqueous solution of 1 g. of trichloroacetic acid is boiled in a fractionating-flask. Carbon dioxide is evolved, and can be identified by its action on lime-water. When the mixture has cooled, the presence of chloroform in the flask can be detected by the odour.

3. **Action of Potassium Hydroxide on Chloroform.**—A few drops of chloroform are heated in a test-tube with a small quantity of dilute potassium hydroxide, potassium chloride

and potassium formate being produced. The mixture is neutralized so as to maintain a slightly alkaline reaction, and heated with a solution of mercuric chloride. Reduction to mercurous chloride, and then to metallic mercury, proves the presence of dissolved formate (**IX.**, 2).

4. **Conversion of Chloroform into Potassium Cyanide.**—1 c.c. of chloroform is heated in a test-tube for a short time with 5 c.c. of concentrated alcoholic ammonia and 1 c.c. of concentrated alcoholic potash. The liquid is transferred to a porcelain dish, and evaporated to dryness on a water-bath. The presence of potassium cyanide in the residue is detected by the method employed in LASSAIGNE'S test for nitrogen (**I.**, 3 *a*).

5. **Chloroform and Silver Nitrate.**—1 c.c. of chloroform is agitated three or four times with water in a test-tube, using about 10 c.c. for each operation; traces of hydrochloric acid, if present, are thus eliminated. More water and 2 or 3 drops of silver-nitrate solution are then added. A precipitate of silver chloride is not formed.

6. **Iodoform-Test for Alcohol.**—To 1 c.c. of alcohol in a test-tube are added 10 c.c. of a moderately concentrated solution of iodine in potassium-iodide solution, and potassium hydroxide drop by drop till the brown colour of the iodine is discharged. A yellow, crystalline precipitate of iodoform is obtained, distinguished by its characteristic odour. Under the microscope, the crystals are seen to be six-sided, dichroïc (reddish-green) plates.

XIV. GLYCEROL.

(151–155.)

1. **Preparation of Allyl Alcohol.**—10 c.c. of glycerol and 12 g. of crystallized oxalic acid are heated in a retort connected with a condenser. At first, formic acid distils (**IX.**, 1), and

soon oily streaks of allyl alcohol are seen on the sides of the retort. The distillation is continued with another receiver, this alcohol passing over. It is characterized by an irritating odour. On heating it with chromic-acid solution, the powerful, penetrating odour of acraldehyde is perceived.

2. **Test for Glycerol.**—1 c.c. of glycerol is heated in a dish with 5 g. of sodium pyrosulphate, $Na_2S_2O_7$; the odour of acraldehyde is soon manifested.

3. **Action of Alkalis on Copper Salts in Presence of Glycerol.**—5 c.c. of dilute copper-sulphate solution are added to 1 c.c. of glycerol. On addition of potassium hydroxide to this mixture, copper hydroxide, $Cu(OH)_2$, is not precipitated. Instead, a soluble copper alkoxide of glycerol is formed, imparting a deep-blue colour to the solution.

XV. SATURATED DIBASIC ACIDS.

(161–168.)

OXALIC ACID (162).

1. **Preparation of Oxalic Acid from Wood.**—A concentrated solution of potassium (not sodium) hydroxide is added to 10 g. of sawdust, so as to form a thick paste, and the mixture heated on a shallow iron dish, and constantly stirred. The first product is potassium formate; on further heating, it loses hydrogen, yielding potassium oxalate (2). The heating is continued for a few minutes after rapid evolution of hydrogen from the mass in large bubbles which burn on ignition has begun, and then stopped, to prevent decomposition of the oxalate formed. When cold, the reaction-mixture is lixiviated with water, filtered through a folded filter, and acidified with dilute acetic acid. On addition of calcium-chloride solution, calcium oxalate is precipitated, insoluble in acetic acid, but soluble in cold, and more readily in warm, hydrochloric acid.

2. Conversion of Formates into Oxalates.—2 g. of dried sodium formate are heated to a high temperature in a test-tube. Hydrogen is evolved, and can be ignited after all the air has been expelled from the tube. The white residue is proved to be sodium oxalate by dissolving it in water, and adding a solution of calcium chloride; a precipitate of calcium oxalate, insoluble in dilute acetic acid, is formed.

3. Calcium, Lead, and Copper Oxalates.—These oxalates are prepared by adding solutions of calcium chloride, lead acetate, and copper sulphate respectively to a ten per cent. solution of ammonium oxalate till precipitation is complete, 50 c.c. of the ammonium-oxalate solution being used for each experiment. The salts are collected on filters, washed thoroughly with water, and spread on porous plates to dry. The last traces of moisture are eliminated by heating them in porcelain dishes on the water-bath.

4. Decomposition of Calcium Oxalate by Heat.—3 g. of calcium oxalate are heated in a hard-glass test-tube fitted with a delivery-tube. When the temperature has risen above 200°, water of crystallization condenses on the sides of the tube; on further heating, carbon monoxide is evolved. The gas is collected in a cylinder, and its identity established by the method of **IX.**, 3. The residue in the tube is calcium carbonate; when cold, it is treated with hydrochloric acid, causing a vigorous evolution of gas. This is proved to be carbon dioxide by its action on lime-water.

5. Decomposition of Lead and Copper Oxalates by Heat.—The experiment described in 4 is carried out in separate tubes with 3 g. of lead oxalate and a like weight of copper oxalate. Both evolve carbon dioxide, as proved by the lime-water test; lead and copper remain in the tubes.

6. Action of Concentrated Sulphuric Acid on Oxalic Acid.—A 100-c.c. distilling-flask is connected with a wash-bottle containing a mixture of potassium-hydroxide solution and lime-water and fitted with a delivery-tube. In the flask are placed

5 g. of oxalic acid and 10 c.c. of concentrated sulphuric acid. The flask is closed with a cork, and heated gently. Gas is evolved; partly carbon dioxide, which renders turbid the lime-water in the wash-bottle; and partly carbon monoxide, which is not absorbed. The latter is collected in cylinders, and identified by the method of **IX.**, 3.

7. Complex Oxalates.—*a*) A solution of ammonium oxalate is added carefully to 2 c.c. of a five per cent. solution of copper sulphate. Copper oxalate is precipitated, and, on further addition of the ammonium salt, redissolves, forming copper ammonium oxalate.

b) 2 g. of "salt of sorrel," $KHC_2O_4,H_2C_2O_4,2H_2O$, are dissolved in 10 c.c. of water. To this solution is added freshly-precipitated ferric hydroxide, obtained by adding ammonium hydroxide to a boiling, dilute solution of ferric chloride, allowing the precipitate to subside, and washing it by decantation. On warming, the ferric hydroxide dissolves, yielding potassium ferric oxalate, $K_3Fe(C_2O_4)_3$. The *green* colour of this solution should be noted; it points to the absence of $\dddot{\mathrm{F}}\mathrm{e}$-ions, and to the presence of complex $[Fe(C_2O_4)_3]'''$-anions.

c) A like solution of "salt of sorrel" is added to 5 c.c. of a ten per cent. solution of ferrous sulphate until the precipitate first formed redissolves. This solution reduces platinum chloride. Its *yellow* colour is due to the complex $[Fe(C_2O_4)_2]''$-anion.

8. Action of Light on EDER'S Solution.—A mixture of 2 volumes of a 4 per cent. solution of ammonium oxalate and 1 volume of a 5 per cent. solution of mercuric chloride (EDER'S solution) is divided into two equal parts, and a few drops of eosin solution are added to one of them. After exposure to light for several hours, both of the liquid samples contain a precipitate of mercurous chloride, the amount of this salt deposited in the solution containing the sensitizer eosin being much larger than in the other solution.

9. Dimethyl Oxalate.—Oxalic acid is dried at 100°, and 3 g.

of the dry acid are dissolved in 10 c.c. of boiling methyl alcohol. On cooling, dimethyl oxalate crystallizes out. Some of the ester is dried by pressure between sheets of filter-paper, and its melting-point taken. M. P. 54°.

10. **Diethyl Oxalate.**—A mixture of 7 g. of anhydrous oxalic acid and 10 c.c. of absolute alcohol is heated slowly in a 50-c.c. fractionating-flask connected with a condenser till the temperature rises to 110°. The distillate is then returned to the flask, and the heating continued till the thermometer reaches 180°. The fraction distilling between this temperature and 190° is collected separately, and is principally diethyl oxalate.

11. **Oxamide.**—The esters obtained in experiments 9 and 10 are dissolved separately in alcohol, and ammonium hydroxide added to each solution. From both a precipitate of oxamide is obtained, insoluble in water, alcohol, and ether.

SUCCINIC ACID (166).

12. **Barium Succinate.**—Ammonium hydroxide is added to 10 c.c. of a cold, saturated solution of succinic acid till neutralization is complete. On addition of barium chloride, a white, crystalline precipitate of barium succinate is formed, the precipitation being facilitated by addition of alcohol.

13. **Basic Ferric Succinate.**—10 c.c. of a solution of succinic acid are carefully neutralized, and ferric chloride added. A brown, gelatinous precipitate of basic ferric succinate is formed.

14. **Succinimide.**—A solution of 10 g. of succinic acid in ammonium hydroxide is evaporated in a porcelain dish on a sand-bath, and heated till the temperature of the fused mass is about 200°. The residue is transferred to a small fractionating-flask, and distilled as rapidly as possible. The distillate is succinimide, M. P. 125°. It can be crystallized from alcohol.

XVI. HYDROXY-ACIDS.

(179-197.)

LACTIC ACID (182).

1. **Decomposition of Lactic Acid by Dilute Sulphuric Acid.**—5 c.c. of lactic acid are heated with a mixture of 5 c.c. of concentrated sulphuric acid and 10 c.c. of water in a retort connected with a condenser. The distillate contains acetaldehyde and formic acid. They can be identified by the silver-mirror test (**X.**, 2), and the mercuric-oxide test (**IX.**, 2), respectively.

2. **Decomposition of Lactic Acid by Concentrated Sulphuric Acid.**—A mixture of 5 c.c. of lactic acid and a like volume of concentrated sulphuric acid is heated in a retort fitted with a delivery-tube. The gas evolved by the decomposition of the formic acid first produced can be proved to be carbon monoxide by the method described in **IX.**, 3.

3. **Oxidation of Lactic Acid.**—Dilute sulphuric acid is added to a solution of 0·5 g. of lactic acid, and the mixture gently heated with a 2 per cent. solution of potassium permanganate. The odour of acetaldehyde soon becomes perceptible.

TARTARIC ACID (188-196).

4. **Potassium Tartrates.**—Potassium hydroxide is added drop by drop to 5 c.c. of a twenty per cent. solution of tartaric acid. A precipitate of potassium hydrogen tartrate is first formed, and, on further addition of potassium hydroxide, redissolves, with production of the neutral tartrate.

5. **Iron Ammonium Tartrate.**—A solution of 9 g. of ferrous sulphate is added to 15 c.c. of a solution of 1 part of tartaric acid in 2 parts of water; excess of ammonium hydroxide produces no precipitate with this mixture. When agitated in presence of air, this liquid absorbs oxygen, becoming light-green, then dark-green, and finally brown. The absorption of oxygen can be demonstrated by carrying out the process in a flask closed with an air-tight cork; on immersion of the neck in water and removal of the cork, the water rises in the flask.

After replacement of the cork, the flask is withdrawn from the water, and an ignited wood-splint introduced into the residual gas; the flame is at once extinguished.

6. **FEHLING'S Solution.**—A solution of copper sulphate is added to one of tartaric acid, and then potassium hydroxide in excess. The dark-blue liquid formed is known as FEHLING'S *solution.*

7. **Action of Heat on Tartaric Acid.**—When heated in a test-tube, tartaric acid becomes brown, and acquires a caramel-like odour. When heated on platinum-foil or nickel-foil, it chars.

8. **Microchemical Test for Tartaric Acid and Racemic Acid.**—Calcium chloride is added to a solution of tartaric acid saturated with ammonia. The calcium tartrate precipitated is only slightly soluble in dilute acetic acid.

The experiment should be repeated with racemic acid, and the crystals of the two calcium salts compared under the microscope.

9. **Relative Solubility of Calcium Tartrate and Calcium Racemate.**—A solution of calcium sulphate is added to solutions of tartaric acid and racemic acid respectively. On the following day, calcium racemate is precipitated, but calcium tartrate remains dissolved.

10. **"Tartar Emetic."**—A solution of potassium hydrogen tartrate is prepared by dissolving 1 g. of tartaric acid in a small quantity of water, neutralizing with potassium hydroxide, and adding a concentrated solution of a second gramme of tartaric acid. The precipitated potassium hydrogen tartrate is redissolved by heating, after addition of a little water. To this solution is added antimony oxide; it dissolves, forming "tartar emetic."

CITRIC ACID (197).

11. **Preparation from Lemons.**—A small quantity of water is added to 10 c.c. of lemon-juice, the mixture filtered, and made alkaline with ammonium hydroxide. On addition of calcium

chloride, no precipitate is formed; on boiling the mixture, tricalcium citrate is precipitated, and is redissolved as the liquid cools.

12. **Action of Concentrated Sulphuric Acid on Citric Acid.**—A solution of 5 g. of citric acid in cold, concentrated sulphuric acid is heated in a distilling-flask, fitted with a delivery-tube. The carbon monoxide evolved is identified by the method described in **IX.**, 3.

13. **Formation of Acetone from Citric Acid.**—A solution of 0·5 g. of citric acid in a small quantity of water is heated to 80°, and a few drops of a 2 per cent. solution of potassium permanganate added. The colour is rapidly discharged. After filtration, the liquid is saturated with ammonia, and a solution of iodine added. Iodoform is produced from the acetone formed by the oxidation.

XVII. CHLORAL HYDRATE.

(201.)

1. **Action of Water on Chloral.**—3 g. of chloral hydrate are covered with concentrated sulphuric acid, and the mixture agitated. An oily layer of anhydrous chloral collects on the surface of the acid. This is separated from the sulphuric acid by the aid of a 50-c.c. tap-funnel, and brought into contact with a *small* quantity of water; heat is evolved, and solid chloral hydrate formed.

2. **Action of Alkali Hydroxide on Chloral Hydrate.**—A small quantity of potassium-hydroxide solution is added to 1 g. of chloral hydrate dissolved in 10 c.c. of water. The odour of chloroform becomes perceptible, and the liquid is rendered turbid by the separation of minute drops of this substance. The presence of formic acid in the solution is proved by warming it, after careful neutralization and addition of a small quantity of mercuric chloride or silver nitrate (**IX.**, 2).

3. **Silver-mirror Test for Chloral Hydrate.**—A dilute solution of chloral hydrate is warmed in a test-tube on a water-bath with a small quantity of an ammoniacal solution of silver nitrate, prepared in accordance with the method described in **X.**, 2. If the tube is clean, a silver mirror is deposited on its sides.

4. **Action of Sodium Hydrogen Sulphite on Chloral Hydrate.**—A concentrated solution of sodium hydrogen sulphite is poured over 3 g. of chloral hydrate, and the mixture vigorously agitated. The hydrate at first dissolves, but the liquid soon becomes a thick paste, owing to separation of the addition-product.

XVIII. ALDEHYDO-ALCOHOLS AND KETO-ALCOHOLS OR SUGARS.

(202–228.)

PROPERTIES OF THE MONOSES (203).

1. **Silver-mirror Test.**—A ten per cent. solution of dextrose is warmed in a clean test-tube in a water-bath with an ammoniacal solution of silver nitrate prepared as in **X.**, 2. A silver mirror forms on the inner surface of the test-tube.

2. **Resinification with Caustic Alkalis.**—A similar solution is boiled with a small amount of a solution of potassium or sodium hydroxide. The liquid turns yellow, then brown, and finally resinifies.

3. **Reduction of FEHLING'S Solution.**—On heating another portion of the dextrose solution with FEHLING'S solution (**XVI.**, 6), reduction takes place, with formation of red cuprous oxide.

4. **Osazones.**—A solution of phenylhydrazine in sulphurous acid is added to another portion of the dextrose solution in a test-tube. On warming the mixture in a water-bath, phenyl-

glucosazone precipitates in the form of microscopic, yellow needles.

METHODS OF FORMATION OF THE MONOSES (206).

5. **Inversion of Sucrose (Cane-sugar).**—A dilute solution of sucrose is boiled for several minutes with a few drops of dilute sulphuric acid. After this treatment, the solution answers to the dextrose-tests described in 1–4.

6. **Glycerose.**—A mixture of 10 g. of glycerol and 20 c.c. of nitric acid of 1·18 specific gravity is heated in a beaker on the water-bath until oxides of nitrogen are evolved, and cooled quickly. After neutralization of the solution with potassium or sodium hydroxide the presence of glycerose can be demonstrated by reactions 1–4.

PENTOSES (207).

7. **Furfuraldehyde-Test.**—To 10 g. of bran contained in a half-litre flask is added a mixture of 5 g. of concentrated sulphuric acid and 70 c.c. of water. The flask is connected with a condenser, and heated. The distillate contains furfuraldehyde (**393**), characterized by its odour. The smell of fresh rye-bread is due to the presence of furfuraldehyde. This aldehyde can be identified in two ways.

a) On addition of a small quantity of aniline to the solution, followed by concentrated hydrochloric acid, the liquid acquires an intense red colour.

b) A solution of phenylhydrazine in sulphurous acid is added to the mixture containing furfuraldehyde, whereupon furfuraldehyde-hydrazone is precipitated in the form of an oil, which soon crystallizes.

HEXOSES (208).

8. **Hydrochloric-acid Test.**—A solution of a hexose is boiled with concentrated hydrochloric acid. The liquid becomes

brown and deposits "humic substances"; lævulic acid remains in solution (**234**).

Dextrose (208).

9. **Calcium Alkoxide of Dextrose.**—Milk of lime is added drop by drop to 10 c.c. of a solution of 1 part of dextrose in 2 parts of water, and the mixture agitated. The lime dissolves, forming the calcium alkoxide or saccharate of dextrose. This is decomposed by carbon dioxide, with precipitation of calcium carbonate.

10. **Glucosesulphuric Acid.**—1 g. of dextrose is triturated in a mortar with cold, concentrated sulphuric acid, added drop by drop till solution is complete. Glucosesulphuric acid is formed, and can be detected by diluting with water, adding barium carbonate until the mixture, thoroughly blended by the aid of the pestle, ceases to be acid, and filtering; the filtrate contains the barium salt of glucosesulphuric acid. Addition of dilute sulphuric acid decomposes the barium glucosesulphate, precipitating barium sulphate.

11. **Copper Alkoxide of Dextrose.**—A small quantity of a solution of one part of dextrose in 2 parts of water is added to 2 c.c. of ten per cent. solution of copper sulphate. On addition of potassium hydroxide to the mixture, no precipitate is formed, the formation of a copper alkoxide of dextrose imparting a dark-blue colour to the solution.

12. **Detection of Dextrose in Urine.**—A bismuth solution, prepared by mixing solutions of bismuth nitrate, Rochelle salt, and sodium hydroxide, is added to a 2 per cent. solution of dextrose, and the mixture boiled. Black bismuthous oxide, BiO, is precipitated.

13. **Oxidation of Dextrose by Nitric Acid.**—A mixture of 1 g. of dextrose and 10 c.c. of nitric acid of 1·3 specific gravity is evaporated to dryness on the water-bath. About 1 c.c. of water is added to the residue, and 5 c.c. of a concentrated

solution of potassium acetate. After a short time, potassium hydrogen saccharate is precipitated.

Lævulose (209.)

14. **Alcoholic Character.**—The alcoholic character of this compound can be demonstrated by the methods employed for dextrose (9–11).

15. **Test for Lævulose.**—1 c.c. of a ten per cent. solution of lævulose is heated with concentrated hydrochloric acid and some crystals of resorcinol. The liquid turns dark-red.

d-Galactose (211).

16. **Oxidation of *d*-Galactose to Mucic Acid.**—A solution of 1 g. of *d*-galactose is boiled for several minutes with nitric acid of 1·3 specific gravity, evaporated to small bulk, diluted with water, and cooled. Mucic acid separates as a crystalline powder, soluble with difficulty in cold water. If *d*-galactose cannot be obtained, lactose should be used instead (**215**).

A small quantity of the mucic acid is washed with water, and a trace of it introduced into a drop of five per cent. potassium-hydroxide solution on a microscope-slide. Under the microscope, the characteristic, prismatic crystals of potassium mucate make their appearance after a few moments.

HEXODIOSES (213–220)

Lactose (215).

17. **Detection of Lactose in Milk.**—A few drops of dilute acetic acid are added slowly to 25 c.c. of milk diluted with a like volume of water, the liquid being thoroughly mixed by stirring. The caseïn and fatty constituents of the milk are thus precipitated. The mixture is filtered through a folded filter. On warming part of the filtrate with FEHLING'S solution, the lactose causes reduction, with formation of red

cuprous oxide. The rest of the filtrate is evaporated with dilute nitric acid to small bulk; *d*-galactose is formed by inversion, and oxidized to mucic acid, which can be recognized by the method of 16.

18. **Lactosazone.**—On warming 5 c.c. of a ten per cent. solution of lactose with a sulphurous-acid solution of phenylhydrazine, an osazone—phenyllactosazone—is formed.

19. **" Sand-sugar."**—The taste of lactose is not so sweet as that of sucrose, and in the mouth it resembles sand, hence the name sand-sugar.

Sucrose (216–220).

20. **Properties Distinguishing Sucrose from the Monoses.**—When heated with caustic alkalis, a ten per cent. solution of sucrose does not resinify; it does not reduce Fehling's solution; and, when warmed with a solution of phenylhydrazine in sulphurous acid, gives no osazone (1–4).

21. **Action of Heat on Sucrose.**—On heating a small quantity of sucrose in a test-tube, it turns brown, forming caramel, and evolving the characteristic odour of this substance.

22. **Tricalcium Saccharate.**—10 c.c. of a twenty per cent. solution of sucrose are agitated with sufficient milk of lime to cause permanent turbidity, and filtered. When the filtrate is boiled, the nearly insoluble tricalcium saccharate, with the formula $C_{12}H_{22}O_{11},3CaO,3H_2O$, is precipitated; on cooling it is dissolved.

23. **Inversion.**—A solution of 2 g. of sucrose is inverted by boiling for several minutes with dilute sulphuric acid. After careful neutralization with sodium hydroxide, the solution thus obtained has the properties characteristic of monoses, described in 1–4, and answers to the lævulose-test with resorcinol.

POLYOSES (224–228.)

Starch (225 and 226).

24. Starch-paste.—5 g. of powdered starch are washed with water on a filter-paper. The washed starch is transferred to a beaker containing 200 c.c. of boiling water, a faintly opalescent solution of starch-paste being obtained.

25. Properties Distinguishing Starch from the Monoses.—If the starch has been washed with sufficient care, this starch-paste does not reduce FEHLING's solution, and is not resinified by alkalis.

26. Conversion of Starch into Dextrose.—*a*) 50 c.c. of the starch-paste solution are boiled with 10 c.c. of ten per cent. sulphuric acid for fifteen minutes. After neutralization with sodium hydroxide, the liquid has the properties characteristic of monoses described in 1–4.

b) A mixture of 50 c.c. of the starch-paste with 10 c.c. of fresh malt-extract, which contains diastase, is heated at 60° for about half an hour. The paste becomes liquefied, and the liquid no longer answers to the iodine-test.

27. Iodine-test for Starch.—A trace of an iodine solution is added to one of starch-paste, a deep-blue coloration being produced. On heating, this disappears, but on cooling returns, provided the heating is not too prolonged.

28. Barium Alkoxide of Starch.—A solution of barium hydroxide is added to a boiling solution of starch-paste. The barium alkoxide of starch is precipitated.

29. Conversion of Starch into Dextrin.—*a*) A small quantity of starch is heated carefully in a test-tube, the residue agitated with cold water, and filtered. The filtrate contains dextrin, proved by the yellow coloration developed by heating with alkalis, its precipitation from solution on addition of alcohol, and the red colour produced by addition of iodine solution.

b) 50 c.c. of concentrated hydrochloric acid is added to 5 g. of starch, the mixture becoming rapidly converted into a transparent, opalescent paste. After the lapse of one or two hours, the paste will have liquefied, and on the following day will no longer answer to the iodine-test for starch, although it will still show the reactions of dextrin. A few days later, the liquid will only contain dextrose.

30. **Potato-starch.**—A small quantity of potato-starch is moistened with a few drops of water, a little of the mixture transferred to a microscope-slide, and examined under the microscope. The starch-granules are seen to have a characteristic shell-like appearance (**225**, Fig. 69).

Cellulose (227 and 228).

31. **Hydrolysis of Cellulose.**—A piece of filter-paper is dissolved in cold, concentrated sulphuric acid by the method described in 10, the solution poured into water, and boiled for half an hour. When neutralized with sodium hydroxide, it answers to the tests for monoses (1–4).

32. **Parchment-paper.**—A strip of filter-paper is immersed in sulphuric acid containing half its volume of water, and at once transferred to a large quantity of cold water, and thoroughly washed. This treatment converts the cellulose into amyloid or parchment-paper, which gives a blue coloration with iodine. Although wet, the parchment-paper is very tough, and cannot be torn readily.

33. **Solubility of Cellulose in SCHWEITZER'S Reagent.**—An ammoniacal solution of copper oxide is prepared by adding freshly-precipitated, washed copper hydroxide to 10 c.c. of concentrated ammonium hydroxide till no more dissolves. When placed in this solution, filter-paper (cellulose) dissolves. On addition of dilute hydrochloric acid, the colour is discharged, and an amorphous, flocculent precipitate of cellulose deposited.

34. **Nitrocelluloses.**—A small piece of cotton-wool is immersed for several seconds in a cold mixture of one part of concentrated nitric acid and two parts of concentrated

sulphuric acid, nitrocelluloses being formed. It is then washed carefully with much cold water, and dried at the ordinary temperature. A part held with tongs in a Bunsen flame burns energetically. Another portion is agitated with a mixture of alcohol and ether, and the liquid—named collodion—poured on a glass plate; on evaporation of the solvent, a transparent skin is left.

The remainder of the nitrocelluloses is moistened with a small quantity of ethyl acetate. A gelatinous mass is formed, which, when dry, burns slowly ("smokeless powder").

35. **Detection of Lignin in Paper.**—A sheet of paper is coated with a solution of aniline in hydrochloric acid. If made from wood, the paper acquires an intense yellow colour.

XIX. PROTEINS.

(246–254.)

1. **Detection of Nitrogen and Sulphur in the Proteins.**—A few cubic centimetres of a solution of egg-albumin—prepared by dissolving white-of-egg in five times its volume of water—is heated with potassium hydroxide. Ammonia is evolved, and can be detected by the aid of a moist strip of red litmus-paper.

The liquid is diluted with water, and lead acetate added. The potassium sulphide formed in the last experiment reacts with the lead salt, precipitating black lead sulphide.

2. **"Salting-out" Proteins with Ammonium Sulphate.**—Solid ammonium sulphate is added to 20 c.c. of the egg-albumin solution. The albumin is precipitated.

3. **Coagulation of Proteins by Alcohol.**—Strong alcohol added to a solution of egg-albumin gives a precipitate of coagulated egg-albumin. A similar precipitate is formed when an aqueous solution of egg-albumin is boiled. Coagulated egg-albumin

is soluble in dilute caustic alkali, concentrated hydrochloric acid, and concentrated sulphuric acid.

4. **Coagulation of Proteïns by Nitric Acid.**—Dilute nitric acid is added to an egg-albumin solution prepared by the method of 1. The egg-albumin is precipitated.

5. **Biuret-reaction.**—A few drops of copper-sulphate solution are added to 5 c.c. of a solution of egg-albumin. Careful addition of dilute potassium hydroxide to the mixture precipitates copper albuminate. Excess of potassium hydroxide redissolves the precipitate, producing a violet-red coloration.

6. **MILLON'S Reagent.**—On boiling an egg-albumin solution with MILLON's reagent—a solution of mercuric nitrate containing nitrous acid—a red, coagulated mass is obtained.

7. **Xanthoproteïn-reaction.**—When an egg-albumin solution is warmed with dilute nitric acid, it coagulates, with production of a yellow coloration.

8. **ADAMKIEWICZ'S Reaction.**—With concentrated sulphuric acid a solution of egg-albumin in glacial acetic acid yields a violet coloration, due to the presence in the mixture of a small proportion of glyoxylic acid.

9. **Decomposition-products of Keratin.**—A feather is heated with concentrated potassium hydroxide. It dissolves, and the solution thus obtained gives the reactions for nitrogen and sulphur, described in 1.

XX. HYDROCYANIC ACID, AND ITS SIMPLE AND COMPLEX SALTS.

(256 and 257.)

1. **Hydrocyanic Acid.**—10 c.c. of a cold, saturated solution of potassium ferrocyanide are poured into a distilling-flask connected with a condenser, and 20 c.c. of twenty per cent. sulphuric acid added. The open end of the condenser is dipped into a test-tube containing water and a few drops of

concentrated potassium or sodium hydroxide. On heating, hydrocyanic acid distils, and is converted into potassium cyanide.

2. **Prussian-blue Test.**—A mixture of a ferrous salt and a ferric salt is added to part of the solution obtained in the last experiment. On acidifying with hydrochloric acid, a precipitate of Prussian blue is formed (**I.**, 3 *a*).

3. **Silver Cyanide.**—A drop of a dilute solution of silver nitrate is added to 10 c.c. of a solution of 1 g. of potassium cyanide in 100 c.c. of water. On agitating the mixture, the precipitate first formed redissolves, yielding a double cyanide of potassium and silver, $KAg(CN)_2$. On further addition of silver nitrate, a permanent precipitate of silver cyanide, $AgCN$, is obtained.

4. **Hydrolysis of Potassium Cyanide.**—25 c.c. of the solution of potassium cyanide prepared for experiment 3 are boiled in a flask. The evolved ammonia turns a strip of red litmus-paper blue.

5. **Conversion of Ammonium Formate into Hydrocyanic Acid.**—3 g. of ammonium formate are submitted to dry distillation in a small distilling-flask connected with a condenser dipping into a test-tube with very dilute sodium hydroxide. The presence of hydrocyanic acid in the distillate can be demonstrated by the Prussian-blue test (2).

6. **Double Ferrocyanide of Potassium and Calcium.**—A small quantity of a calcium-chloride solution is added to a cold, saturated solution of potassium ferrocyanide. The double ferrocyanide, $K_2CaFe(CN)_6$, is precipitated.

7. **Ferrocyanic Acid.**—Concentrated hydrochloric acid is added to 5 c.c. of a strong solution of potassium ferrocyanide. White ferrocyanic acid, $H_4Fe(CN)_6$, is precipitated. When collected on a filter-paper, it soon turns blue, Prussian blue being formed by decomposition and oxidation.

8. **Action of Concentrated Sulphuric Acid on Potassium Ferrocyanide.**—5 g. of potassium ferrocyanide are warmed

with concentrated sulphuric acid in a fractionating-flask. The evolved carbon monoxide can be identified by the method described in **IX.**, 3.

9. **Action of Heat on Potassium Ferrocyanide.**—2 g. of potassium ferrocyanide are heated to redness in a crucible; when cold, the residue is lixiviated with water, and the mixture filtered quickly. The solution contains potassium cyanide, as can be proved by the Prussian-blue and silver-nitrate tests (2 and 3).

10. **Potassium Ferricyanide.**—Bromine-water is added to a solution of potassium ferrocyanide, which converts it into potassium ferricyanide. This change is detected by addition of ferric chloride, which produces a brown coloration, instead of a precipitate of Prussian blue.

11. **Reduction of Potassium Ferricyanide.**—Litharge, PbO, is added to a solution of potassium ferricyanide containing potassium hydroxide. The solid becomes brown, the lead monoxide being oxidized to lead dioxide, PbO_2. After filtering, and adding ferric chloride to the filtrate, a precipitate of Prussian blue is formed, proving the presence of potassium ferrocyanide.

12. **Oxidation of Potassium Ferrocyanide by Potassium Permanganate.**—Sulphuric acid is added to a dilute solution of potassium ferrocyanide. This mixture decolorizes potassium permanganate, forming potassium ferricyanide, which gives a brown coloration with ferric chloride.

XXI. POTASSIUM CYANATE AND POTASSIUM THIOCYANATE.

(258–260.)

1. **Potassium Cyanate.**—Litharge, PbO, is added to 3 g. of fused potassium cyanide in a crucible so long as reduction to metallic lead is rapid. The potassium cyanate, $KCNO$, formed

is extracted with cold water. On addition of sulphuric acid, carbon dioxide is evolved, since the liberated cyanic acid reacts at once with the water to form carbon dioxide and ammonia. The liquid in the flask is made alkaline with sodium hydroxide, and heated. The evolved ammonia turns blue a strip of moist, red litmus-paper held in the mouth of the flask.

2. **Potassium Thiocyanate.**—10 c.c. of potassium-cyanide solution are boiled for some minutes with "flowers of sulphur" and filtered. Addition of ferric chloride to the filtrate gives a blood-red coloration, proving the formation of potassium thiocyanate.

3. **Silver Thiocyanate.**—With silver nitrate a solution of potassium thiocyanate produces a white, cheese-like precipitate of silver thiocyanate, AgCNS, insoluble in dilute nitric acid.

XXII. DERIVATIVES OF CARBONIC ACID.

(263–270.)

CARBON DISULPHIDE (264).

1. **Inflammability.**—A few drops of carbon disulphide are poured into a porcelain basin, and ignited. The liquid burns with a blue flame, forming carbon dioxide and sulphur dioxide, the presence of the latter being made evident by its characteristic, suffocating odour.

2. **Volatility.**—On blowing upon a few drops of carbon disulphide in the palm of the hand, a sensation of cold is experienced.

3. **Solvent Power.**—Some linseed is crushed in a mortar, transferred to a test-tube, and covered with a small quantity of carbon disulphide. After about a minute, the liquid is poured on a clock-glass or watch-glass, and allowed to evaporate spontaneously. The residue is linseed oil.

4. **Barium Trithiocarbonate.**—5 g. of barium sulphide are boiled with water for a few seconds, and the mixture filtered. About 1 c.c. of carbon disulphide is added to the warm filtrate, the mixture vigorously shaken, and allowed to cool. A yellow precipitate of barium trithiocarbonate is deposited.

5. **Potassium and Copper Salts of Xanthic Acid.**—10 c.c. of a twenty per cent. solution of potassium hydroxide in absolute alcohol is agitated with successive quantities of carbon disulphide, till potassium xanthate separates out. The precipitation of the salt is facilitated by addition of a small amount of ether. It is collected on a filter, dried between layers of filter-paper, and dissolved in water. On adding a solution of copper sulphate, a brownish-black precipitate of cupric xanthate is formed. This substance changes so quickly to yellow cuprous xanthate as to render its formation hardly perceptible. In a dilute solution of the xanthate the reaction is much slower.

UREA (266 and 267).

6. **WÖHLER'S Synthesis.**—Potassium cyanate, prepared by the method of **XXI.**, 1, is dissolved in water. Ammonium sulphate is added, producing potassium sulphate and ammonium cyanate. The solution is evaporated almost to dryness on the water-bath, and the urea formed by the intramolecular rearrangement of the ammonium cyanate extracted with alcohol. The solvent is distilled, leaving a residue of urea.

7. **Urea Oxalate.**—The urea obtained in the last experiment is dissolved in a very small quantity of water, and a concentrated solution of oxalic acid added. A crystalline precipitate of urea oxalate is deposited.

8. **Urea Nitrate from Urine.**—About 10 c.c. of urine are evaporated to small bulk on a water-bath, and the residue allowed to cool. On addition of a few cubic centimetres of colourless nitric acid of 1·4 specific gravity, a precipitate of urea nitrate is formed. The mother-liquor is poured off, and

the nitrate purified by crystallization from a small quantity of hot water.

9. **KNOP'S Method for the Estimation of Urea in Urine.**—A solution of bromine in cold potassium hydroxide is added to 10 c.c. of urine contained in a distilling-flask fitted with a delivery-tube. The urea at once begins to decompose, evolving nitrogen, which is collected over water, and tested with a lighted taper.

10. **BUNSEN'S Method for the Estimation of Urea in Urine.**—10 c.c. of urine are heated with baryta-water in a flask. A strip of red litmus-paper held in the mouth of the flask is turned blue by the ammonia liberated. At the same time, the precipitated barium carbonate renders the liquid turbid.

11. **LIEBIG'S Method for the Estimation of Urea in Urine.**—A solution of mercuric nitrate is added to 10 c.c. of a two per cent. solution of urea. A white precipitate of the composition $2CON_2H_4,Hg(NO_3)_2,3HgO$ is formed. When excess of the mercuric nitrate has been added, a drop of the solution brought into contact with one of sodium carbonate gives a yellow precipitate of basic nitrate of mercury.

12. **Action of Heat on Urea.**—1 g. of urea is carefully heated in a test-tube; it melts, and evolves ammonia, which can be identified by means of a strip of red litmus-paper. The fused mass soon re-solidifies, and the heating is stopped. The residue is lixiviated with a *small* quantity of cold water, biuret going into solution. This substance can be identified by the *biuret-reaction.* Potassium hydroxide and one or two drops of a ten per cent. solution of copper sulphate are added to the liquid; the violet-red coloration produced is due to the formation of a copper compound of biuret.

13. **Cyanuric Acid.**—This substance is the principal constituent of the residue in the test-tube after solution of the biuret in the last experiment. It is dissolved in warm water; after cooling, addition of copper sulphate and ammonium hydroxide gives a crystalline, violet precipitate of copper ammonium cyanurate.

CARBAMIC ACID (268).

14. **Calcium Carbamate.**—Ammonium hydroxide is added to 10 c.c. of a ten per cent. solution of calcium chloride. On passing carbon dioxide through the mixture, no precipitate is obtained, the calcium carbamate formed being soluble in water. When the solution is warmed, the carbamate decomposes, precipitating calcium carbonate.

15. **Ammonium Dithiocarbamate.**—A drop of carbon disulphide is added to a concentrated alcoholic solution of ammonia contained in a porcelain dish, and the mixture is evaporated to dryness on a water-bath. The initial product formed is ammonium dithiocarbamate. It is decomposed by the excess of ammonia present into ammonium thiocyanate and ammonium sulphide. The sulphide volatilizes, and the presence of the thiocyanate in the residue is detected by dissolving it in water, and adding a few drops of dilute hydrochloric acid and ferric chloride. The formation of ferric thiocyanate produces a blood-red coloration.

XXIII. URIC ACID GROUP.

(271–273.)

1. **Ammonium Urate.**—A mixture of 50 c.c. of urine and 2·5 c.c. of a concentrated solution of sodium carbonate is placed in a flask, and 5 c.c. of a saturated ammonium-chloride solution added. After a short interval, ammonium urate is precipitated.

2. **Di-potassium Urate.**—A small quantity of uric acid is agitated with water; it does not dissolve. On addition of dilute potassium hydroxide, the readily soluble di-potassium salt is formed, and can be reconverted into uric acid by dilute acids.

3. **Murexide-test for Uric Acid.**—A few cubic centimetres of nitric acid of 1·4 specific gravity are added to 0·5 g. of uric acid in a porcelain dish, and the mixture evaporated nearly to dryness on a water-bath. In addition to other products, alloxantine is formed. When treated with ammonium hydr-

oxide, it forms a purple-red dye—murexide, the ammonium salt of purpuric acid.

4. **Reduction of Silver Nitrate by Uric Acid.**—A small quantity of uric acid is dissolved in a few drops of sodium-carbonate solution. When the liquid is brought into contact with filter-paper moistened with a solution of silver nitrate, a black stain of metallic silver is formed, in consequence of the reducing action of the uric acid.

5. **Murexide-test for Caffeïne.**—A few cubic centimetres of nitric acid of 1·4 specific gravity are added to 0·5 g. of caffeïne in a porcelain dish, and evaporated almost to dryness on a water-bath. A yellow stain of amalic acid, or tetramethylalloxantine, is left. On moistening this with ammonium hydroxide, it becomes purple.

XXIV. BENZENE AND ITS HOMOLOGUES.

(281–288.)

1. **Stability of Benzene towards the Halogens.**—On agitating a few cubic centimetres of benzene with bromine-water, the bromine is dissolved by the benzene, but its colour is not discharged.

2. **Absence of Double Bonds in Benzene.**—Benzene is agitated with a solution of potassium permanganate and sodium carbonate—VON BAEYER'S reagent (**113** and **281**). The violet-red colour remains unaltered.

3. **Nitrobenzene.**—2 c.c. of benzene are added drop by drop to a mixture of 4 c.c. of concentrated sulphuric acid and 2 c.c. of nitric acid of 1·5 specific gravity, the flask being cooled with running water to prevent rise of temperature. The benzene dissolves, and, on pouring the acid mixture into water, nitrobenzene separates and sinks to the bottom. It has a characteristic odour, resembling that of oil of bitter almonds.

4. **Benzenemonosulphonic Acid.**—5 c.c. of benzene are brought gradually into contact with 10 c.c. of fuming sulphuric

acid. At first heat is developed, and the hydrocarbon dissolves quickly; to complete the reaction, the mixture must be warmed gently. It is then poured into twice its volume of water, common salt added, and the liquid heated until hydrochloric-acid gas is evolved. On cooling, sodium benzenesulphonate separates in crystalline plates.

5. **FRIEDEL and CRAFTS'S Reaction.**—1 g. of aluminium chloride is added to 5 c.c. of benzene, and a small quantity of chloroform dropped into the mixture. There is a vigorous evolution of hydrochloric-acid gas, and triphenylmethane is formed.

6. **Formation of Benzene from Calcium Benzoate.**—10 g. of calcium benzoate are mixed with a like weight of soda-lime, and heated in a retort connected with a condenser. Benzene distils, and can be identified by its odour, by the fact that it floats on water, and by converting it into nitrobenzene with a mixture of concentrated nitric and sulphuric acids in accordance with the method described in 3.

7. **Oxidation of Side-chains.**—1 c.c. of toluene is heated with a solution of potassium permanganate and sodium carbonate. The purple colour is discharged, and manganese dioxide precipitated, in consequence of the oxidation of the side-chain and the formation of benzoïc acid.

XXV. MONOHALOGEN COMPOUNDS.

(289.)

1. **Stability of Monochlorobenzene towards Alcoholic Potash or Soda.**—5 c.c. of monochlorobenzene are heated with 10 c.c. of ten per cent. alcoholic potash or soda for a few minutes, and the liquid diluted with water. The monochlorobenzene is precipitated unchanged as an oily liquid. To prove this, it is separated by means of a tap-funnel, dried by contact with granulated calcium chloride for a few minutes, and its boiling-point determined by the method of **III.**, 5. Monochlorobenzene boils at 132°.

After separation of the monochlorobenzene, the aqueous liquid is acidified with nitric acid, and silver nitrate added. It does not become turbid, proving that the caustic alkali has not reacted with the Cl-atom of the monochlorobenzene.

XXVI. MONOHYDRIC PHENOLS.

(292–294.)

1. **Preparation of Phenol by Fusion of Sodium Benzenesulphonate with Sodium Hydroxide.**—10 g. of sodium benzenesulphonate, 3 g. of sodium hydroxide, and a small quantity of water are heated in an iron dish to the temperature of fusion, the mixture being continually stirred. When cold, it is dissolved in water, the solution poured into a fractionating-flask, and dilute sulphuric acid added slowly. Much sulphur dioxide is evolved, and can be recognized by its characteristic odour. The flask is connected with a condenser, and heated. Phenol distils along with water, and is identified by the methods of 4 and 5.

2. **Preparation of Phenol from Calcium Salicylate.**—10 g. of calcium salicylate are heated in a retort connected with a condenser. Phenol distils, and can be recognized by its odour, and by the reactions described in 4 and 5.

3. **Sodium Phenoxide.**—1 g. of phenol is agitated with enough water to form an emulsion; on addition of sodium-hydroxide solution, this dissolves, forming sodium phenoxide. When carbon dioxide is passed through the liquid for a considerable time, phenol is liberated, and the mixture rendered turbid.

4. **Tribromophenol.**—Bromine-water is added to a two per cent. aqueous solution of phenol. Tribromophenol is precipitated.

5. **Ferric-chloride Test for Phenol.**—On addition of a drop of ferric-chloride solution to a one per cent. solution of phenol, an intense violet coloration is obtained.

6. Depression of the Freezing-point of Phenol.—5 c.c of phenol are melted in a test-tube by very careful heating over a tiny flame. After introduction of a thermometer, the liquid is allowed to cool. When crystals begin to form, the mercury ceases falling, and rises, the highest temperature indicated being the freezing-point. For anhydrous phenol, it is 39·6°.

The phenol is again melted, and 1 drop—about 0·05 g.—of water added. The freezing-point is determined as before, and found to be about 4° lower.

7. Action of Nitric Acid on Phenol.—A cubic centimetre of phenol is added drop by drop to 10 c.c. of nitric acid of specific gravity 1·3, the liquid being continually agitated, and finally heated to boiling. On cooling, picric acid is precipitated. When recrystallized from water, it is obtained as yellow, needle-like crystals.

8. Cresol.—With bromine-water and ferric chloride respectively, an aqueous solution of cresol gives reactions similar to those obtained with phenol (4 and 5).

XXVII. MONOAMINO-COMPOUNDS AND THEIR DERIVATIVES.

(296–301).

1. Aniline.—35 c.c. of hydrochloric acid of 1·19 specific gravity are poured into a flask containing 6 g. of nitrobenzene, and 18 g. of tin-powder added in successive small portions. To prevent its contents becoming overheated, the flask is shaken, and cooled with water. The nitrobenzene is reduced to aniline, this combining with the excess of hydrochloric acid to aniline hydrochloride. When all the nitrobenzene has dissolved, and its odour is no longer perceptible, the aniline is set free by potassium or sodium hydroxide, and the mixture distilled. The aniline volatilizes with the steam, rendering the distillate turbid.

2. **Neutral Reaction of Aniline.**—A small quantity of aniline is agitated with water. The solution thus prepared neither imparts a colour to phenolphthaleïn, nor turns red litmus blue.

3. **Aniline Salts.**—On addition of an acid, the turbid liquid obtained in 1 becomes clear, a soluble aniline salt being formed. Potassium or sodium hydroxide reprecipitates the aniline as an oil.

4. **Tribromoaniline.**—With an aqueous solution of aniline or of one of its salts, bromine-water gives a precipitate of tribromoaniline.

5. **Bleaching-powder Test for Aniline.**—A few drops of aniline are agitated with water, and the solution separated from undissolved amine by passing it through a moist filter. A small quantity of a clear solution of bleaching-powder gives a deep-violet coloration with the filtrate.

6. **Potassium-dichromate Test for Aniline.**—2 or 3 drops of aniline are dissolved in dilute sulphuric acid. On addition of potassium-dichromate solution, a precipitate—green, blue, or black according to the concentration—is obtained. The black precipitate is called *aniline-black.*

7. **Acetoanilide.**—A mixture of 9 c.c. of aniline and a like volume of glacial acetic acid is boiled in a flask with a reflux-condenser for several hours. On cooling, crystals of acetoanilide ("antifebrine") are deposited. When recrystallized from a small quantity of alcohol, they melt at 112°.

8. **Carbylamine-Reaction.**—Aniline can be proved to be a primary amine by the carbylamine-reaction (**VII.**, 2).

9. **Diphenylamine.**—0·1 g. of diphenylamine is dissolved in a small quantity of alcohol, and water is carefully added until the liquid has become very turbid. The amine is now suspended in the liquid in a fine state of division, and can be dissolved by addition of concentrated hydrochloric acid

drop by drop. On dilution of this solution with water, the diphenylamine is reprecipitated, the hydrochloride undergoing hydrolytic dissociation.

10. **Nitrosodimethylaniline.**—1·4 g. of sodium nitrite dissolved in water is added gradually to a well-cooled solution of 2·4 g. of dimethylaniline in 12·5 g. of twenty per cent. hydrochloric acid. Yellow nitrosodimethylaniline hydrochloride is precipitated. It is collected on a filter, washed with dilute hydrochloric acid, and purified by crystallization from hot water. The salt is triturated with water, sodium hydroxide is added, and the green nitrosodimethylaniline liberated is dissolved in ether. On distilling the ether, the base is obtained in splendid, yellowish-green leaves. The crystals are boiled with sodium hydroxide, whereby dimethylamine is evolved, and the liquid becomes dark-red owing to the formation of sodium nitrosophenoxide. The dimethylamine can be identified by its characteristic odour, and its alkaline reaction to litmus.

11. **LIEBERMANN'S Test for Aromatic Nitroso-compounds.**—A few drops of concentrated sulphuric acid are added to a solution of 0·5 g. of nitrosodimethylaniline in phenol. After slight heating, the mixture is poured into water. Addition of sodium hydroxide produces a fine dark-blue colour.

12. **Azobenzene, Hydrazobenzene, and Benzidine Sulphate.**——A mixture of 2 c.c. of nitrobenzene and 20 c.c. of twenty per cent. alcoholic potash is gently warmed, and small quantities of zinc-dust added. In consequence of the formation of azobenzene, the liquid develops a red colour. On addition of more zinc-dust, the colour is discharged, and hydrazobenzene produced. When the liquid is poured into a quantity of dilute sulphuric acid sufficient to make it strongly acid, nearly insoluble benzidine sulphate is soon precipitated.

13. **Diphenylurea.**—1 g. of urea and 3 g. of aniline are heated in a test-tube to ebullition, and the evolution of ammonia proved by means of litmus-paper. When the reaction-mixture is cooled by pouring it into a dish, crystallization of diphenyl-

urea causes solidification. After elimination of excess of aniline by means of dilute hydrochloric acid, the residue is washed with water, and recrystallized from alcohol. The melting-point of the product should be 235°.

XXVIII. DIAZO-COMPOUNDS AND HYDRAZINES.

(305–310.)

1. **Benzenediazonium Chloride.**—9·3 g. of aniline are dissolved in about 100 c.c. of hydrochloric acid containing 9·2 g. of HCl. To this solution, maintained between 5° and 10° by the introduction of ice, is added very slowly a concentrated aqueous solution of 7·2 g. of commercial sodium nitrite, the liquid being stirred constantly. The solution of benzenediazonium chloride thus obtained is kept in a vessel surrounded by ice, and used for experiments 2, 3 and 4.

2. **Replacement of N_2-Group in Benzenediazonium Chloride by Hydroxyl.**—A small quantity of the solution of benzenediazonium chloride is warmed in a fractionating-flask connected with a condenser. When the evolution of nitrogen has ceased the solution is distilled, water and phenol passing over. The latter can be identified by its odour, and by reactions **XXVI.**, 4 and 5.

3. **GATTERMANN'S Reaction.**—A paste of finely-divided copper, obtained by sieving zinc-dust into a dilute solution of copper sulphate, is added to a portion of the solution of benzenediazonium chloride. Nitrogen is at once evolved with effervesence. On distilling the liquid with steam, chlorobenzene collects in the receiver.

4. **Diazoaminobenzene.**—Aniline is mixed with ten times its volume of water, and enough hydrochloric acid to give a clear solution. Addition of part of the solution of benzenediazonium chloride prepared in 1 and solid sodium acetate produces a yellow or brown precipitate of diazoaminobenzene.

5. **Aminoazobenzene.**—A small quantity of diazoaminobenzene is warmed gently with about twice its volume of

aniline and some solid aniline hydrochloride. Aminoazobenzene is formed. On addition of concentrated hydrochloric acid and solid salt, steel-blue needles of aminoazobenzene hydrochloride are obtained.

6. Oxidation of Phenylhydrazine by FEHLING'S Solution.—A drop of phenylhydrazine on a watch-glass is mixed with a small quantity of concentrated hydrochloric acid, phenylhydrazine hydrochloride, nearly insoluble in dilute hydrochloric acid, being formed. After pouring off the excess of hydrochloric acid, a small quantity of the salt is dissolved in water in a test-tube, and FEHLING'S solution (**XVI.**, 6) added. Reduction takes place at ordinary temperature, with formation of cuprous oxide, Cu_2O.

XXIX. BENZOÏC ACID AND ITS DERIVATIVES.

(311–313.)

1. Benzonitrile and Benzoïc Acid.—10 g. of sodium benzenesulphonate are mixed with a like weight of dried potassium ferrocyanide, and the mixture submitted to dry distillation in a retort connected with a condenser. Benzonitrile and a trace of phenylcarbylamine distil. The *iso*nitrile is decomposed by warming with two drops of concentrated hydrochloric acid. About 20 c.c. of ten per cent. potassium hydroxide are added, and the mixture is boiled in a flask with a reflux-condenser. Ammonia is evolved, as can be proved by red litmus-paper, while the oily layer of benzonitrile disappears. The flask is cooled, and concentrated hydrochloric acid added slowly; a white, flocculent precipitate of benzoic acid is deposited.

2. Benzoïc Acid from Gum-benzoïn.—*a*) 5 g. of finely-powdered gum-benzoïn are mixed with sand, and heated very gently in a porcelain dish on a sand-bath, care being taken to avoid fusion. The dish is covered with a hollow paper-cone, into which the benzoïc acid sublimes.

b) 5 g. of gum-benzoïn are boiled with milk of lime, the alkaline solution filtered, and hydrochloric acid added. Benzoïc acid is precipitated.

3. **Volatility of Benzoïc Acid with Steam.**—1 g. of benzoïc acid is heated with water in a fractionating-flask connected with a condenser. The acid volatilizes with the steam, and condenses as a white, flocculent precipitate, the distillate having an acid reaction.

4. **Solubility of Benzoïc Acid in Water.**—1 g. of benzoïc acid is heated gently in a test-tube with 1 c.c. of water. At first, two liquid layers are formed, and complete solution of the acid is only attained by boiling with a large excess of water. On cooling, it crystallizes in leaflets.

5. **Ethyl Benzoate.**—1 g. of benzoïc acid is warmed with 5 c.c. of absolute alcohol and a few drops of concentrated sulphuric acid. The ethyl benzoate formed is characterized by a peppermint-like odour.

6. **Benzanilide.**—A few cubic centimetres of water are added to 1 c.c. of aniline, and then alternately small quantities of potassium hydroxide and benzoyl chloride drop by drop. The mixture is agitated constantly, care being taken to maintain it alkaline. Finally, the alkaline liquid is agitated till the odour of benzoyl chloride is no longer perceptible. The white precipitate of benzanilide is collected on a filter, washed with water till the filtrate is no longer alkaline, and crystallized from alcohol. M. P. 158°.

7. **Benzamide.**—3 g. of ammonium carbonate are reduced to fine powder in a mortar, and benzoyl chloride added drop by drop, the mixture being stirred continuously with the pestle till the odour of benzoyl chloride is no longer perceptible. It is lixiviated with cold water to remove ammonium chloride and carbonate, and the residue dissolved in a small quantity of hot water. On cooling, benzamide crystallizes out. M. P. 128°.

This substance is identified by warming with dilute potassium hydroxide. Ammonia is evolved, and addition of hydrochloric acid to the alkaline solution precipitates benzoïc acid.

XXX. BENZALDEHYDE.

(**314** and **315**.)

1. **Silver-mirror Test.**—2 drops of benzaldehyde are added to an ammoniacal solution of silver nitrate, prepared as described in **X.**, 2. Gentle heating in a water-bath produces a silver mirror.

2. **Benzaldehydephenylhydrazone.**—A few drops of benzaldehyde are added to a solution of phenylhydrazine in sulphurous acid. Benzaldehydephenylhydrazone is precipitated, and by crystallization from alcohol is obtained in large, fine crystals, melting at 152°.

3. **Sulphite Compound of Benzaldehyde.**—A cubic centimetre of benzaldehyde is agitated with a very concentrated solution of sodium hydrogen sulphite. The crystalline sulphite compound is precipitated, and the odour of benzaldehyde ceases to be perceptible. On warming with water, the sulphite derivative is decomposed, and the benzaldehyde liberated.

4. **Action of Alcoholic Potash on Benzaldehyde.**—On mixing 1 c.c. of benzaldehyde with 5 c.c. of a ten per cent. solution of alcoholic potash, heat is developed, and the liquid solidifies owing to the precipitation of potassium benzoate. The crystals are collected on a filter, washed with a small quantity of alcohol, and dissolved in water. Addition of hydrochloric acid precipitates benzoïc acid. The alcoholic filtrate contains benzyl alcohol (**325**).

5. **Oxidation of Benzaldehyde.**—*a*) *By the Air.*—A few drops of benzaldehyde are placed upon a glass plate, and allowed to spread. On the following day, the aldehyde will be found to have changed completely into crystals of benzoïc acid.

b) *By Potassium Permanganate.*—A few drops of benzaldehyde are heated with an aqueous solution of potassium permanganate. Manganese dioxide is precipitated, the aldehyde being oxidized to benzoïc acid, which remains dissolved as potassium benzoate. When the odour of benzaldehyde is no longer perceptible, two drops of alcohol are added to reduce the excess of potassium permanganate, and the colourless liquid filtered. On acidifying the filtrate, benzoïc acid is precipitated.

XXXI. BENZENE HOMOLOGUES WITH SUBSTITUTED SIDE-CHAINS.

(321–325.)

1. **Saponification of Benzyl Chloride by Potassium or Sodium Hydroxide.**—1 c.c. of benzyl chloride is warmed for a short time with 10 c.c. of ten per cent. alcoholic potash or soda, and the mixture diluted with a large excess of water. If the heating has been of sufficient duration, no benzyl chloride separates. After acidifying with nitric acid, the solution gives with silver nitrate a heavy precipitate of silver chloride.

2. **Benzyl Iodide.**—A small quantity of benzyl chloride is heated with an alcoholic solution of potassium iodide in a fume-cupboard. Benzyl iodide is formed, and gives off an extremely irritating odour, productive of tears.

3. **Action of Light on Toluene in Presence of Bromine.**—10 c.c. of toluene are poured into a test-tube, and a few drops of bromine added. In daylight, near a window, the mixture becomes decolorized in a few minutes, gaseous hydrobromic acid being evolved.

4. **Resinification of Benzyl Alcohol.**—Concentrated sulphuric acid is added to a few drops of benzyl alcohol. An ester is not formed, but the alcohol becomes resinified.

XXXII. COMPOUNDS CONTAINING AN UNSATURATED SIDE-CHAIN.

(328.)

1. **Oxidation of Cinnamic Acid by Potassium Permanganate.**—0·1 g. of cinnamic acid is agitated with water, and several drops of a one per cent. solution of potassium permanganate added. The colour of the solution is discharged, a precipitate of hydrated manganese dioxide formed, and the liquid acquires an odour of benzaldehyde.

XXXIII. POLYSUBSTITUTED BENZENE DERIVATIVES.

(329–350.)

1. **Reactivity of the Halogen Atom in Halogen Nitro-compounds.**—0·1 g. of picryl chloride is boiled with water for a few minutes. After acidification with nitric acid, the presence of chlorion is detected by addition of a solution of silver nitrate.

2. ***m*-Dinitrobenzene.**—1·5 c.c. of benzene are added drop by drop to a mixture of 5 c.c. of concentrated sulphuric acid and 5 c.c. of fuming nitric acid, the liquid being agitated thoroughly during the process. The solution is heated for a few minutes, allowed to cool, and poured into water. *m*-Dinitrobenzene is precipitated, and is freed from a small percentage of the *ortho*-compound and traces of the *para*-compound by crystallization from alcohol. M. P. 90°.

3. **Reactivity of One Nitro-group in 1:3:5-Trinitrobenzene.**—0·1 g. of 1:3:5-trinitrobenzene is dissolved in boiling methyl alcohol, and a few drops of sodium-methoxide solution are added. The liquid immediately becomes blood-red, and, after an interval, long colourless needles of 3:5-dinitroanisole separate.

4. **Nitrophenols.**—3 c.c. of phenol, liquefied by addition of a small quantity of water, are added slowly to 18 c.c. of nitric acid of 1·17 specific gravity. During the process, the mixture is cooled, and agitated vigorously. A heavy, black oil separates from the aqueous liquid. After washing with water in a small separating-funnel, the oil is distilled with steam (III., 2). *o*-Nitrophenol distils, and can be identified by its odour, and by its yellow crystals melting at 44°. The residue in the flask contains *p*-nitrophenol.

5. **Coloured Salts of *p*-Nitrophenol.**—0·1 g. of colourless *p*-nitrophenol is dissolved in a dilute solution of sodium hydroxide. The liquid has an intense yellow colour.

6. **Picric Acid.**—On carefully heating 0·1 g. of picric acid in a test-tube, the acid melts and sublimes; more rapid heating causes explosive decomposition, leaving a residue of carbon. At the same time, an odour resembling that of nitrobenzene becomes perceptible.

7. **Potassium Picrate.**—Potassium-hydroxide solution is added to an alcoholic solution of 0·5 g. of picric acid. Bright-yellow potassium picrate is precipitated, collected on a filter-paper, and dried by exposure to the air. The dry salt is exploded by percussion, and by heating on a platinum or porcelain crucible-lid. *Only a very minute quantity of the salt must be used for this experiment.*

8. **Taste of Picric Acid.**—0·1 g. of picric acid is dissolved in water; the solution thus obtained has a very bitter taste.

9. **Dyeing with Picric Acid.**—A woollen thread immersed in the liquid is soon dyed bright-yellow.

10. ***iso*Purpuric Acid.**—An aqueous solution of potassium cyanide is added to one of picric acid. A purple coloration, due to the formation of the potassium salt of *iso*purpuric acid, is produced.

11. **Chloropicrin.**—0·5 g. of picric acid is warmed carefully with a solution of bleaching-powder. The pungent odour of chloropicrin, CCl_3NO_2, becomes perceptible.

12. **Ionization of Picric Acid in Aqueous Solution.**—On warming a small quantity of picric acid with light petroleum in a test-tube, a colourless solution is obtained, the acid not being ionized in this solvent. When, however, this colourless solution is agitated with a small quantity of water, the latter acquires the deep-yellow colour characteristic of the anion of picric acid.

13. **Tests for Catechol, Resorcinol, and Quinol.**—With a drop of ferric chloride, aqueous solutions of catechol and resorcinol give a green and a deep-violet coloration respectively. With bromine-water, resorcinol yields a precipitate of tribromoresorcinol.

Solutions of catechol and resorcinol are made alkaline with sodium hydroxide. They acquire a dark colour immediately.

Addition of ammonium hydroxide to a solution of quinol turns it red-brown.

14. **Reducing Power of the Dihydroxybenzenes.**—At ordinary temperature, solutions of catechol and quinol reduce a solution of silver nitrate, with precipitation of metallic silver as a black powder. Quinol also reduces FEHLING's solution.

15. **Pyrogallol.**—On carefully heating 5 g. of well-dried gallic acid in a retort, carbon dioxide—which can be identified by the lime-water test—is evolved, and pyrogallol sublimes. The latter is dissolved in water, and the solution divided into three parts.

When silver-nitrate solution is added to one, metallic silver is precipitated.

Addition of a drop of ferric chloride to the second produces an intense bluish-black coloration.

The third portion is transferred to a thick-walled test-tube, potassium hydroxide added, the tube closed with a closely-fitting cork or rubber-stopper, and the mixture vigorously agitated. The oxygen in the tube is absorbed, the pyrogallol-solution turning brown. On removing the stopper under water, the latter rises in the tube.

16. **Benzoquinone.**—A small quantity of potassium-dichromate solution and a drop of concentrated sulphuric acid are added to a drop of aniline in a dish. The pungent odour of benzoquinone is perceived.

17. **Quinhydrone.**—A solution of ferric chloride is added to an aqueous solution of quinol. After an interval of time, quinhydrone crystals of beautiful metallic lustre separate.

18. **Difference in Basicity of the Three Nitroanilines.**—0·5 g. of *o*-nitroaniline, *m*-nitroaniline, and *p*-nitroaniline respectively are dissolved in about the same quantity of concentrated sulphuric acid, and the solutions poured into about 100 c.c. of water. *o*-Nitroaniline separates almost completely, indicating a high degree of hydrolysis; *p*-nitroaniline gives a yellow colour, due to slight hydrolysis; the solution of *m*-nitroaniline is colourless, owing to absence of hydrolysis.

19. **Reactivity of the Amino-group in Picramide.**—0·1 g. of picramide is warmed with a dilute solution of sodium hydroxide. The formation of ammonia is proved by testing with a moistened strip of red litmus-paper.

20. ***p*-Diazobenzenesulphonic Acid.**—1·7 g. of sulphanilic acid, $NH_2 \cdot C_6H_4 \cdot SO_2OH$ (1 : 4), are dissolved by heating with 25 c.c. of two per cent. sodium hydroxide. A concentrated aqueous solution of 1 g. of sodium nitrite is added, and the mixture poured into excess of cold, dilute sulphuric acid. After an interval, *p*-diazobenzenesulphonic acid is precipitated as a sand-like, crystalline powder.

21. **Oxidation of Aminophenols.**—0·1 g. of *p*-aminophenol hydrochloride is dissolved in water, and a solution of sodium hydroxide added. Owing to atmospheric oxidation, the liquid rapidly becomes brown in colour.

22. **Test for Nitrous Acid with *m*-Phenylenediamine.**—A drop of a solution of sodium nitrite and a drop of dilute sulphuric acid are added to 10 c.c. of a dilute solution of *m*-phenylenediamine. The liquid becomes brown, Bismarck-brown or vesuvine being formed.

23. **Dyeing with Aminoazobenzene.**—An alcoholic solution of aminoazobenzene is diluted with water, and a few drops of dilute hydrochloric acid added. A woollen thread immersed in the liquid for a quarter of an hour is dyed yellow, and the colour cannot be removed by washing with water.

24. **Reduction of Aminoazobenzene.**—A small quantity of aminoazobenzene hydrochloride is brought into contact with tin and hydrochloric acid. It is decolorized, yielding *p*-phenylenediamine and aniline. The mixture is made strongly alkaline with sodium hydroxide, and distilled, using a condenser. The presence of aniline in the distillate can be proved by the bleaching-powder test (**XXVII.**, 5).

25. **Taste of "Saccharin."**—0·1 g. of "saccharin" is dissolved in 1 litre of water, and 30 g. of sucrose are dissolved in a similar volume. When tasted, both solutions are found to have nearly the same degree of sweetness.

26. **Salicylic Acid.**—0·5 g. of salicylic acid is heated gently in a test-tube; it melts, and sublimes. On heating to a higher temperature, it decomposes partly into carbon dioxide and phenol, the characteristic odour of the latter becoming perceptible.

27. **Action of Bromine-water on Salicylic Acid.**—Bromine-water added to a saturated solution of salicylic acid gives a precipitate of the formula $C_6H_2Br_3 \cdot OBr$.

28. **Identification of Salicylic Acid and Phenol.**—Ferric chloride is added to alcoholic and aqueous solutions of salicylic acid and phenol respectively. Salicylic acid gives the violet coloration in both solvents, phenol only in water.

29. **Calcium Salicylate.**—0·5 g. of salicylic acid is added to a mixture of calcium-chloride solution and ammonium hydroxide. On heating, calcium salicylate, $C_7H_4O_3Ca,H_2O$, is precipitated.

30. **Manufacture of Ink.**—1 g. of gallic acid is dissolved in water, and a solution of ferrous sulphate added. When employed as an ink, this liquid leaves a very faint mark on the paper, but on drying the writing becomes black.

31. **Action of Tannin on Gelatin.**—A solution of tannin is added to one of gelatin. The gelatin is precipitated.

32. **Test for Tannin.**—A dilute solution of tannin is turned dark-violet by a drop of ferric chloride. A piece of oak-bark or cinchona-bark, an unroasted coffee-bean, and part of a gall-nut are extracted with boiling water in different dishes. The presence of tannin in all these solutions can be proved by the ferric-chloride test.

33. **Action of Tannin on Quinine.**—On addition of a solution of tannin to one of quinine hydrochloride, the alkaloid is precipitated.

34. **Interaction of Proteïns and Tannin.**—10 c.c. of milk are freed from caseïn and fat by the method described in **XVIII.**, 17. The presence of proteïns in the filtrate can be proved by adding tannin, an insoluble compound of the proteïns and tannin being precipitated.

35. **Decomposition of Anthranilic Acid.** — 0·2 g. of dry anthranilic acid is heated in a test-tube. Part of it sublimes, and part decomposes with evolution of carbon dioxide, and formation of oily drops of aniline.

36. **Phthalic Anhydride.**—0·1 g. of phthalic acid is heated in a dish, covered with a watch-glass, on a sand-bath. Long needles of phthalic anhydride sublime.

37. **Fluoresceïn.**—Some crystals of phthalic anhydride and a like quantity of resorcinol are heated for a few minutes with 1 c.c. of concentrated sulphuric acid. To prevent the liquid becoming dark-coloured, the heating must not be too prolonged, or the temperature too high. On dissolving the mixture in 100 c.c. of water and adding sodium hydroxide, a beautifully fluorescent, yellowish-green solution containing fluoresceïn is obtained.

38. **Phenolphthaleïn.**—A mixture of like quantities of phthalic anhydride and phenol is warmed with concentrated sulphuric acid, phenolphthaleïn being formed. When this is added to a dilute solution of a caustic alkali, a red coloration is produced.

39. **Red Anion of Phenolphthaleïn.**—A few milligrammes of phenolphthaleïn are dissolved in absolute alcohol containing a trace of calcium hydroxide in suspension; the liquid remains colourless. On dilution with water, the calcium compound of the phthaleïn is ionized, with production of a red colour.

XXXIV. HYDROCYCLIC COMPOUNDS.

(365–370.)

1. **Artificial Camphor.**—American or German oil of turpentine is dried by calcium chloride, poured off, and distilled. Being turbid, the first few cubic centimetres of the distillate are rejected. Dry hydrochloric-acid gas, prepared by the method of **IX.**, 15, is led into 10 c.c. of the dry, quite clear turpentine, the flask being cooled by ice. After some time, transparent crystals of pinene hydrochloride or "artificial camphor," $C_{10}H_{16},HCl$, are deposited. The mother-liquor is poured off, and the crystals dried by pressing between layers of filter-paper. In odour and appearance pinene hydrochloride resembles camphor.

2. **Volatility of Camphor with Steam.**—A piece of camphor is placed in water in a fractionating-flask connected with a condenser. On heating, the camphor passes over with the steam.

3. **Camphor and Water.**—A piece of camphor thrown upon the surface of water acquires a rotatory motion, due to disparity of the vapour-tension for the different crystal faces.

4. **Camphoric Acid.**—2 g. of camphor are heated in a flask with dilute nitric acid for some minutes, and evaporated almost to dryness in a porcelain dish. The residue is diluted with water, made alkaline with sodium hydroxide, and the undissolved portion filtered off. If the filtrate is not too dilute, hydrochloric acid precipitates camphoric acid.

XXXV. BENZENE-NUCLEI LINKED TOGETHER BY CARBON.

(371–374.)

1. **Rosolic Acid.**—A mixture of 2 c.c. of phenol, 0·5 g. of oxalic acid, and 5 c.c. of concentrated sulphuric acid is heated in a test-tube. It acquires a red colour. On pouring the liquid into water, and making it alkaline with potassium hydroxide, a dark-red solution is obtained, containing the potassium salt of rosolic acid.

2. **Magenta.**—1 c.c. of aniline is heated in a test-tube with 1 g. of *p*-toluidine and 0·5 g. of mercuric chloride, magenta being formed. On pouring the liquid into water containing a small quantity of hydrochloric acid, a deep-red solution is produced.

3. **Action of Concentrated Hydrochloric Acid on a Solution of Magenta.**—Concentrated hydrochloric acid is added to part of the solution obtained in 2. The liquid becomes yellow, owing to the formation of the hydrochloride of the rosaniline base containing 3HCl. When this is poured into a large quantity of water, the red colour is restored.

4. **Colour-base.**—Excess of solution of ammonium or potassium hydroxide is added to another portion of the magenta solution. The colour-base is formed, and the liquid decolorized.

5. **Leuco-base.**—A third portion of the magenta solution is treated with zinc and hydrochloric acid, without the application of heat. The leuco-base is formed, and the colour discharged.

XXXVI. CONDENSED BENZENE-NUCLEI.

(377–385.)

1. **Action of Heat on Naphthalene.**—0·5 g. of naphthalene is heated in a test-tube. It melts, and sublimes readily.

2. **Naphthalene Picrate.**—3 c.c. of a concentrated ether solution of picric acid are mixed with a like volume of a concentrated solution of naphthalene in that solvent. A yellow, crystalline precipitate of naphthalene picrate is produced.

3. **Naphthalenemonosulphonic Acids.**—A mixture of 0·5 g. of naphthalene and 2 c.c. of concentrated sulphuric acid is heated in a test-tube for a few minutes, allowed to cool, and poured into water. On treatment with barium carbonate by the method of **VI.**, 2, the presence of the dissolved sulphonic acids is proved.

4. **α-Nitronaphthalene.**—1 g. of naphthalene is dissolved in 5 c.c. of concentrated nitric acid, and the solution poured into water. The precipitated yellow α-nitronaphthalene is crystallized from a small quantity of alcohol, being obtained in yellow needles, melting at 61°.

5. **Crude Naphthol.**—0·5 g. of naphthol is agitated with water; only a small quantity dissolves. On addition of potassium or sodium hydroxide, a solution is obtained, from which carbon dioxide reprecipitates the naphthol.

6. **Martius's Yellow.**—1 g. of α-naphthol is dissolved in 3 c.c. of concentrated sulphuric acid, and the solution poured into 3 c.c. of concentrated nitric acid. When this mixture is diluted with water, dinitro-α-naphthol is precipitated. It is filtered off, washed, transferred to a vessel containing water, and dissolved by addition of a small quantity of sodium hydroxide, with formation of the sodium salt, Martius's yellow. A woollen thread dipped into this solution becomes dyed deep-yellow.

7. **Naphthylamines.**—0·5 g. of α-naphthylamine is dissolved in dilute hydrochloric acid. With ferric chloride this solution gives a blue precipitate. A similar solution of pure β-naphthylamine does not react thus.

8. **Congo-red.**—A few centigrammes of congo-red are placed in water, and a drop of concentrated hydrochloric acid added. The liberated acid turns the liquid blue; addition of an alkali restores the red colour.

9. **Naphthionic Acid.**—A mixture of 1 g. of α-naphthylamine and 3 c.c. of concentrated sulphuric acid is heated in a test-tube for a few minutes, and poured into water. On making the liquid alkaline with sodium hydroxide, it exhibits an intense reddish-blue fluorescence, resulting from the formation of sodium naphthionate.

10. **Oxidation of Anthracene by Chromic Acid.**—Small quantities of an acetic-acid solution of chromic acid are added to a solution of 3 g. of anthracene in this solvent, until the energetic reaction has ceased. The liquid is poured into water, and the precipitated anthraquinone collected on a filter.

11. **Test for Anthraquinone.**—A few centigrammes of anthraquinone are heated in a test-tube with zinc-dust and sodium hydroxide, a deep blood-red solution of anthraquinol being formed. On agitating this solution with air, the colour is discharged.

12. **Potassium Salt of Alizarin.**—A few centigrammes of alizarin are placed in water, but the substance does not dissolve. On addition of a dilute solution of potassium hydroxide, the very intense deep-blue colour of the potassium salt is developed.

XXXVII. HETEROCYCLIC COMPOUNDS.

(387–399.)

1. **Pyridine.**—Some drops of pyridine are added to a few cubic centimetres of water, the base dissolving completely. The solution has an alkaline reaction.

2. **Action of Pyridine on Ferric Chloride.**—The aqueous solution of pyridine gives with one of ferric chloride a precipitate of ferric hydroxide.

3. **Action of Pyridine on Mercuric Chloride.**—A solution of mercuric chloride added to a pyridine solution precipitates a white, crystalline compound of pyridine and mercuric chloride.

4. **Test for Pyridine.**—Hydrochloroplatinic acid, H_2PtCl_6, is added to a small quantity of a solution of pyridine; no precipitate is formed. On boiling the mixture for a short time, a yellow powder of the formula $PtCl_4(C_5H_5N)_2$ is deposited. This test is characteristic for pyridine.

5. **Action of the Alkaloid-reagents on Pyridine.**—The alkaloid-reagents (**407**)—among them tannin, phosphomolybdic acid, and picric acid—precipitate pyridine from solution.

6. **Stability of Pyridine towards VON BAEYER'S Reagent.**—A solution of potassium permanganate and sodium carbonate is added to one of pyridine. The violet-red colour is not altered.

7. **Stability of Pyridine towards Oxidizing Agents.**—A solution of pyridine is heated with sodium or potassium dichromate and concentrated sulphuric acid. The colour of the solution undergoes no change.

8. **Pyrrole-red.**—Water is added to a small quantity of "Dippel's oil" (**387**) in a test-tube, and the mixture boiled. A wood-splint moistened with concentrated hydrochloric acid becomes coloured red by the vapour, pyrrole-red being formed.

9. **Indophenin-reaction.**—A cubic centimetre of crude benzene and a like volume of concentrated sulphuric acid are

brought into contact with a fragment of isatin. In presence of thiophen, the layer of sulphuric acid develops an intense blue colour.

10 c.c. of crude benzene are agitated repeatedly with warm, concentrated sulphuric acid, about 2 c.c. being used for each operation. The benzene is separated, and tested by the indophenin-reaction. Either the blue coloration is not produced, or it is much less pronounced than in the first experiment.

10. **Tests for Antipyrine.**—A solution of antipyrine is turned red by ferric chloride, bluish-green by potassium or sodium nitrite and acetic acid.

XXXVIII. CONDENSATION-PRODUCTS OF BENZENE AND HETEROCYCLIC NUCLEI.

(400–405.)

1. **SKRAUP'S Synthesis of Quinoline.**—A mixture of 4 c.c. of aniline, 12 c.c. of glycerol, 2·5 c.c. of nitrobenzene, and 6 c.c. of sulphuric acid is heated carefully in a flask till the reaction begins, the burner being then removed. When it has moderated, the heating is resumed, and continued for five or ten minutes. The liquid is cooled, poured into water, and distilled with steam (III., 2) after addition of excess of sodium hydroxide. The turbidity of the distillate is caused by the presence of minute drops of quinoline. The characteristic odour of the base is perceived.

2. **Quinoline Hydrochloride.**—On addition of hydrochloric acid to the distillate obtained in 1, the liquid becomes clear, soluble quinoline hydrochloride being formed. Sodium or potassium hydroxide reprecipitates the quinoline in oily drops.

3. **Quinoline Picrate.**—With a solution of quinoline hydrochloride, a saturated, aqueous solution of picric acid gives a yellow, amorphous precipitate of quinoline picrate.

4. **Quinoline Dichromate.**—With quinoline salts, potassium dichromate gives a yellow, crystalline precipitate of quinoline dichromate, $(C_9H_7N)_2H_2Cr_2O_7$.

5. **Volatility of Indigo.**—On heating 0·1 g. of indigo in a test-tube, a violet vapour is formed.

6. **Solubility of Indigo in Nitrobenzene.**—0·1 g. of indigo is heated with a small quantity of nitrobenzene. It dissolves, and, on cooling, crystallizes.

7. **Indigosulphonic Acid.**—0·1 g. of indigo is dissolved in 1 c.c. of fuming sulphuric acid. Indigosulphonic acid is formed, so that the indigo is not reprecipitated when the solution is poured into water.

8. **Oxidation of Indigo to Isatin.**—The solution of indigosulphonic acid obtained in 7 is warmed with a small quantity of concentrated nitric acid. It is decolorized, and isatin formed.

9. **"Vat-dyeing."**—0·1 g. of powdered indigo is heated with a solution of sodium hyposulphite, $Na_2S_2O_4$ ("Inorganic Chemistry," **83**). Sodium thiosulphate, miscalled "sodium hyposulphite," must not be used. A strip of linen or cotton is immersed in the solution of indigo-white, and hung up to dry. The oxygen of the atmosphere oxidizes the indigo-white to indigo-blue.

XXXIX. ALKALOIDS.

(**406–415.**)

1. **Alkaloid-reagents.**—A solution of an alkaloid, such as quinine hydrochloride or sulphate, is tested with solutions of the ordinary alkaloid-reagents; for example, tannin, phosphomolybdic acid, mercuric potassium iodide, and a solution of iodine in one of potassium iodide. With each a precipitate is formed.

2. **Nicotine.**—10 g. of tobacco are boiled with 100 c.c. of water containing a small quantity of sulphuric acid. After

filtering, the filtrate is rendered alkaline, and distilled. The distillate contains nicotine, and yields precipitates with platinum chloride, mercuric chloride, and a potassium-iodide solution of iodine.

3. **Fluorescence of Quinine-sulphate Solution.**—0·1 g. of quinine sulphate is dissolved in water containing sulphuric acid. The solution exhibits a blue fluorescence.

4. **Action of Chlorine on Quinine Salts.**—Chlorine-water is added to a solution of a quinine salt until the liquid smells strongly of the gas. On addition of ammonium hydroxide, an emerald-green coloration is produced.

5. **Test for Strychnine.**—A crystal of strychnine nitrate is placed in a porcelain dish, and a few drops of concentrated sulphuric acid added. A small crystal of potassium dichromate produces with this liquid a very intense bluish-violet colour.

6. **Test for Brucine.**—A small quantity of brucine yields a red coloration with concentrated nitric acid; on the application of gentle heat, the colour changes to yellow. Dilution with water, and addition of ammonium sulphide renders the yellow solution violet.

INDEX.

The basis of the arrangement of this index is threefold:

(1) The numbers refer to pages.

(2) In all instances of possible ambiguity as to the identity of the principal references, they are given in old-style figures.

(3) Where a reference is a sub-division of a principal heading, it is indented one *em space* for each word of the principal heading not repeated. Portions of words followed by a hyphen are treated as words for the purposes of this arrangement.

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$CHCl_3$

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