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PRACTICAL ORGANIC CHEMISTRY

Companion Volume

A TEXTBOOK OF ORGANIC CHEMISTRY

The English Translation from the German of

A. BERNTHSEN, Ph.D.

New edition, edited and revised to date by J. J. SUDBOROUGH, Ph.D., D.Sc., F.I.C., Professor of Organic Chemistry in the Indian Institute of Science, Bangalore.

BLACKIE & SON, LTD., LONDON, GLASGOW, BOMBAY

PRACTICAL ORGANIC CHEMISTRY

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BLACKIE AND SON LIMITED
50 OLD BAILEY, LONDON; GLASGOW, BOMBAY
1924

First issued 1909.
Reprinted 1912, 1915, 1917, 1918, 1920 (with alterations), 1921, 1922, 1924 (with alterations).

Printed and bound in Great Britain

PREFACE

This work is a companion book to Sudborough's Edition of Bernthsen's *Organic Chemistry*. It gives examples of the more important types of operations employed in a modern organic laboratory.

The number of experiments given is large, and a single student cannot be expected to perform each experiment. Our own experience is that greater interest is taken by students in their work when different experiments are set to different students. It is not necessary that each student should perform the same example of nitration, sulphonation, reduction, esterification, conductivity, &c.

Our work differs from most laboratory textbooks on Organic Chemistry in being more comprehensive It is not merely an account of the preparation of typical organic compounds; it includes typical preparations, common laboratory operations, equivalent and molecular weight determinations, and numerous simple quantitative experiments with carbon compounds, and indicates the methods to be adopted in identifying the different types of carbon compounds. In addition some of the common physical methods used in the study of carbon compounds are discussed.

J. J. SUDBOROUGH.
T. CAMPBELL JAMES.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH, *December*, 1908.

NOTE TO THE PRESENT EDITION

In this edition the opportunity has been taken to carry out alterations to keep the book in touch with recent advance in the science.

June, 1924.

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ABBREVIATIONS

A.	Liebig's Annalen der Chemie.
A. Supp.	Supplement to Liebig's Annalen der Chemie.
A. Ch. Ph.	Annales de Chimie et Physique
Am.	American Chemical Journal
B.	Berichte der Deutschen Chemischen Gesellschaft.
B A. Rep.	British Association Reports
Bull.	Bulletin de la Société Chimique de France.
C.	Chemisches Zentralblatt.
C. N.	Chemical News.
C. R.	Comptes Rendus de l'Academie des Sciences.
C. Z.	Chemische Zeitung.
Gazz.	Gazzetta chimica italiana
J.	Jahresberichte der Chemie
J. A. C. S.	Journal of the American Chemical Society.
J. C. S.	Journal of the Chemical Society.
J. pr.	Journal für praktische Chemie.
J. R. C. S.	Journal of the Russian Chemical Society.
J. S. C. I.	Journal of the Society of Chemical Industry.
L.-C.	Lassar-Cohn's Arbeits-methoden der Organische-Chemie IV Auflage.
M.	Monatshefte für Chemie.
P.	Proceedings of the Chemical Society.
Rec.	Recueil des Travaux Chimiques des Pays-Bas.
S. B.	Sudborough's edition of Bernthsen's Organic Chemistry.
Trans.	Transactions of the Royal Society.
T. R. S. E.	Transactions of the Royal Society of Edinburgh.
Z.	Zeitschrift für physikalische Chemie.
Z. A.	Zeitschrift für analytische Chemie.
Z. E.	Zeitschrift für Electrochemie.
Z. physiol.	Zeitschrift für physiologische Chemie.
D. R.-P.	Deutsch Reich-Patente.
d.	dextro.
l.	lævo.
dl.	mixture of equal parts of *d.* and *l.*

o.	ortho.
m.	meta.
p.	para.
s.	symmetrical.
as.	asymmetrical.
Ac.	Acetyl, $CH_3.CO$.
Et.	Ethyl, C_2H_5.
Me	Methyl, CH_3
Ph.	Phenyl, C_6H_5.
R.	Alkyl Radical.
n	normal.

WARNING

1. **Fire.**—The student commencing the study of Organic Chemistry is apt to forget that most of his solvents and crystallizing media are highly inflammable. Thus the vapours of ether, light petroleum, carbon disulphide, acetone, alcohol, benzene, toluene, and glacial acetic acid are all inflammable. The risk of a fire is considerably increased when the liquid used is very volatile, as part of the vapour may then escape condensation and take fire when coming into contact with a flame One of the most dangerous liquids is carbon disulphide, as its vapour bursts into flame when brought into contact with a moderately hot surface, even in the absence of a naked light.

A wise precaution is to distil large quantities of ether, carbon disulphide, light petroleum, or acetone on a water bath heated by steam in a room in which no naked flames are allowed. If this is not possible the water bath should be heated by a flame, and the flame extinguished before the flask containing the volatile liquid is placed on the water bath. Another convenient method is to surround the flame by a wire cage (fig. 2, *d*), much in the same manner as in the Davy safety lamp. The vapour is condensed by means of a long condenser kept cool by means of running water (fig. 2, *b*).

2. **Dry Vessels.**—In many reactions good yields of products can only be obtained in the absence of water, and it is thus essential to have all the vessels, *e.g.* flasks, beakers, condensers, &c., quite dry. In other cases solvents are used which are not miscible with water, and it is essential that in such experiments dry vessels should be used. A very simple plan is to wash each vessel after use, and to allow it to drain in a rack, as a rule it will then be dry and ready for use when required. A quicker method of drying vessels is to wash with water, then with alcohol, and to blow air through the warm vessel.

3. **Yields.**—An important point in all preparations is the

question of yield. The most successful operator is he who obtains the best yield of pure product. An error made by many students is to use an unnecessarily large number of vessels, and not troubling to remove as much as possible of the reacting mixture from the one vessel to the other. If a small residue, *e.g.* 2–3 per cent, of the total mixture is left in each vessel, the final yield of product will be considerably diminished.

PRACTICAL ORGANIC CHEMISTRY

I. COMMON METHODS OF PURIFICATION

Before a detailed investigation of an organic compound is undertaken—whether this investigation be a determination of its composition and molecular weight, or an examination of its chemical and physical properties—it is essential that the compound should be pure. Some of the commoner methods of purification employed in the organic laboratory are described in this chapter

A. Extraction with Ether and other Solvents

A method frequently resorted to in order to separate organic from mineral compounds is the process of shaking out with ether (S. B. 28).* Other solvents, such as chloroform and benzene, which are not miscible with water, are used occasionally. The method consists in shaking the aqueous liquid with a given volume of ether in a separating funnel (fig. 1), allowing the two liquid layers to separate, running off the lower aqueous layer by means of the tap at the bottom, and then pouring out the ethereal layer through the neck. By this means a complete separation of the two solutions can be effected. In all cases the aqueous liquid should be extracted a second time with ether, and the ethereal solution added to the first extract. The number of extractions necessary varies considerably with different substances, and depends on the relative solubilities of the substance in water and in ether.

Fig 1

* This refers to p. 28 in Sudborough's Edition of Bernthsen's *Organic Chemistry.*

For any given substance the ratio (*the distribution coefficient*)

$$\frac{\text{concentration of ethereal solution}}{\text{concentration of aqueous solution}}$$

is constant for any given temperature, provided the substance has the same molecular weight in the two solvents, and depends on the relative solubilities of the solute in the two solvents.

The number of times a given aqueous solution should be extracted with ether depends on this ratio, and when the ratio is small, as in the case of succinic acid, the operation must be repeated a number of times.

Experiment 1.—Make a saturated aqueous solution of succinic acid at 15° (cf. Solubility, Chap. III). Determine the concentration of this solution by titration with standard alkali, preferably barium hydroxide (Chap. VI, A), using phenol phthalein as indicator. Shake up the solution for some time with half its volume of ether at 15°, determine the distribution coefficient at this temperature, and then calculate how much of the acid will have been removed when the aqueous solution has been extracted 10 times, if in each extraction the volume of ether is equal to half the volume of the aqueous solution.

Theoretically the extraction is never complete, but in practice the amount remaining in the aqueous solution after several extractions is usually so minute that it may be neglected. The ethereal extract is dried by means of some suitable drying agent, the one most frequently used being granular anhydrous calcium chloride, this, however, cannot be employed if the ethereal solution contain an alcohol or an amine, as these form additive compounds with metallic chlorides. In such cases solid potassium hydroxide or anhydrous sodium sulphate may be used. The dry solution is decanted or filtered from the drying material, and the ether removed by distillation (cf. Warning). The product thus obtained may be further purified by the methods described later. Some points deserving of notice in regard to ether extractions are:—

(1) The metallic salts of acids and the salts of amines cannot, as a rule, be extracted from aqueous solutions by means of ether, although in many cases the acids and bases themselves are readily extracted.

(2) Certain metallic salts, especially halide salts, *e.g.* ferric chloride, stannous chloride, mercuric chloride, mercuric iodide, and also chromic anhydride, are fairly readily soluble in ether.

(3) Ether is soluble in water to an appreciable extent (8·1

per cent), and also water in ether, the aqueous layer which is drawn off is thus always saturated with ether. If the volume of the aqueous liquid is considerable, then the loss of ether due to its solubility is appreciable. This loss may be avoided, to a large extent, by previously saturating the aqueous liquid with common salt, as ether is less soluble in saturated sodium chloride solution than in water. The aqueous solution after extraction should not be heated over a free flame, as the ether vapour which is given off is highly inflammable (see Warning).

(4) If the ethereal solution is not dried before the ether is removed by distillation, the residue obtained contains appreciable amounts of water.

(5) As a rule it is best to use relatively small amounts of ether, as otherwise the distillation of the ether takes some time. If a number of extractions of the same solution have to be made, the volume of the ethereal extracts is usually large. To avoid using a very large flask when distilling off the ether, it is customary to run the dried ethereal extract into a small flask in portions by means of a dropping funnel (see fig. 2, *e*).

(6) When it is desired to make a quantitative estimation of the amount of product extracted, all the vessels, and also the calcium chloride used for drying the ethereal extract, should be thoroughly washed with ether, the ether removed from the total extract by slow distillation from a tared flask, and the residue finally dried in a desiccator. This method can be used with success only when the extracted matter is not readily volatile.

(7) In certain cases the ether and aqueous liquid tend to form an emulsion, and will not readily separate into two distinct layers. The addition of a small amount of alcohol will often bring about the separation.

B. Distillation

Liquids are commonly purified by the process of distillation, but the method is of use only when the substance boils without decomposition. By this means a substance may be freed from a non-volatile impurity, or from substances which are much more or much less readily volatile than the compound to be purified (see Fractional Distillation). In the majority of cases the distillation is carried out under atmospheric pressure,

but in cases where the compound decomposes when heated under atmospheric pressure, but is volatile without decomposition under reduced pressure, the process of distillation under reduced pressure (see p. 7) may be used.

The ordinary process of distillation consists in boiling the liquid, usually in a glass vessel termed the *distillation flask* (*a*), condensing the vapour thus produced by means of a cool surface (*the condenser*, *b*), and collecting the condensed product in a *receiver*, *c* (see fig 2) The distillation flask is usually a round-bottomed flask with a side tube fused into the neck,

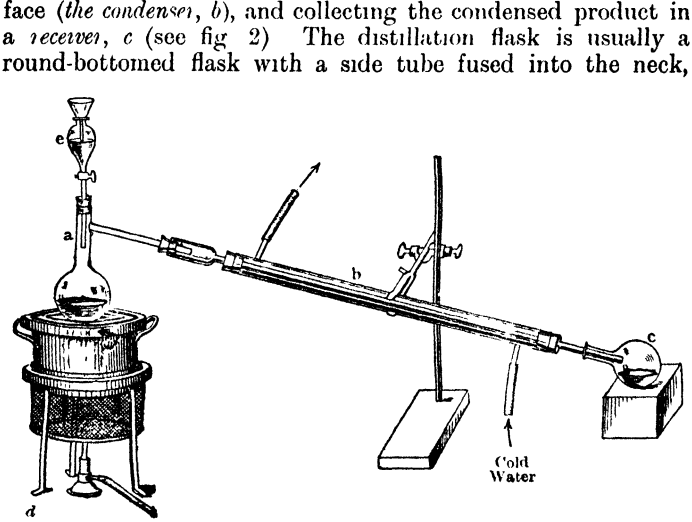

Fig 2

the neck is fitted with a cork which carries the thermometer, and the side tube is fitted to the condenser by means of another cork. It is essential that this connection between flask and condenser should be tight, as otherwise a considerable portion of the vapour will not be condensed. In the majority of cases an ordinary Liebig condenser, *i.e.* a glass tube cooled by an outer jacket of running water, may be used; when the boiling-point of the substance is above 170° there is considerable risk that the inner condenser tube will crack, and an air condenser is therefore employed (cf. fig. 79). This consists of a straight glass tube similar to the inner tube of a Liebig condenser, and is cooled by contact with the surrounding air. When the boiling-point is very high, and only a small amount of liquid has to be distilled, a short air con-

denser made from a test tube may be used (fig. 3). Some points of interest in connection with distillation are:—

(1) For high temperatures a round-bottomed flask should always be used. This may be heated directly with a small flame or by means of a small metal bath made of a readily fusible alloy, *e g.* Wood's metal (Bi 4, Pb 2, Sn 1, Cd 1 parts).

(2) The main fraction which distils within a range of 2–3° should be collected separately, and may be further purified by a second distillation.

(3) In clamping a flask in which a substance of high boiling-point is being distilled the clamp should hold the flask at the coolest part of the neck, *i e.* as far above the union of the neck and side tube as possible, otherwise the neck is almost certain to crack during the distillation, especially if tightly clamped

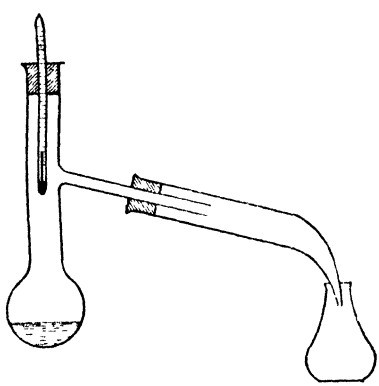

Fig 3

(4) The bulb of the thermometer should be just below the position where the side tube is fused into the neck of the flask, and should not be immersed in the liquid.

(5) A very simple method of preventing bumping and of securing even ebullition is to place two or three small pieces of porous pot in the liquid. These should be introduced before the liquid is heated, as if introduced into the hot liquid they may cause explosive ebullition.

(6) When the distillate tends to solidify in the condenser no special condensing tube should be attached. As a rule the substance will have a very high boiling-point and a moderately long, *wide* side tube to the flask will serve as a condenser, provided the distillation is not carried out too rapidly.

(See also Boiling-point Determinations, Chap. II, B.)

Fractional Distillation.—This is the method resorted to in order to separate miscible liquids the boiling-points of which are somewhat far removed from one another. The method is similar to an ordinary distillation, except that it is advisable to use a fractionating column. A long neck to the flask

serves as a rough fractionating column, but the separation is more readily effected when a special column is used in conjunction with an ordinary round-bottom flask. *Sidney Young** recommends the following forms (fig. 4): (*a*) rod and disc, (*b*) pear-shaped still head. They have the advantages that a fairly good separation can be accomplished by one distillation, and that very little liquid is retained in the column at the end. A simple form of column consists of a moderately wide tube with two or three bulbs blown on and a side tube

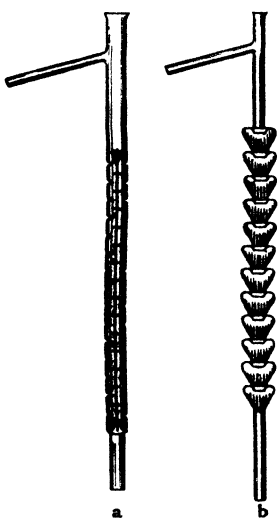

Fig 4

In fractionating it is essential that the distillation should proceed slowly and evenly; it should always be possible to count the individual drops as they pass into the receiver.

The general method adopted will be best seen from the study of a concrete example.

Experiment 2.—The fractionation of "50-per-cent benzol" for the preparation of pure benzene and pure toluene.

100 grams of the mixture is placed in a round-bottom flask provided with a still head, which is attached to a condenser and also fitted with a thermometer The whole apparatus should be thoroughly dry, and some ten small dry flasks should be provided as receivers. The mixture is distilled by heating the flask with a small Bunsen flame, care being taken that the ebullition is quite regular, and that the condensed liquid does not drop into the receiver at a more rapid rate than 1 drop per second.

Separate fractions should be collected every 3° or 5° according to the efficiency of the still head, except with the first and last fractions, which can be collected within a range of 1°. The following gives the number of fractions and the corrected boiling-point for each fraction:—

* "Fractional Distillation", London, 1903, pp. 163, 165, 173.

No	Temperature	Weight		
		1st Distillation	2nd Distillation.	3rd Distillation
1	80·2– 81 2°			
2	81 2– 83·2°			
3	83 2– 86 2°			
4	86 2– 89 2°			
5	89·2– 92·2°			
6	92 2– 95 4°			
7	95·4– 98 6°			
8	98 6–101 6°			
9	101 6–104 6°			
10	104 6–107 6°			
11	107 6–109 6°			
12	109·6–110 6°			
	Pure toluene 110·6°			

The weight of each fraction is noted.

The amounts of the different fractions will vary considerably according to the nature of the still head and of the rate of distillation. If necessary the distillation is repeated, fraction 2 is distilled in the same manner as the original mixture, but using a smaller flask. Any distillate passing over between 80·2° and 81·2° is collected in flask No. 1, and between 81·2° and 83·2° in flask No. 2. As soon as 83·2° is reached fraction 3 is added to the liquid in the distilling flask and the distillation continued, each fraction being collected in its proper receiver according to the temperature at which it passes over. When the temperature reaches 86·2°, fraction 4 is poured into the distilling flask, and the operations are repeated until all 12 fractions have been redistilled. If the separation is still not sufficiently complete, the whole operations can be repeated a third and even a fourth time.

During the distillations the temperature should be kept as constant as possible; the flame must not be blown about, and the distillation flask should be protected from air draughts.

It will not be possible to separate completely a mixture of two liquids which can give rise to a mixture of constant boiling-point. All that can be accomplished in this case is the separation of the excess of the one constituent from the mixture of constant boiling-point.

Distillation under Reduced Pressure.—This is always

resorted to if the compound decomposes when heated at atmospheric pressure, but is volatile without decomposition at lower pressures; it is also used for separating mixtures which are difficult to separate by distillation under atmospheric pressure.

The usual method is to attach the flask and receiver to the condenser by means of air-tight corks. Rubber corks are preferable if they can be used; if, however, the liquid or its vapour attacks rubber, ordinary corks must be employed. It is more difficult to make these air-tight, one of the simplest methods being to coat them with collodion after the apparatus has been fitted up. The receiver is supplied with a side tube, *e.g.* an ordinary distilling flask or a small pump flask can be used, which can be attached to a water or mercury pump, and the pressure reduced to that required. As a rule the pressure used is the lowest obtainable with the pump; a good water pump gives pressures as low as 10–15 mm. of mercury. With a mercury pump or a Geryk pump, pressures under 1 mm. are reached. To measure the pressure some form of manometer can be introduced between the receiver and the pump. A convenient form is that shown in fig 5. In this the difference in level of the mercury in the two arms can be read by means of the sliding mm. scale, and this gives the pressure under which the distillation is being conducted.

In distillations under diminished pressure the liability to bumping is much more pronounced than in ordinary distillations. This can be remedied, as a rule, by the introduction of a piece of porous pot; whenever the distillation is stopped and again started a fresh piece must be introduced, as it is the air-bubbles within the porous material which assist the evolution of bubbles of vapour. Another method adopted is to have a glass tube passing through the cork; this tube is drawn out at its lower end to a capillary which dips into the liquid, and can be closed by means of a piece of rubber tubing and small screw clamp at its upper end, so that the passage of air into the distilling flask is easily regulated. The drawback of this method is that it introduces an error into the boiling-point, as the pressure registered when air is present will be the sum of the partial pressures of the vapour and of the air.

In the majority of distillations under reduced pressure it is necessary to collect different fractions. One method of accomplishing this when the boiling-points are moderately high is to use a second distillation flask as receiver, and to fit up the

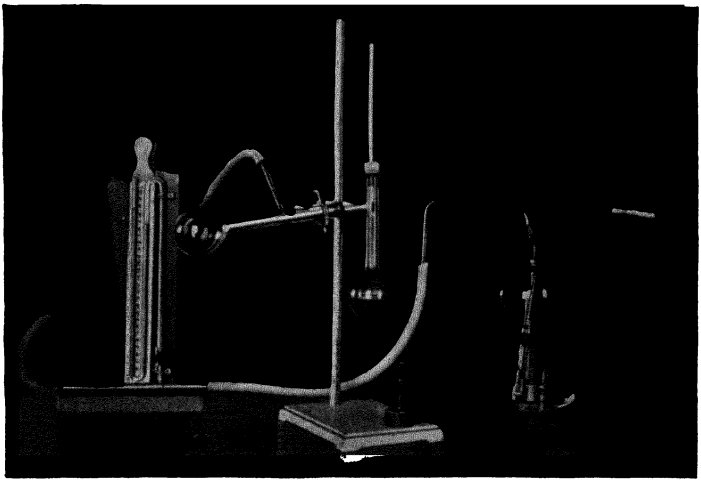

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Fig. 5.

two flasks as shown in fig. 5. The side tube of the receiver is attached to the manometer and pump, and is kept cold by a stream of running water. When the second fraction is to be collected the distillation is discontinued, the apparatus detached from the pump, and the receiver replaced by another similar flask and the redistillation continued when the pressure has again been reduced to the required value. Numerous forms of apparatus have been devised in order to obviate the necessity of interrupting the distillation while the receivers are being changed. The three following forms are those most frequently made use of. (*a*) Bruhl's receiver, fig. 6. The condenser tube is introduced through the rubber cork *c*, and projects into the apparatus, so that the drops of condensed liquid fall into one of the tubes provided as receivers. When the receiver is to be changed the stand and receiving tubes are turned through an angle by means of the handle *b*, whilst the cork *a* is firmly held. (*b*) Bredt's receiver, fig. 7. The condenser tube is fitted into the neck by means of a rubber stopper, and the outlet is just above one of the tubes *a*, *b*, *c*, to which stout test tubes or small flasks are attached by means of corks. The tube *d* is attached to the pump. The receiving tube is changed by turning the whole apparatus through a small angle. Both Bredt's and Brühl's receivers suffer from the disadvantage that if the liquid is fairly readily volatile portions of it collect in all the receivers, when only one is below the condensing tube. (*c*) The apparatus, fig. 8, is one of the most convenient. In this case the condenser is fixed in *a*, and the pump and manometer are attached to *b*; usually

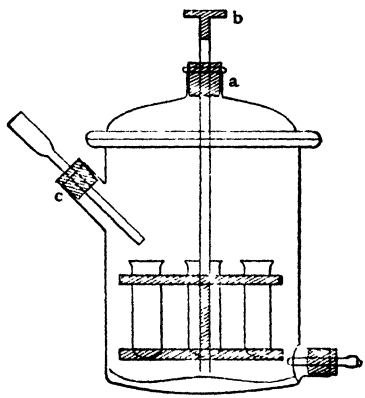

Fig 6

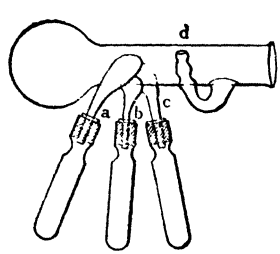

Fig 7

a large bottle of some 10 litres capacity is placed between the pump and the manometer (as in fig. 5), as by this device the alterations in pressure during the changing of the receiver are not so marked. When the receiver is to be changed the cock *c* is turned off, *e* on, and the three-way cock *d* turned so that the receiver is connected with the outer air and not with the pump; the distillation can thus be continued, and the distillate collected in *f*. When the new receiver has been attached to *g*, the cock *d* is turned, so that the receiver is connected with the pump and not with the air, after a short time cock *e* is closed and *c* opened, so that the distillate collected in *f* runs down into the new receiver.

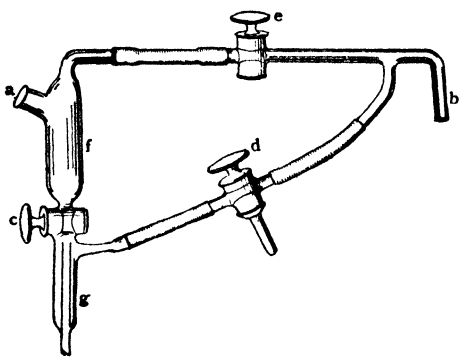

Fig 8

A convenient method of obtaining a vacuum of 1 mm. or less is to fill the whole apparatus with carbon dioxide, then reduce the pressure by means of a water pump, and remove the last traces of carbon dioxide by plunging a flask, which is placed between the receiver and pump, into a Dewar vessel containing liquid air. By this means practically all the carbon dioxide contained in the apparatus is solidified, and a pressure of ·2 or ·3 mm. can be reached. Pressures under ·5 mm. can also be attained by this method when gaseous products, such as carbon dioxide, are produced during the distillation.*

Distillation with Steam (S. B., p. 27).—This consists in blowing a current of steam through the substance to be distilled. It is only applicable to substances which have an appreciable vapour pressure at 100°, or just below. Another

* *Fischer* and *Harries*, B. 1902, **35**, 2158.

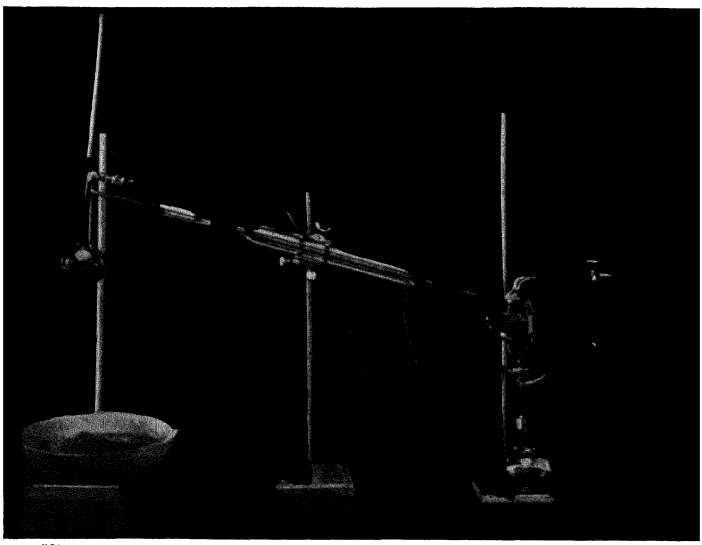

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Fig. 9.

factor which determines the proportions of water and compound which pass over are their relative molecular weights (S. B., p. 28). The method of blowing vapours other than steam, *e.g.* alcohol, toluene, &c., is not generally employed, as the molecular weights of these compounds are comparatively high for the temperatures which are attained, and the distillation would then be tedious.

The steam may be taken from the general laboratory supply, or generated in a metal can. In the latter case the can is provided with an ordinary safety funnel, or with a long glass tube which dips below the level of the boiling water. If the general laboratory supply is used it is necessary to blow this first through a vessel containing a small amount of water, and acting as a trap, *e g* fig 11, otherwise alterations in the pressure of the steam may cause the liquid in the distillation flask to rush back into the steam pipe.

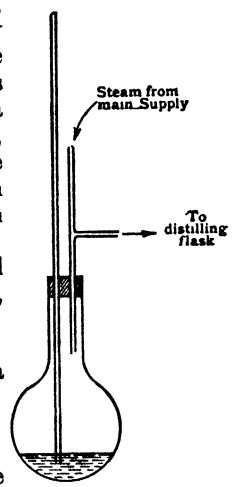

Fig 11

The material to be distilled is placed in a large round-bottomed flask (fig. 10), preferably of resistance glass, and provided with a doubly bored cork, or, if the vapours do not attack rubber, a rubber bung. The tube to carry the steam must dip below the liquid, and is bent at obtuse angles at the upper and lower ends. The tube to carry off the steam and vapour is bent at a fairly sharp acute angle, and fitted into the Liebig condenser by a cork or rubber bung. In this way the distillation flask is tilted on its side to a certain extent, and when the ebullition is rapid there is not the same risk of liquid splashing up into the tube which carries the steam and vapour to the condenser. In order to avoid the condensation of large quantities of water in the distillat... flask, it may be heated gently on a sand tray.

The product which distils over may remain dissolved in the water, *e.g.* acetic acid and the lower fatty acids, or may separate out as an oil (see Aniline, Exp. 133), or as a solid (see Orthonitrophenol, Exp. 101). In the latter case there is a risk that the solid which separates may choke up the condenser tube. This may be avoided by occasionally stopping

the cold water from circulating around the inner condenser tube; as the water in the condenser becomes warm the solid melts and flows down into the receiver, when the cold water is again turned on

It is comparatively easy to tell when the distillation is complete. If an oil or solid separates, the distillation is continued some 10–20 minutes after drops of oil or particles of solid have ceased to appear in the condenser. If the distilled material consists of a soluble acid, the distillation is continued until the distillate no longer gives an acid reaction with litmus paper. To isolate the product from the distillate contained in the receiver, one of the following methods is usually employed (*a*) The solid is filtered off, and the filtrate extracted with ether, if the product is sufficiently soluble to render it worth while to extract the portion in the solution. (*b*) If the distillate separates as an oil, this is usually extracted with ether. If the volume of water is considerable, it is advisable to saturate with common salt before extracting with ether (see p. 3). (*c*) If the distillate contains a soluble acid, this may be exactly neutralized with sodium hydroxide or carbonate, and the solution evaporated to dryness, when the pure sodium salt will be obtained.

Distillation with Superheated Steam. — The method of procedure here is similar to that in ordinary steam distillation,

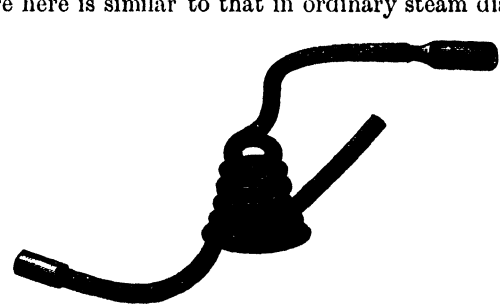

Fig. 12

except that the steam from the boiler is superheated before passing into the distillation flask. The simplest method of superheating is to pass the steam through a coil of copper tube (fig 12) heated by means of a large burner. The boiling-point of the liquid in the flask may also be raised by introducing sulphuric acid or some substance which, with the

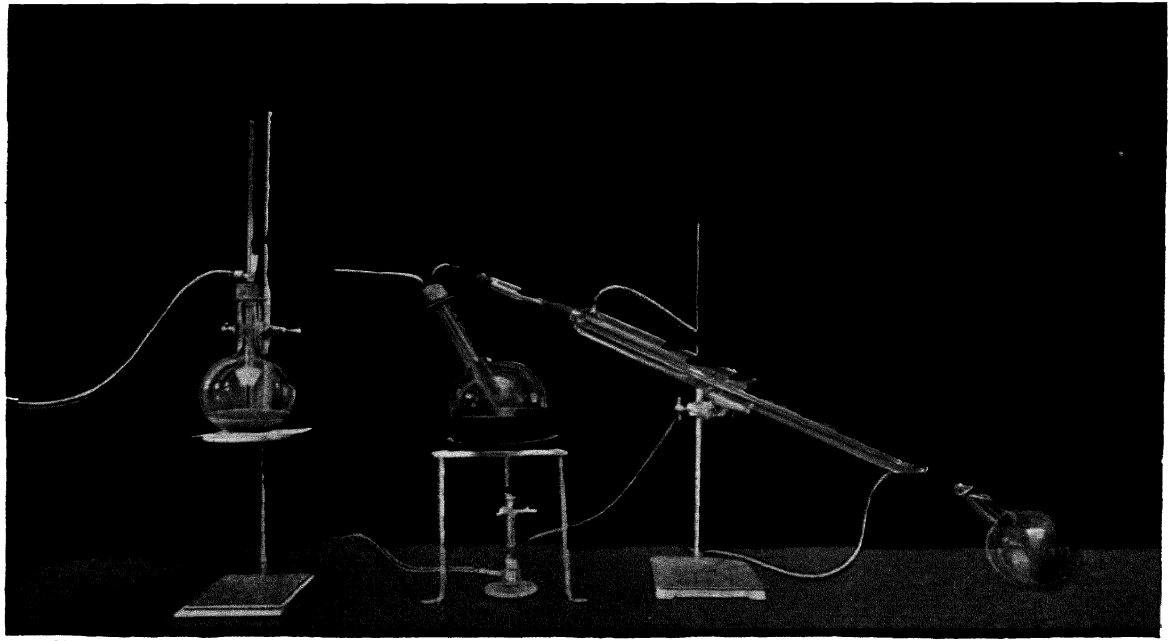

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Fig. 10.

water, will give a liquid boiling at 150°, 170°, or any special temperature required.

Rubber connections cannot very well be used with strongly superheated steam. The union between the copper coil and the glass steam tube leading into the distillation flask can be made by means of an ordinary cork. It is usually advisable for the stopper of the distillation flask to have three perforations, the third being used for a thermometer the bulb of which dips into the liquid.

C. Crystallization

The methods of crystallization are similar to those adopted in the case of inorganic materials, except that solvents like alcohol, benzene, carbon disulphide, acetone, ethyl acetate, light petroleum, &c, are used in addition to water. The commonest type of method is that of *crystallization by cooling*. A warm nearly saturated solution of the solid in a suitable solvent is prepared, this is freed from any insoluble material by filtration, and then allowed to cool in an open vessel, such as a beaker. The majority of substances are less soluble in the cold solvent than in the hot, and thus as the solution cools it becomes supersaturated, and crystals make their appearance. The impurities are largely contained in the mother liquid, and are thus present in the filtrate when the crystals are removed by filtration.

Preparation of Solution.—The hot concentrated solution is prepared by warming the finely divided material with the solvent. If the substance is fairly readily soluble, this is accomplished by gently warming on the water bath; but if it takes some time for the material to dissolve, the mixture should be heated on the water or sand bath in a flask provided with a reflux condenser. In this way loss of solvent is avoided, and also risk of the inflammable vapour of the solvent becoming ignited. If water or a liquid which is not readily volatile is used, the flask may be heated over the free flame; but if on warming the solid melts to a heavy oil, which falls to the bottom, the flask and its contents should be shaken repeatedly, as otherwise the flask is liable to crack.

Care must be taken in the selection of the solvent, and also as regards the amount of solvent used. If the solvent to be used is not definitely stated, preliminary experiments must be undertaken in order to find out which is the most efficient

solvent. These experiments are made by placing a few centigrams of the material in each of several test tubes, and adding small amounts of the common solvents. If the substance dissolves immediately in the cold, or will not dissolve to any appreciable extent on warming, it may be concluded that those solvents are unsuitable.

If, on the other hand, the substance dissolves when the solvent is heated, but separates on cooling in a crystalline form, and to an appreciable extent, then that solvent may be selected. The following points should be noted:—

1. In dissolving the substance previous to crystallizing, the amount of solvent should be so selected that crystals separate on cooling. If too much solvent is used, then the solution will not be saturated when cold, and no crystals will appear Certain solutions have a high degree of supersaturation, and crystals do not readily separate. In such cases the deposition of crystals is facilitated by rubbing the sides of the vessel with a sharp glass rod, or even better by adding a small crystal of the substance, if such can be obtained.

A phenomenon frequently observed in a laboratory is the difficulty with which crystals are deposited when a substance is prepared for the first time, but in subsequent preparations crystals separate readily when the solution is exposed to the air for a short time. This is probably due to the fact that after the first preparation minute particles of the solid are present in the air, some of these are deposited in the solution, and act as nuclei around which the crystals grow.

2. It should be remembered that insoluble impurities are often present, and in these cases large quantities of the solvent should not be added in order to obtain everything in solution.

Filtering the Hot Solution.—The hot saturated solution should not be filtered by means of a porcelain Hirsch or Buchner funnel (fig. 13, *a* or *b*) and the filter pump, as crystals invariably separate and block up the pores of the paper and the holes of the porcelain plate. If only a small amount of liquid is to be filtered, this may be done by using a funnel with a short stem and an ordinary filter paper, or a "folded" filter paper (fig. 13, *c*), and warming both just before filtering. If the amount of liquid is considerable, it is advisable to keep the funnel hot during the filtration. This is most readily accomplished, provided the laboratory has a steam supply, by allowing steam to pass through a metal coil which envelops

the funnel (fig. 14). If a steam supply is not available, then the funnel can be surrounded by a large metal funnel, and the space between the two filled with hot water (fig 15). The tube *a* is used for heating the water by means of a Bunsen burner, but a flame should *never* be placed under this tube

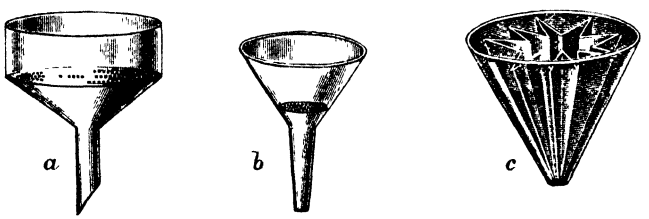


Fig 13

during the actual filtration if the vapour of the solvent is inflammable After filtration the paper is washed with a small amount of the hot solvent and the filtrate allowed to crystallize, preferably in a beaker

Crystallizing -To obtain large, well-developed crystals the vessel should not be disturbed, should be protected from

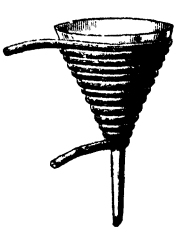


Fig 14

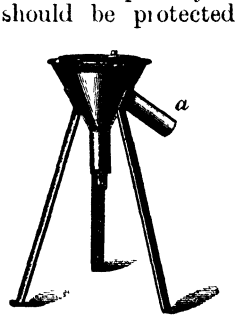


Fig 15

dust by means of a filter paper or clock glass, convex side upwards, and allowed to cool as slowly as possible If small pure crystals are required for analytical purposes, the cooling should be as rapid as possible. This is effected by placing the beaker in cold water, or surrounding it with ice and stirring the solution. The crystals thus produced are very small, but, as a rule, are free from particles of mother liquor, which are very liable to be occluded in larger crystals

If the substance is too soluble at the ordinary temperature, crystallization may be facilitated by cooling down the solution by placing it in an ice chest, or even cooling by means of artificial freezing mixtures (*e g* ice and salt, sodium sulphate and concentrated hydrochloric acid). The methods given on p. 14 for facilitating the formation of the crystals can often be used on the larger scale. In certain cases an oil separates instead of crystals, as the solution cools. This is owing to the fact that the solution is too concentrated, and the solute thus begins to separate from the solution at a temperature above its point of fusion. In many cases the temperature of the solution in which this occurs is below the melting-point of the pure substance It must be remembered, however, that if the solute dissolves even a minute quantity of the solvent, its melting-point will be appreciably lowered.

Removal of Crystals — A mistake frequently made is to allow the whole of the solvent to evaporate before the crystals are removed. It must be borne in mind that the process of crystallization is used in order to purify a compound, and that the impurities are contained in the mother liquor, if this is allowed to evaporate completely all the impurities are left with the crystals. If the crystals are large, the mother liquor can be removed by simple decantation and the crystals washed twice with a small amount of the pure solvent. As a rule it is much better to remove the mother liquor by filtration, using a porcelain funnel (fig 13, *a* or *b*) and suction, and the crystals left on the funnel can be freed from adhering mother liquor by washing several times with small amounts of the solvent. If the liquid filters slowly the form of pump flask shown in fig 16 is very convenient, as the stopcock can be turned and the flask detached from the pump.

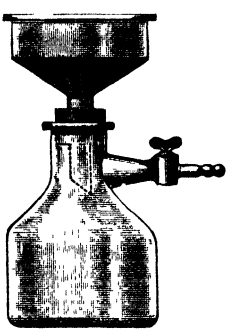


Fig 16

The following points deserve attention:—

(1) When a porcelain funnel with perforated plate is used the paper should be cut so as just to cover the plate. If the amount of material to be filtered is small, a small funnel is used and a stout test tube with a side tube in place of the pump flask.

(2) In removing the crystals from the beaker to the funnel care should be taken that crusts of solid matter which have been deposited on the sides of the beaker do not get mixed with the crystals. If possible these crusts should be removed before filtration

(3) In washing the crystals with the pure solvent considerable care is required if the crystals are at all readily soluble. If too much solvent is used in such a case the crystals will completely dissolve In all cases the crystals should be lightly pressed on the funnel by means of a spatula, and as much as possible of the mother liquor removed before washing is begun. A small amount of solvent is added, whilst the pump is detached and is then sucked through with the aid of the pump, and the operation repeated

(4) When a high boiling or not very volatile solvent, such as nitrobenzene, glacial acetic acid, &c., has been used for crystallization, it is advisable to remove the whole of this and replace it by a more readily volatile liquid. This is done by washing first with the high boiling solvent, then with a mixture or mixtures of the two solvents, and ultimately several times with the volatile solvent, *e g* alcohol or benzene. As a rule the crystals obtained will be practically insoluble in these low boiling liquids.

(5) To dry the crystals they may be placed on filter paper and dried in the air, care being taken that they are protected from dust. They may be dried by being placed in a desiccator over calcium chloride, solid potash, or concentrated sulphuric acid. The drying in such a case is facilitated by partially evacuating the desiccator or by placing in the desiccator a material which will absorb the vapour of the volatile solvent, *e.g.* for benzene ordinary paraffin wax may be used. If the melting-point of the crystals is relatively high, and the solvent is not very readily volatile at the ordinary temperature, the crystals may be dried by placing on a watch glass in the steam oven or on the water bath *Caution.*—Although the melting-point of the pure crystals may be considerably above 100°, yet in the presence of a small amount of a solvent they may melt below 100°.

(6) As a rule a second, and even a third and fourth lot of crystals may be obtained from the mother liquors, if these are evaporated to a certain extent. The crusts obtained in the first crystallization may be added to the mother liquor before it is evaporated As a rule the later fractions will

be less pure than the first fraction, and melting-points of each fraction should be determined, and only those fractions mixed which have practically the same melting-point.

Crystallization by Spontaneous Evaporation —When the substance dissolves as readily in the cold as in the hot solvent no crystals will separate when the solution cools, even when the sides of the vessel are rubbed with a glass rod The solution is still unsaturated, and if a crystal of the pure compound be added it will dissolve. The usual method of obtaining crystals from such a solution is to leave it to evaporate spontaneously at the ordinary temperature The vessel employed, viz a large test tube, beaker, or shallow crystallizing dish, depends upon the volatility of the solvent The less volatile the solvent the wider and shallower the vessel used. The liquid should be protected from dust, usually by a funnel. Filter paper should only be used when it is known that the liquid shows no tendency to "creep" up the side of the vessel and over the edge. All the precautions as to mother liquid, filtering, washing, and drying crystals apply in this case

Crystallization by Use of Two Miscible Solvents —When a substance is too soluble in one solvent and not sufficiently soluble in another to admit of its being crystallized from either independently, it may be possible to crystallize it from a mixture of the two, provided they are miscible The following pairs of solvents are frequently used for this purpose: alcohol and water, benzene and light petroleum, chloroform and light petroleum. The common method of procedure is to dissolve the material in the solvent in which it is readily soluble, to filter if necessary, and then to add the second solvent to the solution until a slight turbidity is produced. The mixture may then be warmed until it is quite clear and allowed to cool. In certain cases the substance separates as an oil, but in other cases in well-developed crystals If it is necessary to allow the solution to evaporate before crystals appear, it is essential that the solvent in which the substance is the more soluble should also be the more volatile. As evaporation proceeds the solvent becomes richer in the constituent in which the compound is less readily soluble, and after a time supersaturation occurs and crystals are formed.

Chloroform and light petroleum (boiling-point 80–90°) form a good crystallizing medium for α-bromallo-cinnamic acid

(Exp. 278). A mixture of alcohol and water is used for crystallizing *m*-dinitrobenzene (Exp 100).

Substances which are extremely readily soluble in water, but insoluble in alcohol, may be dissolved in a mixture of the two solvents and the solution placed in a desiccator containing quicklime. This will absorb the moisture but not the alcohol vapour; the solution becomes richer in alcohol and crystals gradually appear.*

When a substance is very sparingly soluble in benzene, but readily soluble in a mixture of benzene and alcohol, it may sometimes be obtained in a crystalline form by dissolving in the hot mixture of benzene and alcohol, and then shaking the mixture with warm water. This removes the alcohol from the mixture and the substance then crystallizes from the benzene.

Crystallization at Low Temperatures.—Occasionally the substance will crystallize from the solvent at temperatures below 0° only The solution must then be placed in a freezing mixture, and whilst still cold must be filtered by means of a funnel surrounded by a freezing mixture (fig. 17). Under these conditions it is difficult to prevent moisture condensing on the cold materials, and thus the crystals cannot be kept free from moisture.

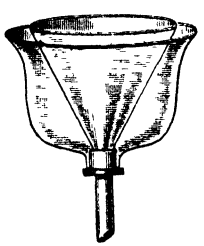


Fig 17

Fractional Crystallization.—The methods of crystallization already described apply to the purification of a single individual substance when mixed with small amounts of impurities The process of fractional crystallization is resorted to when it is desired to separate two crystalline substances both of which are soluble in the solvent used If there is a considerable difference in the solubilities of the two substances a partial separation may be previously effected by partial solution The mixture is treated with an amount of the warm solvent insufficient to dissolve both substances. If the two substances are present in anything approximating equal quantities, the whole of the more soluble and a portion of the less soluble substance will be dissolved, and a considerable quantity of the latter left undissolved. The solution

* *Rumpler*, B. 1900, **33**, 3474.

can then be subjected to fractional crystallization. This consists in collecting several fractions of crystals, either at different temperatures as the solution cools, or after given intervals of time when the solution is left to evaporate spontaneously. The number of fractions collected will vary with the different substances employed, but the following may be taken as a good general rule: Always remove a crystalline fraction by filtration when crystals of a type different from those already present begin to separate. If the fractions which are thus obtained are mixtures they must be again dissolved and allowed to crystallize. The factors which mainly determine which of the two substances crystallizes first are. 1. The relative solubilities, as a rule the less soluble compound will separate first. 2. The relative amounts of the two If a large quantity of the more soluble and only a very small amount of the less soluble compound is present, it is quite possible that the first fraction will consist of crystals of the more soluble compound.

In certain cases it is found that when the mixture is crystallized two entirely different types of crystals separate side by side. The only methods of separation in such a case are by mechanical means, *e g.* difference in specific gravity, thus, if one set of crystals are feathery needles, and the others large prisms, a separation can often be effected by stirring the crystals with the mother liquor and rapidly decanting. The lighter needles are poured off with the liquor and the heavy prisms are left behind. As a last resource the separation of the two kinds of crystals may be accomplished by picking out the individual crystals by hand. This is generally tedious, but is comparatively easy when the crystals are large.

D. Extraction of Solids

A common method of separating solids is by extraction or fractional extraction. In a process of extraction it is advisable, if possible, to select as solvent a liquid which will dissolve the one constituent fairly readily and leave the others undissolved, or will dissolve everything except the substance required. If this method cannot be used a method of fractional extraction must be resorted to. In a process of extraction it is often advisable to use as small an amount as possible of the extracting liquid, and this is accomplished by using the same amount of solvent over and over again. To accomplish

this a piece of apparatus, termed the *extractor*, is introduced between the flask in which the extracting solvent is boiled and the condenser. A form of extractor commonly used for commercial purposes is the Soxhlet extractor (fig. 18).

The solid to be extracted is placed in the extractor; the solvent is boiled; the vapour passes along the side tube *a* into the condenser *b*, *e.g.* a globular metal condenser (Soxhlet condenser), and the condensed liquid collects in the vessel *c* until it reaches the level of the top of the siphon tube *d*, when it is automatically siphoned over into the boiling flask. The process is repeated, and thus the solid in *c* is continually being brought into contact with the pure solvent. After some time all the soluble matter will have been extracted, and the liquid in the boiling flask will be a solution of the extracted matter in the given solvent. After removal of the solvent by distillation the extracted matter can be obtained in a solid form. The common solvents employed are ether, carbon disulphide, and alcohol.

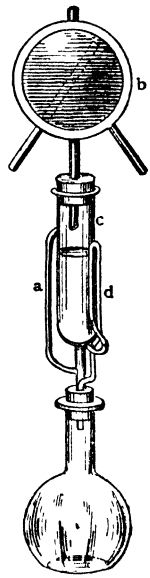


Fig 18

E. Sublimation

A method of obtaining solids in a pure crystalline form is by the process of sublimation. For this purpose it is essential that the substance in question shall have a high vapour pressure at comparatively moderate temperatures. Substances which can be readily purified by this method are trichlor- or tribromaniline, naphthalene, camphor, and benzoic acid. A very simple method of sublimation consists in placing the impure material on a clock glass, covering this with a funnel or beaker, and heating the clock glass gently on the water bath. The substance is volatilized, and the vapour is deposited on the cold inner surface of the funnel or beaker. If the substance has a low melting-point it often

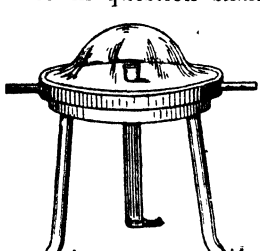


Fig 19

happens that the condensing vessel becomes warm, and the sublimed crystals melt. This difficulty may be overcome by cooling with water. One of the simplest forms of apparatus for this purpose is that suggested by *Bruhl* (fig 19). This consists of a flat hollow metal vessel with inlet and outlet tubes, and pierced in the middle by an opening of the shape of an inverted truncated cone. The substance to be sublimed is placed in a crucible in this cavity, cold water is passed through the metal vessel, a glass dish or beaker is placed over it, and the crucible gently heated. A method of sublimation under reduced pressure is also used occasionally.

II. COMMON METHODS FOR TESTING THE PURITY OF A SUBSTANCE

A. Melting-point

A common method for testing the purity of a known compound is the determination of its melting-point The introduction of small amounts of impurities almost invariably lowers the melting-point.* If, therefore, the melting-point is correct, the substance is usually taken as pure.

In dealing with an unknown compound it is usual to recrystallize it, if possible from several solvents, until its melting-point is no longer affected by subsequent recrystallizations As a rule the compound will then have a sharp definite melting-point, and is considered pure A few substances have somewhat indefinite melting-points; they begin to soften at a certain temperature, and are completely molten only at a much higher temperature; but, as a rule, a melting-point which is not sharp is due to the presence of an impurity.

It must be remembered that the fact that the melting-point is sharp, and is not altered by subsequent crystallization, is not an absolute guarantee that the substance is a pure chemical individual. The possibility of the formation of mixed crystals always exists; such crystals will be formed during the crystallization of a mixture of isomorphous compounds, and no separation can be brought about by repeated crystallization from the

* A few cases are known in which the introduction of an impurity raises the melting-point.

given solvent. A well-known example is a mixture of the α- and β-monocarboxylic acids derived from thiophene when slowly crystallized from water. Such mixtures can frequently be separated by chemical methods.

The two methods commonly employed for determining melting-points are.—

(1) Melting a comparatively large amount of the substance (20 grams) in a tube, and allowing the liquid to solidify with a thermometer in the mixture of liquid and solid The melting-point, which is defined as the temperature at which the liquid and solid phases are in equilibrium, will be registered if the mixture of liquid and solid is kept well stirred A standard thermometer should be used for the purpose, and a correction should be made for the portion of the mercury column which is not immersed in the solidifying liquid (see p. 25).

The thermometer can be clamped, and the liquid and solid intimately mixed by means of a ring stirrer which passes round the thermometer. Readings of the thermometer are taken every half-minute, and the temperature at which the thermometer remains stationary for 2–3 minutes is taken as the melting-point.

Experiment 3.—Determine the melting-point of *o*-nitrophenol by this method

(2) The common method used in laboratories is to place a small amount of the solid in a capillary glass tube closed at one end; this is attached to a thermometer, and gradually heated in a liquid or air bath. Two forms of liquid baths are shown in figs. 20 and 21.

The usual liquid employed is concentrated sulphuric acid. If this becomes dark coloured, a drop of concentrated nitric acid will usually render it colourless. For higher temperatures a mixture of sulphuric acid and potassium sulphate may be used. Sulphuric acid in practically closed vessels (fig 21) can be used for temperatures up to 250°, a mixture of 7 parts by weight of sulphuric acid and 3 of potassium sulphate for temperatures to 325°, and a mixture of 6 of acid and 4 of potassium sulphate for temperatures between 325°–360°.* In fig. 20 the temperature is kept constant by stirring, in fig. 21 no stirring is used, the substance in the tube is at the same level as the bulb of the thermometer, and the bulb of the flask is three-

* As these mixtures resolidify when cold, they should not be allowed to cool in glass vessels, as these will be inevitably cracked during the process of solidification.

quarters filled with the liquid to be heated. The melting-point tube itself is made by taking a length of thin-walled glass tubing, heating a portion of it until quite soft in a blowpipe flame, and then, after removal from the flame, drawing it into a long capillary some 1–2 mm. wide. This long capillary can be broken by means of file marks into suitable lengths, and one end of each of these sealed up by holding the end of the tube in a Bunsen flame for a second or two. The substance is powdered and introduced into this tube; it may be made to

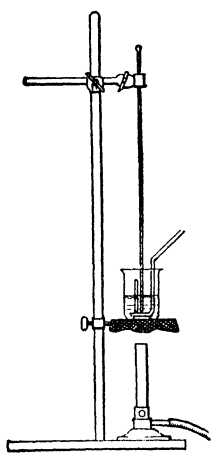


Fig 20

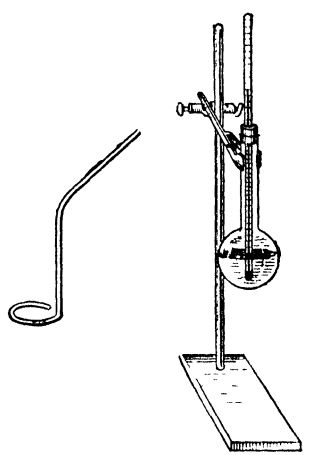


Fig 21

fall to the bottom by gently tapping. The melting-point tube may be attached to the thermometer by (*a*) moistening the thermometer with a drop or two of sulphuric acid, and then the tube will adhere by capillary attraction; (*b*) slipping a small rubber band (*e.g.* cut from a piece of narrow rubber tubing) over the thermometer and tube; (*c*) winding a piece of thin platinum wire round both.

The following precautions should be borne in mind:—

(*a*) Use only a small amount of the substance. The common mistake made is to use too much material; if this is done the temperature of the bath may rise through several degrees whilst the whole of the substance is melting, unless the temperature is extremely carefully regulated. A layer 1 mm. high is ample, and in certain cases it is recommended

to place a portion of the powdered substance in the tube, to shake out the greater part, and to determine the melting-point of the portion which sticks to the inner surface of the tube.

(*b*) Use a standard (normal) thermometer, or an ordinary thermometer which has been calibrated by means of a normal thermometer. The commercial thermometers are occasionally 2° or 3° out.

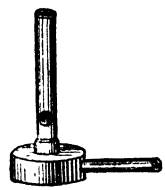


Fig 22

(*c*) The temperature may be raised fairly rapidly until within a degree or two of the actual melting-point, but must then be raised very gradually, so that the melting-point may be read to half a degree. The simplest method of heating is by means of a micro-burner (fig. 22), which can be removed from time to time when the temperature approaches the melting-point.

(*d*) If the whole of the mercury thread of the thermometer is not immersed in the hot liquid, the temperature read off on the thermometer is not the correct melting-point, and should be corrected by means of the formula

$$t \text{ corr} = t + 0\,000156\, a(t - t_0),$$

where 0 000156 is the apparent coefficient of mercury in glass, a is the length of thread measured in degrees not immersed in the hot liquid, t is the melting-point as read off on the thermometer, and t_0 is the mean temperature of the thread above the liquid. A simple method of obtaining correct melting-points is by using short normal thermometers, each ranging over some 50°, and taking care that the whole of the mercury thread is immersed in the hot liquid.

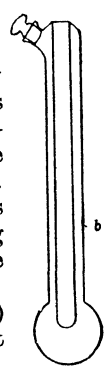


Fig 23

A form of apparatus designed by Roth (fig 23) also admits of correct melting-points being made It is made of one piece of glass, and is some 200 mm long. The sulphuric acid is introduced through the side neck, and is made to fill the space between the two walls up to the mark *b*. When the liquid is heated it expands and rises beyond *b* In this way the thermometer which is supported in the interior hot-air space will have the whole thread of mercury at the melting-point temperature. The side neck is closed by a stopper, but direct connection with the air is obtained by means of two holes,

one in the neck and one in the stopper, or by simply removing the stopper.

It frequently happens that very different melting-points are obtained for the same substance owing to the different rates at which the substance is heated. Thus the melting-point of phthalic acid has been given at various temperatures ranging from 180° to 200°. This phenomenon is especially noticeable when the substance in question decomposes, *e.g.* gives up water, carbon dioxide, &c., on heating In such a case it is advisable to raise the temperature of the bath to nearly the actual melting-point, and then to introduce the substance and raise fairly quickly until melting occurs If the substance and thermometer are placed in a cold bath and the temperature raised slowly much lower melting-points will be obtained; in the case of phthalic acid the reason for this is that as the acid is heated it loses water and yields the anhydride, and the melting-point registered will be that of a mixture of the acid and anhydride

In other cases it has been observed that a given substance has apparently two distinct melting-points. When its temperature is raised it melts to a clear liquid, which immediately solidifies again, and on further raising of the temperature a second melting-point is observed In such a case, unless careful observation is made, it is extremely easy to overlook the first melting-point and to observe the higher one only, as the substance usually resolidifies immediately after melting. The cause of this phenomenon has been discovered in most cases, namely, the conversion of the substance at its melting-point into an isomeride, or in some cases a product of decomposition with a higher melting-point The actual melting-point of the compound is thus the lower temperature, the higher temperature corresponding with the melting-point of an isomeride or decomposition product.

p-Azophenetol melts in a characteristic manner. At 136° it forms a turbid liquid which possesses several of the properties of crystalline substances, more especially double refraction; the turbid liquid is hence termed a *crystalline liquid.* At 165° the melt becomes quite clear, and then possesses none of the above-mentioned properties.

Melting-points are occasionally determined in tubes open at both ends, *e.g.* in the case of a wax which is most easily introduced in a liquid state; or in a tube closed at both ends, more especially when the substance under examination sub-

limes (*e.g.* fumaric acid) or decomposes (*e.g.* dibromosuccinic acid) when heated in a tube open at the upper end If a melting-point is determined under these conditions it should be clearly stated, as the melting-points in open and closed tubes are not always the same.

Melting-point Curves of Mixtures.—Melting-point curves of mixtures are valuable as indicating whether combination occurs between the two constituents of the mixture, and also

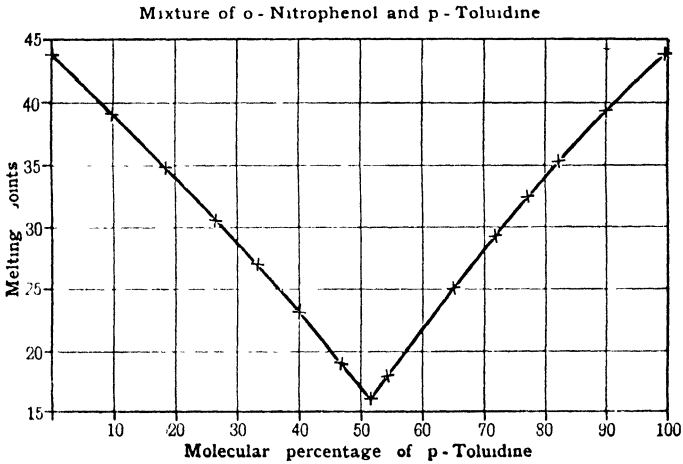


Fig 24

for telling the composition of the compound, if such is formed.

The melting-point curve is obtained by plotting the melting-points of various mixtures against the molecular percentage composition of the mixtures. A mixture containing known weights of the two components is made, and the melting-point determined. The weights taken are transformed into molecular percentages. This is done by dividing the actual amount of each substance by its molecular weight, and then expressing as percentages. The method of determining the melting-point of the mixture varies somewhat. *Philip** determines the freezing point by the Beckmann method (Chap. VIII, B.), *i.e.* the temperature at which the fused mixture

* J. C. S. 1903, **83**, 814.

begins to solidify. *Kreman*,* on the other hand, using a Beckmann freezing-point vessel, warms the mixture until a clear liquid is just obtained and reads off the temperature, care being taken that the mixture is thoroughly stirred as the temperature is raised The temperature of the liquid is then raised several degrees, and the melt placed in an air bath and stirred whilst the temperature falls until the mass begins

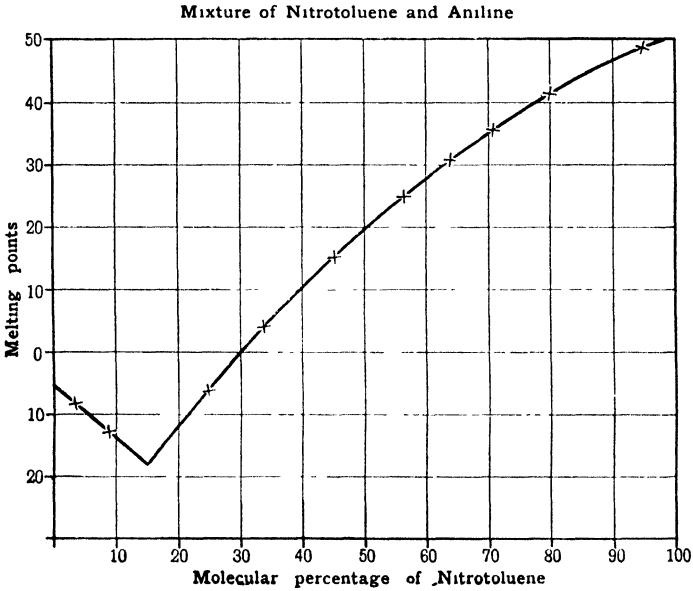


Fig 25

to solidify. The mean of several such determinations of solidifying and melting-points is taken as the correct equilibrium temperature.

The type of curve in figs. 24 and 25 is that usually obtained when the two compounds do not unite to form an additive compound, and consists of two branches with an eutectic point. The type in figs 26 and 27 is that obtained when the constituents form an additive compound. In both the cases given the compound formed consists of an equal

* M. 1904, **25**, 1230.

number of molecules of each constituent; the curve consists of three branches with two eutectic points. The highest point in the middle branch is the melting-point of the definite compound consisting of an equal number of molecules of each component. The addition of a further amount of either

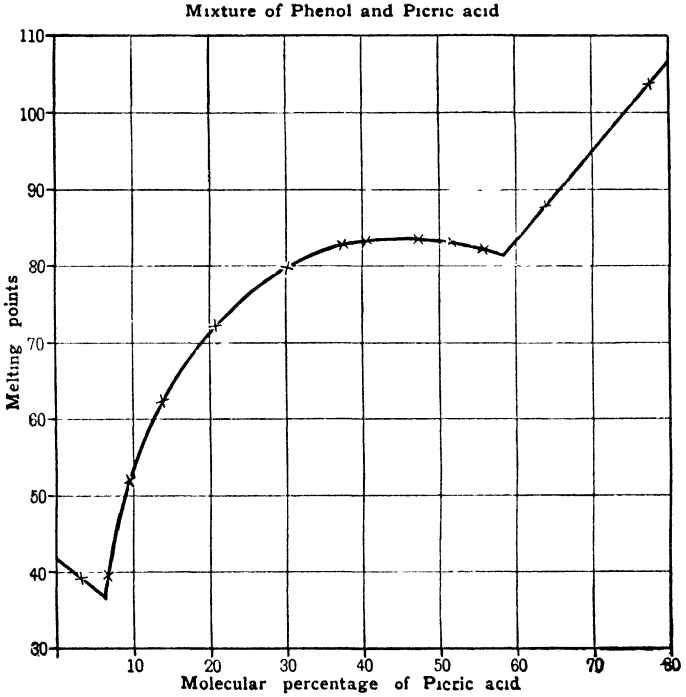


Fig 26

constituent produces a lowering of the melting-point. The nature of the middle branch often indicates the degree of stability of the compound, if the compound is sufficiently stable to be readily isolated the middle branch forms the greater part of the whole curve, as in fig 26, and rises and falls abruptly Where the compound is extremely unstable the middle branch of the curve is smaller and is much flatter in appearance (fig. 27). If the two components can

form more than one compound, then there will be more than three branches, and the maxima of the middle branches will give the melting-points and molecular compositions of the compounds formed.

The formation of mixed crystals complicates the study of melting-point curves.

Experiment 4.—Determine the melting-point curve of one of the following mixtures: (*a*) phenol and α-naphthylamine;

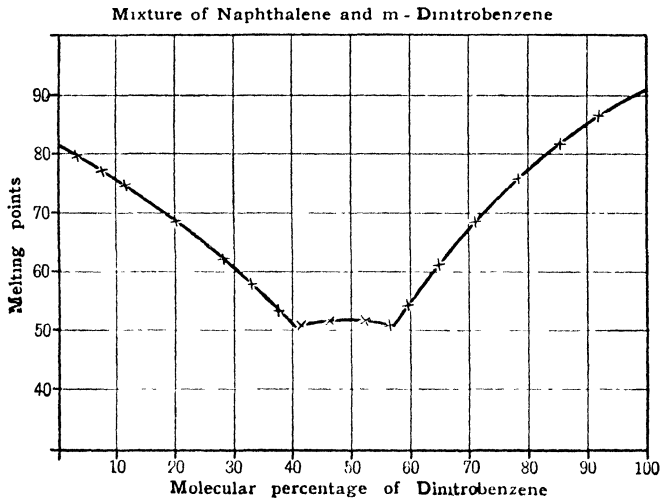


Fig 27

(*b*) α-naphthol and *p*-toluidine; (*c*) naphthalene and picric acid, and state what conclusions you draw from the nature of the curve

B. Boiling-point

The boiling-point, *i.e.* the temperature at which the liquid and its vapour are in equilibrium, may be determined by the following methods:—

I. Distilling the liquid under ordinary or under reduced pressure and noting the temperature at which distillation occurs. If the compound is pure and is volatile without decomposition, practically the whole of the liquid will pass over at a constant temperature; when only a small amount of

liquid remains in the distilling flask the vapour will, as a rule, become superheated, and a temperature rather higher than the correct boiling-point will be registered. The apparatus used is similar to that described under distillation (Chap. I, B.), and attention may be drawn to the following points:—

(1) The thermometer should be a normal one, and the whole of the thread of mercury should be in the vapour; if a portion of the thread is surrounded by cold air a correction must be made for this (p. 25) If short thermometers, similar to those used in melting-point determinations (p. 25), are employed, it is generally easy to fix the thermometer so that the whole thread is immersed in the hot vapour.

(2) The bulb of the thermometer should be in the vapour just below the side tube, it should not be immersed in the liquid.

(3) Superheating of the vapour must be avoided. Low-boiling liquids should not be boiled on a water bath if a correct boiling-point is required, as the steam issuing may surround the flask and superheat the vapour. As a rule, a small direct flame from a micro-burner (fig. 22) is best, and even this should be so regulated that the flame only comes into contact with the portion of the flask filled with liquid. On no account should it lick round the flask and come into contact with the portion where the vapour is present.

The bulb of the thermometer should always be covered with a thin film of pure liquid produced by the condensation of the vapour on the thermometer, this thin film of liquid will be in equilibrium with the pure vapour, and the correct boiling-point will be registered. Certain authorities recommend wrapping a small piece of cotton wool round the bulb of the thermometer in order to secure a film of liquid on the bulb.

(4) Bumping may be avoided and regular boiling facilitated by the introduction of one or two pieces of porous pot.

II. A method adopted when only a small quantity of liquid is available is that due to *Schleiermacher*.* The small amount of liquid or solid is placed in the closed limb of a U tube (fig. 28), the remainder of the limb is filled with mercury, and a thermometer is placed in the open limb. The whole apparatus is gradually heated in a suitable bath, and the tem-

* B. 1891, **24**, 944.

perature read off when the mercury stands at the same level in the two limbs. This is the temperature at which the vapour pressure of the substance is equal to the atmospheric pressure, in other words is the boiling-point of the compound under atmospheric pressure

Only substances which do not react with mercury can be used, and the boiling-point should be sufficiently low—under 220°—so that the vapour pressure of the mercury at that temperature may be neglected. Both substance and mercury should be quite pure. Suitable dimensions of the tube are 6–8 mm. diameter, and total length, before bending, of 50 cm. The tube is thoroughly cleaned and dried, and one end drawn out to a fine capillary 1–2 mm wide, care being taken that no moisture is introduced, and the capillary at its lower end is again drawn out to an extremely fine capillary (hair capillary) some 50 mm. long. The portion which is to form the bend is constructed by holding in the flame and letting the walls fall together to a certain extent, and the bend is then made so that the two arms are vertical and practically touch. The liquid is introduced through the open end and bend, and then the clean mercury, until the level in both limbs is some 2 cm. below the capillary. The liquid is then gently boiled to drive out air, and mercury gradually run in through the open end until the capillary is filled with the liquid and the limb closed by sealing the capillary in the middle. In this manner the apparatus is filled with the liquid and mercury without gas bubbles, or, at most, with a minute gas bubble, due to decomposition products formed during the sealing, which does not interfere. The excess of mercury is run out of the open end by tilting the apparatus, and the tube and thermometer may then be placed in the bath and the boiling-point determined. It is advisable to take the mean of several readings.

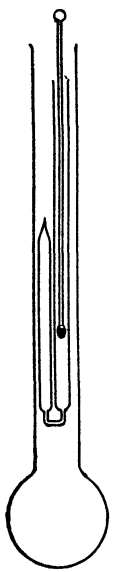


Fig 28

C. Specific Gravity

The specific gravity of a liquid is usually a good criterion of its purity, and may be determined by means of a pyknometer or Sprengel tube. In either case the vessel must be filled

with the liquid at a definite temperature. This is accomplished by filling the vessel at a slightly lower temperature and keeping it for some hours in a thermostat at the temperature required; the increased volume of the liquid due to expansion passes through the hole in the stopper or through the end of the Sprengel tube (fig. 31), and can be removed by filter paper. The weight of the given volume of liquid compared with the weight of the same volume of pure water is the specific gravity, and is denoted by D. The temperature at which the determination was made and also the temperature of the water with which the comparison was made are also denoted, *e.g.* $D_{4^\circ}^{20^\circ} = 1{\cdot}3204$ indicates that the

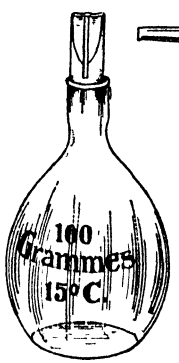


Fig 29

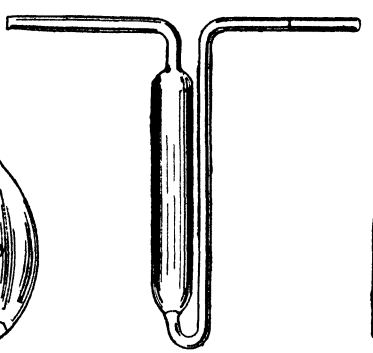


Fig 31

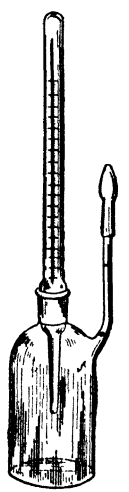


Fig 30

specific gravity of the liquid in question at 20° is 1·3204 when water at 4° is taken as unity.

In the vessels shown in figs. 30 and 31 marks are placed on the side tubes, and the experiment is always arranged so that the liquid meniscus coincides with this mark when the liquid is at the given temperature.

Experiment 5.—Determine the specific gravity of ethyl alcohol purified as described in Exp. 26, or of benzene as purified in Exp. 2.

III. SOLUBILITY OF SOLIDS IN LIQUIDS

The solubility of a given solid in a solvent indicates the number of grams of the solid which dissolve in 100 grams of the solvent to yield a *saturated solution* at the temperature stated

1. **Solubility at the Ordinary Temperature**—A saturated solution may be prepared by making a fairly concentrated hot solution, and cooling down this solution by placing in a vessel of water at the ordinary temperature; care being taken that the solution is thoroughly stirred as it cools, and that solid separates. If solid does not separate, the solution may be either unsaturated or supersaturated. To facilitate the separation of solid, a small crystal may be introduced and a rough glass rod used for stirring. The solution is kept in the water bath for 2 hours, then again vigorously stirred, and finally a suitable amount filtered through a dry filter paper. The first 1–2 c.c. of solution which pass through the paper should be discarded as they are usually not completely saturated. The filtrate which then passes is collected in a weighed crucible, weighing bottle, or other suitable vessel provided with a lid, and the amount weighed. The volatile solvent is then removed by careful evaporation and the dry residue weighed, the weighings being repeated until the residue after cooling in a desiccator is constant in weight. The solubility of a substance which is appreciably volatile at the ordinary or slightly higher temperatures, *e.g.* *p*-toluidine, cannot be determined by this method. The best method for volatile substances is to prepare the saturated solution, and then to determine the concentration of the solution of some chemical method, *e g.* of an acid solution by titration.

Another method of obtaining a saturated solution is to shake the finely powdered solid with the pure solvent in a stoppered bottle for *at least* several hours. The shaking may be carried out by means of any ordinary shaking machine, care being taken to note the temperature; an even better method is to shake in a water thermostat at a fixed temperature. In the latter case the bottle is attached to a rotating axis in the thermostat, the axis being rotated by means of a water turbine, hot-air motor, or electromotor.

If the solvent employed is very volatile it is advisable to

avoid filtration; this may be accomplished by removing a portion of the clear solution by means of a pipette, provided the solid readily falls to the bottom and leaves a perfectly clear solution above.

2. **Solubility at High Temperatures.**—In the determination of the solubility at high temperatures the saturated solution cannot be filtered in the ordinary manner, since the solution cools during the process and part of the solute crystallizes. The simplest form of apparatus is that due to *Pawlewski** (fig. 32) It consists of a test tube A, 10 × 2 cm, and a weighing bottle B, both provided with rubber bungs with two holes. The solvent and solute are placed in A, and B is empty, the bent tube E has its longer limb reaching nearly to the bottom of A, and the end of this limb is covered by two or three layers of fine linen which are firmly tied on.

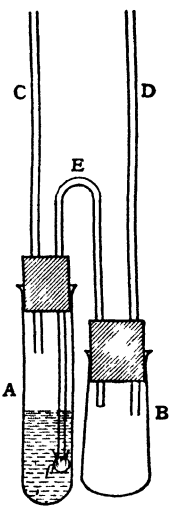


Fig 32

The whole apparatus is suspended in a thermostat at constant temperature, air is drawn out through C so that the solute and solvent are thoroughly mixed. When the solution is saturated the tube D is attached to the pump and a portion of the saturated solution drawn off into B, the layers of linen serving as a filter. The apparatus is disconnected, B dried on the outside, the glass stopper replaced, and the whole weighed. If necessary small condensers can be attached to C and D. The method cannot be used for substances which are readily oxidized nor yet for very volatile solvents.

Experiment 6. — Determine the solubility of potassium oxalate in water at four different temperatures, and construct a solubility curve for this salt. Use two different methods for determining the concentrations of the saturated solutions.

* Pawlewski, B. 1899, **32**, 1040.

IV. DETECTION OF THE COMMON ELEMENTS WHICH OCCUR IN CARBON COMPOUNDS

The common elements which have to be tested for are carbon, hydrogen, nitrogen, halogens, sulphur, and phosphorus, and, in the case of metallic salts of organic acids, the common metallic radicals.

A. Carbon and Hydrogen

The only sure positive test for carbon and hydrogen is oxidation to carbon dioxide and water respectively and testing for these. The oxidation is conducted in a dry glass tube by means of *dry* cupric oxide.

A small amount (1 to ·2 gram) of the liquid or solid is mixed with freshly-ignited powdered cupric oxide and placed in the end of a somewhat narrow hard-glass tube 4–5 inches long and closed at one end. Two or three inches of dry granular cupric oxide are added, and the mouth of the tube closed with a cork and delivery tube. The tube is heated gradually, beginning at the front end, so that the layer of granular oxide of copper is quite hot before the substance itself is heated Moisture can be detected by its condensation in the form of drops of water, or by placing a small amount of anhydrous cupric sulphate in the front part of the tube. Carbon dioxide is detected by passing the products of combustion into lime water or baryta water.

In testing for hydrogen it is essential that all the materials should be dry, and as cupric oxide is hygroscopic it is necessary to heat this thoroughly just before use. Certain carbon compounds char when heated alone or with concentrated sulphuric acid, but this test is of no value as a negative test, as numerous volatile carbon compounds do not char under these conditions.

B. Nitrogen

(*a*) The liquid or solid is heated with soda lime, and ammonia is tested for in the issuing gases. The reaction may be used as a simple positive test, but is of no value as a negative test, as numerous compounds, *e.g.* nitro- and diazo-derivatives, &c., do not evolve their nitrogen in the form of ammonia under these conditions.

(*b*) A small amount of the substance is heated with a small pellet of metallic sodium or potassium. The mixture is heated gradually, in case the reaction is brisk, and then as strongly as possible. The mistakes frequently made by students in this test are—using too large a quantity of the substance and not heating sufficiently. If the compound is volatile and does not readily react with the metal, it simply boils and the condensed vapour falls back on the molten metal and remaining substance without reacting. The amount taken should be such that the whole of it can be vaporized in the small tube, and the sodium can thus be heated much above the boiling-point of the substance. When a drop of the liquid falls back into the strongly heated metal decomposition occurs, and if nitrogen is present sodium cyanide is formed. When once formed this is not destroyed by heat, and the tube should be heated until the glass begins to melt. When comparatively cool the tube is broken and the whole mass extracted with water,* filtered if necessary, and the alkaline liquid warmed with ferrous sulphate solution, and then acidified. If nitrogen was present in the original substance a bluish-green coloration or a blue precipitate of Prussian blue is obtained. The reactions which take place are the production of sodium ferrocyanide from the sodium cyanide and ferrous hydroxide,

$$6KCN + Fe(OH)_2 = K_4FeC_6N_6 + 2KOH,$$

and the production of ferric ferrocyanide (Prussian blue), $Fe_4(FeC_6N_6)_3$, when the solution is acidified, owing to small amounts of ferric salt produced by the oxidation of the ferrous sulphate.

The method does not give satisfactory results when sulphur is also present, and it is then advisable to add a fair amount of iron powder to the substance before it is heated with sodium or potassium (*Jacobsen*). According to *Tauber*,† nitrogen can be detected by this method when compounds quite free from nitrogen are used, as the iron acts as a nitrogen carrier and the atmospheric nitrogen is transformed into cyanide. *Tauber* recommends using a large excess of potassium, *e.g.* ·2 gram freshly cut potassium for some ·02 gram

* Care should be taken in case any metallic sodium or potassium still remains.

† B. 1899, **32**, 3150.

of substance, and finds that under these conditions sulphur does not interfere.

Nitrogen in diazo- and certain pyrrole derivatives cannot be detected by this method.* A method suggested recently† is stated to work in all cases. A mixture of 138 parts by weight of ignited potassium carbonate and 72 of magnesium powder is used in place of metallic potassium; the mixture probably reacts in such a manner as to liberate metallic potassium when heated:

$$K_2CO_3 + 3Mg = 2K + C + 3MgO.$$

Another advantage of this method is that the mixture can be prepared in large quantities and stocked ready for use. A few mgs. of the mixture is intimately mixed with the carbon compound, and then heated in a porcelain crucible or in a glass tube sealed at one end. The mass is ultimately extracted with water, filtered, the filtrate rendered alkaline with sodium hydroxide solution, and tested for cyanide in the usual manner.

C. Halogens

The following methods are used —

(1) A piece of pure copper oxide (*e g* a piece of wire-form cupric oxide, such as is used in the estimation of carbon and hydrogen), which can be held by means of a piece of platinum wire wound round it, is moistened with the substance and held in the lower outer edge of the Bunsen flame. The presence of halogen is indicated by the green coloration imparted to the flame. Even volatile halogen derivatives give the reaction. If the substance is a solid, the cupric oxide is gently warmed and dipped into a small portion of the solid (*Beilstein*).

(2) A small amount of the substance is heated with metallic sodium (as in testing for nitrogen), or with a larger amount of pure lime in a glass tube. The heated mass is afterwards extracted with water, acidified with nitric acid, and the chloride, bromide, and iodide ions tested for in the usual manner. If nitrogen is also present the method of heating with sodium is not recommended, as the cyanide formed interferes with the tests for the haloid ions.

* B. 1902, **35**, 2523. † *Castellana*, Gazz., 1904, **34**, (2), 359. *Ellis* C. N. 1910, **102**, 187, states that the reagent absorbs atmospheric nitrogen.

(3) A mixture of sodium peroxide with 25 times its weight of a compound rich in carbon and hydrogen (*e.g.* naphthalene or cinnamic acid) is prepared and stocked in a bottle with a good stopper. In carrying out the test a small amount of this mixture is heated, by means of the Bunsen flame, with a few particles of the substance in a glass, or, better, iron tube. When cold the mass is extracted with water, the clear solution acidified with nitric acid, and tested in the usual manner. Phosphorus may also be tested for by mixing a portion of the acidified liquid with ammonium molybdate If a portion of the clear extract is acidified with hydrochloric acid, sulphur may be tested for by the addition of barium chloride solution.

N B —The sodium, lime, or sodium peroxide used in testing for halogens should always be previously examined for halogens.

In each case, when the presence of halogen has been established, the exact nature of the halogen, *e.g.* chlorine, bromine, or iodine, should be determined.

D. Sulphur

(1) The presence or absence of sulphur is readily indicated by taking a portion of the clear alkaline filtrate obtained in testing for nitrogen (method *b*), and adding a drop or two of sodic nitroprusside solution The production of a brilliant evanescent purple coloration is a sure indication of the presence of sulphur (*Vohl*).

(2) The substance is oxidized, extracted with water, the clear extract acidified with hydrochloric acid, and the sulphate ion tested for by means of barium chloride solution. The methods of oxidation are as follows: (*a*) With sodium peroxide, as in testing for halogens. (*b*) When the substance is not too volatile, by fusion with sodium carbonate and potassium nitrate. (*c*) The substance is dissolved in hot potassium hydroxide solution, and then cold chlorine is led in, after some time excess of hydrochloric acid is added, the mixture boiled, and then tested for sulphate ions. (*d*) The substance is heated with fuming nitric acid in sealed tubes.

E. Phosphorus

The usual method is to oxidize to phosphoric acid, and to test for this by means of ammonium molybdate. The oxidation can be effected, as in the case of sulphur, by means of (*a*)

sodium peroxide, (*b*) sodium carbonate and nitrate, (*c*) nitric acid under pressure.

F. Detection of Common Metallic Radicals in Organic Salts

As a rule the organic matter is destroyed and the residue examined for the common metallic radicals in the usual manner. The organic matter may be destroyed (*a*) by heating to redness for some time in contact with the air, either on platinum or porcelain. *N.B.*—Platinum must not be used when lead, silver, mercury, &c., are present Any volatile substances, *e.g.* mercury, arsenic, and ammonia, will be lost during the heating. (*b*) By oxidation with a mixture of concentrated nitric and sulphuric acids. This process is quicker, as no charring occurs.

V. ESTIMATION OF THE COMMONLY OCCURRING ELEMENTS

A. Estimation of Carbon and Hydrogen

The estimation of these two elements is usually accomplished by oxidizing a known weight of the pure, dry substance to carbon dioxide and water and weighing the two products, the water by absorption in a calcium-chloride tube and the carbon dioxide in potash bulbs or soda-lime tubes. The operation is carried out in a hard-glass tube heated by means of gas or electricity in a long furnace. The process is usually spoken of as a "combustion", and is conducted in a current of air or oxygen and in the presence of cupric oxide.

The Tube.—The tube used should be of hard glass—the ordinary combustion-tube glass or special Jena glass—open at both ends, the dimensions should be some 12–14 mm. external diameter and some 10 cm. longer than the furnace The tube should be clean and dry, and its ends fitted with rubber stoppers each with a single hole,* care having been taken that the rough edges of the ends of the tube are

* The glass tubes which are introduced into these corks should be pushed in until the end of the tube is just flush with that end of the cork which fits into the combustion tube.

filed smooth or are rounded by heating in the blowpipe flame.

The tube is filled as shown in fig. 33; *a* and *b* are coils of copper gauze each about 2 cm. long; they should be free from grease, and should just fit easily into the tube; they serve to keep the long layer, *c* (some 45 cm. long), of wire-form cupric oxide in position; *d* is a coil of copper gauze some 15 cm. long, which has been strongly heated so that its surface is completely oxidized. The space between *b* and *d* is reserved for the boat which is to hold the substance for analysis. The tube and its contents are dried by passing a stream of dry air through the tube while it is heated in the furnace, and the end *e* protected from atmospheric moisture by a straight calcium-chloride tube. The air used should be freed from moisture and carbon dioxide by passing it first through a wash bottle containing concentrated sulphuric acid, and finally through a soda-lime tower and a U tube filled with granular calcium chloride. A convenient form of apparatus for this purpose is the one shown in fig. 34, which can be used for drying both air and oxygen. This is a great advantage, as occasionally both gases are required at different times in the same combustion, and by means of the clips at *a* and *b* it is possible to admit either gas into the U tube, which is connected to a glass tube passing through the rubber cork at *e* (fig. 33).

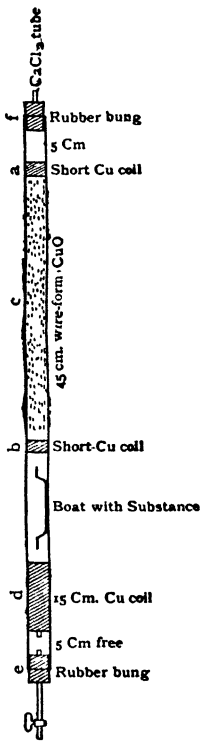


Fig. 33

Collecting the Products of Combustion.—The water is usually collected in a calcium chloride tube (fig. 35), although some chemists use a similar tube filled with pumice and moistened with concentrated sulphuric acid. The side tube *a* fits into the rubber stopper which closes the end *f* of the combustion tube (fig. 33). A common mistake made is to attach the drying tube by means of rubber to a glass tube passing through the cork at *f*. If this is done it is impossible to

weigh accurately the water produced, as part of it will collect in the glass tube and rubber connection. The side tube *b* serves to connect the calcium-chloride tube to the apparatus for absorbing carbon dioxide.

After the tube is filled with *granular* calcium chloride and covered with glass wool, the neck *c*, fig. 35, or *c* and *d*, fig. 36, is closed either by sealing off in a blowpipe flame or by corks pushed down into the necks and covered flush with the top with molten paraffin wax or sealing wax, which is then allowed to solidify. When not in use the tubes *a* and *b* are closed by means of short lengths of stout rubber tubing provided with plugs of glass rod. In this manner the calcium chloride may be protected from atmospheric moisture Before the tube is used the first time, dry carbon dioxide is passed through, as the chloride is apt to contain basic chlorides which absorb carbon dioxide; after the gas has been passed for some 1·5 hour it can be replaced by dry air and the tube is then ready for use. For

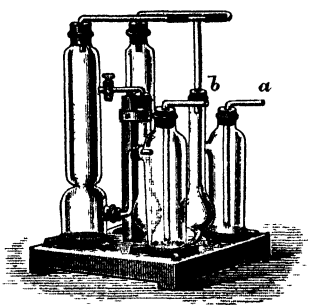


Fig 34

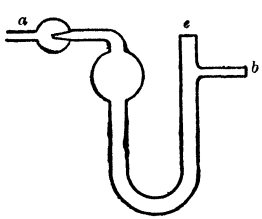


Fig 35

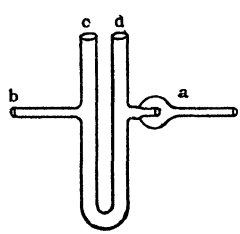


Fig. 36

the purpose of weighing, the tube is suspended to the hook on the balance by means of platinum or aluminium wire. Before weighing, the tube should be dusted and the rubber caps removed. These caps should never be weighed with the tube, as rubber is hygroscopic and varies in weight according to the amount of moisture in the atmosphere. The same rule applies to weighing the apparatus in which

the carbon dioxide is collected. In all unions made by means of rubber tubes, whether the union of the calcium chloride tube to the potash bulbs or the union between the drying apparatus and the tube which leads the dry air into the combustion tube, care should be taken that the gas which has to pass the union does not come into contact with any considerable length of rubber—this is easily arranged by having the ends of the two glass tubes touching one another inside the rubber tubing.

The carbon dioxide is usually collected in potash bulbs or in soda-lime tubes.

Figs. 37–39 represent three of the commonest forms of

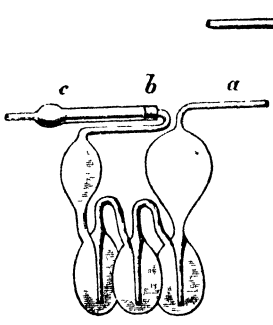


Fig. 37

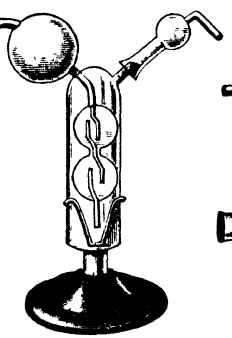


Fig 38

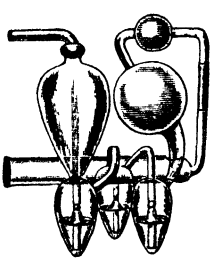


Fig 39

potash bulbs. Fig. 37, Mohr's, is the common type; the three bulbs are three-fourths filled with a concentrated solution of potassium hydroxide (1 · 1·5). This is accomplished by dipping the tube *a* into the alkaline solution, whilst the tube *b* is attached to a pump by means of a rubber connection and a sufficient quantity of the liquid is gently sucked in. The end *b* is carefully cleaned and dried, and the side tube *c* attached after the joint has been very slightly greased. This side tube contains either granular calcium chloride or small pieces of solid potassium hydroxide kept in position by plugs of glass wool. The object is to retain moisture carried away from the potash solution as the gas bubbles through; the solid potash has the further advantage of absorbing any carbon dioxide which escapes absorption in the bulbs. Fig. 39 represents Wetzel's modification of Mohr's apparatus. The advantage it possesses is that the gas bubbles are retained for a longer time in

contact with the alkaline solution. This is effected by means of the funnel-shaped piece of glass in each bulb. The absorption is more efficient, and the combustion can be carried out in a shorter time than is required when the ordinary *Mohr's* bulbs are used. Fig. 38 represents *Bender's* potash bulbs, which are somewhat more convenient for weighing, as they stand upright on an aluminium foot.

At the present time there is a tendency to replace potash bulbs by soda-lime tubes. The usual form of tube is shown in fig. 40. Two tubes are used; the one nearer the combustion tube is filled with soda lime only, the second has the inner limb filled with soda lime, but the outer limb with granular calcium chloride. The tubes can be shut off from

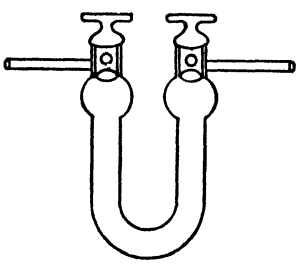


Fig 40

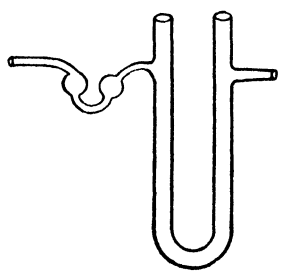
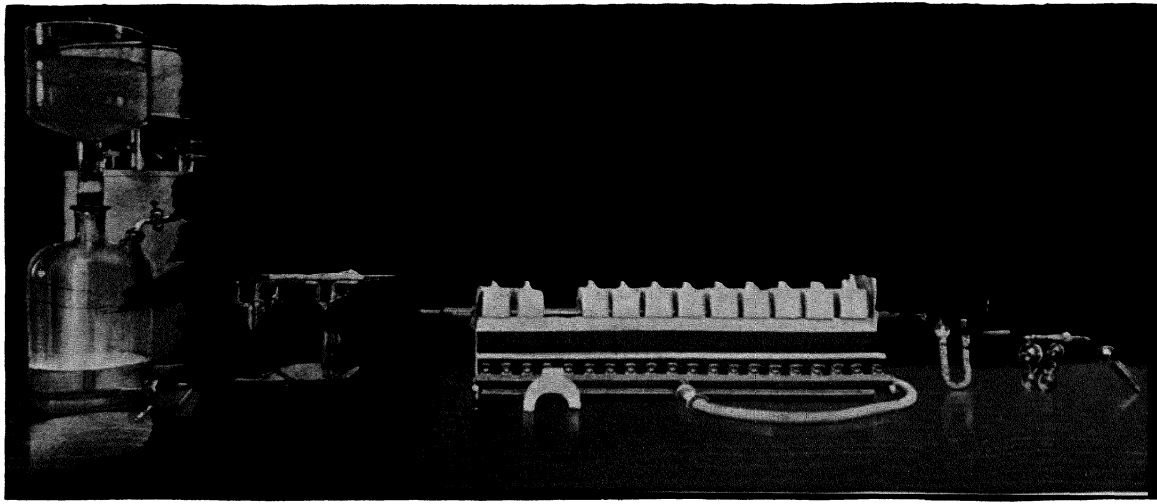


Fig 41

communication with the air by means of the cocks, which must be completely air-tight. The soda lime absorbs carbon dioxide much more readily than the potassium hydroxide solution, and the whole combustion can thus be conducted in a much shorter time and with far less risk of any of the gas not being absorbed.

As the rate at which the products of combustion are passing into the tube cannot be judged, it is advisable to use the form of drying tube shown in fig. 41. After a few drops of water have collected in the small side tube *a*, the rate at which the gases are passing can be readily seen and the flames of the furnace regulated accordingly. With either potash bulbs or soda-lime limbs it is necessary to protect the free end from atmospheric carbon dioxide and moisture during the combustion. This is accomplished by means of a straight tube filled with calcium chloride and soda lime. Before weighing, all tubes should be wiped with a clean dry cloth. All ground joints should be greased with the smallest pos-



B 960

To figure 44

Fig 42.

sible amount of vaseline, so that none of this is exposed; otherwise, when the tube is wiped, a portion of the exposed grease will be removed and a serious alteration in the weight of the tube will occur.

It must be remembered that if the tubes are weighed before the combustion, when filled with air, they must be weighed afterwards filled with the same gas; so that if the combustion has been conducted with oxygen it is necessary to replace this by dry air before reweighing. Any one of the tubes will be appreciably heavier when filled with oxygen than when filled with air.

If either potash bulbs or soda-lime tubes are employed it is necessary to refill them frequently; with the soda-lime tubes after every one or, at least, after every two combustions.

Carrying out the Combustion.—After the combustion tube has been thoroughly dried, the end of the tube nearer the drying apparatus is allowed to cool. During this time the absorption vessels and the substance to be combusted can be weighed. If the substance is a solid it is weighed in a platinum or porcelain boat which has been previously ignited, allowed to cool in a desiccator, and weighed. Care should also be taken that the substance itself is quite dry. The amount required is small, as a rule about 0·2 grm., and the boat and substance are kept in the desiccator until introduced into the tube. If the substance is not too readily volatile the boat may be introduced into the combustion tube whilst still warm. This is accomplished by removing the stopper, withdrawing the oxidized copper coil by means of a glass rod with a hook at the end, pushing in the boat until it nearly touches the small coil *b* (fig. 33), and rapidly replacing the oxidized coil and the cork. Before the boat is introduced it is advisable to attach the absorbing vessels to the front end of the tube, as shown in fig. 42.* All joints should be tight, and, if necessary, the rubber tubes should be wired on. A slow stream of dry air or oxygen, at the rate of about 2 bubbles per second, is passed through the tube. The regulation of this current is most easily made by means of a screw clip. One or two burners are lighted beneath the oxidized copper coil, and also gradually under the layer of granular copper oxide next to the boat. The lighting and regulation of the flames will vary

* The furnace shown in this figure is Fletcher's new furnace. It has the advantage that much less heat is radiated, and so is more convenient for working with.

considerably with the properties of the substance which is being combusted, the more volatile the compound the greater is the care required in turning on the burners; the whole operation must be conducted in such a manner that at no time is the evolution of the products of combustion rapid; if there is an indication that the substance is being volatilized too rapidly one or more flames must be extinguished. The heating may also be accomplished by gradually lowering the fireclay tiles over the tube Ultimately the portion of the tube where the boat is contained is raised to a dull red heat; the front part of the tube should be at a dull red heat during the whole operation, but care should be taken that no part of the tube is raised to a bright red heat, as the glass will then soften and become distorted, and in all probability the gaseous pressure inside the tube will blow holes in the soft glass.

When an electrically heated furnace is used the temperature can be regulated by gradually pushing the small furnace towards the portion of the tube where the substance is. When a gas furnace is employed and the current of air or oxygen is slow, drops of water occasionally collect at the back end of the combustion tube near the cork. These can be driven forward by gently warming the tube by means of a small flame or by means of one of the hot tiles. With an electrically heated furnace this condensation does not occur. One object in placing an oxidized spiral behind the substance is in order to oxidize any volatile material which passes back.

Moisture also tends to collect near the cork at the front end of the tube, but if the temperature of this part of the tube is regulated carefully, the glass will be too hot for water to condense and yet not sufficiently hot to decompose the rubber cork. To prevent the latter a shield of asbestos board may be used. If water does condense it can be driven over into the calcium chloride tube at the end of the experiment by gently heating this end when a more rapid current of oxygen is passed through the tube. The oxygen is continued until the gas issuing from the calcium chloride tube, used as a guard for the potash bulbs or soda-lime tubes, is capable of igniting a glowing splint. The oxygen can then be replaced by air and the absorption tubes removed, allowed to cool, and weighed.*

* The absorbing vessels should not be weighed too soon after the combustion, but should be allowed to stand for several hours or even overnight.

If it is wished to carry out a second combustion on the same day the front part of the tube is kept hot and a straight calcium chloride tube is inserted in the front end whilst the back part of the tube is allowed to cool. A fresh amount of substance is weighed out, and fresh calcium chloride tube and potash bulbs are weighed and attached, and the combustion carried out as already described.

Modifications of the Combustion.—The method described above is the common process for the estimation of carbon and hydrogen when carbon and hydrogen or carbon, hydrogen, and oxygen alone are present in a solid. Various modifications have to be introduced when the substance is a liquid, or when other elements such as nitrogen, sulphur, or halogens are present.

Estimation of Carbon and Hydrogen in a Liquid.—If the liquid is practically non-volatile at the ordinary temperature, and is not hygroscopic, it may be weighed in the open boat, otherwise it is advisable to weigh it in a small tube closed at one end, and provided with a loosely fitting stopper made out of a piece of glass rod flattened at one end (fig. 43). This tube can be introduced into the combustion tube by placing it in the boat in a slightly sloping position, and then pushing both into the tube with the open end of the vessel towards the layer of copper oxide.

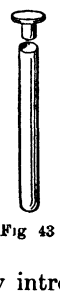


Fig 43

Substances which are extremely volatile are usually introduced into small glass bulbs which have been previously weighed. When the liquid has been introduced the bulb is sealed and reweighed. Before being introduced into the combustion tube the upper part of the neck is broken off and both parts placed in the boat.

Estimation of Carbon and Hydrogen in Presence of Nitrogen.—Certain nitrogen compounds, when combusted in the usual manner, yield higher oxides of nitrogen, which are absorbed either in the calcium chloride tube or in the potash bulbs and thus vitiate the results. The difficulty is readily overcome by placing a freshly reduced coil of copper gauze (some 10–15 cm. long) in the front part of the combustion tube in place of part of the granular cupric oxide. When the nitrogen oxides come in contact with the heated copper they are reduced to free nitrogen, which passes through the various absorbing vessels.

The simplest method of reducing the copper coil is to heat it strongly in the blowpipe flame in order to remove all organic matter, and to drop it while still hot into a large test tube of hard glass surrounded by a duster and containing a small amount (0·5–1·0 c.cm.) of methyl alcohol. The vapour of the methyl alcohol reduces the crust of cupric oxide on the coil, which should then have the characteristic colour of metallic copper. The coil is removed to a dry tube provided with a rubber stopper and glass tube which is attached to the pump. When a good vacuum has been reached, the tube and coil are heated in order to remove moisture and gases, the coil is allowed to cool under the diminished pressure and is then ready to be transferred to the combustion tube During the combustion it is not advisable to pass air or oxygen through the tube, but to turn the stopcock and to pass the oxygen when the whole tube has been heated and when the burners under the reduced copper coil have been turned out

N.B.—If the copper coil is reduced in a current of hydrogen gas, it is necessary to reheat it in some indifferent gas, *e.g.* carbon dioxide, as copper occludes hydrogen

Certain polynitro-compounds are somewhat explosive when heated, and hence cannot be introduced in the ordinary manner in a small boat. The simplest method of preventing a too rapid decomposition is to use a large copper boat which will just pass into the tube. This is partly filled with thoroughly dry powdered cupric oxide. A weighed amount of the nitrogen compound is added and mixed to a certain extent with the oxide by means of a thin glass rod. The mixture is finally covered with more dry copper oxide until the boat is three-fourths full, and the boat can then be placed in the combustion tube and the temperature gradually raised The copper oxide with which the substance is mixed is dried by ignition in a copper or porcelain crucible and allowed to cool in a desiccator. With the exception of the copper boat the remainder of the tube is fitted up as for the determination of hydrogen and carbon when nitrogen is also present.

Estimation of Carbon and Hydrogen in the Presence of Halogens.—If the compound to be combusted contains a halogen, a copper halide will be formed. Most of these are volatile to a certain extent, and are also partially decomposed by oxygen at high temperatures, yielding free halogen. The passage of this halogen into the absorbing tubes can be prevented by placing a coil of silver gauze in the front part of

the tube and keeping this at a moderate temperature, when the halogens will be retained in the form of silver halide. It is usual, however, to replace the copper oxide in the combustion tube by lead chromate,* which has been fused and broken up into small lumps. Under these circumstances lead halides are formed. These are less volatile and more stable than the corresponding copper compound, and there is thus less risk of halogen finding its way into the absorbing vessels. As a precaution it is advisable that the lead chromate in the extreme front part of the tube should not be heated too strongly, and that a silver coil should also be used

Estimation of Carbon and Hydrogen in the Presence of Sulphur.—The compound is combusted in a tube filled with lead chromate, as, if cupric oxide were used, the cupric sulphate would be decomposed and sulphur dioxide would escape and be collected in the absorbing vessels Plumbous sulphate is more stable, but is decomposed to a certain extent at high temperatures, so that it is advisable to have the front portion of the tube at a somewhat lower temperature than the middle portion. After the combustion of a sulphur compound it is always advisable to test the water that condenses in the bulb of the calcium chloride tube and make sure that it is free from sulphurous or sulphuric acid.

Compounds containing alkali or alkali-earth metals are mixed with pure potassium dichromate or lead chromate and then combusted, as otherwise they retain a certain amount of carbon dioxide in the form of the metallic carbonate The use of lead chromate is far less convenient than cupric oxide as it readily attacks the glass of the combustion tube and renders it liable to crack. With a good Jena glass tube it is easy to conduct twelve or more combustions in the same tube when cupric oxide is used, but with chromate the tube often cracks after using once or twice If the tube is heated too strongly the chromate fuses, and when it solidifies again is certain to crack the tube.

When sulphur is present, the same lead chromate should not be used more than three or four times.

* Aliphatic halogen derivatives give excellent results with lead chromate, but a few aromatic compounds rich in bromine yield low results for carbon, owing to the fact that part of the carbon is retained by the fused lead bromide.

B. Dennstedt's Method of Combustion

Within recent years Dennstedt's* method of combustion has come into vogue in many laboratories The principle of the process consists in bringing a mixture of the vapour of the substance and oxygen into contact with platinum, platinized quartz, or platinized asbestos at a suitable temperature The advantages of this method are that no special combustion furnace is required and a great saving of gas is effected. An 86-cm. combustion tube is placed on an iron bed supported by a simple iron frame and heated by means of four burners The iron bed is usually covered with asbestos paper, which keeps the glass from becoming fused to the metal and then cracking when cooled. When the bed becomes bent it should be straightened or replaced by a new bed, as otherwise the glass tube does not touch the bed, and cannot be raised to a sufficiently high temperature.

A layer of platinized quartz (4–5 cm long) is placed about the middle of the tube. Before each experiment the quartz should be tested in order to make sure that it is in an active state. This is accomplished by igniting a small piece of it in a Bunsen flame, turning out the flame, and seeing whether the gas will be ignited when it comes in contact with the hot quartz or asbestos.

Preparation of the Contact Material.—The platinized quartz may be prepared as follows. Large pieces of compact white quartz are raised to a bright-red heat and then dropped into cold water. Pieces the size of a pea are taken and freed from iron by treatment with hot concentrated hydrochloric acid. They are thoroughly washed and dried, and then warmed for some time with an alcoholic solution of pyridine platini-chloride.† The alcoholic solution is more efficient than an aqueous one, as the platini-chloride penetrates more readily into the pores of the quartz. The quartz is then dried and ignited in a porcelain crucible over the blowpipe;

* *Anleitung zur vereinfachten Elementaranalyze*, II. Auf. 1906.

† It is not advisable to use commercial platinic chloride solution, as this frequently contains small amounts of cupric chloride, and the copper left after ignition would destroy the activity of the platinum. The pyridine platinum chloride is precipitated on the addition of pyridine hydrochloride solution to the platinic chloride solution, and may be purified by recrystallization from water.

it should always be tested in order to demonstrate its activity, and if found inactive should be again treated with the pyridine salt.

The lumps of platinized quartz should not be packed too tightly and should be easily capable of being moved to the left or right. Platinized quartz has the drawback that it gradually loses its activity after frequent use, and must then be replatinized. Substances which contain lead, tin, zinc, and other volatile metals can readily destroy the reactivity of the quartz, and this cannot always be regenerated by boiling with hydrochloric acid.

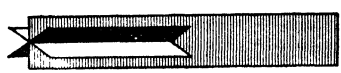


Fig 44

Platinized quartz may be replaced by platinum foil or wire; one of the most efficient forms is that of a six-rayed star of platinum foil. A strip of foil some 10 cm. long, 12–15 mm. broad, and 0·04–0·08 mm. thick has four lateral strips of the same foil luted on so that it forms a star (fig 44). Such platinum "stars" are manufactured by the firm of Heraeus in Hanau, and usually weigh 2–3 grm. The thinner the foil the more efficient the star, but if too thin they are somewhat fragile. The "stars" retain their activity unless

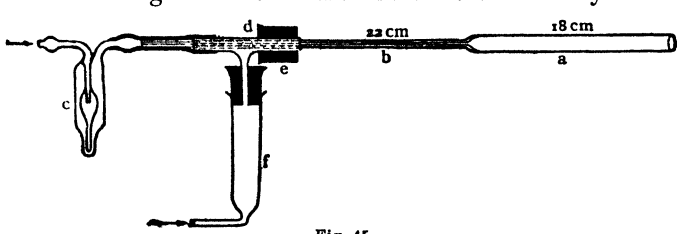


Fig 45

they become poisoned by small amounts of volatile metals, and the activity can, in nearly every case, be restored by extraction with concentrated hydrochloric acid.

Dennstedt (p. 51) recommends conducting the combustion with a double supply of oxygen. This is effected by using a tube of the shape shown in fig. 45.

It consists of an inner tube *a*, 17–18 cm. long and 14 mm. wide if the combustion tube is 16–18 mm., so that there is a clear space of 2–4 mm. between the two. This tube is made of hard glass, is open at one end, and carries the boat con-

taining the substance to be combusted; the other end is attached to a 22–25 cm. capillary tube *b*, to which a small wash bottle *c*, containing a few drops of concentrated sulphuric acid, is connected by means of a rubber tube. This wash bottle renders it possible to tell the rate at which the dry oxygen is passing through the capillary tube. A glass T tube, *d*, is placed over the capillary in such a manner that the one end is closed by the same rubber tubing which attaches the wash bottle to the capillary tube, the other end carries the cork *e*, which fits into the far end of the combustion tube. The side tube of the T is attached to a calcium chloride tube *f* by means of a rubber cork, and this tube, in its turn, is attached to the drying apparatus, so that a second stream of oxygen may be passed into the combustion tube between the inner tube holding the boat and the outer tube.

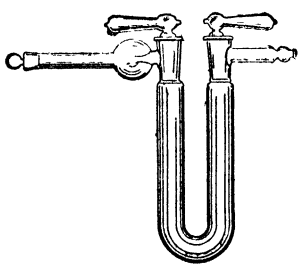


Fig 46

The following absorption vessels are recommended by Dennstedt: A calcium chloride U tube for the water.* This should be provided with the bulb and inner tube shown in fig 46, and with well-ground glass stoppers, as in the soda-lime tubes. To prevent moisture escaping from the bulb whilst the tube is cooling preparatory to weighing, the side tube should be closed either by a rubber tube and glass rod or, better, by a well-fitting glass stopper which can be weighed with the tube. In order to prevent the U tube becoming choked by the hydrated calcium chloride formed by the action of the water, it is recommended to fill the limb next the combustion tube half with calcium chloride and half with cotton wool. These can be removed as they become moist, whereas the calcium chloride in the other limb will require renewing very rarely. It is necessary to see that no calcium chloride dust is present in the side tubes, as this will absorb moisture as the tube is cooling. Plugs of loose cotton wool should be above the calcium chloride in each limb, so that a rapid current of gas will not be able to carry minute particles of calcium chloride into the side tubes.

* A current of dry carbon dioxide should be passed over the calcium chloride and then replaced by dry oxygen before the tube is used.

The carbon dioxide should be absorbed by means of soda lime contained in either of the forms of apparatus *a* and *b* shown in fig. 47. Each of these forms has a capacity of some 15–20 grm of soda lime, an amount which should suffice for a number of combustions. In filling the tube it is advisable to pack the soda lime somewhat loosely, as it expands during the absorption of the carbon dioxide. The soda lime in the lower part of the tube should be slightly moist, but that above quite dry, and when the same absorption tube is used for several combustions the gases should be passed through in the same direction A U tube with ground-in stoppers is attached to the soda-lime absorption tube. One limb of this is filled with

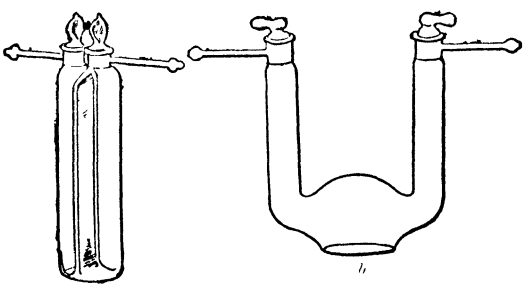


Fig 47

soda lime and the other with calcium chloride; by this means the last trace of carbon dioxide and also the moisture removed from the soda lime are retained. This tube is weighed before and after the combustion, and if the weight increases more than a few milligrams it is a sign that the main soda-lime tube is exhausted Following the U tube is a small wash bottle containing a 1 per cent palladous chloride solution; this indicates the rate at which the unabsorbed gas is passing through, and also whether the oxidation is complete. A cloudiness in the solution indicates incomplete combustion, and the analysis is worthless and need not be completed.

As the absorption vessels are all provided with ground-in stoppers it is simpler to fill them with dry oxygen before weighing the first time, and not to displace the oxygen by air when the combustion is complete.*

* Slight alterations in temperature affect the weight of the absorbing vessels. These should be left for some time after the combustion until they attain the temperature of the balance room.

The Combustion.—After the boat containing the substance has been introduced, the apparatus is tested in order to make sure that all the connections are tight. The oxygen is passed through at a suitable rate and the flame under the contact material is lighted. The temperature is raised gradually until the iron bed under the platinum is red-hot. The end of the platinum nearer the substance should be the hotter, and should be distinctly red-hot. As a rule, this flame suffices to start the decomposition or volatilization of the substance; if not, a second burner, placed about halfway between the end of the tube and the boat is ignited, and the temperature so regulated that the star-shaped end of the platinum continues to glow brightly, a sure sign that the combustion is proceeding normally. The rate at which the temperature is raised by increasing the size of the flame, by moving the burner nearer the boat, or by the use of the iron and asbestos tiles depends largely upon the volatility of the substance to be analysed.

When the substance contains nitrogen, halogens, or sulphur, in addition to carbon, hydrogen, and oxygen, absorption boats are placed in the front part of the combustion tube. In the absence of nitrogen, sulphur, and halogens the front part of the tube is empty, but is heated to about 200° by means of the burner in order to prevent the condensation of water formed during the combustion.

When nitrogen is present a large porcelain boat, 20 cm. long and filled with dry lead peroxide, is introduced into the front part of the tube in order to absorb any nitrogen peroxide formed by the oxidation of the nitrogen. In order to facilitate the absorption of the oxide it is advisable to use a boat which just fits into the tube and without an end, *i.e.* open towards the contact material. The temperature of the boat should be about 300–320°, *i.e.* just below the temperature at which oxygen is evolved. The peroxide should be renewed after every second combustion.

The lead peroxide can also be used for absorbing halogens and oxides of sulphur. When the compound contains sulphur this is converted into sulphur dioxide and trioxide, which react with the peroxide, yielding lead sulphate, which can be estimated. The peroxide used should be free from halogens, carbonate, and sulphate. 5–6 grm., contained in one of the large porcelain boats placed about 6–8 cm. from the contact substance, are used in addition to 2 grm. contained in a small boat, and the temperature is kept at about 320°.

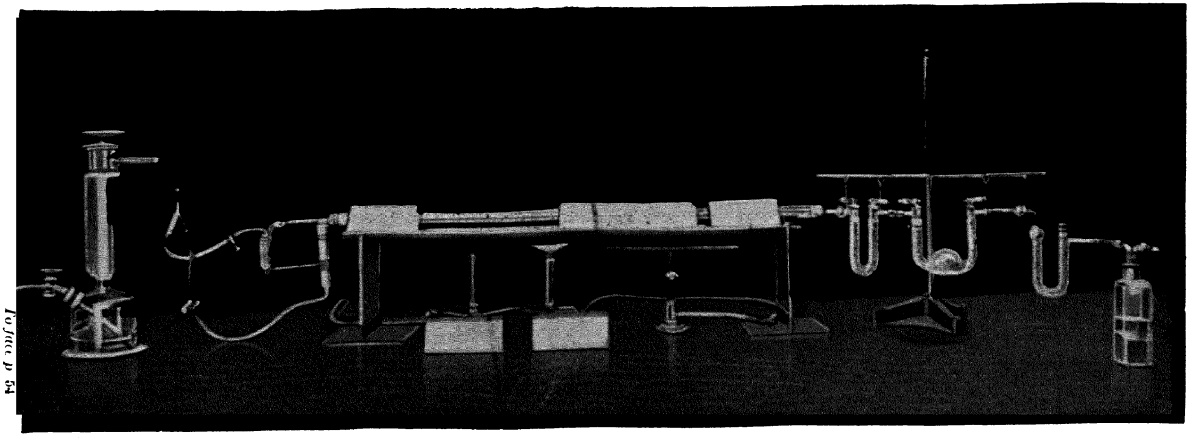


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Fig. 48.

After the experiment is completed the cold peroxide is digested with a 5 per cent sodium carbonate solution for an hour on the water bath, care being taken that any lumps are completely broken up by means of a glass rod When cold the whole is made up to 101 c.cm.* in a graduated flask, filtered through a dry paper, an aliquot part taken, and, after carefully acidifying, the sulphate estimated in the usual manner as barium sulphate.

For the estimation of sulphur alone, without carbon and hydrogen, the method may be simplified by using pure ignited sodium carbonate (4 grm.), heated to 350–400°, as absorbent. The front part of the tube is then attached to a small wash bottle containing water, in order to determine the rate at which oxygen is passing through the tube.

The estimation of chlorine and bromine† can be effected in much the same manner as sulphur. The absorbent is lead peroxide (8 grm.), which, however, must not be heated above 320°, as at higher temperatures the haloids and oxyhaloids of lead fuse. When cold, the mass is extracted with a warm 20 per cent pure sodium or potassium hydroxide solution, the whole is made up to 201 c.cm., and filtered through a dry paper. The chloride or bromide in an aliquot part of the filtrate is estimated in the usual manner after acidification with nitric acid.

If sulphur and halogen are both present, the peroxide is extracted with sodium hydroxide solution; one portion of the filtrate is used for estimating the sulphate and another portion for the halogen.

C. Estimation of Nitrogen

1. **Dumas' Method.**—The process commonly made use of for scientific purposes is the Dumas method, which consists in heating the substance with cupric oxide, reducing any oxides of nitrogen by means of copper coils, and measuring the volume of nitrogen produced. The air within the tube must be removed (*a*) either by means of a good mercury pump, or (*b*) by replacement by some other gas, such as carbon dioxide, which can be readily absorbed by a suitable solvent.

* The 1 c.cm. is the volume occupied by the solid peroxide, viz. 7 grm. of sp. gr. 7.

† Iodine is not completely absorbed by lead peroxide, but "molecular" silver may be used in this case.

The latter method is generally used, as it is somewhat simpler, but in either case the risk is that certain amounts of oxides of nitrogen will be formed, and will not be completely reduced. If nitrous oxide, N_2O, is present it does not interfere with the determination, as the volume is equal to the volume of nitrogen to which it would give rise; if, however, nitric oxide, NO, is present the percentage of nitrogen comes too high, as the volume of this oxide is double the volume of the nitrogen which would be formed by its reduction. Numerous authorities have drawn attention to the presence of small amounts of nitric oxide in the gases collected, but *T Gray*,* who has made a number of experiments on the estimation of nitrogen by Dumas' method, using carbon dioxide as the displacing gas, claims that nitrogen free from nitric oxide is obtained if the following conditions are fulfilled: The copper coil in the front part of the tube should be 5 in. long, should be tightly rolled, and should just fit into the tube, the coil should be strongly heated, and the current of carbon dioxide should be stopped during the actual combustion.

P. Haas † has drawn attention to the fact that certain basic substances belonging to the hydroaromatic series, and containing two methyl groups attached to the same carbon atom, *e.g.*:

$$CH\begin{matrix}\diagup CMe_2\cdot CH_2\\ \diagdown C(OH)\cdot CH\end{matrix}\diagup C\cdot NH\cdot C_6H_5,$$

when combusted in the usual way with cupric oxide, yield an appreciable amount of methane, which is measured with the nitrogen. This difficulty may be overcome by using lead chromate instead of cupric oxide, or by mixing the base with a mixture of cupric oxide and a small amount of cuprous chloride.

Generating the Carbon Dioxide.—The carbon dioxide may be generated within the combustion tube (see fig. 50), and then a tube closed at one end is used and the source of the carbon dioxide is magnesite ($MgCO_3$) in the form of lumps about the size of peas. On the whole it is more convenient to generate the gas outside the tube. This may be done by heating magnesite or sodium bicarbonate in a hard-glass tube connected with the back end of the combustion tube. If the bicarbonate is used it is necessary to place a small wash bottle containing concentrated sulphuric acid between the two

* *J. S. C. I.*, 1898, **17**, 743. † *J. C. S.*, 1906, **89**, 570.

tubes, as otherwise the water produced on heating the bicarbonate might crack the combustion tube. Probably the simplest method is to generate the carbon dioxide in a Kipp apparatus from marble and hydrochloric acid In this case it is essential to test the gas before it is used, in order to make sure that it is free from air. To facilitate the removal of air it is an advantage to boil the marble with water before it is introduced into the Kipp. *Young* and *Caudwell* * recommend generating the dioxide by dropping a concentrated solution of potassium carbonate (sp gr. 1 45–1 5) into a mixture of equal volumes of concentrated sulphuric acid and water contained in a Woulff's bottle (fig. 49)

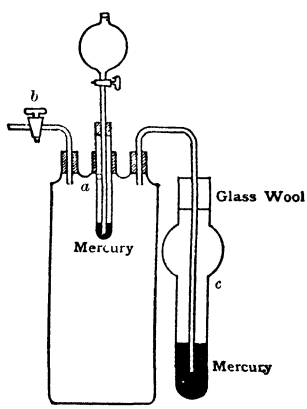


Fig 49

The carbonate solution is placed in the dropping funnel, runs into the mercury trap when the cock is turned, rises in the outer tube, and flows out through the small hole *a* The rate of evolution of gas can be regulated by the cock *b* Should the evolution be too violent the excess of carbon dioxide can escape through the safety tube *c* Care must be taken that when the nitrometer (fig 52 or 53) is being used the pressure is not reduced to such an extent as to draw air in through the safety tube.

The Combustion Tube —If a closed tube is used it is filled as shown in fig 50 The tube is of hard glass, closed at one end. The cupric oxide should be ignited in order to remove all organic nitrogenous matter, but it is not necessary to protect it from atmospheric moisture The simplest method of igniting the oxide is in a large nickel or copper crucible. The coil in the front part of the tube is reduced in the manner described on p. 48, but it is not necessary to dry it in a vacuum. The weight of substance taken should be sufficient to yield at least 20 c.cm. of nitrogen at atmospheric temperature and pressure, but not sufficient to yield more gas than can be collected in the nitrometer employed, viz. 50 c.cm. The known weight of substance and the powdered cupric oxide are mixed

* Young & Caudwell, *J. S. C. I.*, 1907, 26, 184.

in a small mortar, and introduced into the tube by means of a glass or metal funnel, the mortar being rinsed out several times with small amounts of powdered oxide.

If a tube open at both ends is used it is filled as shown in fig. 51. The given weight of substance may be mixed with

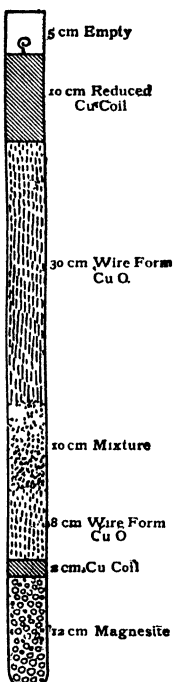


Fig 50

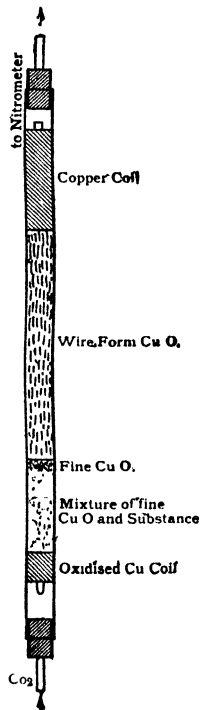


Fig 51

the powdered cupric oxide and introduced directly into the tube, or the mixture may be placed in a large copper boat. In either case it is not necessary to remove the long layer of wire-form cupric oxide when a second determination is to be made; all that is necessary is to remove the powdered oxide, to ignite this, and to pass a current of oxygen over the heated layer of wire-form oxide.

For most purposes the open tube method is the more con-

venient, and is absolutely essential if the substance to be analysed is readily decomposed, as when the closed tube is used there is great risk that the part of the tube in contact with the mixture of substance and copper oxide may become heated too strongly by the burners under the magnesite. When the tube has been placed in the furnace the first essential is to remove the air in the tube This is accomplished by passing a fairly rapid stream of carbon dioxide (from the heated magnesite or from the Kipp) through the tube *before* the measuring vessel (nitrometer) is attached. If this is attempted after the attachment of the nitrometer it will be found to take a much longer time. When most of the air has been displaced, the nitrometer (fig. 52 or 53) is attached, and the burners may be lit beneath the copper coil and part of the layer of cupric oxide, the issuing gas is tested from time to time by filling the measuring tube with the potassium hydroxide solution, and noticing whether all the gas bubbles are absorbed. When no more air is present, the measuring tube is filled with the alkali The burners beneath the tube are gradually lighted until the mixture itself is heated, when the front part of the tube is at a dull red heat. The manner in which the flames are ignited, raised, or lowered must be suited to the individual substance. After the stream of carbon dioxide has been turned off, the bubbles of gas should pass in a regular stream, about 2 per second, into the nitrometer. In no case must a great rush of gas be allowed. After the combustion is completed, and the whole length of the combustion tube has been raised to a dull red heat, the carbon dioxide is again turned on, and the products of combustion swept out gradually into the nitrometer When all the gas issuing is absorbed the tube is clamped and the nitrometer removed. The whole combustion takes on the average about an hour and a half.

The Nitrometer.—Various forms of apparatus are used for collecting and measuring the nitrogen evolved. Fig. 52 represents the *Schwarz* nitrometer and fig. 53 the *Schiff* nitrometer. The liquid used in both cases is a concentrated solution of potassium hydroxide (1 : 2), and a mercury trap at *a* is used in order to prevent the alkali rushing back into the combustion tube owing to the rapid absorption of carbon dioxide.

In the Schwarz nitrometer the measuring tube is filled by opening the stopcock *d* after the apparatus has been attached to the combustion tube at *b*, and pouring in the liquid until

the two tubes are full, then closing the stopcock and running the liquid out of the side tube *c*. In the Schiff nitrometer the combustion tube is attached to the side tube *b*, and the measuring tube is filled by raising the reservoir attached to *c* whilst the stopcock *d* is open. The cock is then closed and the reservoir lowered.

Points to be borne in mind are: (1) Do not have the nitrometer attached whilst the air is being displaced, and if, after testing, air is still found to be present, remove the alkali from the measuring vessel whilst more carbon dioxide is passed through, as otherwise the alkali will be used up and will not be effective when the actual combustion is in progress; (2) do not use sodium hydroxide solution instead of potassium hydroxide, as the carbonate will crystallize out; (3) remove the alkali and wash the nitrometer thoroughly after use, as otherwise the stopcocks will stick; (4) tilt the furnace so that the front part of the tube is at a lower level than the back portion. By this means any water which condenses in the front end of the tube cannot run back on to the hot glass and crack the tube.

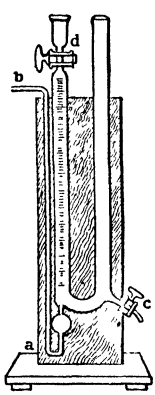


Fig 52

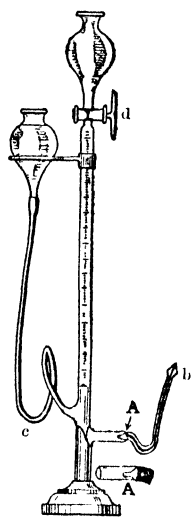


Fig 53

Calculation.—The volume *v* c.cm. of nitrogen measured at *p* mm. pressure and *t*° C. is reduced to normal temperature and pressure, care being taken that the tension of the caustic potash solution (Table I, Appendix) is subtracted from the baro-

metric pressure, or the gas can be transferred from the nitrometer to a graduated tube placed in a tall cylinder of water. The temperature is then the temperature of the water and the pressure the barometric pressure minus the tension of aqueous vapour at that temperature (Table II, Appendix). The percentage of nitrogen is then—

$$\frac{v(p - q)0{\cdot}12505 \times 273}{760(273 + t)w},$$

where q is the tension of aqueous vapour at $t°$, w = weight of substance taken, and 0012505 is the weight of 1 c.cm. of nitrogen at normal temperature and pressure.

The calculation can be facilitated by the use of tables which give the weight of pure nitrogen in milligrammes contained in 1 c.cm. of moist nitrogen under different conditions of temperature and pressure.

2. **Kjeldahl Method.***—The method consists in heating the substance with concentrated sulphuric acid, or a mixture of sulphuric acid and potassium sulphate, until the liquid is clear and colourless The carbon becomes oxidized to carbon dioxide and the nitrogen converted into ammonia (ammonium sulphate). The amount of ammonia formed can be determined by making the liquid strongly alkaline, distilling off the ammonia, and collecting in a known volume of standard acid. The method gives good results with the following groups of organic compounds. Amines, ammonium compounds, pyridine and quinoline derivatives, alkaloids, proteids, and related compounds. It is the method usually employed for estimating nitrogen in feeding-stuffs, organized tissues, animal fluids, &c. It should be remembered that the following groups of compounds do not yield quantitative results unless subjected to a preliminary treatment· Nitro, nitroso, azo, hydrazo, diazonium compounds, and probably cyanogen derivatives and platinichlorides of bases.

From 0 5–1·0 grm. of the substance is heated by means of a Bunsen burner in a 300-c.cm. Kjeldahl flask (fig. 54), made of Jena or resistance glass, with 20–30 c.cm. of a mixture of sulphuric acid† (3 parts) and potassium sulphate (1 part) As

* Z A., 1883, 366.

† All the materials used in the Kjeldahl estimation should be previously tested for nitrogen. The simplest method is to perform a blank estimation with a substance free from nitrogen (*e g.* cane sugar), using known quantities of acid, potassium sulphate, and sodium hydroxide, and if nitrogen is found, to deduct the amount from each subsequent determination.

sulphur dioxide is evolved in large quantity the operation should be conducted in a good fume-cupboard or in an apparatus so arranged that the sulphur dioxide can be absorbed (*Vogtherr*).

In the Vogtherr apparatus (fig. 55) the flask (500 c.cm.) is fitted with a ground-in head which carries a tube bent twice at right angles. The free end of this tube is attached by means of a rubber cork to the pear-shaped absorbing tube, the lower end of which dips into the absorbing liquid contained in a flask. As long as sulphur dioxide is being evolved, sodium hydroxide solution is placed in the absorbing flask When the evolution of sulphur dioxide ceases the small flask

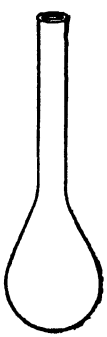


Fig 54

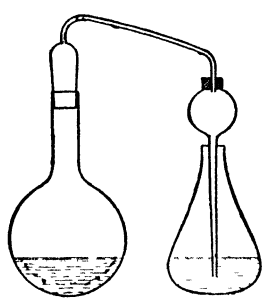


Fig 55

is lowered so that the end of the absorbing tube is just above the surface of the alkali, and the contents of the flask are further heated until colourless. The head and absorbing tube are removed and well washed when the flask is cold, the sulphuric acid is diluted with 100 c.cm. of distilled water, and then some 200 c.cm. of a 15 per cent solution of sodium hydroxide and a little zinc dust run in, the head and absorbing tube replaced, the liquid boiled, and the ammonia collected in an excess of standard acid contained in the absorbing vessel. If Vogtherr's apparatus is not used, it is customary, as soon as the liquid in the Kjeldahl flask is colourless, to allow it to cool, then to pour it into a larger flask and to add an excess of 20 per cent sodium hydroxide solution, care being taken that the acid and alkali are not thoroughly mixed until the absorbing vessel is attached.

The alkaline liquid is then boiled, or steam is blown through,

and the escaping ammonia collected in a known volume of standard acid. It is customary to introduce some form of safety tube (fig. 56) between the distillation flask and the vessel containing the standard acid. The object of such a tube is to prevent particles of the alkaline solution from being carried over.

The addition of one or two grams of zinc dust to the contents of the flask prevents the alkaline liquid from bumping during the distillation. If a Liebig condenser is used the time required for the whole of the ammonia to be driven over is somewhat considerable, owing to the ammonia dissolving in the water which is deposited in the condenser tube Lassar-Cohn recommends distilling for fifteen minutes, using a water condenser, then running the water out of the condenser so that the condensing tube becomes hot, and continuing the distillation for a further five minutes or until the contents of the receiver become hot.

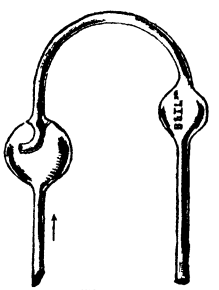


Fig 56

Each cubic centimetre of 0 1 *N.* acid neutralized by the ammonia corresponds with 0 0014 grm. of nitrogen in the given weight of substance used

3. **Soda-lime Method.**—This method is but little used at the present time, and is based on the fact that certain nitrogenous compounds, when heated with alkali, evolve their nitrogen in the form of ammonia. The method is not of general use, as numerous groups of nitrogen compounds, *e.g.* nitro- and azo-derivatives, do not yield up their nitrogen in the form of ammonia when heated in this manner.

Will and *Varrentrapp** suggested the use of soda lime.

A combustion tube 30 cm. long and 6 mm. in diameter is drawn out to a point, and bent at one end as shown in fig. 57 *a*. A small amount of granular soda lime† is placed in the closed end; this is followed by an intimate mixture of a given weight of the substance with about ten times its weight of powdered soda lime, care being taken to rinse out the mortar or vessel in which the admixture has been carried

* A. 1841, 39, 257.

† Ordinary soda lime is quite moist, and should be ignited before use, as otherwise considerable amounts of water will collect in the front part of the combustion tube and may cause it to crack.

out several times with small amounts of powdered soda lime. The remainder of the tube is filled with granular soda lime, and the open end is attached by a rubber cork to the bulbs (fig. 57, *a* or *b*) containing a given volume of standard acid. The amount of substance taken must be less than the amount required to yield ammonia to neutralize the whole of the acid (about 25 c.cm. can be conveniently used in an ordinary *Will and Varrentrapp* bulb, fig. 57, *a*). The tube is placed in a furnace, gently tapped to leave a small air space, and then heated, starting from the front end and gradually extending the heat backwards until the whole tube is hot. The free end of the bulb is then attached to an aspirator, a partial vacuum created, and the closed end of the combustion tube broken off

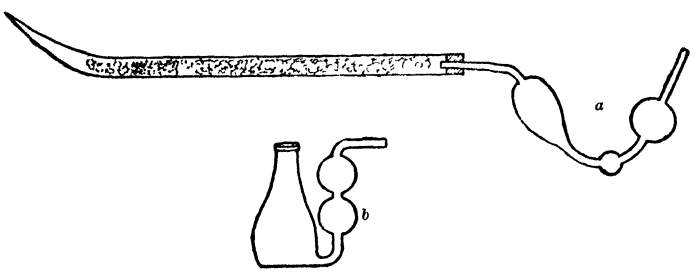


Fig 57

so that a current of air (ammonia free) is drawn through the tube in order to sweep all the ammonia into the absorption bulb. The combustion should not be conducted too rapidly, about 1 bubble per second, and the contents of the absorption bulb should not become cloudy or yellow in colour.

D. Estimation of Halogens

Various methods are used for determining the percentage of halogen in an organic compound. The *Carius* method is generally used, but the method introduced by *Stepanow*,* and further described by *Bacon*,† is considerably simpler in practice, and yields concordant results if the essential details stated below are observed.

1. **Stepanow's Method.**—0·2–0·3 grm. (= *a*) of the substance to be analysed is introduced into a flask and a volume

* B. 1906, 39, 4056. † J. A. C. S. 1909, 31, 49.

of 98 per cent ethyl alcohol added. (Volume of alcohol required is $156a$ c.cm. if chlorine is present, $68a$ c.cm. if bromine, and $44a$ c.cm. if iodine is present.) The flask is attached to a reflux condenser and the solution boiled while a quantity of clean metallic sodium ($19{\cdot}5a$ grm. if chlorine is present, $8{\cdot}5a$ grm. if bromine, and $5{\cdot}5a$ grm. if iodine is present) is added in small pieces through the condenser tube. This addition should extend over *at least* 30 minutes, and the mixture should then be boiled for an hour. After cooling to 50–60°, water is added through the condenser tube, then nitric acid in slight excess and a known volume of standard silver nitrate solution. After filtering off the silver halide, the excess of silver nitrate in the filtrate is titrated with a standard solution of ammonium thiocyanate (*Volhard's* method, cf. *Treadwell* and *Hall*, Quantitative Analysis, p. 543). Hence the percentage of halogen in the compound may be calculated.

As an alternative, or when the solution is coloured, the precipitate of silver halide should be weighed, but in this case it is advisable to remove the alcohol by distillation before the addition of nitric acid, as otherwise explosive silver fulminate may be formed.

The method renders the estimation of two halogens in the same compound a comparatively simple operation. The reduction is effected as already described. The acidified aqueous liquid is mixed with an excess of standard silver nitrate solution and the precipitated silver halides removed, washed, and weighed. In the filtrate and washings the excess of silver nitrate is determined by titration with standard ammonium thiocyanate.

From the weight of silver required for complete precipitation and the weight of the mixed silver halides precipitated the amount of the two individual halides can be calculated. Example·

If a = weight of Ag, and b = weight of mixed AgCl and AgBr.

Then, assuming all b were AgCl, calculate wt. of Ag = c,
and „ „ AgBr „ „ Ag = d.

Then $\frac{c-a}{c-d}100 = x$ = percentage of AgBr in mixture of AgCl and AgBr, and $100 - x$ = per cent of AgCl.

From these numbers the percentage of Cl and Br in the original substance can be calculated.

2. **Carius's Method.**—The method consists in heating the substance under pressure with fuming nitric acid and silver nitrate, and then estimating the amount of silver halide formed either volumetrically (Volhard's method) or gravimetrically using a Gooch crucible.

The estimation is carried out in a sealed tube made of special Jena glass. Such tubes rarely burst if properly sealed, and may be used a number of times. Tubes made of ordinary combustion glass or thick-walled tubes of soft glass should not be used, as they burst more readily and can only be used once or twice. A Jena tube, closed at one end and of a length suitable to fill the bomb furnace (fig. 59), is selected and thoroughly cleaned and dried, in the tube is placed an excess of silver nitrate crystals (in most cases about 0·5 grm. is ample) and not more than 20 drops of pure* fuming nitric acid of sp. gr. 1·5. A common mistake is to use too large a quantity of acid and thus increase the risk of bursting the tube. The acid should be run in by means of a long thistle funnel, and this should be carefully removed so that no drops of acid come in contact with the upper part of the tube.

The substance (not more than 0·2) is weighed in a small clean tube closed at one end and about 7 cm. long and 6–8 mm. diameter. If the substance is comparatively volatile, a loosely fitting glass stopper made from a bit of glass rod can be placed in the open end of the weighing tube. (Cf. fig. 43.) This tube is then introduced into the bomb tube in such a manner that it slides slowly down the inner surface until it comes in contact with the part moistened with the acid. It is not advisable to let it drop to the bottom, as the acid is then liable to creep into the weighing tube and decompose the substance before the bomb tube is sealed. The upper end of the tube can then be sealed off as follows: The end is gradually heated in a small smoky flame of a blowpipe whilst the tube is held at an angle of about 45° and slowly turned in the hand, so that the whole upper end becomes evenly heated; when hot, the blowpipe flame should be used, and when the glass is soft a piece of hot glass rod is fused on. The flame is then directed a little lower down on the tube, while it is still slowly turned in the hand. As soon as it is sufficiently soft it is drawn out into a capillary which can

* It is obvious that all the reagents employed should be free from halogens. As nitric acid often contains hydrochloric acid it should be tested before being used.

be cut by a file some 3 or 4 in. above the shoulder. The shoulder and capillary are far too thin to withstand pressure, and require thickening. This is accomplished by heating the shoulder in the blowpipe flame, whilst the tube is turned gradually in the left hand and the capillary very gently supported by two fingers of the right hand. If the capillary is held tightly the glass will twist and become distorted. As soon as the walls have thickened considerably, and have almost met, the shoulder can be drawn out to form a thick capillary which can then be sealed off in such a way that the end of the tube has the appearance represented in fig 58.

Fig 58

The sealed end is held in the smoky flame until it is covered with a deposit of soot, and then allowed to cool. The tube is ready for heating in the bomb furnace (fig 59) after it has been wrapped in asbestos paper and placed in an iron protecting tube. The flames are lit under the bomb furnace, and the temperature fairly rapidly raised to 320–340° * by adjusting the burners, and kept at that temperature for several hours. The tube is allowed to cool, and opened the following morning.

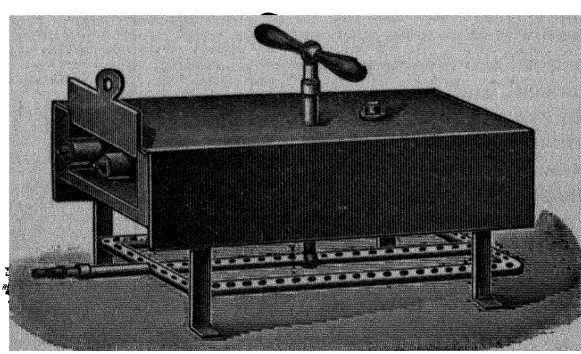


Fig 59

The tubes should never be opened whilst hot, and should not

* Many aliphatic halogen derivatives are completely destroyed at much lower temperatures, viz. 250°. For temperatures above 300° a thermometer filled with nitrogen under pressure should be used, as otherwise the mercury thread breaks at the high temperature.

be touched with the naked hand even when cold, as there is a risk of explosion. To open the tube the capillary end is raised from the protecting iron tube and very gently warmed in order to drive out drops of acid which may have condensed into the capillary, which is then heated in a Bunsen flame until the glass softens and the compressed gases escape by a hole which they themselves blow in the soft glass. When the pressure in the tube has been completely released, as shown by holding a flame near the hole, the upper conical part of the tube is broken off. This is readily accomplished by making a fairly deep file mark at the requisite point, and then heating this mark by means of a red-hot glass rod. The tube cracks at the mark, and by gradually carrying the hot rod round the circumference of the tube the crack may be extended right round, when the upper portion will fall away. The contents of the tube are removed into a beaker by means of distilled water, the small tube is thoroughly washed, and all traces of silver halide removed from both tubes into the beaker, which is then heated until the precipitate has settled to the bottom and the liquid is quite clear. If the silver halide is at all lumpy it should be pressed out with a glass rod, as it is liable to retain small amounts of silver nitrate and nitrite The precipitate is removed on to a quantitative filter paper, or preferably a Gooch crucible, thoroughly washed with distilled water until the filtrate yields no precipitate with dilute hydrochloric acid, and the operation completed in the usual manner for the estimation of silver halides. After the analysis is completed it is always advisable to examine the silver salt, in order to make sure that it does not contain splinters of glass. This may be done by adding potassium cyanide solution to the Gooch crucible, allowing to stand for some time, then sucking the solution through by means of the pump, thoroughly washing the asbestos first with potassium cyanide solution and finally with water, drying, and reweighing. Any increase in weight of the crucible must be due to glass, and this weight can be subtracted from the weight of silver halide previously found.

If a known weight of silver nitrate is placed in the Carius tube, then it is possible to estimate the percentage of halogen by determining by a volumetric process such as Volhard's the amount of silver nitrate left after the tube has been heated.

The Carius method does not give good results with compounds containing iodine (*Seeker* and *Mathewson*, C. N. 1911, **103**, 61).

E. Estimation of Sulphur

1. **Carius Method.**—The substance is heated with fuming nitric acid in a sealed tube, as in the Carius method for estimating halogens After the tube has been opened the sulphuric acid formed is estimated as *barium sulphate* It is advisable to remove the nitric acid before the precipitation is carried out, as it is found that barium sulphate precipitated in the presence of the nitrate carries down with it small amounts of nitrate which cannot be removed by subsequent washing with water. In order to remove the nitric acid the contents of the bomb tube are rinsed into a porcelain dish, hydrochloric acid is added, and the solution evaporated on the steam bath. The solution is then diluted to about 400 c.cm., boiled, and the sulphate precipitated by the addition of a *slight excess* * of boiling barium chloride solution. The precipitate is removed to a Gooch crucible, washed with hot water until a sample of the washings no longer produces a turbidity with dilute sulphuric acid, dried, and weighed.

2. **Sodium Peroxide Method.**—When the sulphur compound is not volatile in the presence of alkali, *e.g.* the salts of a sulphonic acid, the following process is strongly recommended. The substance (0·2–0·8 grm.) is mixed in a nickel vessel with a concentrated sodium peroxide solution, and the mixture evaporated on the steam bath until it has an oily consistency. The dish is then heated over a small flame. No explosion and no spitting should take place, although local heating may occur at one or two points. If the mixture begins to blacken, a further quantity of peroxide solution is added, and eventually the dish and its contents are transferred to a porcelain dish containing sodium peroxide solution. The whole is heated for about fifteen minutes on the water bath, the platinum vessel removed and washed, the liquid acidified with hydrochloric acid, and the sulphate precipitated in the usual manner as barium sulphate (*Edinger*).

F. Estimation of Metallic Radicals in Organic Salts

The estimation of platinum, gold, or silver is readily effected by heating a known weight of the salt, first gently and then

* A large excess of barium chloride should be avoided, as the sulphate tends to retain small amounts of the chloride from concentrated solutions, and this chloride cannot be removed by washing.

more strongly, in a porcelain crucible until all the organic matter has been driven off and a clean residue of the metal is left. The precaution necessary for accurate results is to regulate the heating so that no violent reaction accompanied by spurting occurs.

Many of the heavy metals, such as lead, copper, bismuth, &c., can be precipitated from solutions of their salts by sulphuretted hydrogen. Copper may also be determined by igniting the salt to constant weight with continual access of air, and weighing the residue of oxide (Exp. 68).

Calcium is estimated by igniting a known weight of the salt and weighing as oxide. The complete removal of carbon and elimination of carbon dioxide requires some time, and the ignition and weighing should be repeated until the weight is constant.

Barium is estimated by precipitation as barium sulphate by the addition of hot dilute sulphuric acid to a boiling solution of the salt in water or dilute hydrochloric acid. The precipitate is collected in the ordinary manner or in a Gooch crucible, washed, dried, and weighed.

The ammonia of an ammonium salt may be estimated in the usual manner by boiling a known weight of the salt with excess of potassium hydroxide solution, receiving the evolved ammonia in a known volume of standard acid, and estimating the excess of acid left by titration with standard alkali, using methyl orange as indicator.

The sodium, potassium, calcium, and barium radicals may be estimated by heating weighed quantities of the salts with concentrated sulphuric acid, preferably in a platinum crucible, and weighing as sulphate. This estimation requires some little care in order to avoid loss by the creeping of the mixture. The simplest method is to add a slight excess of sulphuric acid, to heat the crucible from above with a Bunsen flame, and after the sulphuric acid has been removed to add a small pellet of ammonium carbonate in order to transform any acid sulphate completely to the normal sulphate. The heating is then continued.

VI. DETERMINATION OF THE EQUIVALENT OF AN ACID

The usual methods for the determination of the equivalent of an acid are (A) by direct titration with standard alkali, (B) by the preparation of a metallic salt, preferably the silver salt, and its analysis, *i.e.* the determination of the percentage of metallic radical in the salt.

A. By Titration

The most suitable alkali for titrating is barium hydroxide solution, as this can be kept free from carbonate. A roughly 0·1 N solution is prepared and accurately standardized by means of pure oxalic or succinic acid. This standardization should be carefully carried out and checked by a second standardization, preferably with a second pure acid. As an example, 200 c.cm. of exactly 0·1 N oxalic and 200 c.cm. of exactly 0.1 N succinic acid can be prepared by dissolving one-fiftieth of the gram-equivalent of each acid separately in water, and making each up to 200 c.cm in standardized flasks or ordinary measuring flasks which have been carefully calibrated in the laboratory. Known volumes, not less than 20 c.cm. of the acid solutions, are measured from a calibrated burette or pipette, a few drops of an aqueous alcoholic solution of phenol-phthalein added, and the alkali run in from a burette until the pink coloration is just permanent.

The water used throughout these experiments should be freshly distilled and free from carbon dioxide. If the titrations obtained with the two different solutions do not agree, experiments must be conducted in order to determine where the error lies. The most likely possibilities of error are: (1) A mistake in one of the weighings. Whether this is so or not can be settled by making a separate weighing of small amounts of each acid and titrating each quantity with the alkali. (2) One of these acids is impure. This will almost undoubtedly be the case if the readings obtained with different weights of the one acid correspond but do not agree with the results obtained with the second acid. The only method of overcoming this error is to recrystallize the two acids, and when dry to use them for further titrations.

In order to protect the barium hydroxide from contact with the atmospheric carbon dioxide, the apparatus shown in fig. 60

will be found extremely convenient. The tower and tube are filled with soda lime, which is covered with cotton wool so that no finely divided particles are blown into the solution. If the lime in the tube is renewed fairly frequently that in the tower can be used for a long time. The liquid is forced over into the burette by means of the blow ball when the spring clip is open; immediately the burette is full the clip is closed.* Barium hydroxide in such an apparatus can be kept for months, but should be re-standardized occasionally.

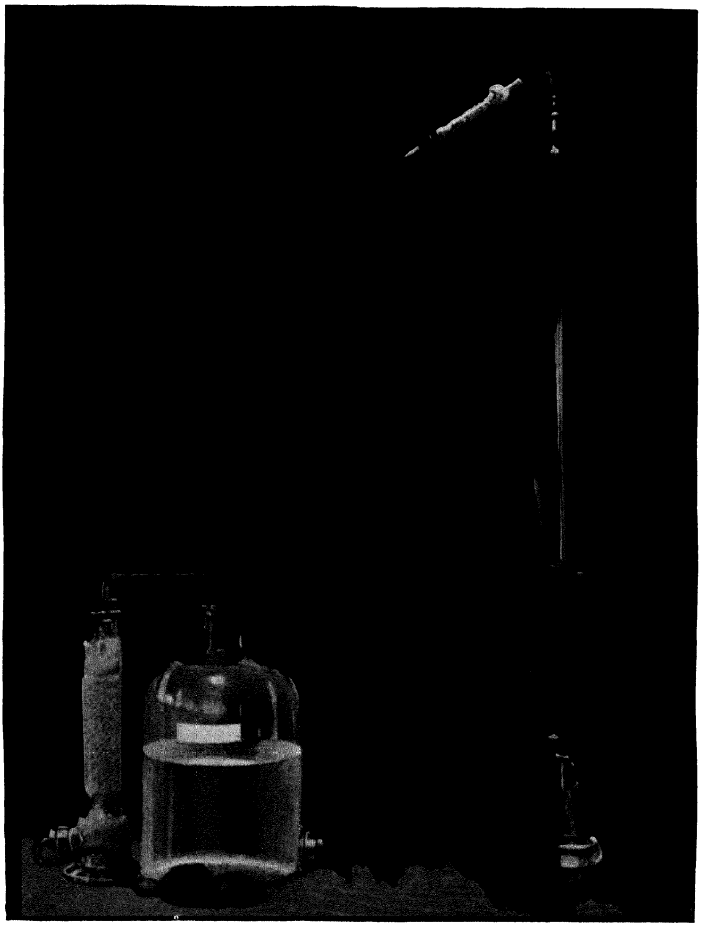
A hot concentrated solution of the hydroxide is prepared and allowed to cool, the saturated solution at 15° is approximately 0·4 N. To obtain an approximate 0·1 N solution the apparatus shown in fig 60 is fitted up, and the whole filled with air free from carbon dioxide by blowing air through the soda-lime tower. 3 litres of distilled water are then siphoned over into the bottle, and ultimately 1 litre of the 0·4 N baryta solution. This is accomplished by fitting a cork and tubes, such as is used in an ordinary wash bottle, to the baryta flask. The short tube is attached to a soda-lime tube and the other tube to the end of the long tube in the large bottle after the burette has been disconnected.

To determine the equivalent of an unknown acid a definite amount is weighed out accurately, the weight actually taken being sufficient to use between 20 and 50 c cm of the standard alkali. To ascertain this amount a rough titration is made with about 0·1 grm. of the acid.

If the acid dissolves in water a solution in freshly distilled water should be employed. If insoluble in water a mixture of alcohol and water or alcohol alone may be used, but in all cases the alcohol should be previously tested in order to make sure that it is free from acid. (Ordinary alcohol is liable to contain small amounts of acetic acid.) The indicator used throughout is phenol-phthalein, as the end point is extremely sharp when a strong alkali like barium hydroxide is used. If sodium hydroxide is used as the standard alkali it should be carefully protected from atmospheric carbon dioxide, as small amounts of carbonate render the end point less delicate, and further, the continual absorption of carbon dioxide materially affects the concentration of the alkali when phenol-phthalein is used as indicator.

If any but freshly distilled water is used for dissolving the

* In fig. 60 a 3-way cock is used, so that a spring clip is not necessary.



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To face p. 72

Fig. 60.

acid a blank experiment should be made in order to determine whether one drop of the alkali solution is sufficient to produce a pink coloration with a given volume of the water and a drop or two of phenol-phthalein. If this is not sufficient the amount of alkali required should be accurately determined, and this subtracted from the volume of alkali required in the actual titrations of the acid.

The average of several readings is taken,* and from the data obtained the amount of acid required to neutralize the gram equivalent of barium hydroxide is calculated.

B By the Analysis of a Salt

Silver Salts.—The most convenient salt to use is the silver salt. The silver salts of organic acids are characterized by the following properties: (*a*) Sparingly soluble in water, hence readily prepared; (*b*) all crystallize without water of crystallization, and hence no need to drive off water of hydration; (*c*) the silver is extremely readily estimated. The preparation of a silver salt is described in Chap XIII. When the salt is thoroughly dry, for example, after being in a desiccator over sulphuric acid for several days, a small amount (0·2–0·5 grm.) is placed in a weighed porcelain crucible, gently heated with the lid on, and the temperature gradually raised until the crucible is red hot and a pure white residue of silver remains. Great care has to be taken at the beginning of the heating, otherwise vigorous decomposition occurs and loss by spirting. In most cases combustible gases are formed and take fire as they are evolved. After the first weighing the crucible is heated again and reweighed in order to make sure that the weight is constant.

From the results of the analysis the weight of salt which contains the gram atom of silver, *i.e.* 107·93 grm. of silver, is calculated. This represents the equivalent weight of the silver salt, and the equivalent of the acid is obtained by subtracting from this number the atomic weight of silver and adding the atomic weight of hydrogen—

$$\text{Equivalent of acid} = \text{Equivalent of Ag. salt} - 107{\cdot}93 + 1{\cdot}008.$$

Barium Salts.—In many cases the barium salts of the acids are insoluble in water, *e.g.* barium oxalate, or are sparingly

* The readings should be approximately the same, and for 20 c.cm. should not vary more than 0·1 c.cm.

soluble and crystallize well (Exp. 69). As barium salts are apt to contain water of crystallization it is advisable to heat the salt in an air oven at a fixed temperature (110–140° is usually sufficient) until the weight is constant.

The salt is analysed and the percentage content of barium determined (see p. 70). The weight of barium salt which contains one equivalent of barium (68·7) is calculated This is the equivalent of the salt, and from this the equivalent weight of the acid is readily obtained—

Equivalent of acid = Equivalent of salt $-68{\cdot}70 + 1{\cdot}008$.

Calcium Salts.—As in the case of barium salts, calcium salts are often readily prepared. These may be analysed by simple ignition to constant weight in a platinum crucible (see p. 70). The weight of salt which yields one equivalent weight of calcium oxide (28·03) is the equivalent weight of the salt. From this the equivalent of the acid may be obtained as above.

VII. DETERMINATION OF THE EQUIVALENT OF A BASE

A. By Analysis of a Platinichloride (Chloroplatinate)

Most organic bases resemble ammonia in the formation of platinichlorides which are sparingly soluble and which crystallize well.

The platinichloride is prepared by dissolving the base in a slight excess of moderately concentrated hydrochloric acid* and adding a fairly concentrated solution of platinic chloride. In most cases if the ordinary laboratory solution of platinic chloride is used (about 2·5 per cent) no precipitate is formed, as the platinichlorides are sparingly soluble in water. With a 10 per-cent solution crystalline precipitates are readily formed.

The precipitate is filtered, washed with a very small amount of water, dried, and analysed in the same manner as the silver salt of an acid. The final residue consists of metallic platinum. The platinichlorides of the organic bases resemble

* In a few cases, *e.g.* α- or β-naphthylamine, the hydrochloride is very sparingly soluble in cold water or hydrochloric acid.

ammonium platinichloride in that they contain 2 grm. equivalents of base in the gram molecule, *e.g.*

$$(NH_3)_2H_2PtCl_6 \text{ and } B_2H_2PtCl_6,$$

where B represents the equivalent weight of the base.

The method of calculation is to find the gram molecular weight of the platinichloride, *i.e.* the number of grams of salt which yield the gram atom (194·8) of platinum.

Then the equivalent of the base

$$= \frac{\text{molecular weight of platinichloride} - (2{\cdot}016 + 194{\cdot}8 + 6 \times 35{\cdot}45)}{2}.$$

B. By Titration

The equivalent of a base may often be determined by preparing a crystalline salt with some mineral acid or even organic acid—*e.g* the hydrochloride, sulphate, acetate, benzoate—purifying the salt, and then titrating the amount of acid present in the salt by means of standard alkali (barium hydroxide solution, p. 71), using phenol phthalein as indicator. The weight of base which is combined with the equivalent weight of the acid will be the equivalent weight of the base.

Salts prepared in aqueous solution may contain water of crystallization, and in such cases the preparation in ether solution is often satisfactory.

Experiment 7.—Prepare aniline sulphate from dilute sulphuric acid and aniline and recrystallize from water. Determine the equivalent of the base by titrating the amount of sulphuric acid present in a known weight of the dry salt.

Experiment 7a.—Prepare aniline hydrochloride by adding a solution of hydrogen chloride in ether to aniline dissolved in the same solvent. Filter off the precipitated hydrochloride by means of a pump, wash with ether and dry. Make a standard solution of the salt in water and titrate with standard baryta.

The methods described above are *not* methods for determining molecular weights. In the case of an acid, for example, it is necessary to know the *basicity*. Similarly with bases, the methods only yield molecular weights when the *acidity* of the base is known. If the base is known to be mono-acidic, its hydro-

chloride will be represented by the formula XHCl, and its platinichloride as $X_2H_2PtCl_6$, where X represents a molecule of the base. The gram molecule of base will therefore be half the amount equivalent to one gram atom of platinum, or, in other words, the equivalent and molecular weights will be identical. If, however, the base is diacid, *e g.* $C_6H_4(NH_2)_2$, the platinichloride will be of the form XH_2PtCl_6, and the molecular weight will be double the equivalent.

VIII. DETERMINATION OF MOLECULAR WEIGHTS BY PHYSICAL METHODS

A. Vapour-density Methods

(S.B., pp. 9 and 10)

The common vapour-density method used in chemical laboratories is the Victor Meyer method (fig. 61)

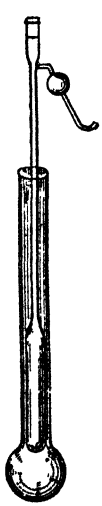
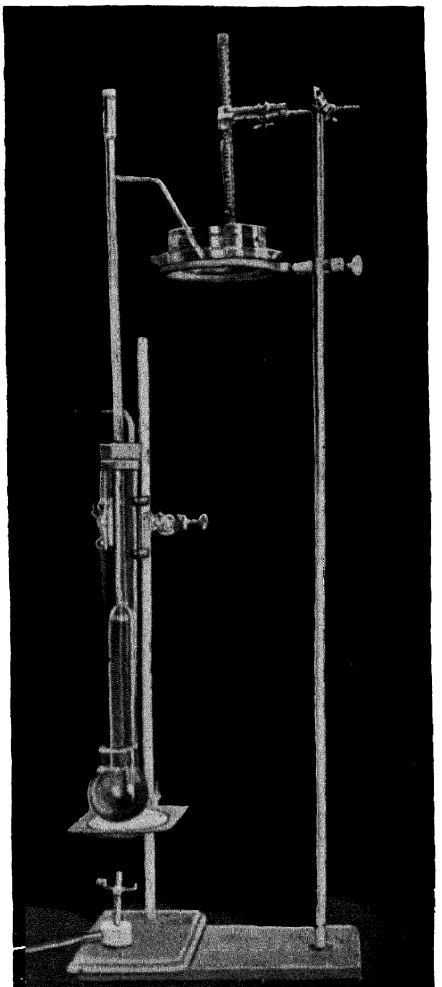


Fig. 62

The inner vessel (fig. 62) is thoroughly cleaned and dried, and a plug of dry asbestos wool is placed in the bottom. In the bulb of the outer jacket or mantle is placed a liquid the boiling-point of which is considerably higher than the boiling-point of the substance under investigation, *e g* water may be used when the vapour density of a volatile liquid like ether (boiling-point 36°) is to be determined. If a higher boiling liquid is required, aniline (boiling-point 185°) may be used, or for still higher temperatures ethyl benzoate (213°), amyl benzoate (262°), diphenylamine (310°), anthracene (335°), anthraquinone (368°), [sulphur 448°].

A glass mantle may be used, but for temperatures above 310° a copper vessel or, in the case of sulphur, an iron vessel must be used. The inner tube is held in position by a clamp, and the liquid in the jacket is boiled so that the greater part of the jacket is filled with the vapour of the boiling substance. The delivery tube attached to the inner vessel is placed under water in a pneumatic trough and the cork placed in the open end of the vessel. By this means it is easy to tell when the air in the inner vessel is at a constant temperature, namely,



H 960 *To face p 76*

Fig 61.

by observing when no more air bubbles escape from the delivery tube.* When a constant temperature has been attained the end of the delivery tube is placed under a graduated measuring tube filled with water.† The cork is then removed, and a known weight of the substance under examination is introduced and the cork immediately replaced. If the substance is a solid a small roll or pastille can often be made by means of a small pastille press (fig 63)‡ and then dropped in. If a liquid is being used it is better to introduce it in a small bulb tube (fig. 64), or a minute stoppered bottle (fig. 65). In either case the vessel used must slide down the neck readily and the amount of material used must never

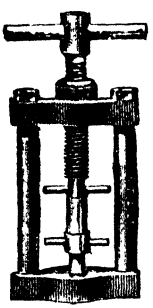


Fig 63

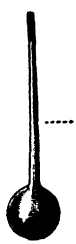


Fig 64

Fig 65

be too large. The vapour to which it gives rise should not more than half fill the bulb of the inner vessel.

If a bulb tube is used it is most readily filled by warming the bulb and then allowing it to cool while the open end is immersed in the liquid. When a small amount of liquid has entered, the bulb is heated until the liquid boils, and then cooled as before, and as the vapour condenses fresh liquid is

* A certain amount of care is required in conducting the experiment, as if the flame under the mantle is blown about by currents of air, the temperature may fall and water may be sucked back into the inner vessel.

† The trough and measuring tube may be replaced by an ordinary Hempel gas burette, in which the displaced air is measured.

‡ Another method of obtaining a solid rod of material suitable for dropping into the inner vessel is to take a glass tube some 2 mm. wide and 6 cm. long. The molten solid is drawn up into this tube and allowed to solidify; to remove the solid the tube is heated very gently above a flame until the surface just melts, when it can be pushed out by means of a copper wire.

drawn up until the whole tube is nearly filled. If the liquid is very volatile the bulb should be sealed during weighing and the sealed end broken off just before introducing into the vapour-density apparatus.

If it is desired to carry out three or four determinations it is not necessary to take the apparatus to pieces. The measuring tube is removed and the trough lowered; a current of air is passed through the inner tube whilst it is still at the constant temperature, and by this means the vapour of the liquid is driven out.

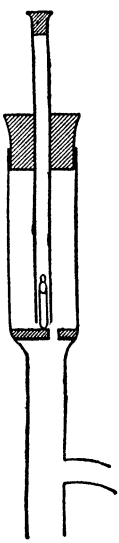


Fig. 66

N.B.—A second determination should never be made before the vapour produced in the first determination has been removed, as otherwise the gas driven over in the second determination consists of a mixture of air and vapour, and when this mixture bubbles through the cold water the vapour is condensed, and thus the volume of gas measured is considerably less than the volume of gas displaced by the vapour produced in the second determination.

The volume of air measured under given conditions of temperature and pressure (viz. the atmospheric pressure and the temperature of the water) is reduced to normal temperature and pressure, care being taken to allow for the pressure of aqueous vapour The value of this pressure for different temperatures is given in Table II, Appendix. The weight of this volume of hydrogen is then readily calculated, since 1 c.cm. of hydrogen at N.T.P. weighs 0·00009 grm., and the ratio—

$$\frac{\text{wt. of substance taken}}{\text{wt. of hydrogen}}$$

gives the vapour density.

Various modifications of the original apparatus have been suggested.

1. In order to avoid removing and replacing the cork, the upper part of the inner tube can be arranged as follows. The small tube or bottle rests on a piece of glass rod, which passes through a second side tube, and when the temperature is constant and it is desired to lower the bottle the glass rod is withdrawn by pulling it through the rubber tube by means of which it is attached to the side tube. This

apparatus should not be used if the substance is very volatile.

2. Another method of releasing the small bulb is suggested by Patterson* (fig. 66). In the upper and wider part of the inner tube a circular piece of cork ($\frac{1}{4}$ in. thick) is introduced. Eccentrically in this cork a circular hole is bored which will admit of the passage of the bulb. The bulb itself is retained in position by means of a glass tube passing in a slightly oblique position through the rubber bung at the top of the apparatus. This tube is also corked, and when it is desired to release the bulb the tube is moved (the elasticity of the rubber cork permits this without any leak) until the bulb is over the opening of the cork, when it falls to the bottom of the V. Meyer tube.

For other vapour-density methods see *P. Blackman.*†

B Freezing-point Method—Cryoscopic Method

(S. B., pp. 10 and 11)

For rough work the following apparatus may be used. A stout test tube some 3·2 cm. in diameter, a metal stirrer made of platinum, a thermometer graduated in tenths of a degree, and a cork to fit the tube. The freezing-point of the pure solvent is first determined Some 20-50 c.cm. of liquid are employed, and the tube is immersed in a bath some 3–4° below the actual freezing-point; *e.g.* if water is the solvent a freezing mixture of ice and salt at about −3° may be used. This is placed in a stout glass vessel, and may be protected by being surrounded with a woollen cloth. The liquid in the tube is kept stirred, and when the temperature registered by the thermometer in the liquid is some 0·3° below the correct freezing-point, the inner tube is removed, and the stirring continued. The temperature falls a little farther until ice begins to separate, when it rises to the correct freezing-point, and will remain at that temperature for a few minutes, provided the ice and liquid are thoroughly mixed by gentle stirring. After the reading has been taken, the ice is melted and the operation repeated. The mean of several readings is taken as the correct freezing-point of the solvent. The operation is then repeated, using a solution of known concentration

* C. N 1908, **97**, 73.

† C. N. 1907, **96**, 223; Z. 1908, **63**, 48 and 635; C. N. 1910, **101**, 121.

in place of the pure solvent. The freezing-point will be lower and again the mean of several readings is taken. The difference between the freezing-point of the solution and of the pure solvent is called the depression of the freezing-point, and is usually denoted by Δ. The molecular weight, M, is calculated by means of the formula—

$$M = \frac{Cp}{\Delta},$$

where C is the molecular lowering for the given solvent, and p represents the number of grams of solute dissolved in 100 grams of solvent.

The value of C for some common solvents is as follows:—

	C.	M.-P.
Water	18·5	0°
Benzene	50	5·48°
Acetic acid	39	16·75°
Ethylene bromide ...	118	7·92°
Naphthalene	69	79·6°
Phenol	72	39·6°
Palmitic acid	44	59·9°
Nitrobenzene	69·1	5·28°

Experiment 8.—Determine the molecular weight of urea by the freezing-point method, using aqueous solutions of about the following strengths, viz. 2·5, 5, and 7·5 per cent.

Experiment 9.—Determine the molecular weight of citric acid by a similar method.

Fairly accurate results can only be obtained when the solvent and solute do not react with one another. If they combine to form a definite compound the results are not correct, owing to the fact that the concentrations of the substance are altered by the formation of the compound. Care should also be taken that the solvent employed does not cause the association or the dissociation of the solute. Thus the molecular weights of strong electrolytes should not be determined in aqueous solutions. Rough determinations of the molecular weights of many organic acids (cf. Exp. 9, where citric acid is used) may be made in aqueous solution, provided the acids are not strongly ionized. The majority of carboxylic acids are not strong acids, and only slightly ionized. A further point to bear in mind is that the solvent must not cause the association of the solute. It is also essential that the crystals

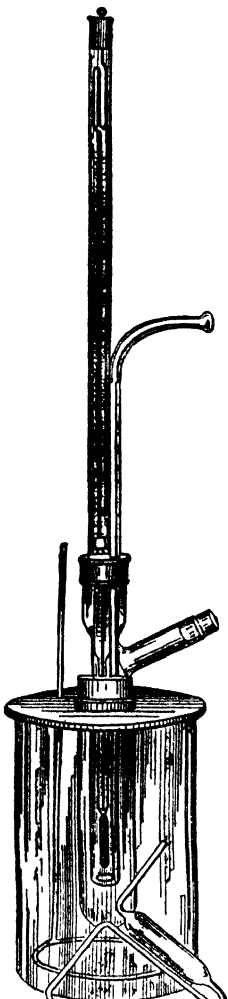


Fig 67

which separate on cooling and stirring should be crystals of the pure solvent and not mixed crystals of solute and solvent; in other words, the solvent and solute must not form solid solutions. The cryoscopic method is usually carried out somewhat more carefully than described above in an apparatus (fig. 67) devised by Beckmann.

The freezing-point tube itself has a wide side tube through which the solute can be introduced, and is fitted into a wider tube by means of a rubber ring. This outer tube serves as an air bath, and keeps the freezing-point tube itself from coming into contact with the freezing mixture. The stirrer for the freezing-point tube is usually made of stout platinum wire, or of a platinum ring fused into a glass holder, which passes through a glass tube carried by the cork. The thermometer used, "the Beckmann thermometer" (fig. 68), is a delicate thermometer graduated in one-hundredths of a degree. As the whole scale of the thermometer has a range of some 6 degrees only, the instrument is so arranged that it can be used for solvents with very different melting-points by an alteration in the amount of mercury contained in the bulb. For example, if it is desired to work with benzene solutions, as the freezing-point of benzene is 5·48° it is necessary that the amount of mercury in the bulb is such that when the temperature is 5·48°, or some 1 to 2 degrees lower, the top of

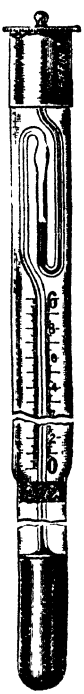


Fig. 68

the mercury thread can be read off on the scale. If there is too much mercury in the bulb the temperature of the thermometer is raised some 2 to 3 degrees above the actual temperature required, the excess of mercury passes over into the reservoir, and if the instrument is gently tapped this excess separates from the main thread and falls into the lower part of the reservoir. When the thermometer is then cooled to the actual freezing-point of the benzene the temperature can be read off on the scale. The numbers on the scale obviously do not represent the correct Centigrade temperatures, but merely relative temperatures. If the amount of mercury in the bulb is too small, the temperature is raised until the thread of mercury reaches from the bulb to the reservoir, the thermometer is then inverted, and some of the mercury is gently tapped into the upper part of the reservoir, so that it joins the thread. The temperature is then allowed to fall to within 2 or 3 degrees of the actual freezing-point, care being taken that the mercury thread does not become broken. When the temperature is some 2–3 degrees above the freezing-point of the solvent any excess of mercury attached to the thread is shaken into the lower part of the reservoir by gently tapping, and the instrument is then ready for use.

The same instrument should not be used for very varying temperatures, as the glass after being heated does not immediately assume its original volume on cooling. It is advisable to have one instrument for comparatively low temperatures and a second one for higher temperatures (*e.g.* boiling-point determinations). Some of the points to be observed in the carrying out of a careful molecular-weight determination by the freezing-point method are:—

1. The temperature of the cooling bath should not be more than 3° below the actual freezing-point of the solution.

2. The liquid, the freezing-point of which is being determined, should not be supercooled more than 0·5°, *i.e.* the inner tube and air jacket should be removed from the outer vessel when the thermometer registers a temperature a few tenths of a degree below the actual freezing-point. The object of preventing too great a supercooling is to avoid the sudden formation of a large quantity of solid solvent. If this happens, the concentration of the solution alters materially, and the actually observed freezing-point is somewhat too high.

3. The stirring should be continuous and fairly regular, not so rapid that the heat due to friction makes any appreciable

difference. The stirring may be a little more rapid just before the liquid freezes, in order to facilitate the separation of solid particles.

4. The mean of at least four readings should be taken in each case, and solutions of two or three different concentrations should be examined. The usual method is to determine the freezing-point of the solvent, then to introduce a small amount of the solute through the side tube, to see that it is all dissolved, and to determine the freezing-point of the solution. A further amount of solute is added, and the freezing-point of the more concentrated solution determined. The process may be repeated several times. The working limits are: (*a*) lower limit, an amount of substance sufficient to produce a depression of at least 0·1°; (*b*) upper limit, the most concentrated solutions must all be such that when cooled crystals of pure solvent and not crystals of the solute separate.

5. If the solvent is hygroscopic, care should be taken to protect it from moisture or means adopted to keep the moisture content constant. Dry air should be passed in through the side tube or the freezing-point determined in the presence of a salt-pair (*e.g.* Na_2SO_4, $10H_2O$ — Na_2SO_4).*

Experiment 10.—Determine the molecular weight of naphthalene in benzene, or the molecular weight of benzoic acid in acetic acid.

Experiment 11.—Calculate the degree of association (x) of benzoic acid in benzene solution from the formula—†

$$x = \frac{\Delta_1 - \Delta_2}{\Delta_1\left(1 - \frac{1}{n}\right)},$$

* Roberts and Bury, J.C.S., 1923, **123**, 2037

† This formula is based on the following considerations:—

In every gram molecule of substance there will be $1 - x$ gram molecule unassociated and $\frac{x}{n}$ associated. $\therefore$ total number of gram molecules is $1 - x + \frac{x}{n}$, or $1 - x\left(1 - \frac{1}{n}\right)$, but the depression of freezing-point is proportional to the number of gram molecules present in a given volume of solution.

$$\frac{\Delta_2}{\Delta_1} = \frac{1 - x\left(1 - \frac{1}{n}\right)}{1}$$

$$x = \frac{\Delta_1 - \Delta_2}{\Delta_1\left(1 - \frac{1}{n}\right)}$$

where n represents the number of molecules which associate to form the complex molecule (in this case $n = 2$). Δ_2 = the observed depression for the given solution, Δ_1 the calculated depression if no association had occurred, and x is the fraction of the total number of molecules which combine to form the larger molecules.

C. Boiling-point Method or Ebulliscopic Method

The principles underlying this method are essentially similar to those for the cryoscopic method. (*a*) For a given pressure the boiling-point of a pure liquid is constant. (*b*) The boiling-point is raised by the introduction of a solute, and for an ordinary solute the raising of the boiling-point is proportional to the amount dissolved in a given weight of solvent. (*c*) For different solutes quantities in the ratio of their molecular weights produce the same raising of the boiling-point. Hence if the molecular raising of the boiling-point is known for a given solvent, the molecular weight of a suitable solute can be determined by means of the formula—

$$M = \frac{Cp}{\Delta},$$

where C is the molecular raising of the boiling-point, p = number of grams of solute in 100 grams of solvent, and Δ is the actual elevation observed.

For ordinary laboratory work *Walker and Lumsden's* modification of *Landsberger's method* is sufficiently accurate, as the results should deviate not more than 5–10 per cent from the theoretical. The method consists in weighing the amount of solute and measuring the volume of solution. The values for C are not the same for this method as for the method when the amount of solvent is weighed.

The following table gives a list of the two values for C for some common solvents:—

	C. For the gram mol. in 100 grm. of solvent.	C^1 For the gram mol. in 100 c cm. of solution.
Alcohol	11·7	15·6
Ether	21·6	30·3
Acetone	17·1	22·0
Benzene	26·7	—

The apparatus (fig. 69) consists of an outer mantle, the lower end of which is connected to a condenser and an inner graduated tube in which the solvent is placed. The solvent or solution in the inner tube is boiled by means of the vapour of the pure solvent, which is led in through the tube B, which dips below the solvent in the inner tube. The thermometer, graduated in 0·1° or 0 01°, is held by the cork which carries the delivery tube, and is arranged so that the bulb is immersed in the boiling liquid. The vapour from the

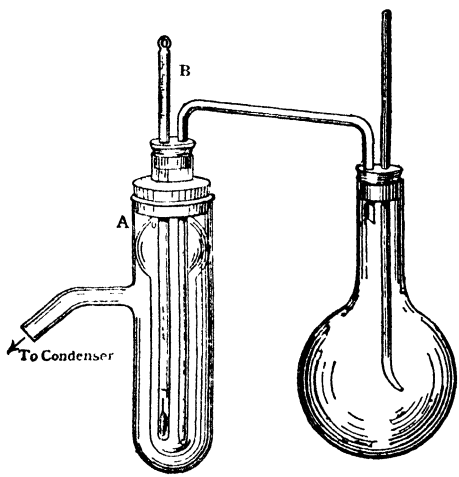


Fig 69

boiling liquid in the inner tube escapes through a small opening at A, and then forms a hot mantle surrounding the inner tube and ultimately passes into the condenser. By this method superheating of the liquid in the graduated tube is avoided, a difficulty which it is not easy to overcome when direct heating with a flame is resorted to. In carrying out an actual determination some 10–12 c.cm of pure solvent are placed in the graduated tube, and the vapour passed in from B until drops of liquid fall from the end of the condenser at the rate of one per second or per two seconds. The temperature is then read off, if necessary with the aid of a lens or small telescope. The greater part of the liquid is then poured back into the distilling flask after the flame has been removed, and only 5–7 c.cm. are left. A weighed quantity of the sub-

stance under examination is then dissolved in this solvent and the boiling-point determined as before. *Immediately* the temperature has been read off the distilling flask is disconnected, so that no more vapour passes over, care being taken that the vapour does not become ignited when the disconnection is made. The volume of liquid is then read off after the thermometer and delivery tube have been removed, and whilst the vessel is in a perfectly upright position. A second determination is made by passing in the vapour again until the liquid drops from the condenser in a regular series of drops, and the temperature and volume are again read.

Experiment 12.—Determine the molecular weight of *o*-toluic acid in ether.

D. Vapour-pressure Methods

The simplest laboratory method for determining molecular weights by vapour-pressure readings is due to *Blackman*,*; other methods have also been suggested, but are somewhat complex for ordinary laboratory work. †

The apparatus consists of two graduated test tubes containing two solutions and joined by a T piece with a bulb in each of the two limbs attached to the test tubes, this attachment being effected by means of wooden corks. All three ends are open, and the solutions are heated in a suitable bath, the temperature of which is registered by a thermometer.

The basis of the method is the fact that the volumes of two solutions with their vapours in communication, when allowed to attain equilibrium, will be directly proportional to the number of dissolved molecules, *i.e.*

$$\frac{v_1}{v_2} = \frac{\frac{w_1}{m_1}}{\frac{w_2}{m_2}} \quad \text{or} \quad \frac{m_1}{m_2} = \frac{v_2 . w_1}{v_1 w_2},$$

where w_1 and w_2 are the respective weights of the substances of molecular weights m_1 and m_2 dissolved in the solvent of volumes v_1 and v_2 after equilibrium has been reached.

* J. C. S. 1905, 87, 1474.

† See *Will* and *Bredig*, B. 1889, 22, 1084; *Barger*, J. C. S. 1904, 85, 286; *Perman*, *ibid.*, 1905, 87, 194.

Suitable weights (0·05 — 0·1 grm.) of two substances, one of known molecular weight and the other the substance the molecular weight of which is to be determined, are placed in the two test tubes and are dissolved in a suitable solvent, care being taken that the liquids do not more than half fill the test tubes. The T piece is attached by means of the wooden corks, and the solutions are boiled in a water or other suitable liquid bath. The volumes of the two solutions are noted after given intervals of time, and from each pair of readings the molecular weight is calculated from the formula.

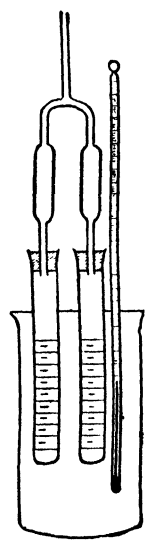


Fig 70

If equal weights of the two substances are used the formula becomes even simpler, since—

$$w_1 = w_2, \text{ and then } \frac{m_1}{m_2} = \frac{v_2}{v_1}.$$

Some necessary precautions to take are—

1. The solvent used should be pure.
2. The first few readings should be neglected, as some little time is required for the solutions to attain equilibrium.
3. No readings should be taken after the amount of liquid in either test tube measures less than 1·5 c.cm.
4. The solutes must not be appreciably volatile in the vapour of the solvent.
5. The bath must be kept about 2–3° above the boiling-points of the solutions, as these are apt to boil irregularly. To minimize violent ebullition and consequent mixing of the solutions thin pieces of platinum wire may be introduced into the solutions, and the apparatus should be tapped gently from time to time against the sides of the bath. It is advisable to have the apparatus hanging freely so that it can be lifted out of the bath instantly, if the ebullition become violent.

Experiment 13.—Determine the molecular weight of β-naphthol in pure ether,* assuming that the molecular weight of resorcinol is 110.

* See Exp. 31.

IX. HYDROCARBONS

A Saturated Hydrocarbons or Paraffins, C_nH_{2n+2}.

(S.B. 30–42.)

Method I.—The common laboratory method for the preparation of the simpler members of the paraffins is by heating an intimate mixture of the sodium salt of a fatty acid with sodium hydroxide, preferably in the form of soda lime.

$$\begin{matrix} C_nH_{2n+1}\cdot COONa \\ HONa \end{matrix} = Na_2CO_3 + C_nH_{2n+2}$$

Experiment 14.—Preparation of methane, CH_4. An intimate mixture of one part, by weight, of **anhydrous** sodium acetate with four parts, by weight, of dry soda lime is heated in a hard-glass flask or tube provided with a cork and delivery tube. The vessel is heated gently and then more strongly, and the gas evolved is collected in the usual manner in cylinders by means of the pneumatic trough. Special attention is drawn to the following points:—

1. The materials must be thoroughly dry, as otherwise water collects and may drop back on to the hot glass vessel and cause it to crack. Crystallized sodium acetate contains three molecules of water of hydration. The simplest method of rendering the crystals anhydrous is to fuse them on a clean sand tray until no more water is given up. The soda lime, which is somewhat hygroscopic, should also be dried by heating it strongly in a metal dish or tray.

2. As methane and air in certain proportions form explosive mixtures, large quantities of gas should not be collected until the air in the generating flask has been allowed to escape. A small test tube full of gas should be collected from time to time and a light applied; if the gas burns quietly it will indicate that practically all the air has been removed and larger quantities of the gas can be safely collected.

3. The gas evolved in this reaction is not pure, but contains appreciable amounts of hydrogen and ethylene.

Experiment 15.—Apply a light to a cylinder of the gas. Note what happens and prove that carbon dioxide is formed.

Bubble the gas through bromine water and see whether the colour of the bromine is destroyed. Expose a mixture of

methane and chlorine to sunlight and observe what happens.

Method II.—For the preparation of a pure paraffin a common method is the reduction of an alkyl halide (Chap. XI) with nascent hydrogen, usually from the copper-zinc couple and alcohol.

$$C_nH_{2n+1}I + 2H = C_nH_{2n+2} + HI.$$

Experiment 16.—Preparation of ethane,* C_2H_6. Granulated zinc (20 grm.) is treated four times with a 2 per cent solution of cupric sulphate, the sulphate being left each time in contact with the zinc until completely decolorized. The zinc, covered with a fine deposit of copper, is washed with water and finally with alcohol, and is then placed in a 200 c.cm. flask fitted up as shown in fig. 71. 100 c.cm. of alcohol mixed with a drop or two of dilute sulphuric acid are added, and ethyl iodide, C_2H_5I (Exp. 34), gradually run in from a dropping funnel. The gas evolved often contains ethyl iodide, and it is advisable to pass it through the tube *a*, which contains more of the copper-zinc couple moistened with alcohol.

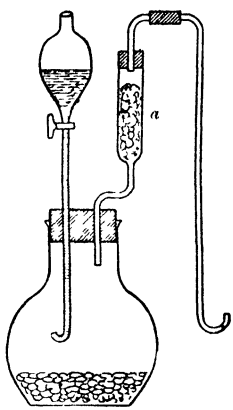


Fig. 71

The method of collection and properties are similar to those of methane.

Method III.—Certain of the lower members of the paraffin series can be prepared by the electrolysis of aqueous solutions of the potassium or sodium salts of fatty acids, *e.g.* ethane from sodium acetate solution.

The hydrocarbon is evolved at the anode, and is formed when the complex acetate anion $CH_3 \cdot COO$ is discharged. The non-charged group $CH_3 \cdot COO$ is unstable, and immediately decomposes into CH_3 and CO_2. The CH_3 groups then unite in pairs to form ethane molecules.

Experiment 17.—Electrolytic preparation of ethane. A saturated solution of sodium acetate, containing about 2 per cent of glacial acetic acid, is placed in a porous pot (1·5 in. in diameter) closed by a cork through which the anode and delivery tube pass. This anode consists of a stout piece of platinum

* Gladstone and Tribe, *J. C. S.* 1884, 45, 154.

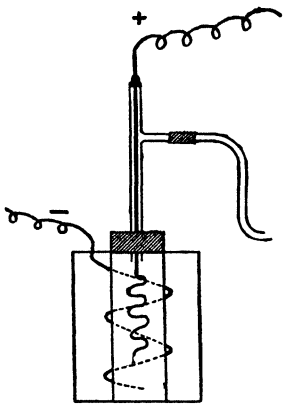


Fig 72

wire wound in the form of a spiral. A convenient device is to fuse the anode into the T-shaped delivery tube (fig. 72).

A piece of nickel wire wound round the cell serves as the cathode. The porous cell is placed in a beaker also containing a saturated solution of sodium acetate, and a current of 60–80 amperes per square decimeter of electrode surface is passed.

As the temperature should not rise above 20° the whole apparatus should be placed in a large vessel of cold water. The gas which issues from the delivery tube consists of a mixture of ethane and carbon dioxide, the latter of which can be absorbed by collecting the gas over a fairly concentrated solution of potassium hydroxide. The hydrogen evolved at the cathode is allowed to escape.

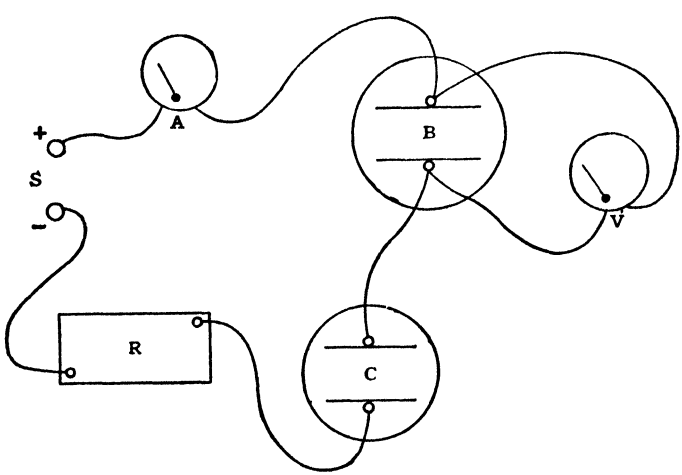


Fig 73

Note.—This method does not always give good yields of paraffin hydrocarbons, *e.g.* when sodium propionate is used the chief product is ethylene and not *n*-butane. This may be

due to the reaction of the discharged methyl radicals with discharged hydroxyl radicals:

$$2CH_3 + 2OH = CH_2{:}CH_2 + 2H_2O.$$

The arrangement of apparatus generally used for electrolytic experiments is shown in fig. 73. It consists of a source of current S (accumulator cells are always used) joined in series with the electrolytic cell B and an ammeter A and regulating resistance (rheostat) R. If an accurate record of the amount of current which has passed through the circuit is required, the ampere-hour meter C (generally a copper voltameter) is included, but this can usually be dispensed with. To determine the difference of potential between the electrodes a voltmeter V may be joined in parallel to the electrodes.

The following terms require explanation:—

Ampere-hours.—This is the product of the number representing the amperes passing the ammeter and the number representing the hours during which the current passes. It provides a measure of the total quantity of electricity which has passed through the circuit.

Current density is the quotient of the current (amperes) passing through the circuit by the area of the electrode measured in square decimetres. It therefore represents the number of amperes per unit area (sq. dm.) of the electrode.

B. Olefine Hydrocarbons, C_nH_{2n}

(S.B. 42–49)

A general method for the preparation of an olefine hydrocarbon is the elimination of water from a saturated monohydric alcohol (Chap. X, A).

$$C_nH_{2n+1}{\cdot}OH - H_2O = C_nH_{2n}.$$

Experiment 18.—Preparation of ethylene, C_2H_4, from ethyl alcohol, $C_2H_5{\cdot}OH$.

A mixture of 25 grm. of ethyl alcohol (rectified spirits), 150 grm. of concentrated sulphuric acid, and a small amount of dry sand is placed in a large round-bottom flask (1·5 litre). The object of the sand is to prevent frothing. The flask carries a rubber cork with two holes; one of these is for the

delivery tube, the other for a dropping funnel. The stem of the dropping funnel should be drawn out to a fine point and slightly bent. By this device the whole stem can be kept filled with liquid, and the gas evolved will not bubble through the liquid in the funnel. The gas which issues is mixed with alcohol and ether vapour, carbon dioxide, sulphur dioxide, and other gases. It is therefore advisable to pass it through a cold, empty wash bottle in order to collect ether and alcohol vapours, a wash bottle containing concentrated sulphuric acid in order to remove these vapours completely, and finally through a wash bottle containing fairly concentrated potassium hydroxide solution to remove the carbon dioxide and sulphur dioxide (see fig. 74). The flask is heated on a sand tray until a steady stream of gas is evolved, and then a mixture of one part by weight of alcohol with two of concentrated sulphuric acid is run in slowly from the tap funnel. The gas may be collected over water, in which it is sparingly soluble (1 volume in 4 at 0°).

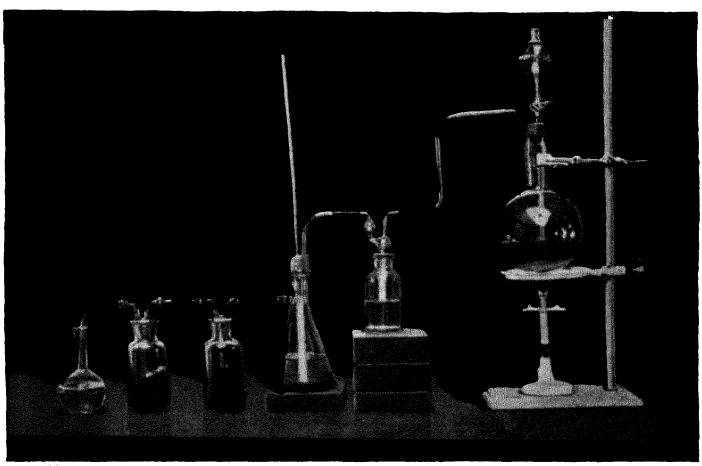
Examine the gas and see whether it is inflammable, whether it forms an explosive mixture with air, whether it is absorbed by bromine water, whether it reacts readily with chlorine, and whether it is readily oxidized by acidified potassium permanganate; also whether it yields precipitates when bubbled through ammoniacal silver nitrate or cuprous chloride.

N.B. Whilst the apparatus for the preparation of ethylene is fitted up, it will be an advantage to proceed with the preparation of ethylene dibromide (Exp. 45, Chap. XI, D).

Experiment 19.—In the above experiment the sulphuric acid may be replaced with advantage by a concentrated solution of orthophosphoric acid* (sp. gr. 1·75). The gas can be evolved in a regular stream free from carbon dioxide and sulphur dioxide. 50–60 c.cm. of the syrupy ortho-acid (sp. gr. 1·75) are placed in a distilling flask with side tube and heated to about 200° by means of a small flame, the temperature being registered by the thermometer, the bulb of which is immersed in the acid. The alcohol is run in very slowly by means of the dropping funnel, the stem of which is drawn out to a fine point reaching to the bottom of the flask.

The gas is passed through a wash bottle surrounded by ice or a freezing mixture in order to condense water, alcohol, and ether vapours. At a temperature of 200–220° a supply of

* *Newth*, P. 1901, 17, 147.



n 960 *To face p* 92

Fig. 74.

gas at the rate of 10–15 litres per hour can be kept up. As the reaction is continuous, practically unlimited amounts of ethyl alcohol can be decomposed by a relatively small amount of phosphoric acid.

Experiment 20.—Preparation of amylene, C_5H_{10}, from amyl alcohol, $C_5H_{11}\cdot OH$.*

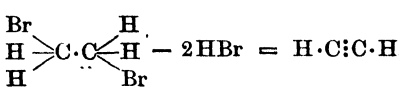
Other dehydrating agents besides sulphuric acid can be employed for withdrawing water from an alcohol. An amylene boiling at 35–38° can be obtained by mixing amyl alcohol (from fusel oil) (1 part) with anhydrous zinc chloride (1·5 part) in the form of small lumps, leaving for twenty-four hours, then heating on a sand tray, collecting the low boiling distillate, and carefully fractionating. The product is a mixture of several isomeric amylenes, but consists mainly of trimethyl-ethylene $(CH_3)_2{:}C{:}CH\cdot CH_3$. Compare the chemical properties of amylene with those of ethylene.

See also Grignard's synthesis, Chap. XXIX, E.

C. Acetylene Hydrocarbons, C_nH_{2n-2}

(S.B. 49–53)

A general method for the preparation of an acetylene hydrocarbon is by the elimination of two molecules of hydrogen bromide from one molecule of an olefine dibromide, *e.g.* ethylene dibromide, under the influence of an alkali:



As a rule, the first molecule of hydrogen bromide is eliminated more readily than the second, and thus in the above-mentioned example vinyl bromide, $CH_2{:}CHBr$ is formed as a by-product. The best yields of hydrocarbon are obtained when sodium ethoxide, $C_2H_5\cdot ONa$, is used.

Experiment 21.—Preparation of acetylene, C_2H_2, from ethylene dibromide, $C_2H_4Br_2$.†

10 grm. of metallic sodium are dissolved in 100 grm. of ethyl alcohol, contained in a round-bottom flask, the metal being added gradually in the form of thin strips. When most

* *Würtz*, A. 1863, 128, 225. † *Marsden*, Diss. Heidelberg, 1892.

of the sodium has been added it may be necessary to heat the alcohol. The flask is then provided with a cork carrying a dropping funnel and reflux condenser, *e.g.* a small Soxhlet condenser (fig. 18). The dropping funnel should be drawn out to a fine point, and contain 20 grm. of ethylene dibromide (Exp. 45). The upper end of the condenser is connected by a glass tube to two wash bottles containing a small amount of ethyl alcohol and surrounded by a freezing mixture of ice and salt. The contents of the flask are heated on a sand tray or in a boiling bath of salt and water, and the ethylene dibromide is dropped in gradually. The gas which issues from the second wash bottle is tested from time to time until all the air has been removed, when it can be collected in cylinders or in a gasholder. The gas is somewhat soluble in water, but is less soluble in a saturated solution of common salt.

Experiment 22.—Preparation of acetylene from calcium carbide, CaC_2.

Several metallic carbides when brought into contact with water generate acetylene. The commonest of these carbides is calcium carbide. Water is gradually added by means of a tap funnel to pieces of calcium carbide placed in a flask provided with a cork with two holes. This cork carries the tap funnel and also the delivery tube. The rate at which the gas is evolved can be regulated by the quantity of water added. The air should be displaced before cylinders of the gas are collected. The gas prepared by this method will differ somewhat in properties from the gas prepared by the previous method, as it contains small amounts of impurities, especially hydrogen sulphide and phosphide.

The following properties should be examined:—

1. Inflammability and nature of flame.
2. Its instability and decomposition by electric sparks.
3. Ready decolorization of bromine solutions. A small amount of acetylene tetrabromide, $C_2H_2Br_4$, can be prepared by slowly bubbling the gas through bromine (see Preparation of ethylene dibromide, Exp. 45). After washing with sodium hydroxide solution and water, and subsequent drying with calcium chloride, it forms a heavy oil, $D_{4^\circ}^{17^\circ}$ 2·971, and boiling-point 114° under 12 mm. pressure.
4. Oxidation with acidified permanganate.
5. Formation of solid silver and cuprous derivatives when passed through small amounts of ammoniacal silver nitrate and cuprous chloride solutions. *N.B.* These precipitates will

be discoloured when they are obtained from impure acetylene. Only small amounts should be prepared, as in the dry state they are extremely explosive.

D. Benzene Hydrocarbons, C_nH_{2n-6}. (S. B 343–352.)

Many of these are prepared from coal tar by processes of fractional distillation. For the preparation of pure benzene from commercial 50 per cent benzol see Exp. 2.

Three methods for synthesising homologues of benzene are used

I **The Fittig Synthesis.***—This consists in subjecting a mixture of an alkyl halide and a halogen derivative of a benzene hydrocarbon to the action of metallic sodium in the presence of dry ether:

$$\begin{matrix} C_2H_5\ Br \\ Na \end{matrix} + \begin{matrix} Br\ C_6H_5 \\ Na \end{matrix} = 2NaBr + C_6H_5 \cdot C_2H_5.$$

Experiment 23.—Preparation of ethylbenzene, $C_6H_5 \cdot C_2H_5$, from ethyl iodide and monobromo-benzene.

24 grm. of metallic sodium (this is an excess) in the form of thin sheets are added to 100 c.cm. of pure dry ether† contained in a ½-litre round-bottom flask provided with a long reflux condenser, preferably a double-surface condenser, which is finally closed with a calcium chloride tube (fig 78). 50 grm. of monobromo-benzene (Exp 38), and somewhat more than an equivalent quantity of ethyl iodide, viz. 55 grm (Exp. 32), are added, and the mixture left overnight. (*N.B.* The water should not be allowed to run through the condenser during the night.) Next morning the liquid is removed from the blue solid which has been formed. The latter is washed twice with small amounts of dry ether, and these washings are added to the main bulk of liquid. The solid consists of a mixture of sodium bromide and iodide and unaltered sodium, and should be transferred to a dish and added in small quantities to a large vessel of cold water. *Do not* tip the whole mass of solid from the flask into water, as a vigorous action will occur and a serious explosion and fire may result.

The liquid which was poured off from the solid is distilled from a steam bath or water bath heated by steam (see Warn-

* *Tollens* and *Fittig*, A. 1864, **131**, 303.

† For purification see Exp 31.

ing, Introduction). After the ether has been removed the residue is fractionated from a small distilling flask without the aid of a fractionating column, and the portion boiling at 133–135° collected separately. Yield 60 per cent of theoretical, viz. 20 grm. Boiling-point, 135°.

II. **Friedel and Craft's Synthesis.**—This is similar to the synthesis of a ketone described in Exp. 183, except that an alkyl chloride or iodide is used in place of the acid chloride (see also Exp. 254 *a*).

III. **Grignard's Synthesis.**—See Exp. 250.

E. Examination of a Liquid Hydrocarbon

The group to which an unknown hydrocarbon belongs can often be determined by an examination of some of its chemical properties. Some of the more important of these are.—

1. The manner in which the hydrocarbon burns, *e g.* non-luminous, luminous, or smoky flame. All benzene hydrocarbons burn with an extremely smoky flame, all the lower paraffins with a non-luminous or luminous but non-smoky flame.

2. Behaviour towards bromine. Most olefine and acetylene hydrocarbons readily decolorize a solution of bromine in water or in chloroform. Paraffins and benzene hydrocarbons do not.

3. Olefines and acetylene hydrocarbons are readily oxidized by acidified permanganate, and hence decolorize a dilute acidified solution of this reagent when added to or bubbled through the solution. Paraffins and also benzene hydrocarbons, unless they contain a double bond in the side chain, *e.g* cinnamene, $C_6H_5 \cdot CH{:}CH_2$, will not readily decolorize permanganate.

4. Formation of explosive metallic derivatives. This reaction is characteristic of acetylene and its monoalkyl derivatives, but is not given by dialkyl derivatives of acetylene, *e.g.* $CH_3 \cdot C{:}C \cdot CH_3$.

5. Formation of nitro-derivatives and sulphonic acids is characteristic of benzene derivatives. Thus if the hydrocarbon dissolves in concentrated nitric acid or a mixture of concentrated nitric and sulphuric acids, and the solution when poured into water yields a yellow oil or solid, it may be safely concluded that the hydrocarbon is aromatic.

X. ALCOHOLS AND ETHERS

A. Saturated Monohydric Alcohols, $C_nH_{2n+1}OH$.

(S. B 66–81.)

Method I.—Several of these alcohols can be obtained by the action of micro-organisms on sugars. The most important example is the fermentation of cane sugar by ordinary brewers' yeast (compare S B 76–77)

Experiment 24.—Preparation of ethyl alcohol by fermentation of sugar. This process takes place in two stages:

(*a*) Inversion, $\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$,

(*b*) Fermentation, $C_6H_{12}O_6 \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_6O} + 2CO_2$

400 grm. of cane sugar are dissolved in 2 litres of water, and the solution placed in a Winchester quart bottle. 30 grm. of brewers' yeast made up to a paste with a small quantity of water are added, and the loosely stoppered bottle is allowed to stand in a warm place for one or two days. The temperature most favourable for fermentation is between 25° and 30°. The liquid is then distilled in portions of about 500 c cm. at a time from a large distilling flask (1 litre) provided with a long neck. The side tube is connected to a water condenser and receiver Some pieces of porous pot are added to prevent bumping, and the heating is conducted regularly on a sand bath. About one-third of the contents of the flask is distilled over and collected in each case. The united distillates, the total volume of which should be about 700 c cm., are again subjected to fractional distillation from a litre flask fitted with a rod and disc fractionating column (fig. 4 *a*) (observe precautions described under Fractional Distillation, Chap. I, B), the distillation being continued until the thermometer registers a temperature of 80°. The product is placed in a 500 c.cm. distilling flask, and about 100 grm. of quicklime added in the form of small lumps. The flask is fitted to a condenser and receiver and allowed to stand overnight. In the morning the alcohol is distilled off from the residue of partially slaked lime by heating the flask in a paraffin or metal bath.

Experiment 25.—Determine the density of the product by means of a pyknometer (figs. 29, 30, 31). From this result

determine the percentage of alcohol in the liquid by consulting tables of specific gravities of mixtures of alcohol and water. Hence calculate the yield of alcohol in the above experiment.

The alcohol obtained in this manner is not anhydrous. Ordinary absolute alcohol contains about 0·2 per cent of water.

Experiment 26.—To remove the last traces of water from ethyl alcohol. Commercial absolute alcohol (99·8 per cent) is treated in a reflux apparatus (fig. 78) with about 1 per cent of its weight of metallic calcium in the form of freshly prepared turnings. The condenser is fitted with a calcium chloride tube to prevent access of moisture, and the mixture is kept vigorously boiling on a water bath until the solid deposit in the flask, which is at first dark-coloured, becomes practically white The alcohol is then distilled over into a dry receiver, which is protected from access of moisture by a calcium chloride tube. The portion passing over at a constant temperature is collected and treated again in a similar manner with a smaller quantity of calcium turnings (0·5 per cent). The solid formed in this case should be white, and on distillation the alcohol should pass over at constant temperature.

Methyl alcohol is purified in a similar manner.

Physical Properties of Ethyl Alcohol.—A colourless mobile liquid with spirituous odour Boiling-point, 78·3° under 760 mm., 13° under 21 mm., solidifies at −112·3°; $D_{4^\circ}^{15^\circ}$, 0·790 It is extremely hygroscopic; contraction takes place on mixing with water, and heat is developed.

Physical Properties of Methyl Alcohol.—A colourless liquid. Boiling-point, 66°; $D_{4^\circ}^{15\cdot5^\circ}$, 0·7952.

Method II.—A very common method for the preparation of an alcohol is by the replacement of halogen by hydroxyl This is usually effected by means of an aqueous solution of an alkali (*e.g.* potassium hydroxide or carbonate), or by means of metallic oxides (*e.g.* plumbous or silver oxides) and water.

Experiment 27.—Preparation of benzyl alcohol from benzyl chloride.

$$2C_6H_5CH_2Cl + H_2O + K_2CO_3 = 2C_6H_5CH_2OH + 2KCl + CO_2.$$

10 grm. of benzyl chloride are boiled in a reflux apparatus (fig. 78, without calcium chloride tube) with about one and a half times the theoretical weight of potassium carbonate dissolved in 100 c.cm. of water, until the smell of benzyl chloride

has disappeared. About six hours will be necessary. The liquid is extracted with ether (Chap I, A), the ethereal extract dried by standing over anhydrous potassium carbonate, and then decanted into a small distilling flask, and the ether removed by distillation (cf. Warning). The residue is fractionated from the same flask, the water condenser being replaced by a short air condenser (fig 3), the portion boiling between 200° and 210° being collected separately. Yield, 5–6 grm.

Physical Properties.—A colourless liquid with an aromatic odour, boiling-point 206·5°, $D^{0°}_{4°}$ 1·0628. It is only sparingly soluble in water, but is miscible in all proportions with alcohol and ether

Method III.—Primary alcohols result from the reduction of aldehydes (Chap XXI), while ketones (*ibid*) yield secondary alcohols (cf. Exp 225 and 226), *e.g*:

$$CH_3\cdot CH{:}O + 2H \longrightarrow CH_3\cdot CH_2\cdot OH$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{:}O + 2H \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\cdot OH$$

In the case of the aromatic aldehydes the reduction of a molecule of aldehyde takes place simultaneously with the oxidation of a second molecule, when the aldehyde is shaken with potassium hydroxide solution (*Cannizaro's reaction* *).

Experiment 28.—Preparation of benzyl alcohol, $C_6H_5\cdot CH_2\cdot OH$, and benzoic acid, $C_6H_5\cdot CO_2H$, from benzaldehyde, $C_6H_5\cdot CH{:}O$.

$$2C_6H_5\cdot CH{:}O + KOH \longrightarrow C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot CO_2K.$$

20 grm. of benzaldehyde (Exp. 173 or 174) are added to a solution of 18 grm of potassium hydroxide in 12 c.cm. of water in a thick-walled bottle closed with a cork (*not* a glass stopper), and the mixture shaken vigorously until a permanent emulsion is formed. It is then allowed to stand overnight, when a thick precipitate of potassium benzoate separates out. The mixture is treated with water and shaken until a clear solution is obtained, and is then extracted with ether at least *three* times. The ethereal solution of benzyl alcohol is dried over anhydrous potassium carbonate, then poured into a distilling flask and fractionated. After the removal of the ether the water condenser is replaced by an air condenser, and the

* B. 1881, **14**, 2394.

fraction which distils at 200–210° collected separately. Yield, 8–9 grm.; boiling-point, 206·5°.

The alkaline liquid left after extraction with ether is acidified with moderately concentrated hydrochloric acid. When cold, the precipitated benzoic acid is separated by means of a porcelain funnel and suction pump, washed with water, and dried on a porous plate. It is recrystallized from hot water or purified by sublimation (cf. Chap. I, E). Yield, 8–10 grm; melting-point, 121°. (For properties and reactions cf. Chap. XII, Exp. 50.)

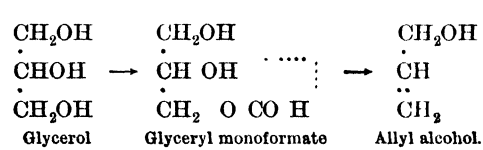
Method IV.—Grignard's synthesis (*a*) of secondary alcohols (Chap XXIX, C), (*b*) of tertiary alcohols (Chap. XXIX, D).

B. Unsaturated Monohydric Alcohols

These alcohols may be prepared by methods analogous to those mentioned above. They may also result from the decomposition of saturated poly-hydroxy-derivatives.

Experiment 29.—Preparation of allyl alcohol from glycerol.*

Glycerol, when heated with formic or oxalic acids, yields glyceryl monoformate, and this decomposes at 220°, yielding allyl alcohol, carbon dioxide, and water.



A mixture of 200 grm. of glycerol, 50 grm. of oxalic acid crystals, and 0 5 grm of ammonium chloride or sulphate, is heated in a large distilling flask attached to a condenser and receiver. A thermometer fixed through the neck of the flask dips *into* the liquid. At first, rapid evolution of carbon dioxide gas occurs, and the temperature indicated by the thermometer remains stationary for a while at 130°. After some time the evolution of gas slackens, and the temperature rises gradually to 195°, when evolution of gas practically ceases. At 205–210° gas begins to be evolved again, oily

* *Tollens* and *Henninger*, A. 1870, 156, 135.

drops appear in the condenser tube, and the disagreeable odour of allyl formate may be detected. The heating is continued carefully, the temperature remaining at 220–230° for some time; later it rises gradually to 260°, when the heating is discontinued.

The distillate which passes over above 220° is a mixture of allyl alcohol with water; some allyl formate, glycerol, and acrolein are also present

The residue in the flask consists mainly of unchanged glycerol, and should be treated with more oxalic acid (40 grm.), and the distillation repeated.

The product is redistilled from a small distilling flask fitted with a thermometer, the process being continued until a test portion of the liquid passing over no longer yields an oily layer on treatment with solid potassium carbonate This occurs when the thermometer indicates a temperature of 105°. The distillate is treated with solid potassium carbonate, and the allyl alcohol separates out as an oil, which is removed from the aqueous liquid by means of a tap funnel. The oil is treated with more anhydrous potassium carbonate, and, after standing for a short time, decanted into a small distilling flask and redistilled The portion boiling between 92° and 96° is collected separately. Yield, about 15 grm.

It is a colourless, mobile, oily liquid with a pungent odour. Boiling-point, 96–97°; $D^{25°}$, 0·854.

C. Recognition of Alcohols

(*a*) **General Reactions.**—(Apply these tests to absolute ethyl alcohol.)

(i) Alcohols react with metallic sodium, with evolution of hydrogen and formation of alcoholates.

$$2C_2H_5\cdot OH + 2Na \longrightarrow 2C_2H_5\cdot ONa + H_2.$$

(ii) They react vigorously with phosphorus halides (*e.g.* phosphorus pentachloride), with the production of halogen derivatives and evolution of hydrogen halide.

$$C_2H_5\cdot OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl.$$

(See also Exp. 36.)

(iii) With acyl chlorides they react with the formation of fragrant-smelling esters. (See Exp. 79.)

(*b*) **Tests for Unsaturated Alcohols.**—(Apply to allyl alcohol.)

(i) They decolorize bromine water.

(ii) They are oxidized by acidified potassic permanganate solution.

(*c*) The specific alcohols can be identified by means of their physical constants, or by the preparation of some solid derivative whose melting-point can be taken (see Chap. XIX, Acetyl and Benzoyl Derivatives).

Special Tests for Methyl Alcohol, CH_3OH.

Warm a little of the alcohol with *p*-nitro-benzoyl chloride A solid ester is produced. Recrystallize from alcohol, and determine the melting-point of the dried crystals Melting-point, 96°.

Special Tests for Ethyl Alcohol, C_2H_5OH.

(i) The characteristic odour of ethyl acetate may be detected when the alcohol is warmed with concentrated sulphuric acid and an acetate (see Exp 74).

(ii) With *p*-nitro-benzoyl chloride it yields a solid ester. Melting-point, 57°.

(iii) The iodoform test Add a little solution of iodine in aqueous potassium iodide solution to an aqueous solution of ethyl alcohol. Then add potassium hydroxide solution drop by drop until the colour of iodine just disappears Warm in a water bath to about 80° and then cool. A yellow crystalline precipitate of iodoform is produced. If the alcohol solution is very dilute the formation of the precipitate will take some time; in any case the characteristic odour of iodoform will be detected.

Note.—This test is also given by certain other substances, *e.g.* acetone, acetaldehyde, and isopropyl alcohol, but *not* by methyl alcohol.

D. Ethers or Alkyl Oxides, R·O·R, or R·O·R′ (S.B. 83–87)

These ethers are the anhydrides of the alcohols.

One of the commonest methods for the preparation of ethers is by the action of concentrated sulphuric acid on a

monohydric alcohol. The reaction proceeds in two stages, as represented by the equations—

$$C_2H_5OH + \begin{matrix}H\\HO\end{matrix}\!\!>\!SO_2 \rightarrow \underset{\text{Ethyl hydrogen sulphate}}{\begin{matrix}C_2H_5O\\HO\end{matrix}\!\!>\!SO_2} + H_2O$$

$$OH\cdot SO_2\cdot OC_2H_5 + C_2H_5\cdot OH \rightarrow \underset{\text{Ethyl ether}}{(C_2H_5)_2O} + SO_2(OH)_2$$

When a mixture of alcohols is used a certain amount of a mixed ether, *e.g* $C_2H_5\cdot O\cdot C_3H_7$ (ethyl propyl ether) is formed.

Experiment 30.—Preparation of ethyl ether from ethyl alcohol.

100 grm. of concentrated sulphuric acid are gradually added to a similar weight of ethyl alcohol (rectified spirit 96 per cent), with constant shaking and cooling. The mixture is placed in a 500 c cm. distilling flask fitted with a two-holed cork. Through one hole passes the stem of a dropping funnel, which has been drawn out to a fine point, and which dips below the surface of the liquid; through the other hole a thermometer is fixed, the bulb of which should also be immersed in the liquid The side tube of the distilling flask is attached to a very long condenser through which a rapid stream of water is flowing The flask is heated on a sand bath When the temperature reaches 140° ether begins to distil over, and alcohol is then added through the tap funnel at about the same rate as the distillate passes over. The flame is adjusted so that the temperature is maintained at 140°, and the reaction should be continued until about 200 c.cm. of alcohol have been added.

Since the vapour of ether is heavy, and very inflammable, it is advisable to stretch a damp cloth across the working bench, between the flame and the receiver.

The distillate contains alcohol, water, carbon dioxide, and sulphur dioxide in addition to ether. It is purified by shaking, in a separating funnel, with a little dilute potassium hydroxide solution. After separation into two layers, the lower aqueous layer is run off, and the ether shaken with about 50 c.cm. of saturated common salt solution (see p 3). After running off the latter, the ether is allowed to stand for some time (overnight is desirable) in a distilling flask with granular calcium chloride. It is then redistilled from a previously warmed water bath or steam bath (cf. Warning), when the whole should pass over between 34° and 35°.

Physical Properties.—A colourless liquid with a characteristic odour; boiling-point, 35°; $D_{4°}^{15°}$, 0·720. Slightly soluble in water (1 part in 12 of water at 15°), less soluble in salt solution.

Experiment 31.—Purification of ether. In many cases where ether is used as a solvent it is necessary that it should be entirely freed from traces of water and alcohol. For this purpose the ether should be shaken several times with *small* amounts of water in order to remove alcohol. It is then placed in a thick, well-stoppered bottle with a large quantity of *freshly fused* calcium chloride and allowed to stand overnight. It is then filtered through a folded filter paper into another similar bottle also thoroughly dried (see Warning), and allowed to stand over metallic sodium. Small amounts of the metal are added from time to time in the form of wire from a sodium press (fig 92), until no further evolution of hydrogen occurs. When required for use the necessary amount is poured into a dry distilling flask and distilled over phosphorus pentoxide.

(For Phenolic Ethers see Chap. XVII.)

Chemical Characteristics of Ethers (S.B. 85).

The ethers are neutral, inert liquids, which when quite dry do not react with sodium, phosphorus pentachloride, or acyl chlorides (cp. alcohols). They are not acted upon by the ordinary reagents for aldehydes and ketones (see Chap. XXI, A2, B2). They are only hydrolysed with difficulty. When saturated with hydrogen iodide gas at 0° they yield alcohol and alkyl iodide (see Chap. XVII, G).

XI. HALOGEN DERIVATIVES

A. Replacement of Hydroxyl by Halogen

Method I.—By the action of the halogen hydrides on alcohols (S.B. 58).

$$C_nH_{2n+1}OH + HBr \rightleftharpoons C_nH_{2n+1}Br + H_2O.$$

As the reaction is reversible, it is necessary to remove one of the products from the sphere of action as soon as formed. This is effected by absorbing the water by means of dehydrating agents.

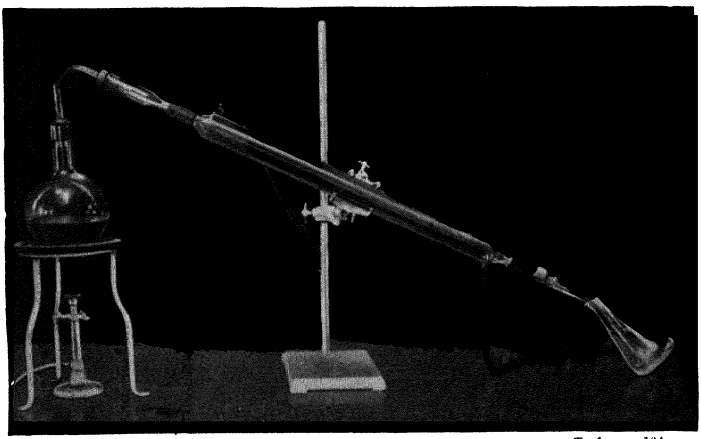


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Fig. 75.

Experiment 32.—Preparation of ethyl bromide, C_2H_5Br, from ethyl alcohol

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

To obtain a good yield of the product in this preparation it is advisable to use rather more sulphuric acid and alcohol than is required by the equations.

120 grm. of concentrated sulphuric acid are placed in a round-bottomed flask of about 750 c cm. capacity and 50 grm. of alcohol (rectified spirit about 95 per cent) added gradually with constant shaking and cooling. 60 grm. of powdered potassium bromide are then added, the flask connected with a condenser through which a rapid stream of water is flowing, and the open end of the condenser fitted with an adapter which dips under ice-cold water in a flask. (See fig. 75.) The mixture is heated quickly on a sand bath, frothing occurs during the reaction, and the ethyl bromide passes over and collects as a heavy oily layer at the bottom of the water in the receiver. The distillation is continued till no more oily drops pass over

The oil is freed from the aqueous layer by means of a separating funnel; it is washed by shaking with its own volume of water, again separated, and then shaken with dilute sodium carbonate solution. During the latter operation the separating funnel should be inverted and the stopcock remain open. After another washing the ethyl bromide is dried by allowing to stand over a small quantity of granular calcium chloride until the liquid becomes clear. It is then decanted into a distilling flask and distilled in the ordinary manner. Yield, about 40 grm., *i.e.* 80 per cent of the theoretical yield calculated on the amount of potassium bromide taken. It is a colourless liquid, boiling-point, 39°; $D^{13°}$, 1 470.

The above reaction is applicable not only to alcohols of the aliphatic series but also to those of the aromatic series, *e.g.*:

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + HCl \rightleftharpoons \underset{\text{Benzyl chloride.}}{C_6H_5CH_2Cl} + H_2O$$

According to Norris, all alcohols react with fairly concentrated hydrobromic and hydriodic acid, giving fairly good yields of the corresponding alkyl halides even in the absence of dehydrating agents, provided an excess of acid (3–4 equivalents) is used. The reaction takes place most readily with

tertiary alcohols and least readily with primary Hydrochloric acid does not give good yields of chlorides with primary alcohols.

Experiment 32 *a*.—**Alternative method for the preparation of ethyl bromide.***

A mixture of 20 grm. of ethyl alcohol and 300 grm. of hydrobromic acid (= 4 molecules), of constant boiling-point 126°, and sp. gr. 1·49, are gradually heated in a distillation flask or retort connected with a condenser. The heating is continued until no more oily drops pass over. The distillate is then washed, dried, and distilled as in Exp 32. Yield, 86 per cent. Only a small portion of the acid distils over, and if the residue left in the flask is slowly distilled the excess of hydrobromic can be obtained in the form of the solution of constant boiling-point, and may be used for subsequent experiments.

The halogen hydrides, especially hydrogen chloride and bromide, also react with many di- and poly-hydroxy-alcohols.

The number of hydroxyl groups replaced depends on the conditions under which the experiments are conducted, *e.g* the temperature, concentration of acid, &c. Thus the final product of the action of hydrogen chloride on glycerol is unsymmetrical dichlorhydrin (*Berthelot*).

$$\begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 2HCl \longrightarrow \begin{array}{l} CH_2OH \\ CHCl \\ CH_2Cl. \end{array} + 2H_2O$$

Hydriodic acid acts in a somewhat different manner, causing reduction as well as substitution. By acting on glycerol with this acid isopropyl iodide is obtained.

$$\begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} \xrightarrow{3HI} \begin{array}{l} CH_2I \\ CHI \\ CH_2I \end{array} \xrightarrow{2HI} \begin{array}{l} CH_3 \\ CHI \\ CH_3 \end{array}$$

Experiment 33.—Preparation of isopropyl iodide, $CH_3 \cdot CHI \cdot CH_3$.†

In this case the reaction is carried out by the action of phosphorus tri-iodide and water on the hydroxy-compound

20 grm. of glycerol diluted with an equal volume of water are mixed with 30 grm. of iodine in a retort attached to a

* *Norris*, Am. 1907, **38**, 640. Compare also *Taboury*, Bull. 1911, [iv], **9**, 124. † *Morkownikoff*, A. 1866, 138 364.

condenser. 5·5 grm. of yellow phosphorus (Caution: Cut into small pieces and weigh under water, do not touch with the hands) are added little by little. Each piece of phosphorus reacts vigorously immediately it is introduced, and produces flashes of light. The iodine dissolves completely if the retort is shaken vigorously after the addition of about one-third of the phosphorus, and the remainder may then be added more quickly The contents of the retort are distilled until no more oily drops pass over and the distillate is replaced in the retort and redistilled. The product of the second distillation is washed with water, then with dilute sodium hydroxide solution, again with water, dried over granular calcium chloride, and redistilled. It forms a colourless liquid. Boiling-point, 89°; $D^{0°}$, 1·744. Yield, 12–15 grm.

Phenolic hydroxyl groups cannot be replaced by means of the halogen hydrides

Method II.—By the action of phosphorus halides on hydroxy-compounds (S B. 58).

The replacement of hydroxyl by halogen can more readily be effected by the action of phosphorus halides on the hydroxy-compound. For the introduction of bromine or iodine it is not necessary actually to isolate the phosphorus halide, but merely to use the elements in the necessary proportions. Usually red phosphorus is added to the hydroxy-compound and the theoretical amount of halogen introduced gradually.

1. **Preparation of Alkyl Halides.**

Experiment 34.—Preparation of ethyl iodide from ethyl alcohol:

$$PI_3 + 3C_2H_5OH = 3C_2H_5I + P(OH)_3$$

2 grm of *yellow* phosphorus (weighed under water, cut into small pieces, and dried with filter paper) are added gradually to the theoretical amount of iodine contained in a 250 c.cm. round-bottomed flask. The flask is attached to a reflux condenser (fig 78), and when cold 25 c cm. (excess) of absolute alcohol are added gradually through the condenser tube. After the vigorous reaction has moderated, the flask is heated on a water bath with occasional shaking, until all the phosphorus iodide has been decomposed (1·5–2 hours). The ethyl iodide is then distilled off in the usual manner, either by immersing the flask in the boiling-water bath, or by heating on a sand bath. The distillate is freed from alcohol by washing several times with water. Should it be coloured brown

by iodine it is again shaken with water to which a few drops of sodium hydroxide solution have been added. It is then dried over granular calcium chloride, decanted into a distilling flask and redistilled. Yield, about 28 grm., *i.e.* 95 per cent of theory, calculated from the amount of iodine taken.

It is a colourless liquid, boiling-point 72°, $D^{0°}$ 1 944, and is slightly soluble in water but miscible in all proportions with alcohol and ether.

The replacement of hydroxyl by means of phosphorus halides is one of the most general reactions met with By its means all the hydroxy-groups of aliphatic poly-hydric alcohols, the hydroxy-groups of phenols, and the hydroxy-groups of all types of acids can be replaced by halogen, *e.g.*:

$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3PCl_5 \longrightarrow \underset{\text{Trichlorhydrin}}{C_3H_5Cl_3} + 3POCl_3 + 3HCl$$

$$\underset{\text{Phenol}}{C_6H_5\cdot OH} + PCl_5 \longrightarrow \underset{\text{Chlor-benzene}}{C_6H_5Cl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{3CH_3\cdot C(=O)OH} + 2PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3\cdot COCl} + P_2O_3 + 3HCl$$

$$\underset{\text{Benzoic acid}}{C_6H_5\cdot CO\cdot OH} + PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5\cdot COCl} + POCl_3 + HCl$$

$$\underset{\text{Benzene-sulphonic acid}}{C_6H_5\cdot SO_2\cdot OH} + PCl_5 \longrightarrow \underset{\text{Benzene-sulphonic chloride}}{C_6H_5\cdot SO_2Cl} + POCl_3 + HCl$$

In the case of phenols, however, the yields are unsatisfactory, owing to the phosphorus oxychloride, formed as a by-product, reacting with the residual phenol and giving rise to esters of phosphoric acid, *e g.*:

$$POCl_3 + 3C_6H_5OH \longrightarrow 3HCl + PO(OC_6H_5)_3.$$

2. Preparation of Acyl Halides. (S.B. 178.)

Experiment 35.—Preparation of acetyl chloride from acetic acid. See equation above. *To be conducted in a fume chamber.*

60 grm. of glacial acetic acid * are placed in a distilling flask of 200 c.cm. capacity, connected by the side tube to a

* The acetic acid, if not solid on a cold day, should be purified by fractional distillation. The fraction boiling-point 116–117°, should be collected separately, cooled by surrounding the vessel with ice water, and the liquid portion decanted off. The process of freezing can be repeated several times, and ultimately an acid of melting-point 17° can be obtained. It is hygroscopic, and should be protected from atmospheric moisture.

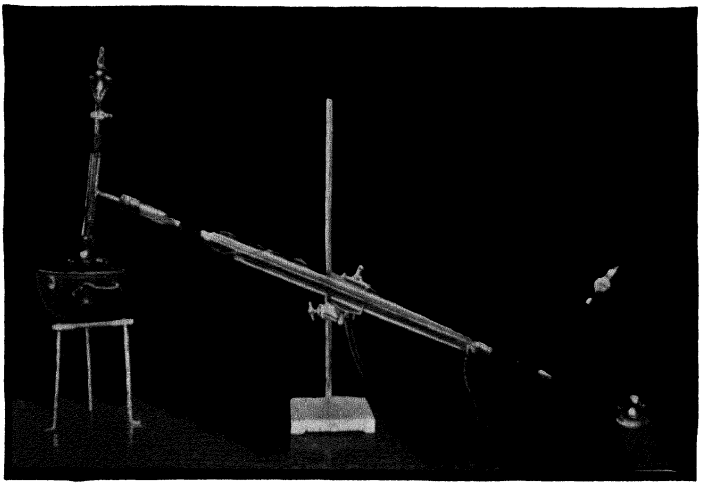

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Fig. 76.

condenser, and 46 grm. of phosphorus trichloride added gradually from a dropping funnel. During the addition the flask is cooled by immersion in a water bath containing cold water. The temperature of the bath is then raised to 40–50°, and maintained at this until the evolution of hydrogen chloride slackens and the contents of the flask separate into two layers The water bath is then heated to boiling, and the distillate collected in a second distillation flask communicating with the air through a calcium chloride tube attached to the side tube of the flask (fig. 76). The acetyl chloride is redistilled from the latter flask fitted with a thermometer, the same precautions being observed in collecting the distillate, and the portion passing over between 53° and 56° is collected separately. Yield, about 50 grm., *i.e.* 65 per cent of theory.

A colourless liquid which fumes strongly in air. Boiling-point, 55°; $D^{0°}$, 1·13

Experiment 36.—Preparation of benzoyl chloride from benzoic acid. See Equation above. *To be conducted in a fume chamber.*

A quantity of phosphorus pentachloride is introduced into a tared distilling flask of 200 c.cm. capacity, and its weight determined About 40 grm should be taken. The theoretical amount of benzoic acid is then weighed out and introduced gradually into the flask. The reaction proceeds with great vigour, dense fumes of hydrogen chloride being evolved. The contents of the flask become liquid, and consist of a mixture of the acyl chloride with phosphorus oxychloride, which are separated by fractional distillation without a fractionating column. The oxychloride distils over first, the temperature then rises, and the fraction passing over between 190° and 200° is collected separately. Yield, about 75 per cent of theory.

A colourless liquid which fumes in air. Boiling-point, 198°; $D^{19°}$, 1·214.

Experiment 37.—Preparation of benzene-sulphonic chloride from sodium benzene sulphonate,

$$C_6H_5\cdot SO_2\cdot ONa + PCl_5 \rightarrow C_6H_5\cdot SO_2Cl + POCl_3 + NaCl.$$

About 20 grm. of phosphorus pentachloride are weighed out into a tared flask. The theoretical amount of sodium benzene-sulphonate (Exp. 109*a*) is added gradually and after the reaction is completed, the contents of the flask are cooled and poured into an excess of cold water. The acyl halide,

which is fairly stable towards water, is not affected, while the other products of the reaction go into solution. The oil is separated by means of a tap funnel, and is purified by distillation under diminished pressure. Yield, about 15 grm., *i.e.* 85 per cent of theory.

The chloride is a colourless oil which solidifies at low temperatures to crystals. Melting-point, 14·5°; boiling-point, 120° under 10 mm. pressure.

B. Replacement of Hydrogen by Halogen—Chlorination—Bromination

(S. B. 55–57, 169, 355)

Halogen derivatives may readily be obtained by the direct replacement of hydrogen by the action of halogens on hydrocarbon groups. The reaction is of the type—

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl,$$

a molecule of halogen hydride being formed for each atom of hydrogen replaced. The action is generally accelerated by (*a*) sunlight, (*b*) heat, (*c*) the presence of "halogen carriers"—iodine, iron powder, sulphur, phosphorus, antimony pentachloride, aluminium chloride or bromide, the aluminium-mercury couple,* are the substances chiefly used.

This substitution reaction is not well adapted for the preparation of halogen derivatives of the paraffin hydrocarbons, because mixtures of compounds are almost invariably produced and these are often difficult to separate The method is more often applied in the case of the closed-ring hydrocarbons. Here the products formed depend entirely on the conditions of the reaction.

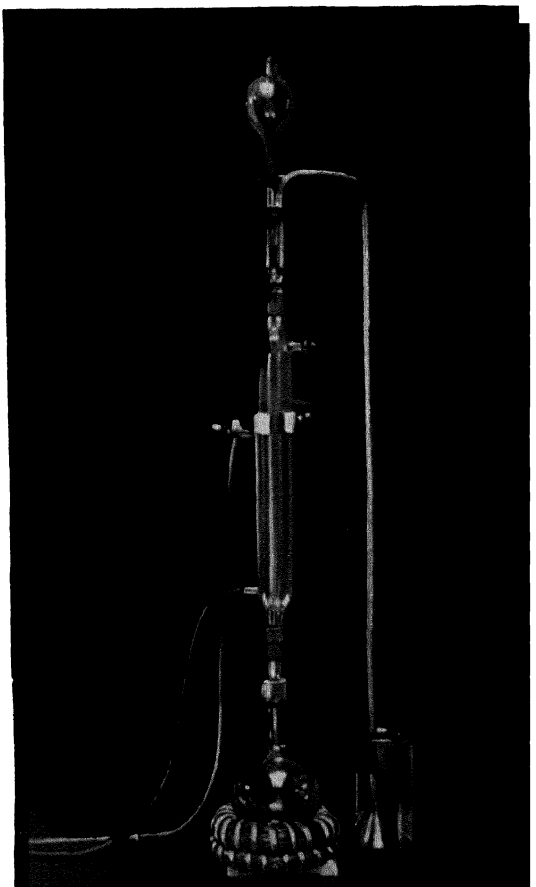
Experiment 38.—Preparation of bromobenzene, C_6H_5Br, from benzene.†

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr.$$

50 grm. of pure, dry benzene and about 0·5 grm. of an aluminium-mercury couple are placed in a small flask. The couple is prepared by allowing small rolls of aluminium foil

* *Cohen* and *Dakin.*

† *Cohen* and *Dakin*, J. C. S. 1899, 75, 894.



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To face p 110

Fig. 77.

to stand in a strong solution of mercuric chloride for about a minute, then removing quickly and washing with water, alcohol, and finally with benzene. The flask is fitted to a reflux condenser provided with a dropping funnel and tube for leading off the hydrogen bromide (fig. 77), and 60 grm. of *dry* bromine * dropped in. The addition should extend over half an hour. The mixture becomes quite warm and copious evolution of hydrogen bromide takes place, the gas being absorbed by the water in the beaker.

When the mixture has cooled it is shaken with excess of dilute potassium hydroxide solution, separated, dried with granular calcium chloride, and, when clear, decanted into a distilling flask and distilled. The portion boiling between 140° and 170° is redistilled, and the fraction boiling at 150–160° collected Yield 30–35 grm., *i.e.* 60 per cent of theory calculated on amount of bromine taken.

When pure it is a colourless liquid, boiling-point 154–155°; $D^{12°}$, 1·502.

When the aromatic hydrocarbon contains a side chain, the product of the action of halogens depends on the conditions under which the experiment is conducted When the reaction takes place at ordinary temperatures in the presence of halogen carriers the halogen substitutes in the ring. In bright sunlight and at the boiling-point of the hydrocarbon the halogen enters the side chain

Experiment 39.—Preparation of benzyl chloride, $C_6H_5 \cdot CH_2Cl$, from toluene.

$$C_6H_5 \cdot CH_3 + Cl_2 \longrightarrow C_6H_5 \cdot CH_2Cl + HCl.$$

50 grm. of toluene (from Exp. 2) are introduced into a tared retort, the neck of which is tilted upwards and fitted to a reflux condenser. The retort is heated on a sand bath and the contents kept boiling gently while chlorine gas (prepared by the action of strong hydrochloric acid on *granular* manganese dioxide, and dried by bubbling through a wash bottle containing concentrated sulphuric acid) is led in by a tube fitted through the tubulus of the retort. The liquid gradually turns yellow, and hydrogen chloride is evolved. The

* Bromine is dried by shaking up with an equal volume of concentrated sulphuric acid in a tap funnel, allowing to stand for some time, and then running off the lower layer of bromine.

It is more convenient to measure out the bromine in a graduated cylinder. D = 3.

passage of the chlorine is continued until the contents of the retort (which is periodically weighed) have increased by the theoretical amount (18–19 grm.). The liquid is then transferred to a distilling flask and fractionated, the portion boiling between 165° and 185° being collected separately. This portion is redistilled, and the fraction boiling between 176° and 180° is nearly pure benzyl chloride Yield about 40 grm, *i.e.* 60 per cent of theory

It is a colourless liquid, boiling-point 176°; $D^{14°}$, 1·107; the vapour is very irritating to the mucous membranes of the nose and eyes.

Experiment 40.—Preparation of benzal chloride, $C_6H_5 \cdot CHCl_2$, from toluene.

$$C_6H_5 \cdot CH_3 + 2Cl_2 \longrightarrow C_6H_5 \cdot CHCl_2 + 2HCl.$$

The experiment is conducted in a similar manner to the last, the chlorine being led in until the theoretical increase of weight is attained (37 grm). The product is fractionated, some unchanged toluene and benzyl chloride pass over first, and the portion boiling at 205–213° is collected separately (use an air condenser). The product is purified by redistillation. It is a colourless liquid, boiling-point 213°, $D_{4°}^{16°}$, 1 295.

When the benzene ring already contains certain substituents, especially amino- or phenolic groups, the entrance of halogen into the ring takes place with great ease. Thus a solution of aniline in dilute hydrochloric acid yields a precipitate of the insoluble *s*-tribromaniline when treated with bromine water.

$$C_6H_5 \cdot NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3 \cdot NH_2(1:2:4:6) + 3HBr$$

Sulphanilic acid, $C_6H_4(NH_2) \cdot SO_3H(1:4)$, when treated with bromine in a similar manner, yields dibromosulphanilic acid,

$$C_6H_4(NH_2)SO_3H + 2Br_2 \longrightarrow C_6H_2(NH_2)(SO_3H)Br_2(1:4:2:6) + 2HBr,$$

and phenol yields *s*-tribromophenol (melting-point, 95°) The bromine atoms always tend to take the *o*- and *p*-positions with respect to the amino- and hydroxyl radicals

Experiment 41.— Preparation of tribromaniline, $C_6H_2(NH_2)Br_3$ (1:2:4:6), from aniline *

10 grm. of aniline (Exp. 133) are dissolved in sufficient

* *Loring Jackson* and *Moore*, Am. 1890, **12**, 166.

dilute hydrochloric acid, and the solution is made up to 500 c.cm with water. The solution is placed in a pump flask, the side tube of which is attached to a pump, and the mouth of the flask is closed by a cork carrying a leading tube connected with a small wash bottle containing the theoretical amount of bromine (3 molecules for 1 molecule of aniline). A rapid stream of air, saturated with bromine vapour, is drawn through the apparatus until the liquid assumes a permanent yellow colour. The precipitate of tribromaniline is filtered off on a porcelain funnel, washed with water, and dried on a porous plate Yield almost theoretical. It crystallizes from hot alcohol in stout colourless needles Melting-point, 119°.

Alternative method for the preparation of s-tribromaniline.— The aniline is dissolved in 3–4 times its weight of glacial acetic acid, and while the solution is kept well stirred a solution of the theoretical amount of bromine in twice its volume of glacial acetic acid is run in The mixture becomes quite hot, and, if necessary, can be surrounded by cold water. The mass should be finally coloured yellow and of a pasty consistency It is poured into water, filtered, washed with water, dried on a porous plate, and recrystallized

Experiment 42.—Preparation of dibromosulphanilic acid, $C_6H_2Br_2(NH_2)(SO_3H)$ (1:4:2:6), from sulphanilic acid.

20 grm of sulphanilic acid (Exp 114) are dissolved in the smallest possible quantity of dilute sodium hydroxide solution, and then diluted with water to about 2 litres and a slight excess of dilute hydrochloric acid is added; usually no precipitate of sulphanilic acid appears The mixture is placed in a Winchester quart bottle attached to a pump and to a small wash bottle containing the theoretical amount of bromine, and a rapid stream of air saturated with bromine vapour drawn through the solution When all the bromine has disappeared the liquid is filtered, if necessary, and evaporated· On cooling, colourless crystalline needles of dibromosulphanilic acid separate. Yield, 90 per cent of theory.

Halogen substitution products of the aliphatic carboxylic acids may also be prepared by the direct action of the halogen on the acids, *e.g.*—

$$\underset{\text{Acetic acid}}{CH_3\cdot COOH} + Cl_2 \longrightarrow \underset{\text{Monochloracetic acid.}}{CH_2Cl\cdot COOH} + HCl.$$

By continued action of the halogen di- and tri-substituted acids are obtained.

The Hell-Volhard-Zelinsky Reaction.—The direct halogenation of acids takes place with difficulty, but the action proceeds readily if the acyl halides (p. 108) or acyl anhydrides (Chap. XIV, A) are treated with the halogen. The action on the acid is greatly facilitated by sunlight, and especially by the addition of red phosphorus. In the latter case the reaction proceeds in two stages:

(*a*) The production of the acyl halide by the action of the phosphorus halide on the acid (Cf. Exps. 35 and 36)

(*b*) The halogenation of the acyl halide

The complete reaction may be represented by the following equation:—

$$3X\cdot CH_2\cdot COOH + P + 8Br \longrightarrow 3X\cdot CH_2Br\cdot COBr + HPO_3 + 2HBr.$$

The halogen acid may be obtained from the acyl compound by treatment with water. (Cf. properties of acyl halides, p. 120.)

The reaction is of great importance for the preparation of halogen derivatives of acids, and is also of theoretical interest, for the halogen always enters the molecule in the α-position to the carboxylic group, *e.g.*—

$$\underset{\text{Propionic acid}}{CH_3\cdot CH_2\cdot CO_2H} \longrightarrow \underset{\alpha\text{-Bromo-propionyl bromide}}{CH_3\cdot CHBr\cdot COBr}*$$

$$\underset{\text{Succinic acid}}{COOH\cdot CH_2\cdot CH_2\cdot COOH} \longrightarrow \underset{\alpha\text{-Bromo-succinyl bromide}}{COBr\cdot CH_2\cdot CHBr\cdot COBr}\dagger$$

Acids which have no hydrogen atom in the α-position, *e g.* trimethyl-acetic acid, $(CH_3)_3C\cdot COOH$, cannot be brominated by this method.

Experiment 43.—Preparation of monobromacetic acid, $CH_2Br\cdot CO_2H$, from acetic acid.

$$3CH_3\cdot CO_2H + P + 8Br = 3CH_2Br\cdot COBr + HPO_3 + 2HBr.$$

For success in this preparation the materials used must be thoroughly purified and dried. The acetic acid is purified by distillation and freezing (see note, Exp. 35), and the bromine is dried by shaking with concentrated sulphuric acid (see note, Exp. 38). The red phosphorus should be warmed with dilute ammonia solution, then washed well with water and dried in a steam oven.

* *Zelinsky*, B. 1887, **20**, 2026. † *Volhard*, A. 1887, **242**, 141.

A mixture of 20 grm of pure acetic acid and 3 grm. of red phosphorus is placed in a round-bottomed flask of about 300 c.cm. capacity, fitted up as shown in fig. 77. (NOTE.—*Rubber stoppers should not be used*.) The bromine is added from the dropping funnel, very gradually at first, the flask being cooled by immersion in cold water. The reaction proceeds with great vigour, but moderates after about half the bromine has been added, when the remainder may be run in more quickly. The flask is then warmed on a boiling-water bath until the colour of bromine vapour in the interior of the flask disappears. After cooling, the bromacetyl bromide is poured into a distilling flask and distilled under diminished pressure (see p. 8, and fig. 9). The product is weighed and the theoretical amount of water required to convert it into bromacetic acid added gradually. The mixture solidifies to a white crystalline mass. This is purified by distilling under ordinary pressure from a small distilling flask provided with an air condenser (fig. 79), the portion distilling between 190° and 210° being collected.

It forms colourless crystals, melting-point 50–51°, boiling-point 208. The yield is variable.

Note.—The bromacetyl bromide and bromacetic acid must not be allowed to touch the hands, as they cause serious wounds.

Experiment 44.—Preparation of α-bromostearic acid, $CH_3 \cdot (CH_2)_{15} \cdot CHBr \cdot CO_2H$, from stearic acid.

30 grm. of stearic acid and the requisite amount of red phosphorus are placed in a flask fitted with a reflux condenser and dropping funnel (fig. 77). The flask is immersed in a water bath containing water at 60–70° so that the stearic acid melts, and the theoretical amount of dry bromine is added gradually from a dropping funnel, when addition is complete, the mixture is heated on a boiling-water bath for about three hours. The product is poured into water and the monobrom-stearic acid filtered off and dried on a porous plate.

It crystallizes from carbon disulphide in colourless plates. Melting-point, 61°.

C. Replacement of Amino-groups by Halogens

This reaction is carried out by the agency of the diazo-reaction (Chap. XX, E).

D. Addition of Halogens or Hydrogen Halides to Unsaturated Compounds

(S. B. 57–58)

Examples of this type of reaction are afforded by the following equations:—

$$\underset{\text{Ethylene}}{CH_2{:}CH_2} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3{\cdot}CH_2Br}$$

$$\underset{\text{Propylene}}{CH_3{\cdot}CH{:}CH_2} + Br_2 \longrightarrow \underset{\text{Propylene dibromide, 1:2-dibromo-propane}}{CH_3{\cdot}CHBr{\cdot}CH_2Br}$$

$$\underset{\text{Acetylene}}{CH{\vdots}CH} + 2Br_2 \longrightarrow \underset{\text{Acetylene tetrabromide}}{CHBr_2{\cdot}CHBr_2} \text{ (cf. Exp 22 (4))}$$

Experiment 45.—Preparation of ethylene dibromide from ethylene.

$$CH_2{:}CH_2 + Br_2 \longrightarrow CH_2Br{\cdot}CH_2Br.$$

Ethylene is prepared and purified as described in Exp 18 The gas is bubbled slowly through two wash bottles with ground-glass stoppers (fig 74), each containing 20 grm. of bromine and 20 c cm. of water, until the colour of the bromine completely disappears. Should the contents of the flask in which the ethylene is being generated char badly (a slight amount of charring is inevitable), the operation is stopped and a fresh supply of gas made.

When decolorization is complete the contents of the wash bottles are removed to a separating funnel, the oily layer removed, and shaken with dilute sodium carbonate solution until colourless. The lower layer of ethylene dibromide is removed, dried over granular calcium chloride, and distilled. Yield, 40–45 grm.

The dibromide is a colourless oil. Boiling-point, 131°, D, 2·189

The method of preparation can be made less tedious either by preparing the gas, as described in Exp. 19, or by collecting the ethylene in a large gas holder, measuring its volume, and bubbling it very slowly through rather less than the theoretical amount of bromine.

In the preparation of a dihalogen derivative by this method the two halogen atoms become attached to two adjacent carbon atoms, except when two conjugate double bonds are present (*e.g.* cinnamylidene-acetic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}$

$CH \cdot CO_2H$, Exp. 235), when the bromine enters into the 1·4 positions

$$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot COOH + Br_2 \longrightarrow C_6H_5CHBr \cdot CH:CH \cdot CHBr \cdot COOH.$$

For the preparation of cinnamic acid dibromide, see Exp. 272.

For the preparation of acetylene tetrabromide, see Exp. 22 (4)

For rate of addition of bromine, see Chap. XXXVI, B.

E. Special Methods

Chloroform results from a process of simultaneous oxidation and chlorination of alcohol or acetone by means of bleaching-powder solution. Iodoform is obtained in a similar manner by using an alkaline solution of iodine

Experiment 46.—Preparation of chloroform, $CHCl_3$, from ethyl alcohol *

$$4C_2H_5OH + 16CaOCl_2 = 13CaCl_2 + 3(H \cdot CO_2)_2Ca + 8H_2O + 2CHCl_3.$$

100 grm. of bleaching powder are rubbed into a paste with about 300 c.cm. of water and placed in a large flask of 2 litres capacity fitted to a condenser and receiver. 20 grm. of rectified spirit (or of acetone) are added, and the mixture gradually heated on a sand bath. The reaction is accompanied by much frothing, and the distillation is continued as long as oily drops of chloroform pass over The product is separated from the aqueous layer, shaken with dilute sodium hydroxide solution, dried over granular calcium chloride, and purified by redistillation Yield, about 20 grm.

It is a colourless liquid with a sweetish odour. Boiling-point, 61–62°, $D^{0°}$, 1·526

Experiment 47.—Preparation of iodoform, CHI_3, from ethyl alcohol.

5 grm. of alcohol are added to a solution of 10 grm. of potassium carbonate in 40 c.cm. of water, and to the mixture 10 grm. of iodine are added in small portions with stirring. The whole is heated gradually to a temperature of 80° and then allowed to cool. Iodoform separates in the form of small

* *Liebig*, A. 1832, 1, 199.

yellow crystals; it is filtered with the aid of the suction pump and washed with a small quantity of distilled water.

It forms brilliant yellow leaflets with a characteristic odour. It melts at 120°, is insoluble in water, but dissolves readily in alcohol and ether, and is volatile with steam

Experiment 48.—Preparation of methyl iodide.*

$$KI + (CH_3)_2SO_4 \longrightarrow CH_3I + CH_3KSO_4.$$

A solution of 50 grm. of potassium iodide in its own weight of water is warmed in a distillation flask fitted to a condenser, and 40 grm. of methyl sulphate † are run in slowly from a dropping funnel. The methyl iodide distils over and can be purified as in Exp. 32 As methyl iodide is very volatile, a rapid stream of cold water should be kept circulating through the condenser, and the receiver may be partly filled with ice and water. Yield, 39 grm

It is a colourless liquid, boiling-point 45°, and closely resembles ethyl iodide.

F. Replacement of Chlorine or Bromine by Iodine

Experiment 49.—Preparation of iodo-acetic acid, $CH_2I \cdot COOH$, from chlor-acetic acid.

$$CH_2Cl \cdot COOH + KI \longrightarrow CH_2I \cdot COOH + KCl.$$

20 grm of chlor-acetic acid are heated in a flask fitted with a reflux condenser on a water bath for an hour with 100 c.cm of absolute alcohol and 40 grm of powdered potassium iodide. After cooling, the product is filtered from the precipitate of potassium chloride and remaining iodide, and the filtrate evaporated to a small bulk on a water bath. On cooling, crystals of iodo-acetic acid separate. These are purified from potassium iodide by dissolving in ether, filtering, and evaporating the filtrate.

Iodo-acetic acid consists of white crystalline plates, melting-point 84°. The vapours are irritating to the eyes, and the solid causes serious burns if handled. The later stages of the experiment should therefore be carried out in a well-ventilated fume chamber.

* *Weinland* and *Schmid*, B. 1905, **38**, 2827.

† *N.B.* Methyl sulphate is exceedingly poisonous, and all operations with it should be conducted in a good fume cupboard.

G. Chemical Reactions of the Halogen Derivatives

Organic compounds containing halogens, considered from the point of view of the halogen only, may be divided into three groups:

(i) Compounds derived from open-chain hydrocarbons by the substitution of halogen for hydrogen, *e.g.* ethyl iodide, C_2H_5I. The group includes closed-ring compounds containing halogen in the side chain, *e.g.* benzyl chloride, $C_6H_5CH_2Cl$. Substances containing several halogen atoms in the molecule, *e g* chloroform, $CHCl_3$, and compounds containing other organic radicals, *e.g.* bromacetic acid, $CH_2Br \cdot COOH$, may be included in this class.

(ii) Compounds derived from closed-chain hydrocarbons and their derivatives by substitution of halogen for hydrogen in the ring, *e g* bromobenzene, C_6H_5Br; chlorotoluene, $C_6H_4Cl \cdot CH_3$.

(iii) Acyl halides—compounds produced by the replacement of the hydroxy-group of acids by halogen, *e.g.* acetyl chloride, $CH_3 \cdot COCl$; benzene-sulphonic chloride, $C_6H_5 \cdot SO_2Cl$.

Mixed compounds may be obtained, *e.g.* bromacetyl bromide, $CH_2Br \cdot COBr$.

Group I.—The simple halogen compounds of this group are generally heavy liquids which are only sparingly soluble in water but readily soluble in alcohol and ether. They give no precipitates of silver halides when shaken with silver nitrate solution. (Exceptions: methyl iodide, which gives a copious precipitate, and ethyl iodide, which gives a slight precipitate.) They are practically unaffected by cold water, but are gradually hydrolysed when boiled with water:

$$C_2H_5Br + H_2O \rightleftharpoons C_2H_5OH + HBr.$$

When treated with cold dilute alkalis—shaking with cold dilute potassium hydroxide solution—they are partially hydrolysed, but the amount of oil is not appreciably diminished:

$$C_2H_5Br + KOH \longrightarrow C_2H_5OH + KBr.$$

If the aqueous liquid, after such treatment with alkali, is acidified with nitric acid and silver nitrate added, a precipitate of silver halide is obtained.*

* The alkali used must be free from halides.

Warming with excess of alkali causes complete hydrolysis.

Group II.—The simple compounds of this class are either colourless liquids or crystalline solids, insoluble in water, but soluble in alcohol and ether. They are extremely stable, and the halogen cannot be removed from the molecule at all readily. Thus they are not affected by alkalis (test the aqueous liquid as above, after addition of nitric acid, with silver nitrate solution). The halogen can be replaced by treatment with absolute alcohol and metallic sodium (see p. 64).

Group III.—The acyl halides are generally fuming liquids (yielding fumes of hydrogen halide in contact with moist air) or crystalline solids. They are extremely reactive, the aliphatic members of the class reacting vigorously with water, *e.g.*

$$CH_2Br \cdot COBr + H_2O = CH_2Br \cdot CO_2H + HBr.$$

The aromatic members (*e.g.* benzoyl chloride, $C_6H_5 \cdot COCl$) are only attacked slowly by cold water, while the sulphonic derivatives (*e.g.* benzene-sulphonic chloride, $C_6H_5SO_2Cl$) are comparatively stable. All the acyl halides are completely hydrolysed by treatment with boiling water or by shaking with dilute alkalis. The oil disappears under this treatment, and the resulting solution, acidified with nitric acid, gives a copious precipitate of silver halide with silver nitrate solution:

$$C_6H_5COCl + 2KOH = C_6H_5COOK + KCl + H_2O.$$

The acyl halides react readily with ammonia, yielding acyl amides (Chap. XIV, B):

$$C_6H_5COCl + 2NH_3 = \underset{\text{Benzamide}}{C_6H_5CONH_2} + NH_4Cl.$$

These are generally crystalline solids of definite melting-point, and can therefore be used for the characterization of the acyl halides from which they are prepared.

The acyl halides react readily with primary amines, yielding substituted amides (Chap. XIX, A), and when treated with alcohols or other hydroxy-compounds, fragrant smelling esters are obtained (Chap. XIII, C).

XII. CARBOXYLIC ACIDS

Characteristic of these acids is the presence of the carboxylic group $-C\overset{O}{\underset{OH}{<}}$, and their reactivity is largely due to the readiness with which the hydrogen radical of the carboxylic group can be replaced The basicity of any given acid depends upon the number of such carboxylic groups present in the molecule.

A. Oxidation of Hydrocarbons

Method I—As a rule, a saturated aliphatic hydrocarbon cannot be oxidized directly, on the other hand, olefine and acetylene hydrocarbons are readily oxidized, the molecule in each case is ruptured if a moderately strong oxidizing agent is used, and a mixture of acids or ketones containing a smaller number of carbon atoms is obtained (S B. 162). The rupture always occurs between the two carbon atoms originally united by the double or triple bond, and thus the method is used in order to determine the exact position of the double or triple bond in the molecules of unsaturated hydrocarbons and their derivatives. The method is, however, not generally used for the preparation of acids

The oxidation of homologues of benzene is a method frequently adopted for the preparation of aromatic acids (S. B. 435), the reaction consisting in oxidizing one or more side chains into carboxylic groups by means of common oxidizing materials In many cases the oxidation is facilitated by the introduction of a halogen atom into the side chain.

Experiment 50.—Preparation of benzoic acid, $C_6H_5\cdot COOH$, from benzyl chloride, $C_6H_5\cdot CH_2Cl$

Benzyl chloride may be oxidized by means of an alkaline solution of potassium permanganate. The reactions are represented by the equations—

$$C_6H_5\cdot CH_2Cl \rightarrow C_6H_5\cdot CH_2\cdot OH$$

$$3C_6H_5\cdot CH_2\cdot OH + 4KMnO_4 = 3C_6H_5\cdot COOK + 4MnO_2 + KOH + 4H_2O.$$

A mixture of 5 grm. of benzyl chloride (Exp. 39), with a solution of 4 grm. of anhydrous sodium carbonate in 50 c cm. of water, is boiled gently in a reflux apparatus, the theo-

retical amount of potassium permanganate required by the equation dissolved in 150 c.cm. of water is added gradually, and the mixture boiled until the purple colour of the permanganate has disappeared, and has been replaced by the brown precipitate of hydrated manganese peroxide. A stream of sulphur dioxide is then led into the hot liquid, until the precipitate of manganese peroxide is completely dissolved. On cooling, crystals of benzoic acid separate These are removed by filtration, using a porcelain funnel, washed with a little water, and recrystallized from hot water. Yield, about 4 5 grm —almost theoretical.

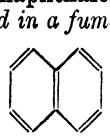
The acid forms colourless needles, melting-point 121° It sublimes at a higher temperature, is very sparingly soluble in cold water, but fairly soluble in hot water, alcohol, and ether, and is volatile with steam.

The acid is soluble in caustic alkalis, yielding soluble salts, from which the free acid is reprecipitated on the addition of mineral acids. Its silver, calcium, lead, and ferric salts are insoluble, or very sparingly soluble, in water. When heated with soda-lime the acid yields benzene:

$$C_6H_5CO_2H + 2NaOH = C_6H_6 + Na_2CO_3 + H_2O.$$

Experiment 51. — Preparation of phthalic acid, $C_6H_4(CO_2H)_2$, from naphthalene,* $C_{10}H_8$.

To be conducted in a fume chamber.



$$\rightarrow C_6H_4\begin{cases}CO_2H\ (1)\\CO_2H\ (2).\end{cases}$$

The process is one of oxidation by means of concentrated sulphuric acid, using mercuric sulphate or metallic mercury as a catalytic agent.

20 grm. of naphthalene and 10 grm. of mercuric sulphate are placed in a large retort (500 c cm), with a mixture of 260 grm. of concentrated sulphuric acid and 40 c.cm. of water. A thermometer fixed by a cork through the tubulus of the retort dips into the liquid, and a flask is used as receiver. As the mixture is gently heated, the naphthalene dissolves, oxidation begins at about 200°, and at 250° the evolution of carbon dioxide and sulphur dioxide is rapid. Phthalic acid and its anhydride distil over together with sulphuric acid, and

* D. R.-P. 91,202; L.-C., p. 613.

are condensed in the receiver, which is cooled, if necessary, with water The temperature is finally raised to 300°, and the heating continued until the contents of the retort become almost solid. The residue of mercuric sulphate can be used for a further operation. The distillate is diluted with twice its volume of water, and boiled for some time. After cooling, the solid is filtered by means of a porcelain funnel, washed with a little cold water, and dried. Yield, 8–10 grm., *i.e.* 35–40 per cent of theory. It crystallizes from hot water in short prisms, melts at 213° when heated very quickly and sublimes on further heating, yielding its anhydride (see Exp. 85). It is very sparingly soluble in water, but dissolves in alcohol and ether.

The acid dissolves in caustic alkalis, yielding soluble salts. The silver and barium salts are insoluble in water. When heated with soda-lime it yields benzene:

$$C_6H_4(CO_2H)_2 + 4NaOH = 2Na_2CO_3 + 2H_2O + C_6H_6.$$

B. Oxidation of Primary Alcohols and Aldehydes

Method II.—Although the paraffins themselves are not readily oxidized, many of their oxygenated derivatives are readily converted into carboxylic acids by further oxidation. Every primary alcohol, whether of the aliphatic or aromatic series, when oxidized yields an aldehyde and then a monobasic acid, both containing the same number of carbon atoms as the original alcohol:

$$R\cdot CH_2\cdot OH \longrightarrow R\cdot C\begin{matrix}H\\ \diagdown O\end{matrix} \longrightarrow R\cdot C\begin{matrix}OH\\ \diagdown O\end{matrix}.$$

Experiment 52.—Oxidation of ethyl alcohol, $CH_3\cdot CH_2OH$, to acetic acid, $CH_3\cdot CO_2H$.

10 grm of powdered potassium dichromate are treated with a mixture of 20 grm. of concentrated sulphuric acid and 20 c.cm. of water in a small flask fitted with a reflux condenser (fig 78). 20 c.cm. of 25 per cent alcohol are run in slowly by means of a dropping funnel, and the mixture is then heated for about fifteen minutes. The product is distilled, and an aqueous solution of acetic acid passes over.

Pure acetic acid (glacial) is a colourless liquid with the odour of vinegar. It solidifies at low temperatures. Melting-point, 16·7°; boiling-point, 119°. $D_4^{15°}$, 1·0553.

Chemical Reactions.—Most of the salts are readily soluble, the silver salt somewhat sparingly. The ferric salt forms a blood-red solution, which deposits a brown precipitate of basic acetate when boiled. When heated with alcohol and concentrated sulphuric acid, acetates yield the characteristic odour of ethyl acetate (Exp. 74).

C. By the Elimination of Carbon Dioxide from a Dibasic Acid

Method III.—Many dibasic acids are perfectly stable, and show very little tendency to lose carbon dioxide, others, *e.g.* oxalic and malonic acids, evolve carbon dioxide readily when heated, yielding corresponding monobasic acids.

$$\begin{matrix}\text{COO H}\cdot\text{COOH (oxalic)} \\ \text{COO H}\cdot\text{CH}_2\cdot\text{COOH (malonic)}\end{matrix} \longrightarrow \begin{matrix}\text{H}\cdot\text{COOH (formic)} \\ \text{CH}_3\cdot\text{COOH (acetic)}\end{matrix}$$

This reaction appears to be characteristic of dibasic acids in which the two carboxyl groups are directly united, as in oxalic acid, or in which they are both attached to the same carbon atom, as in malonic acid and its substituted derivatives (cf Malonic ester synthesis, Chap XXV).

Experiment 53.—Preparation of formic acid from oxalic acid.

A good yield of formic acid cannot be obtained by merely heating oxalic acid, as a certain portion of the oxalic acid sublimes unchanged. The oxalic acid is therefore heated with glycerol when carbon dioxide and glyceryl monoformate are obtained, and the latter when boiled with water yields formic acid and glycerol:

$$\begin{matrix}\text{COOH} \\ \text{COOH}\end{matrix} + \text{C}_3\text{H}_5(\text{OH})_3 = \text{CO}_2 + \text{H}_2\text{O} + \text{C}_3\text{H}_5(\text{OH})_2\cdot\text{O}\cdot\text{C}\begin{matrix}\nearrow\text{H} \\ \searrow\text{O}\end{matrix}$$

$$\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{O}\cdot\text{C}\begin{matrix}\nearrow\text{H} \\ \searrow\text{O}\end{matrix} + \text{H}\cdot\text{OH} = \text{C}_3\text{H}_5(\text{OH})_3 + \text{H}\cdot\text{C}\begin{matrix}\nearrow\text{O} \\ \searrow\text{OH}\end{matrix}$$

30 grm. of glycerol are weighed in an evaporating dish and dehydrated by heating on a sand bath until a thermometer immersed in the liquid indicates a temperature of 175–180°. The mass is then introduced into a distilling flask of about 200 c.cm. capacity and 30 grm. of crystallized oxalic acid ($H_2C_2O_4\cdot 2H_2O$) added. The side tube of the flask is attached to a condenser, and a thermometer introduced through

the neck of the flask dips *into* the liquid. The mixture is heated gradually on a sand bath, and the temperature maintained at about 110° until the evolution of carbon dioxide gas slackens When this occurs the contents of the flask are allowed to cool somewhat and a fresh portion of 30 grm. of oxalic acid added. The heating is renewed, the reaction recommences, and an aqueous solution of formic acid distils over into the receiver. The reaction is a continuous one, and an abundant supply of the distillate may be obtained by the addition of similar quantities of oxalic acid at intervals. The water of crystallization of the oxalic acid serves to hydrolyse the glyceryl monoformate The residue in the flask after each distillation contains this ester (see Esters, Chap XIII, C).

The product in this experiment is an aqueous solution of formic acid

For the preparation of crystallized specimens of the lead and copper salts cf Chap XII, Exps. 62, 64.

Experiment 54.—Preparation of anhydrous Formic acid. Place 20 grm of the dry lead salt in a vertical glass tube drawn out at the bottom, pass in a stream of dry hydrogen sulphide from the top. Collect the oil which flows away from the bottom, and distil from a small flask containing a few grams of lead formate

The anhydrous acid is a colourless liquid with a penetrating odour, boiling-point 100° It is miscible in all proportions with water and alcohol.

The acid and its salts when heated with concentrated sulphuric acid yield pure carbon monoxide:

$$HCO{:}OH \rightarrow H_2O + CO.$$

The salts, with the exception of the silver salt and sparingly soluble lead salt, are readily soluble in water. The ferric salt, obtained by adding ferric chloride to a neutral solution of a formate, forms a blood-red solution which deposits a reddish precipitate of basic ferric formate on warming (cf Acetate, 52). Silver formate readily decomposes, depositing metallic silver

Experiment 55.—Add silver nitrate to a neutral solution of a formate. A white precipitate is obtained which darkens on exposure to light. Dissolve the precipitate by addition of a few drops of ammonia solution, and warm the resulting solution in a thoroughly clean test tube in a water bath; a silver mirror is deposited.

Formates also show other reducing properties. With a solution of mercuric chloride, a white precipitate of mercurous chloride is obtained.

Distinction between Formates and Acetates.—These two classes of salts may be distinguished by their reaction in *neutral* solution with silver nitrate. Formates yield a white precipitate which is easily reduced to metallic silver, while acetates in dilute solution yield no precipitate The former decompose when treated with concentrated sulphuric acid and alcohol, yielding carbon monoxide, while the latter yield the fragrant-smelling ester.

D. The Hydrolysis of an Ester of the Acid

Method IV.—The esters (Chap. XIII, C) of many acids occur naturally, and the acids may be obtained by the hydrolysis (saponification) of such esters either by means of dilute mineral acids or of alkalis (S. B. 176)—

$$CH_3 \cdot COOC_2H_5 + KOH = CH_3 \cdot COOK + C_2H_5OH,$$

the products formed being the acid, or its alkali salt, and the alcohol. Many of the natural fats and oils are esters of the trihydric alcohol glycerol, $C_3H_5(OH)_3$, with certain saturated and unsaturated monobasic acids, and when hydrolysed with alkalis, as in the manufacture of soap, yield the alkali salts of the acids and glycerol (S. B. 158).

Experiment 56.—Preparation of oleic acid from olive oil.

$$C_3H_5(O \cdot CO \cdot C_{17}H_{33})_3 + 3KOH \longrightarrow C_3H_5(OH)_3 + 3C_{17}H_{33}CO_2K$$

30 grm. of olive oil are boiled for 1–2 hours with a solution of 10 grm. of potassium hydroxide in 100 c.cm. of alcohol in a flask fitted with a reflux condenser (fig. 78). The alcohol is then evaporated on a water bath, and the excess of alkali in the residue carefully neutralized by the addition of dilute acetic acid (test with phenol phthalein). Excess of a concentrated solution of lead acetate crystals (30 grm.) is then added and the precipitate, which consists of a mixture of the lead salts of oleic, palmitic, and stearic acids, filtered by means of the pump. It is washed with alcohol to remove any unchanged olive oil, and then transferred to a separating funnel and shaken vigorously for some time with a large volume of ether, which dissolves the lead oleate. The result-

ing mixture is filtered through a fluted filter paper, the precipitate washed several times with ether, and the ether evaporated from the filtrate and washings. A residue of pure lead oleate is obtained which yields an oily layer of oleic acid when acidified with *pure* dilute nitric acid. The oil is removed by means of a separating funnel, shaken with anhydrous calcium chloride, and purified by distillation under diminished pressure (fig. 9). Boiling-point, 223° under 10 mm pressure. Yield, 10–15 grm.

It is a clear oily liquid at ordinary temperatures, but solidifies on cooling It melts at 14° and decomposes when distilled under ordinary pressure. $D_4^{15°}$, 0 895.

Chemical properties.—Oleic acid is an unsaturated acid; thus it decolorizes bromine water and reduces alkaline permanganate solution. (Cf allyl alcohol, Chap. X, C (*b*).) The lead salt is soluble in ether. Nitrous acid converts oleic acid into the stereo-isomeric elaidic acid. (Cf. stereo-isomerism of acids, Chap. XXXII, C.)

Experiment 57.—Preparation of elaidic acid from oleic acid

5 grm. of oleic acid are mixed with 1 to 2 c cm. of sodium nitrite solution, a little dilute nitric acid is added, and the mixture shaken well. In a short time the oil changes into a solid, which is removed and dried. Melting-point, 51°; boiling-point, 225° under 10 mm pressure.

This acid is also unsaturated and decolorizes bromine water and alkaline permanganate solution

E. The Hydrolysis of the Corresponding Nitrile.

(S.B., 142, 436.)

Method V.—Nitriles (cf. Chap. XIV, D) are readily hydrolysed to the corresponding acids on treatment with mineral acids or alkalis, *e.g.*:

$$C_6H_5 \cdot CH_2 \cdot CN + 2H_2O \longrightarrow C_6H_5CH_2 \cdot CO_2H + NH_3.$$

Experiment 58.—Preparation of phenyl-acetic acid, $C_6H_5 \cdot CH_2 \cdot CO_2H$, from benzyl chloride.*

15 grm. of potassium cyanide (98 per cent) are dissolved in 15 c.cm. of water in a flask fitted with a reflux condenser.

* *Mann*, B. 1881, **14**, 1645; *Staedel*, B. 1886, **19**, 1951.

To the warm solution a mixture of 25 grm. of benzyl chloride (Exp. 39) and 25 grm. of alcohol are added, and the whole is heated on a boiling-water bath for three hours. The upper alcoholic layer is removed and distilled, the crude nitrile, boiling-point 210–235°, being separately collected.

25 grm. of this product and 75 grm. of a mixture of con centrated sulphuric acid (3 volumes) and water (2 volumes) are heated in a flask fitted with a very long reflux condenser until the reaction just begins; the source of heat is then removed immediately. A very vigorous reaction takes place, when this has moderated, the mixture is heated for a few minutes longer. As the solution cools, the acid separates in the form of crystalline plates; when quite cold this is filtered with the aid of the pump, dissolved in sodium carbonate solution in order to remove a small amount of phenylacetamide, and reprecipitated by the addition of dilute sulphuric acid. It crystallizes from ligroin in colourless plates, melting-point, 76°; boiling-point, 265 5° (corr.). Yield, 90 per cent of theory.

For a further example of this method, cf. Exp. 271, *b*.

F. The Oxidation of Complex Carbon Compounds

Method VI.—Many complex oxygenated carbon compounds of the type of the carbohydrates yield oxalic acid when subjected to the action of vigorous oxidizing agents, especially concentrated nitric acid.

Experiment 59.—Preparation of oxalic acid from cane sugar, $C_{12}H_{22}O_{11}$. (*To be conducted in a fume chamber.*)

40 grm. of finely-powdered cane sugar are added to 200 grm. of concentrated nitric acid in a large flask. The mixture is warmed on a water bath until the reaction begins, after which it is allowed to proceed without the aid of external heat. Oxidation takes place with great vigour and abundant nitric fumes are evolved. When the reaction has moderated, the solution is evaporated on a water bath to a small bulk, on cooling, crystals of oxalic acid separate. These are filtered off on a porcelain funnel (a further yield is obtained by evaporating the mother liquor still further) and recrystallized from a little water. Yield about 10 grm.

The acid forms colourless crystals ($H_2C_2O_4 \cdot 2H_2O$) which lose their water of crystallization when heated at 100–105°.

Melting-point (of hydrated crystals), 101·5°. It is soluble in water and alcohol, sparingly soluble in ether

The acid and its salts, when heated with concentrated sulphuric acid, yield a mixture of carbon monoxide and carbon dioxide.

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

Warm solutions of the acid (or its salts) decolorize acid solutions of potassium permanganate.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

The calcium salt is insoluble in water and in acetic acid.

G. Kolbe's Synthesis of Hydroxy-acids of the Benzene Series.* (S. B. 438, 455)

Method VII.—The phenolic acids are formed when a current of dry carbon dioxide is passed over heated sodium phenoxides. The reaction takes place in three stages.

1. $C_6H_5\cdot ONa + CO_2 \longrightarrow C_6H_5\cdot O\cdot CO_2Na.$

This reaction occurs when the phenate is heated in a stream of the gas at 110° for an hour. At a higher temperature (200°) intramolecular change takes place.

2. $C_6H_5\cdot O\cdot CO_2Na \longrightarrow C_6H_4\langle^{OH}_{CO_2Na}\ ^{(1)}_{(2)}.$

The latter compound reacts with an unchanged molecule of sodium phenoxide, yielding the di-sodium derivative and free phenol

3. $C_6H_4\langle^{OH}_{CO_2Na} + C_6H_5ONa \longrightarrow C_6H_4\langle^{ONa}_{CO_2Na}\ ^{(1)}_{(2)} + C_6H_5OH.$

In this reaction, therefore, only one-half of the phenol is converted into the acid, the remainder distils over unchanged.

In Schmidt's modification of the method† (S. B. 456), the

* *Kolbe*, A. 1860, **113**, 125; 1860, **115**, 201, &c.
† J. pr., 1885 [2], **31**, 397.

product of reaction (1) is heated in an autoclave under pressure of carbon dioxide at 130°, and is thereby converted directly into mono-sodium salicylate.

Experiment 60.—Preparation of salicylic acid,

$$C_6H_4\begin{matrix}OH \\ CO_2H\end{matrix}\begin{matrix}(1) \\ (2)\end{matrix}$$

from phenol, C_6H_5OH.

23·5 grm. of pure phenol are added gradually to a solution of 10 grm. of pure sodium hydroxide in a little water (15 c.cm.) contained in a porcelain or nickel dish. The mixture is evaporated down over a free flame *with continual stirring*, the later stage being conducted with a large luminous flame kept in constant motion. The mass should be prevented from setting into a cake by stirring, when quite solid it is finely pulverized in a mortar, then heated in the nickel dish until quite dry, and quickly transferred into a dry tubulated retort which is immersed as far as possible in an oil or metal bath. Since the success of the experiment wholly depends on the sodium phenate being quite dry, it is advisable to heat the retort in the oil bath for half an hour at 140°, while a current of *dry* hydrogen is passed in through a leading tube fixed in the tubulure. The bath is then allowed to cool to 110°, and the hydrogen replaced by a current of dry carbon dioxide which is passed through the retort for about an hour. The temperature is then raised very gradually while a slow current of the gas is passed in, until at the end of four hours it reaches 200°, at which temperature the mixture is kept for two hours The regenerated phenol is driven over into the neck of the retort during the later stages and is removed by warming gently with a flame. The fine powder left in the retort is poured into a beaker, dissolved in water, and treated with excess of concentrated hydrochloric acid. Salicylic acid crystallizes out on standing and is filtered off on a porcelain funnel, washed with water, and crystallized from hot water.

It is best purified by distillation with superheated steam* (cf. p. 12), and forms colourless crystalline needles, melting-point 155°. It is sparingly soluble in cold water, more readily in alcohol, and is a powerful antiseptic.

The aqueous solution gives a violet coloration with ferric chloride (colour test for phenolic groups).

* *Rautert*, B. 1875, **8**, 537.

H. Recognition of Acids

If soluble in water, the aqueous solution of an acid usually gives an acid reaction with litmus solution. *Note.*—The fact that the aqueous solution has an acid reaction is no proof that the original substance was a free acid, it may have been an acid salt, an anhydride, chloride, or ester which was readily hydrolysed by water to the free acid; or it may have been the salt of a feeble base, *e.g* aniline hydrochloride, as all such salts are largely hydrolysed by water yielding the free acid.

Acids insoluble in water should dissolve in cold dilute sodium carbonate solution with effervescence, leaving no oily or solid residue, such as would be given by the salts of aniline and its homologues. (Carry out the test with a small quantity of the substance on a watchglass.)

To determine the actual acid present, reliance should be placed on physical constants rather than on mere colour reactions. The following should be determined: (*a*) The melting-point or boiling-point, (*b*) elements present; (*c*) the relative solubility in water; (*d*) whether a strong or a weak acid (test with various indicators), (*e*) the solubility or insolubility of the silver, calcium, barium, and ferric salts (for this purpose prepare a *neutral* solution of the ammonium salt by dissolving the acid in a very slight excess of ammonia solution, and boiling off excess of ammonia), (*f*) reducing properties (try the silver mirror test); (*g*) saturated or unsaturated nature (examine the action towards bromine water and towards acidified potassium permanganate).

Finally, determine the equivalent of the acid by titration of a known weight of the acid in aqueous or alcoholic solution, with standard baryta solution, using phenol-phthalein as indicator (Chap. VI, A), *or*, prepare and analyse the silver salt (Chap. VI, B).

If a solution of an acid is given, attempts should be made to isolate the pure acid from the solution, by evaporation if the acid is not volatile, or by extraction with ether. Then the physical constants and equivalent should be determined. For physical constants of common acids see pp. 349–351.

XIII. DERIVATIVES OF ACIDS

A. Metallic Salts

The metallic salts are formed by the substitution of metallic radicals for the hydrogen atoms of the carboxylic groups of the acid. When the acid is monobasic it gives rise, as a rule, to *normal* salts only. With polybasic acids *normal* and *acid* salts can be obtained:

$$CH_3 \cdot CO_2H \longrightarrow CH_3 \cdot CO_2Ag$$

$$CO_2H \cdot CH_2 \cdot CH_2 \cdot CO_2H \begin{cases} \longrightarrow CO_2K \cdot CH_2 \cdot CH_2 \cdot CO_2K \\ \longrightarrow CO_2H \cdot CH_2 \cdot CH_2 \cdot CO_2K. \end{cases}$$

N.B. Many dibasic acids do not form acid silver salts, *e.g.* succinic acid yields the normal salt, $CO_2Ag \cdot CH_2 \cdot CH_2 \cdot CO_2Ag$, even when silver nitrate solution is added to a solution of the potassium hydrogen salt.

Method I.—When the acid and salt are both readily soluble in water the simplest method for preparing the salt is by dissolving equivalent amounts of the acid and the metallic hydroxide or carbonate in small amounts of water, mixing and allowing to crystallize.

If the pure acid is not available, only an aqueous solution, the concentration of this solution, must be determined by titration with standard barium hydroxide (Chap. VI, A), using phenol phthalein as indicator. When the concentration is known then the amount of metallic hydroxide or carbonate required to neutralize a given quantity of the solution can be calculated.

Experiment 61.—Preparation of potassium acetate.

A solution of 20 grm. of glacial acetic acid in water is mixed with a warm, concentrated aqueous solution of the equivalent amount of pure dry potassium carbonate; crystals of the normal acetate, $CH_3 \cdot CO_2K$, separate as the solution cools. Filter by means of the pump, and dry on a porous plate.

Method II.—When both acid and salt are soluble in water, but the metallic oxide, hydroxide, or carbonate is insoluble, the simplest method is to digest an aqueous solution of the acid with an *excess* of the oxide, hydroxide, or carbonate * on

* It is generally safer to use the carbonate, as when an excess of the oxide or hydroxide is used there is the possibility that a basic salt may be formed. Thus from acetic acid and litharge the basic acetate, $CH_3 \cdot CO \cdot O \cdot Pb \cdot OH$, can be obtained.

the water bath, to filter whilst hot through a folded filter paper in a hot water funnel, and to allow the filtrate to cool.

Experiment 62.—Preparation of lead formate, $(H \cdot COO)_2Pb$.

Part of the acid distillate from Exp. 53 is digested on the water bath with an excess of lead carbonate, the solution filtered hot, and the filtrate allowed to cool. Long colourless prismatic crystals separate, and can be readily filtered by means of a Büchner funnel, washed, and dried.

Experiment 63.—Determine the percentage of lead in the dried specimen of salt you have prepared—

(*a*) By ignition and conversion into oxide.
(*b*) By heating with sulphuric acid and weighing as sulphate.

Experiment 64.—Preparation of cupric formate, $(H \cdot COO)_2Cu, 4H_2O$.

The remainder of the aqueous distillate from Exp. 53 is digested with an excess of freshly precipitated cupric oxide which has been thoroughly washed. Ordinary cupric oxide powder may also be used, but the solution of the oxide will take longer. The hot filtrate when kept deposits large, transparent, blue prisms of the cupric salt.

Method III.—When the salt is sparingly soluble, or practically insoluble in cold water, the simplest method is to prepare the salt by double decomposition, using an aqueous solution of the ammonium salt of the organic acid and a solution of some soluble salt of the metal, usually the chloride or nitrate. The solution of the ammonium salt of the acid is prepared by taking a known weight of the acid, adding water and a *slight* excess of ammonium hydroxide, until the solution is faintly alkaline. If too much ammonia has been added, the excess may usually be removed by gently heating the solution. The salt is then precipitated by adding a slight excess of the metallic chloride or nitrate dissolved in water.

Experiment 65.—Preparation of silver benzoate, $C_6H_5 \cdot CO_2Ag$.

Use 3 grm. of benzoic acid purified by sublimation, prepare a solution of the ammonium salt and add a solution containing a slight excess of silver nitrate. Filter by means of the pump, wash with cold distilled water, and dry on a porous plate in a desiccator.

Experiment 66.—Determine the percentage of silver in the dry silver salt by ignition, and from the result of the

experiment calculate the equivalent of benzoic acid (Chap. VI, B).

Experiment 67.—Preparation of cupric tartrate.

$$\begin{matrix} OH\cdot CH\cdot CO\cdot O \\ OH\cdot CH\cdot CO\cdot O \end{matrix}\!\!>\!Cu,\ 2H_2O.$$

Use equivalent quantities of cupric sulphate crystals, $CuSO_4$, $5H_2O$, and Rochelle salt, $NaKC_4H_4O_6$, $4H_2O$, sufficient to yield 5 grm. of the cupric salt. Filter as in preparation of silver benzoate, wash with distilled water until free from sulphate, and dry on a porous plate *in the air*.

Experiment 68.—Determine the percentage of cupric radical in the above hydrated salt by ignition and weighing the residual cupric oxide

Experiment 69.—Preparation of barium succinate.

$$\begin{matrix} CH_2\cdot CO\cdot O \\ CH_2\cdot CO\cdot O \end{matrix}\!\!>\!Ba.$$

From 5 grm of succinic acid prepare a solution of the ammonium salt, add a very slight excess of barium chloride crystals, $BaCl_2$, $2H_2O$, dissolved in water, filter, wash with distilled water until free from chloride, and dry in a desiccator.

Experiment 70.—Determine the percentage of barium radical in the dry salt by dissolving in hydrochloric acid, treating with sulphuric acid, and weighing the barium sulphate.

Experiment 71.—Preparation of the acid potassium salt of tartaric acid.

Dissolve 5 grm. of crystallized tartaric acid, $CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$, in a small amount of warm water, and add the theoretical amount of potassium hydroxide solution (1 equivalent for 2 equivalents of acid). The sparingly soluble acid salt separates, and may be filtered, washed with a little water, and dried.

Acid Salts of Monobasic Acids.—As a rule, an inorganic monobasic acid yields normal salts only, monobasic organic acids, on the other hand, frequently yield both normal and acid salts, *e.g.* acetic acid gives the three salts, $KC_2H_3O_2$, $KH(C_2H_3O_2)_2$, and $KH_2(C_2H_3O_2)_3$. The majority of such acid salts are decomposed readily by water.

Experiment 72.— Preparation of ammonium hydrogen benzoate,* $(C_6H_5CO_2)_2H \cdot NH_4$.

10 grm. of benzoic acid (2 molecules) are dissolved in alcohol and treated with the theoretical amount (1 molecule) of an alcoholic solution of ammonia. The mixture is kept for some time, when ammonium hydrogen benzoate separates as colourless plates.

The salt melts indefinitely at 190°. It is sparingly soluble in alcohol, insoluble in ether and chloroform, and is decomposed by water yielding the free acid and normal salt.

B. Salts of Organic Acids with Organic Bases

The combination of an amine (cf. Chap. XVIII) and an acid depends to a great extent on the strengths of the acid and base. Thus the simpler aliphatic amines combine readily with most organic acids, but when weaker bases are used the salts are not always easily isolated.

Experiment 73.—Preparation of phenylammonium benzoate,† $C_6H_5 \cdot CO \cdot O \cdot NH_3C_6H_5$.

$$C_6H_5NH_2 + C_6H_5CO_2H \longrightarrow C_6H_5 \cdot CO \cdot O \cdot NH_3C_6H_5.$$

Equivalent quantities of aniline and benzoic acid are stirred together in a test tube with a thermometer. The temperature rises as the mixture turns solid, showing that combination has taken place. The resulting salt is unstable, and is decomposed partially when crystallized from ligroin. The decomposition can be avoided by recrystallizing from ligroin containing 5 per cent of free aniline.

It consists of long, colourless, silky needles, melting-point 90°, it is fairly soluble in warm water, readily in most organic solvents.

C. Esters or Alkyl Salts. (S. B, pp. 172–176, 443.)

The esters are derived from acids by the exchange of the replaceable hydrogen atoms of carboxylic groups for alkyl radicals, in the same manner as metallic salts result by exchanging the hydrogen for metallic radicals. Monobasic acids

* *Farmer*, J. C. S. 1903, **83**, 1442.

† *Lloyd* and *Sudborough*, J. C. S. 1899, **75**, 596.

give rise to normal or neutral esters only; dibasic acids can give both normal and acid esters.

Normal Esters.—

Method I.—By the action of the acid on the alcohol, *e.g.*:

$$\underset{\text{Acetic acid}}{CH_3CO_2H} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \rightleftharpoons \underset{\text{Ethyl acetate.}}{CH_3CO_2C_2H_5} + H_2O$$

As the reaction is reversible, it is necessary in certain cases, in order to obtain a good yield, to use a dehydrating agent to take up the water formed during the reaction.

Experiment 74. — Preparation of ethyl acetate, $CH_3 \cdot CO_2C_2H_5$.

A half-litre flask is fitted with a cork carrying a dropping funnel * and a wide delivery tube leading to a long condenser (fig. 75). A mixture of 50 c.cm. of alcohol (rectified spirit) and 100 c.cm. of concentrated sulphuric acid is introduced into the flask, which is then heated in an oil or metal bath until it attains a temperature of 140° (the thermometer is placed in the bath). The bath is maintained at this temperature while a mixture of alcohol and glacial acetic acid, in equal proportions by volume, is added through the tap funnel, at about the same rate as liquid distils over. About 500 c.cm of the mixture should be added.

The distillate is treated as follows: To remove any acetic acid carried over, it is treated in a large beaker with a dilute solution of sodium carbonate, with continual stirring, until the upper layer of ester no longer shows an acid reaction The mixture is then poured into a separating funnel and the lower aqueous layer run off, after which the ester is shaken with a strong solution of calcium chloride (100 grm. in 100 c.cm. of water) to remove alcohol. The lower layer is again run off as completely as possible, and the ester dried by allowing to stand (preferably overnight) over granular calcium chloride. It is then filtered through a fluted filter paper into a dry distilling flask and distilled from a boiling-water bath in the usual manner, the portion boiling between 74° and 79° being collected separately. Yield, 80 per cent of theory.

It is a colourless liquid, with a pleasant, fruity odour. Boiling-point, 77°; $D_{4^\circ}^{17^\circ}$, 0·905. It is slightly soluble in water, but is miscible in all proportions with alcohol and ether.

* The dropping funnel should have a long stem drawn to a fine point, which dips under the surface of the liquid in the flask.

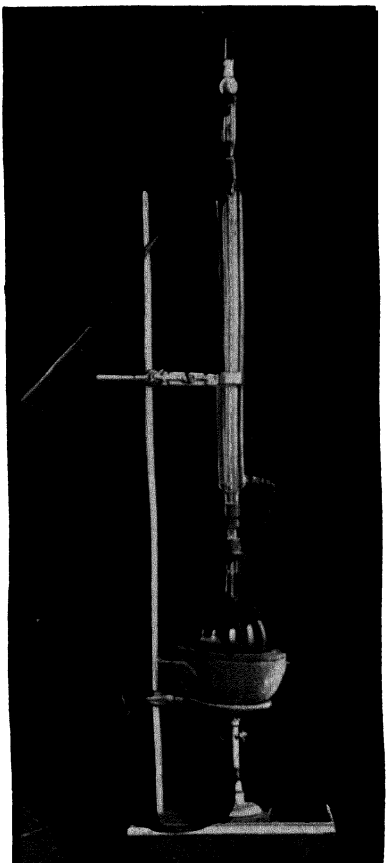


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Fig 78.

For the further purification of ethyl acetate see Chap. XXIV, A.

The yield of product may also be improved by taking excess of one of the reacting substances, *e.g.*:

Experiment 75.—Preparation of methyl oxalate,* $\begin{matrix}\mathrm{COOCH_3}\\ \mathrm{COOCH_3}\end{matrix}$.

$$\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix} + 2\mathrm{CH_3OH} = \begin{matrix}\mathrm{COOCH_3}\\ \mathrm{COOCH_3}\end{matrix} + 2\mathrm{H_2O}.$$

50 grm. of oxalic acid crystals are finely powdered, spread on a large clockglass, and heated in an air oven to a temperature of 110–120° for about an hour, to remove the water of hydration. (Test when completed by ascertaining the loss of weight.)

The anhydrous acid is then heated in a reflux apparatus on a boiling water bath (fig. 78), with 40 grm. (excess) of pure methyl alcohol for two hours. The product is subjected to fractional distillation. When a temperature of 120° is attained the water condenser is replaced by an air condenser (fig. 79), and the distillate obtained above this temperature collected in a porcelain dish. As it cools it solidifies, and is separated from any remaining liquid by filtering over the pump and pressing on porous plate. The product is recrystallized from methyl alcohol or dilute alcohol, when it forms colourless crystalline plates, melting-point 54°, boiling-point 163°. Yield, 15–20 grm., *i.e.* 30–40 per cent of theory.

Method II.—**The Fischer-Speier Method.**† This consists in boiling the anhydrous acid with two to three times its weight of absolute alcohol in the presence of a small amount of concentrated sulphuric acid or dry hydrogen chloride, which act as catalytic agents in accelerating the reaction.

Experiment 76.—Preparation of ethyl benzoate, $\mathrm{C_6H_5 \cdot CO \cdot OC_2H_5}$.

$$\mathrm{C_6H_5 \cdot CO \cdot OH + H \cdot OC_2H_5} \rightleftharpoons \mathrm{C_6H_5 \cdot CO \cdot OC_2H_5 + H_2O}.$$

A mixture of 50 grm. of pure benzoic acid, 100 grm. of absolute ethyl alcohol, and 10 grm. of concentrated sulphuric acid are boiled for three hours in a round-bottomed flask, attached to a reflux condenser (fig. 78). The greater part of the alcohol is then distilled off, and the residue poured into about five times its volume of cold water. The liquid is neutralized

Erlenmeyer, J. 1874, 572. † B. 1895, 28, 3252.

with solid sodium carbonate and the oil extracted with ether. The ethereal solution is separated, dried with anhydrous potassium carbonate, the ether removed, and the residue distilled. 55 grm. (*i.e.* 90 per cent of theory calculated on the amount of the acid used) pass over as a colourless liquid, boiling-point 213°; D, 1·066. The ester is very slightly soluble in water, but is soluble in alcohol and ether.

Experiment 77.—Preparation of diethyl succinate,* $CO_2Et \cdot CH_2 \cdot CH_2 \cdot CO_2Et$.

60 grm. of succinic acid are treated with 100 c.cm. of 96 per cent alcohol, and 4 c.cm. of concentrated sulphuric acid, and the mixture heated for three hours on a water bath in a flask fitted with a reflux condenser. After cooling, the product is poured on to 30 grm. of soda crystals in a beaker, the oil separated, washed with a little ice water, dried with calcium chloride, and distilled. The portion boiling between 200° and 220° is collected. Yield 75–80 grm., *i.e.* 90 per cent of theory.

It forms a colourless oil with fragrant odour, and is insoluble in water. Boiling-point, 216°, $D_{4°}^{25·5°}$, 1·0475

Experiment 78.—Preparation of diethyl tartrate, $CO_2Et \cdot (CHOH)_2 \cdot CO_2Et$.

Dry hydrogen chloride (cf. Chap XXXIX) is led slowly into a flask containing absolute alcohol until an increase in weight of 3 per cent is obtained To 100 grm. of the resulting solution 20 grm. of tartaric acid, which has been dried previously in an air oven at 110° for an hour, are added, and the mixture heated in a reflux apparatus on a water bath for six hours (fig. 78). The whole is then distilled under reduced pressure; ethyl alcohol and water pass over first, the temperature rises rapidly, and the greater portion passing over at 192–193°, under a pressure of 60 mm., is collected separately. Yield, 22 grm., *i.e.* 80 per cent of theory.

It is a fragrant-smelling liquid, boiling-point 280°/760 mm.; $D_{4°}^{14°}$, 1·2097. It is dextro-rotatory $[\alpha]_D^{20°} = +7·659$, and is sparingly soluble in water, but dissolves readily in alcohol and ether.

For determination of specific rotatory power, see Exp. 275.

The ordinary Fischer-Speier method for isolating the ester cannot be used in the above case as the ester dissolves in water and is readily hydrolysed to the acid and alcohol.

* *Volhard.*

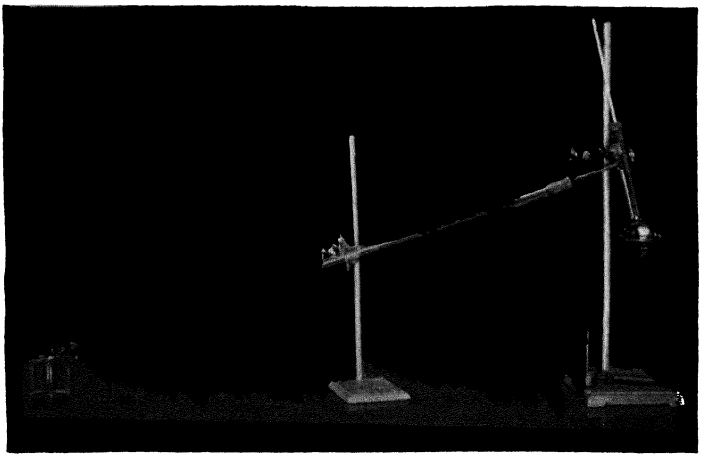

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Fig 79

A methyl ester can usually be transformed into the corresponding ethyl ester when it is dissolved in an excess of ethyl alcohol and a fragment of metallic sodium added.* The reactions which occur are those indicated in the equations—

$$R\cdot C\begin{matrix}O\\ \diagdown\\ OMe\end{matrix} + EtONa \longrightarrow R\cdot C\begin{matrix}ONa\\ \diagdown\\ OEt\\ \diagup\\ OMe\end{matrix} \longrightarrow R\cdot C\begin{matrix}OEt\\ \diagdown\\ O\end{matrix} + MeONa$$

The same transformation occurs when a solution of a methyl ester in ethyl alcohol is saturated with hydrogen chloride.† Ethyl esters can be converted into methyl esters by similar methods, but in neither case can transformation occur when a diortho-substituted benzoic ester is used.‡

Certain acids, especially diortho-substituted benzoic acids, are not esterified by the catalytic process. (Cf. Steric Retardation, S. B. 447.) In such cases the esters may be obtained by Methods III or IV.

Method III.—By the action of the alcohol on the acyl chloride.

A good yield of ester can generally be obtained when the acyl chloride (Chap. XI, A, 1) is boiled for a short time with a slight excess of the alcohol

Experiment 79.—Preparation of methyl benzoate from benzoyl chloride.

$$C_6H_5CO\,Cl + H\,O\cdot CH_3 = C_6H_5CO\cdot OCH_3 + HCl$$

10 grm. of benzoyl chloride are boiled for 10 minutes with 10 grm of methyl alcohol (excess) in a small distilling flask fitted to a reflux apparatus. The product is fractionally distilled. When the excess of methyl alcohol has been removed, the water condenser is replaced by an air condenser (fig. 79), and the product boiling above 190° is collected. Yield about 10 grm., *i.e.* almost theoretical.

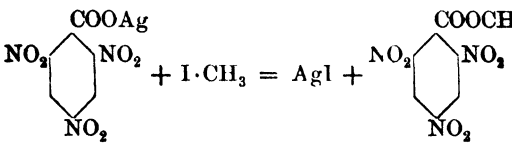
It is a colourless oil with fragrant odour, boiling-point 199°; D, 1·1026; insoluble in water.

Method IV.—A universal method of preparing esters is by the action of alkyl iodides on the silver salts of the acids; or in the case of methyl esters by the action of methyl sulphate¶ (2 molecules) on an aqueous solution of the sodium salt of the

* *Purdie*, J. C. S. 1885, **47**, 855. † *Patterson*, J. C. S. 1901, **79**, 280.
‡ *Sudborough* and *Davies*, P. 1905, **21**, 87.
¶ *Werner* and *Seybold*, B. 1904, **37**, 3658; *Graebe*, A. 1905, **340**, 244.

acid; the mixture is shaken, warmed to 30–40°, and the ester removed.

Experiment 80.—Preparation of methyl trinitrobenzoate,* $(NO_2)_3C_6H_2 \cdot COOCH_3$.



5 grm. of trinitrobenzoic acid (1·2·4·6) are converted into the ammonium salt by the addition of the theoretical amount of ammonium hydroxide solution (excess is to be avoided as a deep-red solution is then formed). A slight excess of silver nitrate in aqueous solution is added. The precipitated silver salt is removed, washed and dried in the usual manner. The dried salt and 10 grm. of methyl iodide are placed in a small flask fitted with a reflux condenser and heated on a gently-boiling water bath for an hour. The excess of methyl iodide is then distilled off, the residue extracted with boiling alcohol and filtered to remove silver iodide. As the solution cools, the ester separates in the form of yellow plates, melting-point 157°. Yield almost theoretical.

D. Acid Esters

Acid esters derived from dibasic acids may be obtained by the following methods:—

Method I.—By the partial esterification of the acid.

Experiment 81.—Preparation of ethyl hydrogen tartrate, $C_2H_5H \cdot C_4H_4O_6$.†

A solution of tartaric acid in an equal amount of absolute alcohol is heated for six hours at 65–70° in a water bath. The product is diluted with water and excess of barium carbonate added. The barium tartrate and excess of carbonate are removed, the filtrate evaporated and allowed to crystallize. The barium ethyl tartrate which separates is dried and decomposed with the theoretical amount of dilute sulphuric acid. The filtrate from the barium sulphate when evaporated

* *Sudborough*, J. C. S. 1895, **67**, 600.
† *Guérin-Varry*, A. 1837, **22**, 238.

gently yields the ester as colourless rhombic prisms, melting-point 90°.

Method II.—By the addition of alcohol to the anhydride of a dibasic acid.

Experiment 82.—Preparation of methyl hydrogen succinate,* $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO_2CH_3$.

$$\begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} \!\!>\!\! O + CH_3 \cdot OH = \begin{matrix} CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2CH_3 \end{matrix}$$

5 grm. of succinic anhydride (Exp. 86) are boiled with twice the theoretical weight of pure methyl alcohol for 45 min. The product is kept in a desiccator until the excess of alcohol is removed and then crystallized from hot carbon disulphide, when the ester is deposited as glistening white plates, melting-point 58°. Yield almost theoretical.

Method III—By the partial hydrolysis of the normal ester.

Experiment 83.—Preparation of ethyl hydrogen succinate,† $CO_2Et \cdot (CH_2)_2 \cdot CO_2H$.

$$CO_2Et \cdot (CH_2)_2 \cdot CO_2Et + KOH \longrightarrow CO_2Et \cdot (CH_2)_2 \cdot CO_2K + EtOH.$$

50 grm. of diethyl succinate (Exp. 77) (1 molecule) are diluted with 40 c.cm. of alcohol in a large distilling flask, and treated with a strong solution of 16 grm. of potassium hydroxide sticks in alcohol. The mixture becomes warm and some salt separates After standing for 3 hours, the alcohol is distilled off on the water bath, a current of carbon dioxide being meanwhile passed through the apparatus The residue is taken up with water, and the solution shaken up with ether to remove any unchanged diethyl ester. The aqueous solution contains potassium ethyl succinate (as required for Exp 248); to obtain the free ester, it is acidified with hydrochloric acid and extracted with ether; the ethereal extract is dried, the ether evaporated, and the residue distilled under diminished pressure. Boiling-point, 170° under 30 mm. Yield, 60–70 per cent of theory.

E. Recognition of Salts

The majority of salts leave inorganic residues (metal, oxide, or carbonate) when ignited on platinum or porcelain. Am-

* *Bone, Sudborough,* and *Spankling,* J. C. S. 1904, 85, 539.
† *Walker,* J. C. S. 1892, 61, 709.

monium salts are completely volatile, but can be readily distinguished by the fact that they yield ammonia when treated with *cold* potassium hydroxide or when rubbed with slaked lime. (Cf. amides and nitriles, Chap. XIV, B and D.)

To determine the nature of the metallic radical examine the residue obtained after ignition of the substance either alone or with concentrated sulphuric acid. To determine the acid from which the salt is derived, prepare, if possible, a specimen of the pure acid, determine its physical constants (*e.g.* the melting-point, boiling-point), and the percentage of silver in the silver salt If the acid is sparingly soluble in water, a specimen can be obtained readily by treating the salt, or better, an aqueous solution of the salt, with a mineral acid. If soluble in water, it can often be obtained by extracting the acidified solution with ether, and removing the ether after the solution has been dried.

For physical constants and characteristics of common acids, see pp 349–351

Colour reactions and solubilities of certain salts may be made use of, but should not be the only methods adopted.

F. Recognition of Esters

The esters are mostly volatile liquids with fruity odours, generally insoluble, or only sparingly soluble, in water. They are hydrolysed by alkalis yielding the free alcohol and the alkali salt of the acid. The simplest method of treatment is to hydrolyse the ester with aqueous alkali and to determine the nature of the alcohol and acid formed.

The simplest and best method of hydrolysing the ester is to boil a given quantity of it with excess of 10 per cent aqueous potassium hydroxide in a flask fitted with a reflux condenser (fig. 78). If the ester is insoluble in water the completion of the hydrolysis can be seen from the disappearance of the oily layer, unless the alcohol formed during the hydrolysis is also insoluble in water or potassium hydroxide solution (*e.g.* benzyl or amyl alcohol).

When the reaction is finished any oil is removed and its boiling-point taken, and it is examined in order to determine whether it is unaltered ester or an alcohol. If no oil is present, the product is partially distilled, using a water condenser, and when about one-third of the liquid has distilled

over the distillation is stopped. The distillate will contain any volatile alcohol (*e.g.* methyl, ethyl, propyl), and the residue will contain the potassium salt of the acid.

To determine the alcohol, the distillate is subjected to fractional distillation, using a rod and disc column (fig 4, *a*). The first fraction is completely dehydrated by means of anhydrous potassium carbonate, redistilled, and tested for methyl, ethyl, or propyl alcohol.

To determine the acid, a small amount of the alkaline residue is acidified with hydrochloric acid.

(*a*) If a precipitate is formed, it indicates that the acid from which the ester is derived is insoluble in water. The whole residue is then acidified, the precipitated acid removed and examined carefully.

(*b*) If no precipitate is obtained, it indicates that the acid is soluble in water. The acidified mixture is extracted with ether in order to obtain a specimen of the pure acid.*

(*c*) If no precipitate is obtained, and it is found impossible to extract the acid by means of ether, then the acid must be detected by means of—(1) colour reactions; (2) solubilities of salts, (3) reducing properties. (Cf. Chap. XXXVIII, p. 352, properties of common acids.)

N.B.—In trying colour reactions and solubilities of salts, it must be remembered that the alkali used for the hydrolysis will probably not be pure, but will contain chloride, carbonate, &c

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XIV. DERIVATIVES OF ACIDS—(*Continued*)

A. Acid Anhydrides or Acyl Oxides
(S. B. 180, 444.)

1. **Anhydrides of Monobasic Acids.**—These are theoretically derived from the acids by the elimination of one molecule of water from two molecules of the acid; but they cannot be prepared by the action of dehydrating agents on the acids.

Modes of Formation.—*Method I.*—By the action of the acyl

* Acids such as oxalic and succinic are not readily extracted by ether, but, after shaking some two or three times with ether, sufficient acid can be obtained to determine some of its physical data.

chloride (Chap. XI, A) on the anhydrous sodium salt of the acid, *e.g.*—

$$CH_3 \cdot COCl + CH_3 \cdot CO \cdot ONa \longrightarrow (CH_3 \cdot CO)_2O + NaCl.$$

By using the chloride and sodium salt of different acids mixed anhydrides are produced, *e.g.*—

$$CH_3 \cdot COCl + CH_3 \cdot CH_2 \cdot COONa = \begin{matrix} CH_3 \cdot CO \\ C_2H_5 \cdot CO \end{matrix} \!\!>\!\! O + NaCl.$$

Experiment 84 — Preparation of acetic anhydride, $(CH_3CO)_2O$, from acetyl chloride.

The sodium acetate should be freshly dehydrated as described in Exp. 14, care being taken that no charring occurs during the process.

50 grm. of anhydrous sodium acetate are introduced into a retort connected with a water condenser A dropping funnel is fixed through the tubulure of the retort, and by means of the funnel 30 grm. of acetyl chloride (Exp 35) are added drop by drop. When the addition is completed, the dropping funnel is removed, the mixture stirred with a glass rod, and the tubulure closed with a glass stopper. The retort is then heated with a luminous flame kept in constant motion. The distillate is collected in a distillation flask, the side tube of which is fitted with a drying tube containing calcium chloride. A little fused sodium acetate is added to the product, which is redistilled from the collecting flask into a flask protected from atmospheric moisture (fig. 75) It is a colourless liquid with suffocating odour, boiling-point 138°; D, 1·073.

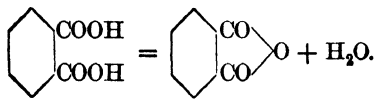
2. **Anhydrides of Dibasic Acids.**—Certain dibasic acids, *e.g.* succinic acid and its substituted derivatives and phthalic acid, yield cyclic anhydrides by the elimination of one molecule of water from one molecule of the acid.

$$\underset{\text{Succinic acid}}{\begin{matrix} CH_2 \cdot CO \cdot OH \\ CH_2 \cdot CO \cdot OH \end{matrix}} = H_2O + \underset{\text{Succinic anhydride.}}{\begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} \!\!>\!\! O.}$$

The property seems to be characteristic of acids which can yield an anhydride containing a ring built up of five atoms. (S.B. 322.)

Modes of Formation.—*Method I.—Formation of the anhydride by heating the acid.*

Experiment 85.—Preparation of phthalic anhydride from phthalic acid.



10 grm. of phthalic acid (Exp. 51) are heated in a sublimation apparatus (fig. 19). The sublimate, which consists of long white needles, is the pure anhydride Melting-point, 128°.

Method II.—Succinic acid does not yield the pure anhydrides on sublimation; the sublimates, in these cases, consist of mixtures of the anhydride with the original acid.* The anhydrides are obtained in a pure state by heating the acid with a dehydrating agent. Various dehydrating agents can be used, *e g.* phosphorus pentachloride or oxychloride, acetyl chloride or acetic anhydride. The last is generally the most convenient.

Experiment 86.—Preparation of succinic anhydride from succinic acid.† (Cf equation above.)

10 grm. of finely-powdered succinic acid are boiled for two hours with excess (15 grm.) of acetyl chloride in a flask fitted with a reflux condenser The product is poured into a shallow dish or clock-glass and kept in a desiccator over soda-lime until the excess of acetyl chloride and acetic acid are com pletely removed, it is then recrystallized from chloroform and forms long needles, melting-point 119°. Yield almost theoretical.

3. **Chemical Properties of the Acid Anhydrides.**—The acyl anhydrides of the aliphatic series are, for the most part, colourless liquids which are readily soluble in alcohol and ether; the corresponding compounds of the benzene series are solids, generally melting considerably lower than the acids from which they are derived. They are insoluble in water, but are gradually hydrolysed by it to the corresponding acid.

$$(CH_3 \cdot CO)_2O + H_2O = 2CH_3CO_2H.$$

When treated with dilute alkalis they are readily converted into salts of the corresponding acids.

* *Volhard*, A. 1887, 242, 148. † *Anschütz*, A. 1884, 226, 8.

B. Acid Amides. (S. B. 182–185.)

The acid amides are to be regarded as acids in which the hydroxyl groups of the carboxylic radicals (—COOH) have been replaced by the amido-group ($-NH_2$). Amides can also be obtained from sulphonic acids (Chap. XVI).

Modes of Formation.—*Method I.—By the dehydration of the ammonium salt of the acid.**

Experiment 87.—Preparation of acetamide, $CH_3 \cdot CONH_2$, from ammonium acetate.*

$$CH_3 \cdot CO \cdot ONH_4 = CH_3CO \cdot NH_2 + H_2O.$$

50 grm. of glacial acetic acid are weighed into a large evaporating basin and warmed gently on a hot-water bath. Finely powdered ammonium carbonate is added gradually with continual stirring until the mixture just shows an alkaline reaction. (Dilute a small portion with water and test with litmus paper.) About 65–70 grm. of ammonium carbonate will be necessary. The mixture is then heated on the water bath until another test portion just shows an *acid* reaction. After cooling, the crystals are drained and pressed on filter paper.

50 grm of this ammonium acetate and 56 grm. of glacial acetic acid are boiled in a litre flask with a reflux condenser for five hours, and the product is distilled rapidly. The distillate is then fractionated, using a simple form of column with two bulbs. *This operation should be carried out as slowly as possible.* Three fractions are collected: (1) the fraction passing over below 180°, (2) between 180° and 213°, (3) above 213°. The second fraction (180–213°) is again fractionated, and the portion passing over at about 213° added to fraction 3.

This fraction solidifies as it cools, and the crystals are dried by pressing between filter paper. Yield, 30 grm., or 60 per cent of the theoretical. This method is much more convenient than the older Hofmann method, according to which the ammonium acetate was heated in sealed tubes. The acetic acid used appears to act as a catalyst.

The crystals of acetamide possess the peculiar odour characteristic of mouse excrement. This is not the odour of the pure substance, but of an impurity which accompanies it. The substance recrystallized from ether is odourless; it forms

* *Hofmann*, B. 1882, **15**, 979; *Rosanoff, Gulick*, and *Larkin*, C. N. 1911, **104**, 1. Alternative method described by *Hitch* and *Gilbert*, J.A.C.S. 1913, **35**, 1780.

colourless crystals; melting-point, 82°; boiling-point, 223°. It is deliquescent, soluble in water, alcohol, and ether.

Method II.—By the action of concentrated ammonia solution on acyl chlorides. This method is particularly suitable for the preparation of the amides of the higher fatty and of the aromatic acids.

Experiment 88 - Preparation of benzamide, $C_6H_5CO\cdot NH_2$, from benzoyl chloride

$$C_6H_5COCl + 2NH_3 \longrightarrow C_6H_5CO\cdot NH_2 + NH_4Cl.$$

5 grm. of benzoyl chloride (Exp. 36) are added, drop by drop, to 20 c.cm. of strong ammonia solution (D, 0·880) contained in a beaker. After cooling, the precipitated product is filtered with the aid of the pump, washed well with water, and dried on a porous plate. It crystallizes from hot water as colourless, glistening plates, melting-point 130°, boiling-point 288°, and is readily soluble in hot water, alcohol, and ether Yield, 4 grm.

Experiment 89.—Preparation of benzene-sulphonamide, $C_6H_5SO_2\cdot NH_2$, from benzene-sulphonic chloride.*

$$C_6H_5SO_2Cl + 2NH_3 \longrightarrow C_6H_5SO_2\cdot NH_2 + NH_4Cl.$$

5 grm. of benzene-sulphonic chloride (Exp. 37) are treated exactly as described under the last experiment. The product forms colourless glistening plates, melting-point 150°.

Method III.—By the action of concentrated ammonia solution on esters. This method is used mainly for the preparation of amides which are not readily soluble in water, *e.g.* amides of certain dibasic acids. If the ester is a solid it may be dissolved in a little alcohol. Methyl esters react more readily than ethyl.

Experiment 90. — Preparation of oxamide from ethyl oxalate.

$$C_2H_5O\cdot CO\cdot CO\cdot OC_2H_5 + 2NH_3 = NH_2\cdot CO\cdot CO\cdot NH_2 + 2C_2H_5OH.$$

3 grm. of ethyl oxalate are added gradually to about 3 c.cm. of concentrated ammonia solution, and the mixture well shaken until the ester is transformed into a snow-white crystalline solid. The precipitate is filtered with the aid of the pump, washed with alcohol, and dried.

It is a white crystalline solid, which partly sublimes on

* *Gerhardt* and *Chancel*, J. 1852, 434.

heating, but the greater part is decomposed; it is very sparingly soluble in water and alcohol.

Experiment 91.—Preparation of succinamide from ethyl succinate.*

$$C_2H_5O\cdot CO\cdot(CH_2)_2\cdot CO\cdot OC_2H_5 + 2NH_3 = NH_2\cdot CO\cdot(CH_2)_2\cdot CO\cdot NH_2 + 2C_2H_5OH.$$

Proceed exactly as in Exp. 90. The product is recrystallized from hot water, and the crystalline needles obtained dried in a steam oven.

It forms colourless needles, melting point 242–243°; is sparingly soluble in cold water, more readily in hot, and is insoluble in absolute alcohol and in ether.

Chemical Properties of the Acyl Amides (S. B. 183–184).—The acyl amides are generally crystalline substances with definite melting-points, and are therefore of use for the characterization of the acids from which they are derived On the whole, they are less readily soluble in water than the ammonium salts of the corresponding acids.

1. When boiled with alkalis they are completely hydrolysed, giving off ammonia.

$$X\cdot CONH_2 + KOH = X\cdot CO_2K + NH_3.$$

2. Treated with nitrous acid,† they yield the corresponding acid, with evolution of nitrogen. (Cf. Amines, Chap. XVIII.)

$$X\cdot CONH_2 + HNO_2 = X\cdot CO_2H + H_2O + N_2.$$

Experiment 92.—Apply these reactions to benzamide, and isolate the benzoic acid formed.

3. With bromine and alkali the acyl amides yield amines (*Hofmann's* reaction, Chap. XVIII, A. 1).

Quantitative Estimation of Amido-groups.—The determination of the percentage of the amido-group ($\cdot NH_2$) in an amide is carried out as follows:—A known weight of the amide is distilled with excess of strong potash solution, and the ammonia evolved absorbed in a known volume of standard hydrochloric acid. When completed, the excess of acid is titrated with standard alkali, using methyl orange as indicator (cf. Kjeldahl estimation of Nitrogen, Chap. V, C. 2).

Recognition of Amides.—The amides give off ammonia

* *Fehling*, A. 1844, **49**, 196.

† A solution of potassium or sodium nitrite is added, and then the mixture acidified with a dilute mineral acid.

when boiled with dilute potassium hydroxide, but are not generally decomposed in the cold (cf. Ammonium salts). They are distinguished from ammonium salts and nitriles (this chap., D) by examination of their comparative solubilities and melting-points.

To determine the specific amide, isolate and examine the acid formed by reactions 1 and 2 above, and if necessary determine the percentage of $-NH_2$ present.

C. Imides

Dibasic acids which yield anhydrides also form *Imides*, which may be regarded as anhydrides in which the $>O$ atom has been replaced by the divalent imido-group $>NH$.

Method I.—By the dry distillation of ammonium salts or amides of dibasic acids.

Experiment 93.—Preparation of succinimide from ammonium hydrogen succinate.*

$$\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COONH_4\end{matrix} = \begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}\!\!>NH + 2H_2O.$$

25 grm. of succinic acid are dissolved in a small quantity of water, and neutralized with ammonia solution. Any excess of ammonia is boiled off, and then an equal quantity of succinic acid (dissolved in water) is again added. The solution is evaporated to dryness on a steam or water bath, and the residue dried in a steam oven. The dry salt is transferred to a retort and distilled quickly, using a *large luminous* flame. The sublimate is recrystallized from dry acetone, and forms colourless rhombic plates, melting-point 125–126°; boiling-point, 287–288°. Yield, 10–15 grm.

Method II.—By the action of dry ammonia on an acid anhydride.

Experiment 94.—Preparation of phthalimide† from phthalic anhydride.

$$C_6H_4\!<\!\begin{matrix}CO\\ CO\end{matrix}\!\!>O + NH_3 = C_6H_4\!<\!\begin{matrix}CO\\ CO\end{matrix}\!\!>NH + H_2O.$$

20 grm. of phthalic anhydride (Exp. 85) are placed in a large boiling tube, which is fitted with a cork bored with two

* *Fehling*, A. 1844, **49**, 198.

† This imide is an important synthetical agent for the preparation of various amino-compounds (*Gabriel*, cf. S. B. 463).

holes, one carrying a leading tube which reaches to within 1 cm. of the substance. The tube is heated in an oil bath to 130°, while a current of dry ammonia is led in. The temperature of the bath is raised gradually until after about an hour it reaches 230°; the tube is then withdrawn, and the contents crystallized from ether. Yield, 12 grm., *i.e.* 60 per cent of theory.

White crystalline needles, melting-point 233°.

Chemical Properties of the Imides.—The imides resemble the amides in their behaviour towards hydrolysing agents. The properties of the :NH group are so modified by the proximity of the two carbonyl (:CO) groups that the imido hydrogen is often replaceable by metallic radicals.

Experiment 95.—Preparation of the potassium salt of phthalimide,* $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK$.

A quantity of phthalimide is dissolved in alcohol and treated with the theoretical amount of alcoholic potassium hydroxide solution. A white crystalline salt separates out, which is only sparingly soluble in water, and insoluble in alcohol and ether.

Imides yield amino-acids when treated with bromine and alkali (*Hofmann's* reaction, cf. Exp. 131).

Quantitative Estimation of Imido-groups.—This is carried out in a similar manner to the estimation of amido-groups (p. 148).

For Substituted Amides and Imides, cf. Chap XIX.

D. Nitriles or Alkyl Cyanides. (S. B. 100–102, 436.)

The nitriles or alkyl cyanides contain the monovalent $\cdot C\vdots N$ group attached to an alkyl radical.

Modes of Formation.—*Method I.*—By the dehydration of an acid amide by means of phosphoric anhydride or phosphorus pentachloride.

Experiment 96.—Preparation of acetonitrile from acetamide.†

$$CH_3CO\cdot NH_2 = CH_3\cdot CN + H_2O.$$

10 grm. of dry acetamide (Exp. 87) are added to 15 grm

* *Landsberg*, A. 1882, **215**, 181.
† *Dumas*, A. 1847, **64**, 332.

of phosphoric anhydride in a small distilling flask. The substances are mixed by shaking, and the flask connected with a condenser. On warming gently with a small flame a vigorous reaction ensues; the acetonitrile is distilled over by means of a *large luminous* flame kept in constant motion. The distillate is treated with about half its volume of water, and then solid potassium carbonate is added until no more dissolves. The upper layer of nitrile is separated by means of a small tap funnel and redistilled with a little fresh phosphorus pentoxide from a small distilling flask. Yield, 5 grm.

It is a colourless liquid with an agreeable odour, and is miscible with water, alcohol, and ether; boiling-point, 82°; $D_{4°}^{15°}$, 0·789.

Method II.—From halogen derivatives by the action of potassium cyanide (cf. Exps. 58 and 271*b*).

Method III.—By the addition of hydrogen cyanide to aldehydes (cf. Exp. 271).

Method IV.—By application of the diazo-reaction (cf. Exp. 160).

General Chemical Properties of the Nitriles (S. B. 101, 445).—The nitriles are liquids, usually insoluble in water, possessing an ethereal odour, and distilling without decomposition. They are hydrolysed when boiled with acids or alkalis or superheated with water yielding the corresponding acids or their salts, with evolution of ammonia, *e.g.*:

$$CH_3 \cdot CN + 2H_2O = CH_3 \cdot CO_2H + NH_3.$$

Experiment 97.—Warm a few drops of acetonitrile with dilute potassium hydroxide solution until no more ammonia is evolved. Neutralize the resulting solution with hydrochloric acid, and test for an acetate (cf. p. 124).

On reduction, the nitriles yield primary amines,* *e.g.*:

$$CH_3 \cdot CN + 4H \longrightarrow CH_3 \cdot CH_2 \cdot NH_2 \text{ (ethylamine).}$$

Experiment 98.—Treat a solution of a few drops of a nitrile in alcohol with metallic sodium. Test the resulting solution for a primary amine by the carbylamine reaction (cf. p. 189).

Recognition of Nitriles.—The nitriles resemble the ammonium salts, amides, and amic acids (*e.g.* oxamic acid, $NH_2 \cdot CO \cdot CO \cdot OH$), and cyano-acids (cyanacetic acid, $N{:}C \cdot CH_2 \cdot CO_2H$), in their behaviour towards alkalis. The last two may readily be distinguished, since they possess the carboxylic

* *Mendius*, A. 1862, 121, 129.

group; the distinction between the others depends chiefly on a study of the physical constants of the substance and the identification of the acid obtained by hydrolysis.

XV. NITRO-DERIVATIVES—NITRATION

The reaction with nitric acid provides a fairly general method of distinguishing between aliphatic and aromatic compounds. As a rule, treatment of the former class of compounds with nitric acid leads to oxidation, whereas in the latter case nitro-derivatives are produced, *e.g.*:

$$\underset{\text{Benzene}}{C_6H_5\,H} + HO\cdot N\lesssim^{O}_{O} \longrightarrow \underset{\text{Nitrobenzene.}}{C_6H_5\cdot N\lesssim^{O}_{O}} + H_2O$$

One or more nitro-groups may enter the molecule, according to the conditions of the experiment and the nature of the compound to be nitrated. The introduction of subsequent nitro-groups after the first becomes progressively more difficult, and the number of nitro-groups that can be introduced into a closed-ring compound is usually limited (cf. Preparation of nitro-phenols, Exp. 101, and picric acid, Exp. 103). When the aromatic compound contains a saturated side chain, nitration usually affects the benzene ring; under special conditions only (*e.g.* heating with dilute nitric acid, sp. gr. 1 075, in a sealed tube at 105° for several hours) does the nitro-group enter the side chain.*

A. Nitration of Aromatic Compounds

For the preparation of aromatic nitro-derivatives the following reagents are usually employed:—

If the substance is readily nitrated: dilute nitric acid, sodium or potassium nitrate and diluted sulphuric acid; solutions of nitric acid in glacial acetic acid, ether, acetone, or acetic anhydride.†

If the substance is nitrated with moderate ease: concentrated nitric acid.

If the substance is nitrated with difficulty, or if di- or tri-nitro-derivatives are required: fuming nitric acid; a mixture of con-

* *Konowaloff*, B. 1894, 27, Ref. 194. † *Orton*, J. C. S., 1902, 81, 806.

centrated nitric and sulphuric acids; a mixture of fuming nitric and concentrated sulphuric acids.

A solution of nitric acid in concentrated sulphuric acid is very frequently used, and is highly efficient as a nitrating agent. It probably contains the compound $SO_2<^{OH}_{O\cdot NO_2}$.

The methods may be further modified by (*a*) varying the temperature, (*b*) varying the amount of nitric acid employed.

Experiment 99.—Preparation of nitrobenzene, $C_6H_5\cdot NO_2$, from benzene.

100 grm. of concentrated nitric acid (sp. gr. 1·4) are added gradually to 150 grm. of concentrated sulphuric acid, the mixture is cooled, and then added in small portions to 50 grm. of pure benzene contained in a 500 c.cm. flask. The contents of the flask are well shaken and cooled, after each addition, by immersion in cold water; under no circumstances must the temperature be allowed to rise above 50°, otherwise some dinitrobenzene is formed. When the addition is completed, a vertical air condenser is attached to the flask, which is then immersed in a water bath kept at 50–60° for about an hour The flask is withdrawn from the bath at intervals and shaken well. After cooling, the contents of the flask are poured into a separating funnel, and the lower layer of acid removed The oily nitrobenzene is washed free from acid by shaking, once with water, then with dilute sodium carbonate solution, and again with water. (During these operations the nitrobenzene forms the *lower* layer.) The liquid is now turbid, and is freed from water by allowing to stand over granular calcium chloride until it becomes clear. It is then fractionally distilled from a distilling flask provided with a long air condenser (fig. 79); the fraction boiling between 204° and 207° is collected separately.

The nitrobenzene is a yellow oil with an odour of bitter almonds. It solidifies in a freezing mixture to a solid. Melting-point, 3°; boiling-point, 206–207°; $D^{15°}$, 1·208. Yield, about 65 grm., *i.e.* 80 per cent of theory.

*Modified Method.**—In the above preparation a considerable excess of acid was employed. The operation can be conducted with almost the theoretical amount of nitric acid provided the mixture is well stirred.

50 grm. of pure benzene are placed in a round-bottomed

* *Schultz* and *Flachsländer*, J. pr. 1902, [2], 66, 156.

flask provided with a cork which carries (*a*) a thermometer, the bulb of which dips into the benzene; (*b*) a short condenser; (*c*) a dropping funnel. A *Witt* stirrer, worked by a water turbine or hot air motor, passes through the condenser tube and keeps the liquid rapidly agitated. A *cold* mixture of 55 grm. of concentrated nitric acid (sp. gr. 1·456) and 72 grm. of sulphuric acid (sp. gr. 1·842) (= 42·8 grm. *pure* HNO_3, whereas the theoretical amount required is 40·4 grm.) is added drop by drop from the funnel whilst the flask is cooled; the temperature is ultimately allowed to rise to 35–40°; the mixture is poured into water, and the nitro-benzene isolated as above. No dinitro-product is produced. Yield, 95–96 per cent of theory.

When the compound to be nitrated already contains a substituent group, the position taken by the nitro-group depends on the nature of that group. (Cf. S. B. 446.) The presence of alkyl radicals in the benzene nucleus facilitates nitration, so that the nitro-derivatives of toluene, xylene, and mesitylene are more readily prepared than the nitro-derivatives of benzene.

Experiment 100.—Preparation of *m*-dinitrobenzene from nitrobenzene.*

$$C_6H_5 \cdot NO_2 \longrightarrow C_6H_4\langle^{NO_2\,(1)}_{NO_2\,(3)}$$

20 grm. of nitrobenzene are added gradually to a mixture of 40 grm. of concentrated sulphuric acid and 35 grm. of fuming nitric acid, contained in a 1000 c.cm. flask, with continual shaking. The mixture is heated on a boiling-water bath until a test portion poured into water separates as a solid cake (about half an hour is required). It is then poured, while still hot, into a large quantity of cold water. The dinitrobenzene which solidifies is filtered off on a porcelain funnel, washed with cold water, and dried on a porous plate. Yield about 24 grm., *i.e.* almost theoretical. The product, which is a mixture of the three isomeric dinitrobenzenes (mainly the meta- compound), is crystallized from alcohol, when the meta-dinitrobenzene separates as pale-yellow flat needles, melting-point 90°.

The presence of phenolic hydroxy-groups considerably facilitates nitration. In order to obtain mono-nitro-derivatives of phenol, dilute nitric acid must be employed.

* *Muspratt* and *Hofmann*, A. 1846, 57, 214.

Experiment 101.—Preparation of *o*- and *p*-nitrophenols from phenol.*

$$C_6H_5\cdot OH \longrightarrow OH\cdot C_6H_4\cdot NO_2 \text{ (1:2 and 1:4).}$$

60 grm. of dry sodium nitrate crystals are introduced into a large beaker of 1½ litre capacity and dissolved in 150 c.cm. of water. 75 grm. of concentrated sulphuric acid are added gradually and the mixture cooled in running water. A warm solution of 40 grm. of phenol in 5 grm of alcohol is added gradually to the mixture from a tap funnel. During the addition the acid mixture is stirred vigorously (automatically), and the temperature must not be allowed to rise above 25°. It is kept overnight, when the product collects as a dark oil (or solid) at the bottom of the vessel, and consists of a mixture of *o*- and *p*-nitrophenols with much tarry matter. It is freed from acid by shaking three or four times with cold water and decanting About 250 c.cm. of fresh water are then added and the mixture subjected to steam distillation (fig. 10). The *o*-nitrophenol passes over with the steam and condenses as a yellow solid in the condenser tube, from which it is periodically removed by turning off the supply of cold water and allowing the water in the condenser to become warm. The distillation is continued as long as solid passes over, the product is then filtered by means of the pump and dried on a porous palate The product is practically pure, but may be crystallized from dilute alcohol, and is thus obtained as bright-yellow needles, melting-point 45°. Yield, 15 grm.

The aqueous liquid remaining in the flask, which contains much *p*-nitrophenol in solution, is removed while hot, and the tarry residue extracted three or four times with boiling water or with hot dilute hydrochloric acid (about 100 c.cm. at a time). The united extracts are decolorized by boiling with about 20 grm. of animal charcoal for half an hour, filtered while hot through a fluted filter paper, and made alkaline by addition of sodium hydroxide solution. The liquid is evaporated down to a small bulk (about 100 c.cm.); if tarry matter separates it is removed by filtration. It is then acidified (while hot) with concentrated hydrochloric acid and allowed to cool. *p*-nitrophenol separates in the form of long almost colourless needles, which are filtered off and recrystallized from hot water. Yield about 8 grm. Melting-point, 114°.

Preparation of Salts of Nitrophenols.—The nitrophenols

* *Hart*, J. A. C. S. 1910, **32**, 1105.

are much more strongly acidic than the phenols (cf. Chap. XVII), and can decompose metallic carbonates.

Experiment 102.—Prepare crystals of potassium *o*-nitrophenate and sodium *p*-nitrophenate by dissolving the respective phenols in concentrated hot solutions of the metallic carbonates and allowing to crystallize.

The final product of the nitration of phenol is picric acid, $C_6H_2(OH)(NO_2)_3$ (1:2:4:6), which is also formed when *o*- and *p*-nitrophenols are further nitrated.

Experiment 103.—Preparation of picric acid (*s*-trinitrophenol), $OH \cdot C_6H_2(NO_2)_3$, 1:2:4:6, from phenol

10 grm. of phenol are dissolved in 20 grm. of concentrated sulphuric acid by warming in a porcelain basin. The product (phenol-sulphonic acid) is cooled and then added gradually to 50 grm. of concentrated nitric acid (sp gr. 1·4) in a 500 c.cm. flask. A considerable amount of heat is generated during the operation and oxides of nitrogen are abundantly evolved After the reaction has moderated the mixture is heated on a boiling-water bath for two hours On cooling, picric acid separates as a yellow crystalline mass The liquid is diluted with water and the crystals are filtered off at the pump, well washed with cold water, and recrystallized from hot water, when it is obtained in the form of yellow needles It melts at 122·5°, is sparingly soluble in cold water, but dissolves readily in hot water and in alcohol. Yield 15 grm., *i.e.* 60 per cent of theory.

Picric acid is more strongly acidic than the mono-nitrophenols. It is largely used as an explosive.

B. Aliphatic Nitro-Compounds

Aliphatic nitro-compounds are usually prepared indirectly (see Exp. 104), but numerous cases of direct substitution have been observed among the higher paraffins.* The usual indirect method is by the action of an alkyl iodide on dry silver nitrite.†

Experiment 104.—Preparation of nitro-ethane, $C_2H_5 \cdot NO_2$, from ethyl iodide.

$$C_2H_5I + AgNO_2 \longrightarrow C_2H_5 \cdot NO_2 + HgI.$$

* *Worstall*, Am. 1898, 20, 202; 1899, 21, 211.

† *V. Meyer*, A., 1874, 171, 18.

The silver nitrite is prepared by adding a slight excess of a lukewarm concentrated solution of potassium nitrite to a similar solution of silver nitrate and allowing the mixture to cool. The precipitate of silver nitrite is collected on a filter, washed rapidly, and dried on a porous plate.

42 grm. of dry silver nitrite are placed in a round-bottomed flask fitted with a reflux condenser, and 34 grm. of ethyl iodide are added gradually through the condenser tube. During the process the flask is not disturbed, as it is important that the silver nitrite should be gradually penetrated by the iodide. The latter is admitted at such a rate that the liquid boils vigorously, but not too violently. The mixture is finally warmed for some time on the water bath, and the products separated by fractional distillation. Ethyl nitrite ($C_2H_5 \cdot O \cdot N:O$, isomeric with nitro-ethane), boiling-point 18°, distils over first, and afterwards nitro-ethane is collected at 110–114°. Yield, 8–9 grm., *i.e.* 50 per cent of theory.

When pure it is a colourless liquid. Boiling-point, 113–114°. $D^{13°}$, 1 058.

C. General Characteristics of the Nitro-Compounds

1. The aliphatic nitro-derivatives and the aromatic compounds with the nitro-group in the side chain are acidic in properties, with the exception of the tertiary nitro-derivatives, *i.e.* compounds of the type $R_1R_2R_3C \cdot NO_2$, which are neutral compounds.

Experiment 105.—To about 2 c.cm. of a solution of sodium ethoxide in absolute alcohol add a few drops of nitro-ethane A white precipitate appears, which consists of the sodium derivative, $CH_3 \cdot CH:N\begin{matrix}O\cdot \\ \diagdown O\cdot Na.\end{matrix}$

These metallic derivatives are explosive when dried; they are quite differently constituted from the hydrogen compounds from which they are formed, and are thus pseudo-acids (cf. S. B. 96, 363, 634).

2. The simpler nitro-compounds of the aromatic series are, for the most part, pale-yellow liquids or solids, of high boiling-point, which distil unchanged and are often volatile with steam. With increase in the number of nitro-groups the colour deepens to an intense yellow or red, and the compounds decompose on heating, often explosively. All these nitro-compounds are heavier than water, and only sparingly

soluble in it; most are readily soluble in alcohol, ether, and glacial acetic acid.

3. Nitro-compounds when reduced in acid solution, *e.g.* by the action of tin and hydrochloric acid, are converted into the corresponding primary amines (see Exp. 133).

$$\underset{\text{Nitro-ethane}}{C_2H_5\cdot NO_2} \longrightarrow \underset{\text{Ethylamine.}}{C_2H_5\cdot NH_2}$$

$$\underset{\text{Nitrobenzene}}{C_6H_5\cdot NO_2} \longrightarrow \underset{\text{Aniline}}{C_6H_5\cdot NH_2}$$

These can be tested for by the carbylamine reaction (p. 189), or recognized by the melting-point of their acetyl or benzoyl derivatives (cf. Chap. XIX).

4. Reduction of a nitro-compound in neutral solution, *e.g.* boiling the nitro-body with zinc dust and water, yields a hydroxylamine derivative (Exp. 221).

$$\underset{\text{Phenyl hydroxylamine}}{C_6H_5\cdot NO_2 \longrightarrow C_6H_5\cdot NH\cdot OH}$$

Experiment 106.—Heat a nitro-compound for a few minutes in a test tube with zinc dust and water. Filter and test the clear filtrate by warming with *Fehling's* solution (p. 311). A precipitate of cuprous oxide is formed indicating the presence of a hydroxylamine derivative, a compound which possesses reducing properties.

The poly-nitro-compounds often form beautifully crystallizing additive compounds with many aromatic hydrocarbons, but more especially with amines and phenols.

Experiment 107.—Prepare the additive compounds of (*a*) naphthalene and picric acid; (*b*) α-naphthylamine and trinitrobenzene by dissolving equivalent quantities in alcohol or benzene and allowing to crystallize.

Elimination of the Nitro-Group from an Aromatic Nitro-Compound.—The nitro-derivative is reduced to an arylamine (Exp. 133) and the amino-group, subsequently eliminated by means of the diazo-reaction (Exps. 168, 169).

D. Determination of the number of Nitro-Groups present in a Molecule*

The percentage of nitro-radical can be determined in many cases by estimating the amount of stannous chloride required to reduce the nitro- to amino-groups.

* Callan, Henderson and Strafford, J.S.C.I., 1920, **39**, 86, T. (resumé of methods); Bruce, C.N., 1919, **118**, 133.

$$X \cdot NO_2 + 3SnCl_2 + 6HCl = X \cdot NH_2 + SnCl_2 + 2H_2O.$$

The solution of stannous chloride is prepared by dissolving 25 grm. of tin in 250 c.cm. concentrated hydrochloric acid and making up to a litre. The strength of this solution should be determined *during the time occupied by the reduction*, by titration with standard iodine solution.

$$2SnCl_2 + 2I_2 = SnCl_4 + SnI_4.$$

A known weight of the nitro-compound (0·2–0·4 grm.) is dissolved in 40 c.cm. of alcohol in a flask fitted with a reflex condenser, and also an inlet tube for carbon dioxide. The air in the apparatus is removed by passage of carbon dioxide, and a known volume (excess) of stannous chloride solution introduced. The mixture is heated on a boiling water bath for 2½ hours, cooled, and made up to 200 c.cm. with distilled water. The excess of stannous chloride is then titrated with decinormal iodine solution, using starch solution as indicator.

Knecht and Hibbert* describe an alternative method using titanous chloride as reducing agent. Both methods fail in certain cases (*e.g.* α nitro-napthalene) where chlorination takes place as well as reduction. It is suggested that this error may be avoided by the use of titanous sulphate.

If the molecular weight of the nitro-compound is known, the number of nitro-groups present in the molecule may be readily calculated.

Experiment 108. — Determine the percentage of nitro-radical in *m*-dinitrobenzene.

XVI. SULPHONIC ACIDS—SULPHONATION

A. Aromatic Sulphonic Acids. (S. B. 401.)

One of the characteristic properties of benzene and its derivatives is the readiness with which they react with sulphuric acid, yielding sulphonic acids. The process is termed sulphonation, and the products contain the monovalent group—$SO_2 \cdot OH$, *e.g.*—

$$C_6H_5H + HO \cdot SO_2 \cdot OH = C_6H_5 \cdot SO_2 \cdot OH + H_2O.$$

* *New Reduction Methods in Volumetric Analysis*, London, 1918, p. 25.

The reaction proceeds with varying degrees of readiness in the case of different substances, one or more sulphonic groups being introduced into the compound according to the conditions under which the reaction is conducted. The chief agents used for sulphonation are—concentrated sulphuric acid, fuming sulphuric acid, sulphuryl chloride, $HO \cdot SO_2 \cdot Cl$, and mixtures of sulphuric acid with other dehydrating agents, *e.g.* acetic anhydride.

For the isolation of the products, the fact that the sulphonic acids generally form soluble calcium, barium, or lead salts is utilized. The strongly acid liquid, consisting of the sulphonic acid with excess of sulphuric acid, may be poured into excess of cold water containing pieces of ice. Under these circumstances a few sulphonic acids will crystallize If the product is soluble in water and no separation occurs, the hot solution is digested with excess of calcium or barium carbonate (or lead carbonate or oxide may be used), and filtered whilst hot to remove the precipitated sulphate The calcium, barium, or lead salt of the sulphonic acid is then allowed to crystallize from the solution.

To obtain the free sulphonic acid, the recrystallized salts are decomposed with the calculated quantity of sulphuric acid, the precipitated sulphate filtered off, and the solution evaporated. Solutions of lead salts may be decomposed by hydrogen sulphide, and an aqueous solution of sulphonic acid obtained by filtering off the precipitated lead sulphide.

Experiment 109.—Preparation of benzene-sulphonic acid,* $C_6H_5 \cdot SO_2 \cdot OH$.

120 grm. of fuming sulphuric acid of D 1·88–1·89 (containing 5–8 per cent of SO_3) are placed in a small flask fitted with a reflux condenser, and 30 grm. of benzene are added gradually with continual shaking, care being taken that the first quantity of benzene dissolves before any further amount is added. During the addition the flask is cooled by immersion in cold water; after all the benzene has dissolved (about fifteen minutes are required) the product is treated in different ways according to whether a salt or the pure acid is required.

(*a*) **Sodium benzene-sulphonate,** $C_6H_5 \cdot SO_2 \cdot ONa$. The reaction mixture is added very slowly by means of a tap funnel to 400 c.cm. of a saturated solution of common salt contained

* *Gattermann*, B. 1891, **24**, 2121.

in a stout beaker immersed in ice-cold water. After some time, or more quickly if the sides of the beaker are rubbed with a glass rod, sodium benzene-sulphonate separates in the form of glistening plates. After standing for several hours the crystals are filtered off (use a Buchner funnel and pump) and washed with a little saturated salt solution. Yield, 75 grm.

The substance may be freed from common salt by recrystallization from absolute alcohol, in which sodium chloride is insoluble. The crude salt also contains sulpho-benzide, $(C_6H_5)_2:SO_2$, which can be removed by extracting the dried salt with ether.

(*b*) **Benzene-sulphonic acid.**—To obtain the free acid the reaction mixture is poured into a large excess of water (½ litre) and neutralized by the gradual addition of excess of finely-powdered barium carbonate made into a cream with water. The product is warmed and filtered quickly while hot through a folded filter paper The barium benzene-sulphonate, $(C_6H_5SO_2\cdot O)_2Ba$, is deposited as the solution cools (evaporate down if necessary), and is purified by recrystallization from hot water. To obtain the free benzene-sulphonic acid, a quantity of the salt is treated with its exact equivalent of dilute sulphuric acid, the precipitated barium sulphate filtered off, and the sulphonic acid obtained by evaporating the solution to a small bulk and allowing the acid to crystallize.

Alternative Methods for the Preparation of Benzene-sulphonic Acid.—

(*a*) If the sulphuric acid is mixed with some porous material, *e.g.* kieselguhr, the sulphonation proceeds much more readily than when the acid is used alone.* The kieselguhr should be treated previously with acid, well washed with water, and ignited.

Experiment 110.—A quantitative yield of benzene mono sulphonic acid can be obtained by shaking together 15 grm. of pure benzene, 90 grm. of sulphuric acid (sp. gr. 1·842), and sufficient ignited kieselgühr to form a thin paste, and allowing this to stand for twenty-four hours The acid or its salts can be isolated as in Exp. 109.

(*b*) Sulphonic acids can be very readily prepared by using polysulphates, *i.e.* compounds of acid sulphates with sulphuric acid of the type $NaH_3(SO_4)_2$, instead of sulphuric acid itself.†

* *Wendt*, D. R.-P., 71,556. † *Lambert*, D. R.-P., 113,784.

Mono-, di-, and tri-sulphonic acids can be prepared by the use of this reagent.

Experiment 111.—Preparation of benzene-mono-sulphonic acid.

$$C_6H_6 + KH_3(SO_4)_2 \rightarrow C_6H_5 \cdot SO_3H + KHSO_4 + H_2O$$
$$C_6H_5SO_3H + KHSO_4 + Ca(OH)_2 \rightarrow C_6H_5SO_3K + CaSO_4 + 2H_2O.$$

1 part by weight of benzene and 2·5 parts by weight of potassium polysulphate are boiled in a flask fitted with a reflux condenser until all the benzene is dissolved The cold product is dissolved in water and *neutralized* with milk of lime, the precipitated calcium sulphate is removed, and the filtrate, which contains potassium benzene-sulphonate, is evaporated to dryness, or until crystals separate.

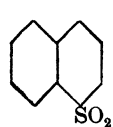
Experiment 112.—Preparation of benzene-*m*-disulphonic acid, $C_6H_4(SO_2 \cdot OH)_2$ (1:3)

1 part by weight of benzene and 5 parts by weight of potassium polysulphate are gradually heated together until a temperature of 200–240° is attained, and then kept at this temperature for some little time The potassium salt is isolated as in Exp. 111. A small amount of the *p*-acid is formed in addition to the meta.

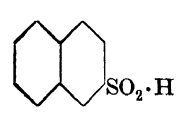
On treatment of the meta-disulphonic acid with 1·5 parts of potassium polysulphate at 280–300°, it is further sulphonated to the 1:3:5 benzene-trisulphonic acid.

Naphthalene Sulphonic Acids

Naphthalene yields two mono-sulphonic acid derivatives, viz.:—



Naphthalene α-sulphonic acid



Naphthalene β-sulphonic acid.

A mixture of the two acids is obtained when naphthalene is heated at 80° with concentrated sulphuric acid. They may be separated by fractional crystallization of their calcium or barium salts, as the β sulphonates are less soluble than the α salts. The α salt or acid is transformed into the β compound when heated with concentrated sulphuric acid, so that the chief product obtained by sulphonating naphthalene at 160° is the β acid.

Experiment 113.—Preparation of β naphthalene-sulphonic acid *

60 grm. of concentrated sulphuric acid are warmed in a round-bottomed flask, and 50 grm. of finely powdered naphthalene added gradually, the flask being well shaken. The mixture is heated in a paraffin or metal bath (without condenser) at 170–180° for four hours. After cooling, the product is carefully poured into a litre of water, and the unaltered naphthalene which separates removed by filtration. The liquid is made alkaline with milk of lime, prepared by slaking quicklime (calculate the amount necessary to neutralize the sulphuric acid taken) with hot water. The mixture is filtered while hot through a damp filter-cloth, and the precipitate in the cloth thoroughly squeezed out into another dish. It is then boiled up with 500 c.cm of water, and again filtered and pressed. The united filtrates are clarified by passing through an ordinary filter paper, then evaporated to a small bulk and allowed to stand overnight. The crystalline calcium salt $[(C_{10}H_6SO_2 \cdot O)_2Ca]$ which separates is filtered at the pump, washed with a little water, and finally dried on a porous plate. Yield variable.

Preparation of sodium β naphthalene-sulphonate, $C_{10}H_7 \cdot SO_2 \cdot ONa$.

$$(C_{10}H_7 \cdot SO_2 \cdot O)_2Ca + Na_2CO_3 = CaCO_3 + 2C_{10}H_7 \cdot SO_2 \cdot ONa.$$

A portion of the calcium salt is dissolved in hot water, and a concentrated solution of the theoretical weight of anhydrous sodium carbonate added, until a test portion filtered off gives no further precipitate with sodium carbonate solution. After cooling, the precipitated calcium carbonate is filtered off, and the solution evaporated until crystals begin to form. After standing for several hours the crystals of sodium salt are filtered; a further yield of crystals is obtained by evaporating the mother liquor and allowing it to stand The crystals are dried in a steam oven. Yield, about 70 per cent of theory.

Preparation of the free β-naphthalene-sulphonic acid.—A portion of the calcium salt is treated with rather less than the theoretical amount of sulphuric acid diluted with five times its volume of water and warmed on a water bath. The aqueous solution of the acid obtained after filtering is evapo-

* B. 1870, 3, 195.

rated to a small bulk on a water bath, when non-deliquescent plates, melting-point 161°, are deposited. The acid is not volatile with steam.

When the substance to be sulphonated already contains a substituent group, the position taken by the $\cdot SO_2 \cdot OH$ group (or groups) depends on the nature of the group already present (cf. S. B. 446).

Amino- and hydroxy-derivatives of benzene are sulphonated more readily than benzene itself. In the case of aniline, the final product is the *p*-sulphonic acid, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot OH$, but several intermediate products are formed.* (Cf. S. B. 403.)

Experiment 114.—Sulphonation of aniline Preparation of sulphanilic acid, *p*-aminobenzene-sulphonic acid.

$$C_6H_5 \cdot NH_2 \longrightarrow NH_2 \cdot C_6H_4 \cdot SO_2 \cdot OH \ (1:4).$$

80 grm. of concentrated sulphuric acid are placed in a round-bottomed flask, and 25 grm. of aniline added cautiously The mixture, consisting of aniline sulphate with excess of sulphuric acid, is heated in an oil or paraffin bath at a temperature of 180–190°, until a test portion diluted with water and treated with sodium hydroxide solution remains clear, and no aniline separates (four to five hours are necessary). The product is then cooled, and poured gradually with stirring into excess of cold water, when the sulphanilic acid separates as fine greyish crystals. These are removed and recrystallized from hot water to which a little animal charcoal has been added to remove the colour. Yield, about 25 grm.

It forms colourless rhombic crystals containing 2 molecules of water of hydration. The substance has no definite melting-point, but decomposes at high temperatures.

Experiment 115.—Sulphonation of camphor, $C_{10}H_{16}O$; Preparation of *d*-camphor-sulphonic acid, $C_{10}H_{15}O \cdot SO_2 \cdot OH$ † (*Reychler's acid*).

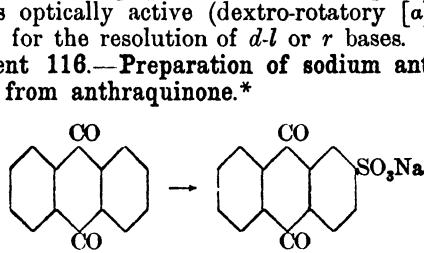
30 grm. of powdered camphor are added gradually to a mixture of 20 grm. of concentrated sulphuric acid, with 40 grm. of acetic anhydride. The camphor dissolves readily, and the mixture is allowed to stand for two to three days at the ordinary temperature, during which *d*-camphor-sulphonic acid crystallizes out. The liquid is then drained away from the

* *Bamberger*, B. 1897, **30**, 2274.

† *Reychler*, Bull. 1898, (iii), **19**, 120; *Armstrong* and *Lowry*, J. C. S. 1902, **81**, 1442.

crystals, which are filtered at the pump over a pad of asbestos or glass wool; they are washed with acetic acid till colourless, and purified by recrystallization from acetic acid or ethyl acetate. Yield, 16–18 grm., *i.e.* 50 per cent of theory. It is thus obtained as large prisms, which decompose at 190–193°. The acid is optically active (dextro-rotatory $[\alpha]_D = +21°$), and is used for the resolution of *d-l* or *r* bases.

Experiment 116.—Preparation of sodium anthraquinone-sulphonate from anthraquinone.*



25 grm of finely powdered anthraquinone (Exp. 195) are added to 25 grm. of fuming sulphuric acid containing 45–50 per cent SO_3 (sp. gr. 1·98–2) in a round-bottomed flask. The mixture is heated in an oil bath, the temperature of which is gradually raised so that at the end of an hour it reaches 160°. The product is carefully poured into excess of hot water, and the unchanged anthraquinone which separates removed by filtration. The filtrate is neutralized with sodium hydroxide and allowed to cool, when the greater portion of the sodium anthraquinone-sulphonate crystallizes out. A further yield of crystals is obtained by concentrating the filtrate. Yield, 20 grm.

The final filtrate contains the sodium salt of anthraquinone-disulphonic acid, which may be obtained (mixed with sodium sulphate) by evaporating to dryness.

Sodium anthraquinone sulphonate crystallizes from water with one molecule of water of crystallization.

B. Aliphatic Sulphonic Acids. Modes of Formation.

(S. B. 98.)

Method I.—These aliphatic acids cannot be obtained by direct sulphonation, but are usually prepared by the oxidation of mercaptans or by the action of alkyl iodides on metallic sulphites.

* *A. G. Perkin.*

Experiment 117.—Preparation of ethyl-sulphonic acid, $C_2H_5 \cdot SO_2 \cdot OH$.*

$$2C_2H_5I + 2(NH_4)_2SO_3 + 2H_2O = 2C_2H_5 \cdot SO_2 \cdot OH + 2NH_4OH + 2NH_4I.$$

20 grm. of ethyl iodide are added to a solution of 20 grm. of crystallized ammonium sulphite in 40 c.cm. of water, in a flask attached to a reflux condenser, and the mixture boiled until all the ethyl iodide has disappeared (about six hours are necessary). The liquid is then diluted with water, 30 grm. of lead oxide added, and the mixture heated until all ammonia has been expelled. When cold the lead iodide is removed by filtration, and the lead salt of ethyl-sulphonic acid, $(C_2H_5SO_2O)_2Pb$, which is present in the filtrate, decomposed by passing hydrogen sulphide until no more precipitate is formed. The lead sulphide is filtered off, and the solution of ethyl-sulphonic acid neutralized by addition of excess of barium carbonate (20 grm.). After filtration, the clear solution of barium ethyl sulphonate is evaporated Yield, 22 grm., 90 per cent of theory.

For a number of years the constitution usually attributed to the additive compounds of aldehydes and ketones with sodium bisulphite (cf. Exp. 179) was that of sulphonic acid salts.

$$R \cdot C\lessgtr^{H}_{O} + NaHSO_3 \longrightarrow R \cdot CH\lessgtr^{OH}_{SO_2 \cdot ONa}$$

The additive compounds are now supposed to contain the grouping $R \cdot CH(OH)(O \cdot SO \cdot ONa)$.†

Method II.—Metallic sulphites also form additive compounds with certain olefine derivatives.‡

$$R \cdot CH{:}CH \cdot CO_2H + K_2SO_3 \longrightarrow R \cdot CH_2 \cdot CH\lessgtr^{CO_2K}_{SO_3K}$$

Experiment 118.—Preparation of phenylsulphopropionic acid from cinnamic acid.

Molecular proportions of cinnamic acid (Exp. 235) and normal potassium sulphite are boiled in a reflux apparatus with ten times their weight of water for twelve hours, allowed to cool,

* *Hemilian*, A. 1873, **168**, 146.

† *Knœvenagel*, B. 1904, **37**, 4059; *Reinking, Dehnel*, and *Labhardt*, B. 1905, **38**, 1069.

‡ *Valet*, A. 1870, **154**, 63.

and acidified with acetic acid. A colourless crystalline precipitate of the acid potassium salt, $C_6H_5 \cdot CH_2 \cdot CH<^{CO_2H}_{SO_3K}$, separates and is recrystallized from hot water. A further yield of the product may be obtained by evaporating the filtrate, extracting the potassium acetate with alcohol, and crystallizing the residue from water.

The salt may be crystallized from boiling dilute hydrochloric or sulphuric acids without decomposition. When heated, it melts and decomposes with the development of aromatic odours.

C Characteristics of the Sulphonic Acids

The sulphonic acids are colourless oils or solids, generally hygroscopic and readily soluble in water. They are *strong* acids, the basicity depending on the number of sulphonic groups present. They are not hydrolysed when boiled with aqueous alkalis or acids (cf. the alkyl hydrogen sulphites, isomeric with the aliphatic sulphonic acids), but are decomposed when fused with alkalis, the aliphatic compounds yielding alcohols, and the aromatic, phenols or phenolic derivatives (cf. Exp 121)

$$2C_2H_5SO_2 \cdot OK + 2KOH = 2C_2H_5OH + K_2SO_3 + H_2O + SO_2$$
$$C_{10}H_7SO_2 \cdot ONa + NaOH = C_{10}H_7OH + Na_2SO_3.$$

They give rise to salts, esters, acid chlorides, amides, anilides, &c, in much the same way as the carboxylic acids. The acids, as a rule, have no definite melting-points, and hence to diagnose the different acids it is usual to convert the sodium salts into the sulphonic chlorides (cf. Exp. 37), and then into the sulphonamides (cf. Exp. 89), as these latter are easily crystallized and have definite melting-points.

D. Removal of the Sulphonic Acid Group

The sulphonic acid group $\cdot SO_2 \cdot OH$ can be removed from many, although by no means from all sulphonic acids by heating the compound with superheated steam.

Experiment 119.—Removal of the sulphonic acid group from a derivative of sulphanilic acid; Preparation of 2 : 6-

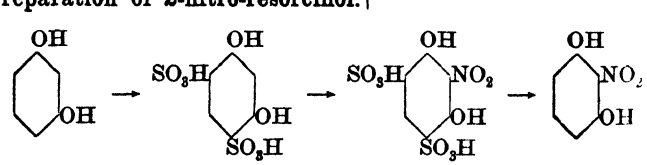
dibromaniline from 2 : 6-dibromo-1-amino-benzene-4-sulphonic acid.*

$$NH_2 \cdot C_6H_2Br_2 \cdot SO_3H + H_2O \longrightarrow NH_2 \cdot C_6H_3Br_2 + H_2SO_4.$$

A mixture of 90 grm. of concentrated sulphuric acid, 26 grm. of water, and 20 grm. of dry dibromo-sulphanilic acid (Exp. 42) is heated in a flask by means of an oil bath to 170°. The flask is fitted with a cork bored with three holes, for the steam inlet and outlet tubes and for the thermometer. It is not advisable to have the thermometer dipping directly into the acid, but to protect it by means of a glass tube closed at the lower end and passing through the cork. Superheated steam (p. 12) is blown through the solution, and the temperature rises gradually to 178°, but on no account must it rise above 180°. Part of the dibromaniline passes over with the steam, and is collected in the condenser and receiver. The greater part remains in the flask, and may be obtained by pouring the contents of the flask into cold water after the steam has passed through for one and a half hours. Yield, 83 per cent of the theoretical.

The dibromaniline crystallizes from ligroin in colourless needles, melting-point 83–84°.

Experiment 120.—Removal of the sulphonic acid groups from 2-nitro-1 : 3-dihydroxybenzene-4 : 6-disulphonic acid Preparation of 2-nitro-resorcinol.†



22 grm. of finely divided resorcinol (1 : 3 dihydroxy-benzene) are added gradually to 150 grm. of fuming sulphuric acid (sp. gr. 1·875). When all is dissolved, the solution is allowed to cool and the disulphonic acid separates in a crystalline form. To the semi-solid mass, which is cooled by means of running water, and agitated by means of a mechanical stirrer, a mixture of 12·6 grm. of nitric acid (sp. gr. 1·52) and 40 grm. of fuming sulphuric acid (sp. gr. 1·875) is added gradually, care being taken that the temperature is kept

* *Heinichen*, A. 1889, **253**, 275.
† *Kaufmann* and *de Pay*, B. 1904, **37**, 725.

between 10° and 15°. The mixture becomes yellow coloured, and ultimately a clear solution is obtained. After some time, 60 c.cm. of water are added for each 100 grm. of the mixture, the whole is then heated and distilled with superheated steam (as in Exp 119). 2-nitro-resorcinol passes over with the steam, and, after crystallization from dilute alcohol, is obtained in the form of orange-red needles, melting-point 85°.

E. Estimation of the Number of Sulphonic Acid Groups in the Molecule

If the molecular weight of the substance has been determined, and no carboxylic groups are present, the number of sulphonic acid groups can be determined in most cases by direct titration with standard alkali, and then calculating the number of grams of $\cdot SO_3H$ in one gram molecule of the acid.

XVII. PHENOLS AND PHENOLIC ETHERS
(S B 405–419)

The phenols are the aromatic hydroxy-derivatives in which the hydroxy-group is directly attached to the benzene nucleus, *e.g.* $C_6H_5 \cdot OH$, $CH_3 \cdot C_6H_4 \cdot OH$, &c. Isomeric with certain phenols are the aromatic alcohols (S. B. 419–420), in which the hydroxy-groups are attached to carbon atoms of side chains (cf. Exp. 27).

The phenols are classified as mono-, di-, tri-hydric, &c, according to the number of hydroxy-groups present in the molecule.

A. Modes of Formation

Method I.—By fusion of sulphonic acids with alkali hydroxides, e.g.—*

$$C_6H_5 \cdot SO_2 \cdot ONa + NaOH \longrightarrow C_6H_5 \cdot OH + Na_2SO_3$$
$$C_6H_5 \cdot OH + NaOH \longrightarrow C_6H_5 \cdot ONa + H_2O.$$

The product formed in each case is the sodium derivative of a phenol, from which the phenol is liberated by the addition of

* *Kekulé, Wurtz.*

a mineral acid. The acid also decomposes the sulphite, producing considerable amounts of sulphur dioxide, so that the decomposition should be carried out in a well-ventilated fume chamber.

Substances which contain two or more sulphonic acid radicals yield polyhydric phenols when fused with potash, and halogen derivatives of mono-sulphonic acids also yield dihydric phenols when fused in the same manner. It does not necessarily follow that the hydroxy-groups occupy the same relative positions in the molecule as the original sulphonic acid or halogen radicals, since, at the high temperature at which the reaction occurs, *molecular rearrangement* can readily take place. Thus all three chlorobenzene-sulphonic acids yield *m*-dihydroxy-benzene (resorcinol) when fused with potash. Constitutional formulæ based on the products of fusion with potash are always liable to be incorrect, on account of the fact that molecular rearrangement often occurs at the high temperatures employed (cf S. B. 162).

Experiment 121.—Preparation of β-naphthol, $C_{10}H_7 \cdot OH$, from sodium naphthalene-β-sulphonate *

90 grm. of fairly pure sodium hydroxide powder is treated with about 3 c.cm of water in a large nickel or copper crucible (about 8–10 cm. diameter and 12–15 cm. deep). The crucible is heated carefully and the contents stirred, the stirrer consisting of an iron tube closed at one end and fixed into a cork at the other, so that when the iron tube gets hot the cork protects the hand. A little mercury is poured into the tube and a thermometer immersed in it; the temperature of the fused mass can by this means be determined with accuracy. It is advisable to cover the hand with a glove or duster during stirring, for molten caustic soda is inclined to sputter.

When the temperature of the fused caustic soda reaches 280°, 30 grm. of sodium naphthalene-β-sulphonate (Exp. 113) are added gradually in portions of 5 grm. After each addition the temperature is allowed to reach 280° before the next portion is added. When all has been introduced the temperature is raised; this is accompanied by much frothing and evolution of steam, and at 310° the reaction begins. This temperature is maintained for about ten minutes, and the mixture becomes completely liquid and separates into two layers. The molten mass is then poured on to a copper or iron tray and allowed

* *Schaffer*, A. 1869, 152, 280.

to solidify. The solid is broken up, dissolved in 500 c.cm. of water, and treated gradually with concentrated hydrochloric acid until the liquid becomes acid to litmus, in order to transform the sodium β-naphtholate into the free phenol. When cold, the precipitated β-naphthol is filtered off, washed with a little water, and recrystallized from hot water. It forms colourless plates, melting-point 122°, boiling-point 286°. Yield about 15 grm., *i.e* 80 per cent of theory.

Special Test.—A few drops of ferric chloride impart a greenish colour to a solution of β-naphthol.

Method II.—From primary amines by application of the diazo-reaction, e g. preparation of phenol from aniline, Exp 157.

Special tests for phenol, C_6H_5OH.

(i) A few drops of ferric chloride impart a violet colour to its neutral solution.

(ii) Bromine water precipitates 2 : 4 : 6-tribromophenol from even very dilute solutions.* (Cf. p. 112.)

Method III.—Certain *o- and p-dihydric phenols* can be prepared by *reducing the corresponding quinones* (Chap. XXIII).

Experiment 122.—Preparation of quinol (hydroquinone), $C_6H_4(OH)_2$ (1:4), from quinone.†

$$C_6H_4\begin{matrix}O\ (1)\\ O\ (4)\end{matrix} \longrightarrow C_6H_4\begin{matrix}OH\ (1)\\ OH\ (4)\end{matrix}.$$

An aqueous solution of quinone (Exp. 193) is saturated with sulphur dioxide gas and the solution allowed to stand for some hours Should the odour of the gas disappear the saturation is repeated. The resulting solution is extracted with ether, the ether distilled off, and the residue recrystallized from a very little water containing sulphur dioxide, with addition of animal charcoal if necessary. Yield almost theoretical.

It forms colourless plates, melting-point 169°, which decompose when quickly heated, and is soluble in water, alcohol, and ether.

Special Test.—Ferric chloride oxidizes quinol to quinone (detected by its odour).

Method IV.—Elimination of carbon dioxide from phenolic carboxylic acids.

$$(OH)_3 \cdot C_6H_2 \cdot CO_2H \longrightarrow C_6H_3(OH)_3 + CO_2.$$

* For estimation of phenols by standard bromine solution see *Wilkie*, J. S. C. I. 1911, **30**, 398. † *Nietzki*, B. 1886, **19**, 1467.

Experiment 123.—Preparation of pyrogallol, $C_6H_3(OH)_3$ (1:2:3), from gallic acid.*

A mixture of one part of gallic acid with two parts of powdered pumice is heated in a retort on a sand bath. Through the tubulus of the retort a tube is fixed, through which a current of dry carbon dioxide (from a Kipp's generator) is passed in. The neck of the retort becomes filled with long, glistening needles; if the temperature rises above the melting-point of pyrogallol, the crystals melt and the substance solidifies again in the receiver to a crust Yield, about 40 per cent of theory. Melting-point, 133°. It is soluble in water, alcohol, and ether.

B. Characteristic Reactions of the Phenols

The solubility of the phenols in water tends to increase, and the solubility in ether to diminish with increase in the number of hydroxy-groups present in the molecule The readiness with which they are oxidized in alkaline solution also increases with the number of hydroxy-groups

Colour Reactions of the Phenols.—(i) **With Ferric Chloride.**—Aqueous solutions of phenols yield colorations varying from red to violet with ferric chloride solution. The colorations produced by ferric chloride are more or less characteristic. Monohydric phenols, with the exception of thymol and nitrophenols, give violet or blue colorations, ortho-dihydric phenols green, meta- violet, and trihydric green, violet, or even black. Para-dihydric phenols are oxidized to the corresponding quinones.

(ii) **Liebermann's Reaction.**—Most phenols, when warmed with concentrated sulphuric acid and a little potassium nitrite (or a nitrosamine, cf. p. 189), and then diluted with water and made alkaline, yield intense blue, purple, or green colorations.

Experiment 124.—Warm a crystal of phenol with 1 c.cm. of concentrated sulphuric acid and a drop of potassium nitrite solution. Pour into water and add potassium hydroxide solution until alkaline A blue coloration is produced.

(iii) **Formation of Dyes.**—

(*a*) Alkaline solutions of phenols condense with dia

* *Liebig*, A. 1857, 101, 48.

zonium compounds yielding azo-dyes (Exp. 165.)

(*b*) With phthalic anhydride most phenols yield phthaleins (Exp. 259), but *m*-dihydric phenols yield fluoresceins (Exp. 260). The last reaction is used as a test for *m*-dihydric phenols such as resorcinol.

The phenols are more distinctly acidic than the alcohols; they dissolve, for example, in solutions of alkali hydroxides yielding *phenoxides* or *phenolates*.

$$C_6H_5OH \longrightarrow C_6H_5ONa.$$

The phenoxides derived from simple phenols are decomposed by very weak acids, *e.g.* by passing a current of carbon dioxide (cf. Acids). The entrance of acidic groups (*e.g.* nitro-groups) into the molecule strengthens the acidic properties, *e.g.* the salts of the nitro-phenols (Exp. 102) are not decomposed by carbon dioxide, while picric acid (sym-trinitrophenol, Exp. 103) is a strong acid. A mixture of a phenol and a carboxylic acid may frequently be separated by treatment with sodium carbonate solution, the acid dissolving to form its sodium salt while the phenol is not affected; or the mixture may be dissolved in sodium hydroxide solution and the solution saturated with carbon dioxide, in which case the free phenol is precipitated. The method only applies in cases where the phenol is sparingly soluble in water or where it can be extracted with ether; thus, it is of little use for the separation of the polyhydric phenols from acids.

Experiment 125.—Separate a mixture of benzoic acid and β-naphthol by the above method.

C. Phenolic Ethers and Esters

The hydrogen atoms of the hydroxy-groups of phenols can be replaced by alkyl groups when *phenolic ethers* are obtained, or by acyl groups when *phenolic esters* are formed. For the latter, see Acetyl and Benzoyl Derivatives, Chap. XIX.

Phenolic Ethers. Cf. Ethers, Chap. X, D.

The commonest type of phenolic ether is that in which the hydrogen atoms of the hydroxy-groups are replaced by alphyl-groups, *e.g.* phenetole, $C_6H_5 \cdot OC_2H_5$; resorcinol dimethyl ether,

m-$C_6H_4(OCH_3)_2$; but diaryl ethers, *e.g.* $(C_6H_5)_2O$, are also known.

Formation of Alkyl Ethers.

Method I.—By the action of alkyl halides on sodium phenoxides.

$$C_6H_5ONa + C_2H_5I \longrightarrow C_6H_5OC_2H_5 + NaI.$$

Experiment 126.—Preparation of phenetole, $C_6H_5 \cdot O \cdot C_2H_5$, from phenol.

2·3 grm of sodium in fine shavings are dissolved in 30 c.cm. of absolute alcohol contained in a flask fitted with a reflux condenser. After the sodium has dissolved and the solution cooled, the theoretical amount of phenol and slight excess of ethyl iodide ($1\frac{1}{4}$ molecule) are added, and the mixture heated on a water bath until the solution is no longer alkaline (about two hours) The alcohol and excess of ethyl iodide are then distilled off on the water bath and the residue treated with water. A layer of phenetole separates on the surface of the aqueous solution. This is extracted with ether, the ethereal solution shaken with dilute sodium hydroxide solution, and then washed with water, dried with calcium chloride, and distilled. The colourless liquid distilling between 169° and 172° is collected separately. Boiling-point, 172°; $D^{0°}_{4°}$, 0 9822.

Method II.—By the action of alkyl sulphates on the metallic phenoxides. As methyl sulphate is a cheap reagent, methyl ethers are invariably prepared by this method.

Experiment 127.—Preparation of pyrogallol trimethyl ether (1 : 2 : 3 - trimethoxy - benzene), $C_6H_3(OCH_3)_3$, from pyrogallol.*

Caution.—Methyl sulphate is exceedingly poisonous.

31 c.cm. of methyl sulphate, $(CH_3)_2SO_4$, are added gradually to a well-shaken solution of 12 grm. of pyrogallol in 35 c.cm. of 40 per cent sodium hydroxide solution. The mixture becomes warm and a dark precipitate is deposited. This is filtered, washed with water, and dissolved in ether in order to remove insoluble impurities. The ether is distilled off from the solution, and the residue crystallized from dilute alcohol, when it is obtained as colourless crystals, melting-point 47°, boiling-point 235°. Yield, 12 grm., *i.e.* 75 per cent of theory.

D. Removal of Hydroxyl Radicals from Phenols

This is usually accomplished by distilling the phenol with an excess of zinc dust, when the corresponding hydrocar-

* *Ullmann*, A. 1903, 327, 116.

derivative is obtained in the distillate.* Phenol treated in this manner yields benzene, the naphthols yield naphthalene, and the hydroxy-ketone, alizarin, yields anthracene (cf. Exp 222*a*).

E Estimation of Hydroxy-groups in Phenols and Alcohols

Method I.—By preparing the acetyl derivative (Chap. XIX), and determining the amount of acetic acid formed when the acetyl derivative is hydrolysed (Exp 153).

Method II.—By treating a known weight of the hydroxylic compound with an excess of methyl-magnesium-iodide dissolved in amyl ether or phenetole, and measuring the amount of methane evolved.†

$$R{\cdot}OH + CH_3{\cdot}Mg{\cdot}I \rightarrow R{\cdot}OMgI + CH_4$$
$$R''\begin{matrix}OH\\OH\end{matrix} + 2CH_3{\cdot}MgI \rightarrow R'':(OMgI)_2 + 2CH_4.$$

Experiment 128.—Determination of the percentage of hydroxy-group in a given compound

(*a*) **Preparation of amyl ether solution of methyl-magnesium-iodide** (Cf Chap. XXIX, A)

Commercial amyl ether is boiled for some time with metallic sodium, then removed and left over phosphorus pentoxide, and finally distilled (boiling-point, 172–173°). A crystal of iodine is added to a mixture of 100 grm. of the dry amyl ether, 6 grm of dry magnesium, and 35·5 grm of methyl iodide in a round-bottomed flask. If the reaction does not begin spontaneously, the mixture is warmed gently and finally heated in a rapidly-boiling water bath for one to two hours, using a reflux condenser and protecting from atmospheric moisture. Any excess of methyl iodide is then distilled off on the water bath and the clear solution decanted into a well-stoppered bottle and kept in a desiccator. *N B*.—The solution is gradually acted upon by moisture, carbon dioxide, and oxygen, and should be protected from these as far as possible.

(*b*) **Estimation of hydroxy-groups.**—0·1 to 0·25 grm. of the perfectly dry substance is introduced into a stout glass flask or bottle of 200 c.cm. capacity, fitted with a rubber bung

* *Baeyer*, A. 1866, **140**, 295.

† *Hibbert* and *Sudborough*, J. C. S. 1904, **85**, 933; *Zerewitinoff*, B. 1907, **40**, 2023.

which carries a delivery tube, which can be connected by stout rubber tubing with the measuring tube of a Hempel gas burette filled with dry mercury * (fig. 80). Dry amyl ether (10–20 c.cm.) is added, or if the hydroxy-compound is insoluble in ether, *dry* pyridine† may be used, and the substance dissolved by heating gently. About 15 c.cm. of the amyl ether solution of methyl-magnesium-iodide are placed in a *separate* tube which is introduced into the flask or bottle. The latter is then fixed in a constant-temperature bath, the rubber bung introduced and connected with the measuring tube of the gas burette, which contains dry mercury. After the bottle has attained the temperature of the bath, the temperature and position of the mercury in the measuring tube is noted. The two solutions are then mixed by tilting the bottle, and the mixture is thoroughly shaken. For this purpose it may be withdrawn from the bath. When no more gas is evolved the bottle is replaced in the bath, and when the volume of gas in the burette is constant (after five to seven minutes) the volume, temperature, and pressure are observed.‡ From these data the weight of methane evolved can be calculated, and since 16 grm. of methane are equivalent to 17 grm of hydroxyl, the weight and percentage of hydroxyl in the compound can be determined.

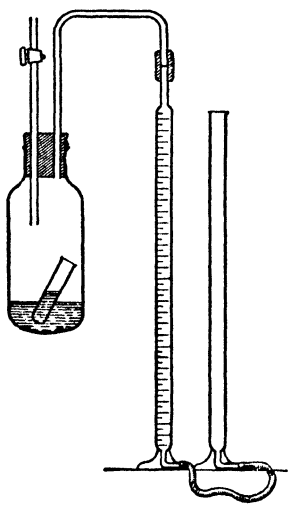


Fig 80

If the molecular weight of the substance is known, the number of hydroxy-groups present in the molecule can be readily calculated.

* It is an advantage to have a glass T-piece connected by rubber to the two glass tubes of the Hempel burette, and to attach a glass stopcock to the remaining end of this T, so that mercury can be run out of the apparatus through the cock.

† Pyridine is dehydrated by heating with barium oxide, distilling, and preserving over a further quantity of the oxide.

‡ If pyridine be used as solvent, the volume falls to a minimum, but then tends to increase. In this case the minimum reading must be taken.

F. Hydrolysis of Methoxy- and Ethoxy-Derivatives

The alkyl-oxy-groups may be removed from a compound by—

Method I.—Heating the substance with fairly concentrated hydriodic acid (cf. Estimation of Methoxy-groups, Chap XVII, G).

Method II.—Heating the substance with anhydrous aluminium chloride.*

Experiment 129 — Preparation of catechol, o-$C_6H_4(OH)_2$, from guaiacol, $OH \cdot C_6H_4 \cdot OCH_3$.

12 grm of finely powdered and freshly prepared aluminium chloride (Chap XXXIX) are added gradually to 15 grm. of guaiacol in an Erlenmeyer flask, surrounded by ice. The mixture is well shaken during the addition, and should be well cooled, so that the reaction does not begin until after the whole of the chloride has been added. It is then removed from the ice, again well shaken, and then heated for two hours at 210–220°, using a reflux air condenser. When cold, the solid mass is removed, broken up, and added to dilute hydrochloric acid and warmed. The unaltered guaiacol is removed by filtration, the filtrate saturated with common salt, and extracted three times with ether Yield, 11–12 grm. of crude catechol, *i.e.* 70 per cent of theory. It may be purified by distillation or by crystallization from toluene, and then forms colourless crystals, melting-point, 104°; boiling-point, 245°.

G. Estimation of Methoxy-Groups

This is generally accomplished by Zeisel's method.† The ether is heated with hydriodic acid of constant boiling-point, and the methyl iodide thus formed is led into an alcoholic solution of silver nitrate, and the precipitated silver iodide estimated in the usual manner.

$$X \cdot OCH_3 + HI \longrightarrow X \cdot OH + CH_3I$$
$$CH_3I + AgNO_3 + H_2O \longrightarrow AgI + CH_3OH + HNO_3.$$

The method has been simplified by Hewitt and Moore,‡ and further by Perkin,¶ whose apparatus is shown in fig. 81.

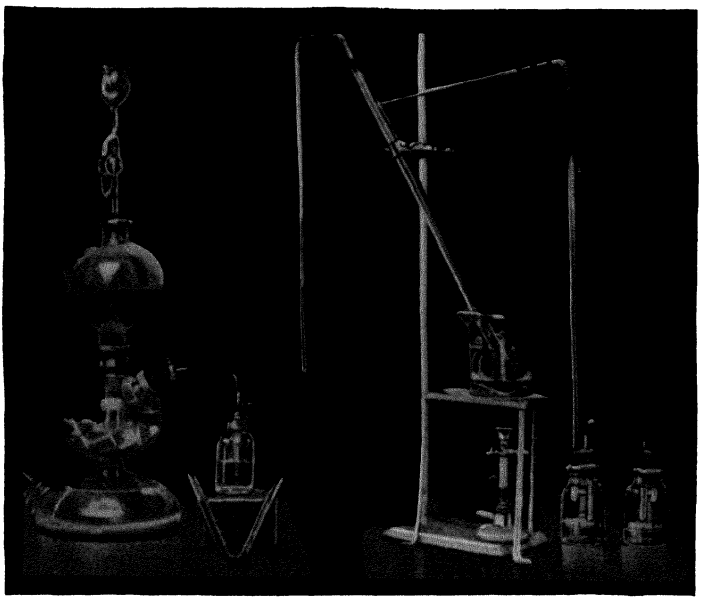
* *Hartmann* and *Gattermann*, B. 1892, **25**, 3532.
† *Zeisel*, M. 1885, **6**, 989; 1886, **7**, 406.
‡ J. C. S., 1902, **81**, 318. ¶ J. C. S., 1903, **83**, 1367.

Experiment 130.—Determination of the percentage of methoxyl in a compound by Perkin's method.

A distilling flask with a very long neck (20–25 cm.) is fitted with a tube leading into the bulb, through which a stream of carbon dioxide is passed from a Kipp's generator. The side tube of the distilling flask is attached directly to a pair of absorption flasks arranged as in fig. 81. (Note carefully the position of the siphon tube connecting the two flasks.)

15 c.cm. of concentrated hydriodic acid (previously purified by distilling over a little red phosphorus, the portion of constant boiling-point, 126° at 760 mm. pressure, is taken) are placed in the distilling flask, and 0·3–0·35 grm. of the substance weighed in a small tube added. The stopper carrying the carbon dioxide leading tube is then fixed into the neck of the flask, and the absorption flasks charged, one with 20 c.cm., the other with 15 c.cm. of alcoholic silver nitrate solution. The distilling flask is then fixed in a bath of glycerol, which is heated to 130–140°, while a constant current of carbon dioxide is passed through at the rate of three or four bubbles in two seconds. After a time the solution in the first flask becomes turbid, but the liquid in the second flask is scarcely affected. The temperature of the glycerol bath is then raised gradually until it causes the hydriodic acid to boil gently, but not so vigorously as to cause distillation of the acid into the side tube of the flask. The operation is often completed in three-quarters of an hour; generally the heating is continued for an hour. The flasks are then disconnected, and a V tube containing a few c.cm. of silver nitrate solution substituted. The heating is continued for about twenty minutes, and if no appreciable amount of silver halide forms during that time the operation may be considered complete; otherwise the latter operation is repeated. The precipitate of silver iodide is treated with water, the alcohol removed by evaporation, and after treatment with dilute nitric acid the silver iodide is collected and weighed in the usual manner.

Ethoxy-determinations may be carried out with the same apparatus and in a similar manner, but the results obtained are generally somewhat low; probably a small amount of the ethyl iodide is reduced by the hydriodic acid.



H 960

To face p 178

Fig. 81.

XVIII. AMINES AND QUATERNARY AMMONIUM COMPOUNDS. (S. B. 104–111; 365–380)

The amines are compounds derived from ammonia by the replacement of the hydrogen atoms of the latter by alkyl radicals Like ammonia, they possess distinctly basic properties, and combine with acids yielding crystalline salts. They are classified as *primary*, *secondary*, *tertiary*, or *quaternary* bases, according as they contain one, two, three, or four monovalent alkyl radicals attached to the nitrogen atom. The first three groups are derived from ammonia and the last from the ammonium hydroxide Characteristic of the primary amines is the *amino*-group, $\cdot NH_2$, *e g.* methyl-amine, $CH_3 \cdot NH_2$; of secondary amines the *imino*-group, $:NH$, *e g.* methyl-aniline, $C_6H_5(CH_3)NH$. Tertiary amines have the N radical attached to three alkyl groups, *e.g.* dimethylaniline, $C_6H_5 \cdot N(CH_3)_2$; the quaternary compounds contain four alkyl groups, *e.g.* tetra-methyl-ammonium iodide, $N(CH_3)_4I$.

A. Primary Amines: Modes of Formation

Method I.—A general method applicable for both alphyl- and aryl-amines is from acid amides or imides (Chap XIV, B and C) by Hofmann's reaction.* An acid amide is converted by bromine, in the presence of alkali, into a brom-amide.

$$R \cdot C(=O)NH_2 + Br_2 = R \cdot C(=O)NH \cdot Br + HBr.$$

The bromamide by further action of alkali loses HBr, and probably yields an iso-cyanate (alkyl carbimide), which is then hydrolysed by an excess of alkali to an amine and a carbonate.

$$R \cdot CO \cdot NHBr \longrightarrow R \cdot N{:}C{:}O + HBr$$
$$R \cdot N{:}C{:}O + H_2O \longrightarrow R \cdot NH_2 + CO_2.$$

The amine can be obtained by distilling the product, or by separation as a salt

Experiment 131.—Preparation of methylamine hydrochloride, $CH_3 \cdot NH_2, HCl$, from acetamide.

20 grm. of dry acetamide (1 mol.) (Exp. 87) are mixed with 54 grm. of bromine (1 mol.) in a 500 c.cm. flask, and a solution

* *Hofmann*, B. 1882, **15**, 407, 752; 1884, **17**, 1407, 1920; 1885, **18**, 2734.

of 20 grm. of potassium hydroxide (1 mol.) in 200 c.cm. of water is added gradually, the flask being cooled during the addition by immersion in cold water. The reddish-brown liquid changes gradually to a yellow colour. The mixture, which now contains acetbromamide, is dropped slowly from a tap funnel into a concentrated solution of potassium hydroxide (60 grm. in 100 c.cm.), contained in a large distilling flask (500 c.cm. capacity). During this process heat is generated, and the temperature of the mixture must on no account be allowed to rise above 75°. The liquid is then kept at a temperature of 65–70°, until the yellow colour disappears (about half an hour). The side tube of the distilling flask is attached to a condenser which terminates in an adapter fitted into a gas absorption tube. The liquid is distilled over a wire gauze, and the volatile ammonia and methylamine absorbed in 100 c.cm. of dilute hydrochloric acid. When the drops of distillate are no longer alkaline, the hydrochloride solution is evaporated to dryness on a water bath, and the colourless crystalline residue of methylamine hydrochloride and ammonium chloride extracted several times with hot *absolute* alcohol, in which ammonium chloride is practically insoluble. The methylamine hydrochloride crystallizes from the alcoholic solution; the crystals are removed, washed with a little alcohol, and dried in a desiccator.

It consists of colourless deliquescent plates, melting-point 200°, and sublimes above 220°, with slight decomposition.

Acid imides when treated in a similar manner yield amino-acids.

Experiment 132. — Preparation of anthranilic acid, $C_6H_4\langle^{CO_2H\ (1)}_{NH_2\ (2)}$, from phthalimide.*

$$C_6H_4\langle^{CO}_{CO}\rangle NH \rightarrow C_6H_4\langle^{CO_2H}_{NH_2}$$

28 grm. of potassium hydroxide (5 mol.) are dissolved in 280 grm. of water, and 16 grm. of bromine (1 mol.) added gradually while the solution is cooled and well stirred. (The mixture contains 1 mol. of potassium hypobromite and 3 mol. of potassium hydroxide.) To the well-cooled solution 15 grm. of phthalimide (1 mol.) (Exp. 94) are added gradually, care being taken that the mixture is cooled and well shaken. Then 12 grm. of potassium hydroxide (2 mol.) in 120 c.cm. of water

* *Hoogewerff* and *van Dorp*, Rec. 1891, **10**, 6.

are added, and the mixture warmed to 80°. The solution is acidified with acetic acid and excess of a strong solution of cupric acetate (20 grm.) added. After shaking, it is allowed to stand for some time, when cupric anthranilate separates as a pale-green precipitate. This is filtered off on a Buchner funnel, washed with cold water, and then suspended in a small amount of warm water and decomposed by completely saturating with sulphuretted hydrogen. (Allow to stand for a short time after passing the gas to ensure the thorough decomposition of the salt.) The cupric sulphide is filtered off, washed with a little water, and the aqueous filtrate and washings evaporated to a small bulk on a water bath and allowed to stand. Anthranilic acid separates as colourless crystals, melting-point 145°, it is soluble in water, and the aqueous solution possesses a sweet taste. Yield, 85 per cent. of theory.

The substance possesses both acidic and basic properties.

Method II.—By the reduction of nitro-compounds (Chap. XV), usually in acid solution. This method also is applicable for the preparation of both alphyl and arylamines, but is generally used in the aromatic series only.

For the reduction of each nitro-group six atoms of nascent hydrogen are necessary, and the reaction may be expressed as follows:—

$$X \cdot NO_2 + 6H = X \cdot NH_2 + 2H_2O.$$

The amine produced combines with excess of acid to form a salt, *e.g.* $X \cdot NH_2 \cdot HCl$, from which the amine is obtained by the addition of an excess of caustic alkali.

Almost any combination of metal and acid which gives rise to nascent hydrogen may be used, but in the laboratory a mixture of tin and hydrochloric acid is usually employed. In this case the metal is first converted into stannous, and then into stannic chloride. The complete reaction may be represented thus:—

$$2X \cdot NO_2 + 3Sn + 14\,HCl = 2(X \cdot NH_2HCl) + 3SnCl_4 + 4H_2O.$$

The hydrochloride of the amine combines with the stannic chloride, forming a *stannichloride*, $(RNH_2,HCl)_2SnCl_4$.

Various methods are adopted in order to obtain the free amine from the acid mixture. If it is volatile with steam, the reaction product is treated with excess of an alkali hydroxide, which, in addition to liberating the free amine, redissolves the stannic hydroxide at first precipitated with the formation of

stannates, and the amine is then distilled over with steam Solid amines are obtained directly by filtering off from the alkaline fluid. Direct extraction of the alkaline tin solution with ether is not advisable, owing to the formation of difficultly separable emulsions of the alkaline solution with ether. For the separation of non-volatile amines it is therefore necessary to precipitate the tin from the diluted acid solution by means of hydrogen sulphide. The stannous or stannic sulphide is separated by filtration, the amine hydrochloride subsequently decomposed with alkali, and the free amine extracted with ether.

Experiment 133 — Reduction of nitrobenzene to aniline (phenylamine), $C_6H_5 \cdot NH_2$

40 grm. of nitrobenzene (Exp. 99) and 75 grm. of granulated tin are placed in a round-bottomed flask of 2 litres capacity fitted with a long air-condenser, and 200 c cm of concentrated hydrochloric acid (sp. gr. 1 16) are added *gradually* through the condenser tube in quantities of about 10 c cm. at a time The mixture is shaken well after each addition; it soon becomes warm, but active ebullition must be prevented by cooling the flask when necessary under the tap, otherwise some nitrobenzene and aniline are lost. Towards the end the reaction moderates, and the remainder of the acid may then be added more quickly. To ensure complete reduction, the flask is heated on a water bath until no odour of nitrobenzene can be detected, a little more tin being added if necessary. To obtain the amine from the stannichloride, $(C_6H_5 \cdot NH_2, HCl)_2SnCl_4$, the contents of the flask are diluted with water (100 c.cm.), and then made strongly alkaline by the gradual addition of sodium hydroxide solution (150 grm. in 200 c.cm. of water). The addition is carried out slowly so as to avoid active ebullition and consequent loss of amine. The alkali is added until the stannic hydroxide at first precipitated is completely redissolved, and the mixture shows a strongly alkaline reaction. The aniline separates out during this process as a dark oil, and is removed by distillation with steam (p. 11, fig. 10), the operation being continued until the liquid which passes over is no longer milky in appearance but perfectly clear. The distillate, which consists of two layers—an oily layer of aniline, together with an aqueous solution of the base—is saturated with common salt (about 25–30 grm. for each 100 c.cm. of distillate) and extracted with ether. The ethereal solution is separated and

dehydrated by allowing to stand for some time with solid potassium hydroxide. The clear liquid is decanted into a distilling flask, the potash and the vessel being washed with a little ether, the ether removed, and the aniline distilled, an air-condenser being used (fig. 79). Yield, 32–35 grm., *i.e.* about 90 per cent of theory.

It is a colourless, oily, strongly refracting liquid, which becomes yellow on standing, and possesses a peculiar odour. Boiling-point, 182°; D^{15}, 1·0265. It is only sparingly soluble in water

Special Tests for Aniline (for General Tests, cf. p 188, 189).

(i) Dilute solutions of aniline or its salts give a violet coloration with a solution of bleaching powder.

(ii) Bromine water gives a precipitate of tribromaniline with even very dilute solutions of aniline or its salts (cf. Exp. 41).

(iii) The addition of potassium dichromate solution to a few drops of aniline dissolved in dilute sulphuric acid produces a precipitate—green, blue, or black (aniline black), according to the concentration.

Poly-nitro-compounds are completely reduced by the above process to the corresponding poly-amino-compounds, *e.g.* the complete reduction of *m*-dinitrobenzene yields *m*-phenylenediamine.

$$C_6H_4(NO_2)_2(1:3) \longrightarrow C_6H_4(NH_2)_2(1:3).$$

Experiment 134.—Preparation of *m*-phenylenediamine.

25 grm of *m*-dinitrobenzene (Exp. 100) are treated with 100 grm of granulated tin, and 200 c.cm. of concentrated hydrochloric acid, as described in the last experiment. The reduction is completed by heating the product on the water bath for an hour. On cooling, crystals of the *stannochloride*, $C_6H_4(NH_2)_2$, $2HCl$, $2SnCl_2$, separate as slender needles, these are removed with the aid of the pump and dissolved in warm water.

The solution is diluted with water, and a current of sulphuretted hydrogen led through until the tin is completely precipitated. The sulphide is removed, the filtrate made alkaline by the addition of sodium hydroxide solution, and extracted several times with ether. After drying with solid potassium hydroxide the ethereal solution is fractionated (use an air-condenser after removal of the ether), the portion boiling at 280–284° being collected separately. This solidifies on standing—generally a long time is required—to rhombic crystals. Melting-point, 63°; boiling-point, 282–284°.

If it is desired to reduce but one or two out of several nitro-

groups, special methods are necessary. An alcoholic solution of ammonium sulphide is the reagent generally used, as this substance reduces the nitro-groups in stages, and the reaction can be stopped at the desired point.

Experiment 135. — Preparation of *m*-nitraniline, $C_6H_4{<}^{NH_2\ (1)}_{NO_2\ (3)}$, from *m*-dinitrobenzene.*

$$C_6H_4{<}^{NO_2}_{NO_2} + 3H_2S = C_6H_4{<}^{NH_2}_{NO_2} + 2H_2O + 3S.$$

20 grm. of *m*-dinitrobenzene (Exp. 100) are dissolved in 60 grm. of 90 per cent alcohol, and 10 grm. of strong ammonia solution (D, 0·880) added. The flask and its contents are weighed; then hydrogen sulphide is led in, until the solution is saturated. The flask is allowed to stand in a warm place until the smell of sulphuretted hydrogen has disappeared; it is then cooled and again saturated with hydrogen sulphide, the process being repeated until the theoretical increase of weight of the contents of the flask (12 grm.) is attained.

The *m*-nitraniline is precipitated by the addition of water to the alcoholic solution. It is purified from any unchanged dinitrobenzene by solution in dilute hydrochloric acid, and precipitation with ammonia. Yield, 70–80 per cent of theory. It crystallizes from hot water in long straw-coloured needles, melting-point 114°; dissolves in most organic solvents, and forms salts with mineral acids.

B Secondary Amines

1. Conversion of a Primary Arylamine into a Secondary Alphyl-arylamine.

Experiment 136. — Preparation of methylaniline, $C_6H_5NH\cdot CH_3$, from aniline.†

$$C_6H_5N{<}^{H}_{CO\cdot CH_3} \longrightarrow C_6H_5N{<}^{Na}_{CO\cdot CH_3}$$

$$C_6H_5N{<}^{Na}_{CO\cdot CH_3} + I\cdot CH_3 \longrightarrow C_6H_5N{<}^{CH_3}_{CO\cdot CH_3} + NaI$$

$$C_6H_5\cdot N{<}^{CH_3}_{CO\cdot CH_3} + KOH \longrightarrow C_6H_5N{<}^{CH_3}_{H} + CH_3CO_2K.$$

* *Beilstein* and *Kurbatow*, A. 1875, **176**, 44. For the mechanism of the reaction cf. *Cohen* and *M'Candlish*, J. C. S. 1905, **87**, 1257.

† *Hepp*, B. 1877, **10**, 328.

20 grm. of acetanilide (for preparation from aniline, see Exp. 144), 5 grm. of sodium wire, and 100 grm. of pure xylene (dried over sodium) are heated in a flask fitted with a reflux condenser for 2–3 hours in an oil bath at 130°. After cooling, rather more than the theoretical weight of methyl iodide is added, and the mixture digested for a short time, until no more methyl iodide condenses in the condenser tube. The xylene is then distilled off.

The methyl acetanilide is decomposed by boiling with concentrated alcoholic potash solution for about 24 hours in a reflux apparatus. The alcohol is distilled off, and the residue neutralized by addition of hydrochloric acid. The residual xylene is then distilled off with steam, the solution made alkaline, and the methylaniline distilled over with steam. It is taken up with ether, dried with fused sodium sulphate or potassium hydroxide, and fractionated. It is a yellowish oil, boiling-point 192° $D_{4^\circ}^{15^\circ}$, 0·976. Yield almost theoretical.

Experiment 136*a* — Prepare methyl-phenyl-nitrosamine, $C_6H_5 \cdot NMe \cdot NO$, by treating an acid solution of methyl aniline with nitrous acid. The product is a yellow oil which solidifies in cold. Melting-point 12–15°.

Experiment 137 —Preparation of ethyl-α-naphthylamine.

$$C_{10}H_7NH_2 + C_2H_5I \longrightarrow C_{10}H_7 \cdot NH \cdot C_2H_5 + HI.$$

A mixture of 20 grm. of α-naphthylamine, 33 grm. of ethyl iodide, and excess of sodium carbonate (40 grm.) in 500 c.cm. of water is heated in a reflux apparatus on a water bath for 3 hours. The ethyl-α-naphthylamine is extracted with ether, dried with potassium hydroxide, the ether and excess of ethyl iodide removed, and the residue fractionated, preferably under diminished pressure. Yield almost theoretical. It is a pale-yellow oil, boiling-point 301–302° at 760 mm., 200° at 75 mm.

2. **Conversion of a Primary Arylamine into a Secondary Arylamine.**

Experiment 138.—Preparation of diphenylamine, $(C_6H_5)_2NH$, from aniline.*

$$C_6H_5 \cdot NH \cdot CO \cdot CH_3 + C_6H_5Br \longrightarrow (C_6H_5)_2N \cdot CO \cdot CH_3 + HBr$$
$$(C_6H_5)_2N \cdot CO \cdot CH_3 + H_2O \longrightarrow (C_6H_5)_2NH + CH_3 \cdot CO_2H.$$

10 grm. of acetanilide (Exp. 144), 5 grm. of dry potassium carbonate, 20 grm. of phenyl bromide, and a little cuprous

* *Goldberg* and *Sissoeff*, B. 1907, **40**, 4543.

iodide, in nitrobenzene solution, are boiled for 15 hours in a reflux apparatus. The product, a dark-brown liquid, is distilled with steam until no more nitrobenzene passes over. The residue in the distillation flask, consisting of the acetyl derivative of diphenylamine, is a thick brown oil. It is taken up with ether, the solution filtered, dried with calcium chloride, and the ether removed. The residue is crystallized from alcohol, and is obtained as yellow plates, melting-point 102°

The crystals are dissolved in 30 c cm of alcohol, and decomposed by boiling with 30 c.cm of concentrated hydrochloric acid for 2–3 hours The product is distilled with steam, a yellow oil passing over which solidifies in the condenser. It crystallizes from alcohol in yellow crystalline plates, melting-point 54°, boiling-point 310°. Yield, 7·5 grm., *i.e.* 60 per cent of theory.

C. Tertiary Amines

Conversion of an Arylamine into a Tertiary Alphylarylamine.

Primary arylamines which contain an ortho-substituent can be readily transformed into tertiary amines by heating with methyl iodide and sodium carbonate solution (*Noelting's* method).*

Experiment 139. — Preparation of dimethyl-*o*-toluidine, $CH_3 \cdot C_6H_4 \cdot N(CH_3)_2$ (1:2), from *o*-toluidine, $CH_3 \cdot C_6H_4 \cdot NH_2$ (1:2).

$$C_6H_4\langle^{CH_3\ (1)}_{NH_2\ (2)} + 2CH_3I + Na_2CO_3 \rightarrow C_6H_4\langle^{CH_3\ (1)}_{N(CH_3)_2\ (2)} + 2NaI + H_2O + CO_2.$$

A mixture of 15 grm. of *o*-toluidine with a little more than the theoretical weight of methyl iodide, and slight excess of sodium carbonate, dissolved in 250 c.cm of water, is heated in a reflux apparatus on a water bath, until methyl iodide no longer condenses in the condenser tube (about 2 hours) The liquid is made alkaline with sodium hydroxide, and the amine extracted with ether; the ethereal solution is dried with solid caustic potash and distilled, when the amine is obtained as a pale-yellow liquid, boiling-point 183°. Yield, 80 per cent of theory.

A portion of the product is tested for the presence of

* *Noelting*, B. 1891, **24**, 563.

secondary amine by heating with acetic anhydride (cf. Exp. 146), and distilling. If towards the end of the distillation the boiling-point rises much beyond that of the tertiary amine, it indicates the formation of the acetyl derivative of the secondary amine, in which case the residue of the base should be again heated with methyl iodide and sodium carbonate solution.

D. Quaternary Ammonium Compounds

1. Formation of Quaternary Salts

(*a*) From a primary amine.

Experiment 140.—Preparation of trimethyl-β-naphthyl-ammonium iodide, $C_{10}H_7 \cdot N(CH_3)_3I$, from β-naphthylamine

$$C_{10}H_7 \cdot NH_2 + 3CH_3I \longrightarrow C_{10}H_7 \cdot N(CH_3)_3I + 2HI.$$

5 grm. of β-naphthylamine are boiled with rather more than the theoretical amount of methyl iodide, and 20 c.cm. of water, in a reflux apparatus, until the whole of the amine goes into solution (3–4 hours). On cooling, the sparingly soluble quaternary salt crystallizes in colourless needles. It is filtered, washed with a very little water, and dried on a porous plate. Yield almost theoretical.

The salt decomposes when heated. On exposure to the air it turns dark coloured owing to the liberation of iodine.

(*b*) From a tertiary base and an alkyl halide.

Experiment 141.—Preparation of dimethyl-benzyl-phenyl-ammonium chloride from dimethylaniline and benzyl chloride *

$$C_6H_5NMe_2 + C_6H_5 \cdot CH_2 \cdot Cl \longrightarrow N(CH_3)_2(CH_2 \cdot C_6H_5)(C_6H_5)Cl.$$

A mixture of equivalent quantities of dimethylaniline and benzyl chloride (Exp. 39) is left for 2–3 months at the ordinary temperature in an open dish in a desiccator. The mass is then practically solid, it is pressed on porous plate, washed with ether, and recrystallized from alcohol or water, when it is obtained as colourless plates containing a molecule of water of crystallization. Melting-point, 110°.

2. Preparation of Quaternary Bases.†

Experiment 142.—Preparation of tetra-methyl-ammonium hydroxide, $N(CH_3)_4OH$.

* *Michler* and *Gradmann*, B. 1877, **10**, 2079.

† *Walker* and *Johnston*, J. C. S. 1905, **87**, 955; *Crichton*, P. 1907, **23**, 236.

40 grm. of pure dry tetra-methyl-ammonium chloride (estimate the chlorine accurately by titration) are dissolved in 80 c cm. of absolute methyl alcohol A filtered solution of potassium hydroxide in methyl alcohol is made, and its strength accurately determined by titration with standard acid; the theoretical amount of this is added to the salt solution. A white precipitate of potassium chloride separates, and is filtered off after the mixture has stood for 1½ hour, the precipitate being washed with a little methyl alcohol. The filtrate is mixed with 45 c cm. of water and then subjected to distillation under reduced pressure from a water bath at 35°. After 2 hours, 35 grm. of water are added, and the distillation continued for 1 hour. The solution is now practically free from methyl alcohol. It is removed to a crystallizing dish, and allowed to cool in a desiccator. Partial crystallization takes place; the crystals (about 15 grm.) are filtered off, and the solution, after standing for some days in the desiccator, deposits a further supply (15 grm.) of the crystals.*

The crystalline substance is the penta-hydrate of the base, $N(CH_3)_4OH$, $5H_2O$. It melts at 62–63°.

E. Characteristics of the Amines

As a group the amines possess basic properties, and with acids form salts, from which the free bases are liberated by the addition of a strong alkali, such as potassium hydroxide.

The aliphatic amines (alphylamines) are not frequently met with in the laboratory; they differ from the aromatic (arylamines) in being more decidedly basic. Thus their aqueous solutions are strongly alkaline, whereas those of the arylamines are not.

An amine can generally be characterized by the readiness with which it forms salts with mineral acids This salt formation is indicated by the fact that the amine, although only sparingly soluble in water, dissolves readily in dilute hydrochloric acid. A few amines, of which α- and β-naphthylamine are the most important, yield somewhat sparingly soluble hydrochlorides, and hence do not dissolve in cold hydrochloric acid. That salt formation has occurred can be shown in such

* In this experiment it is advisable to protect the solutions from atmospheric carbon dioxide as far as possible, as both potassium hydroxide and the quaternary base readily absorb carbon dioxide.

a case by comparing the melting-point of the original compound with (*a*) the melting-point of the product obtained by dissolving the base in hot hydrochloric acid, and allowing to cool; (*b*) the melting-point of the product obtained by decomposing the hydrochloride with potassium hydroxide solution.

Distinction between primary, secondary, and tertiary amines.

1. The carbylamine test for primary amines.* A few drops of the amine are warmed (in a fume chamber) with alcoholic potash solution and a few drops of chloroform If the fœtid odour of a carbylamine is observed, it is a sure indication of the presence of the amino-group, $\cdot NH_2$, in the original amine.

$$R\cdot NH_2 + CHCl_3 + 3KOH \longrightarrow R\cdot N{:}C + 3KCl + 3H_2O.$$

2. Primary amines condense with carbon disulphide with the formation of di-alkylated thioureas. The latter are decomposed by boiling with concentrated hydrochloric acid, yielding isothiocyanates (mustard oils), which can be readily recognized by their odour.

$$2R\cdot NH_2 + CS_2 \longrightarrow H_2S + S{:}C(NH\cdot R)_2$$
$$CS\cdot(NHR)_2 + HCl \longrightarrow R\cdot N{:}C{:}S + RNH_2, HCl.$$

Apply Exps. 237 and 238 to the amine on a small scale in a test tube.

3. If the amine is not primary, *Liebermann's* nitrosamine test for a secondary amine is tried. The amine is dissolved in dilute hydrochloric acid, and a little sodium nitrite solution is added. If a secondary amine is present, a yellow oily nitrosamine is formed.

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!NH + HO\cdot N{:}O \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!N\cdot N{:}O + H_2O.$$

The oil is extracted with ether, and the ethereal solution washed well with water to free it from nitrous acid, and the ether removed † The oily residue is then warmed with concentrated sulphuric acid and phenol, poured into water, and made

* *Hofmann*, B. 1870, 3, 767.

† These operations are necessary in order to remove all traces of nitrous acid or nitrite. If they are omitted a coloration will always be obtained, whether a nitrosamine is present or not (cf. Exp. 124).

alkaline with sodium hydroxide, when a deep blue or violet blue coloration is obtained.*

N.B.—Nitrous acid reacts with warm solutions of primary amines, yielding alcohols or phenols (cf. Chap. XX, D). It has no characteristic reaction with aliphatic tertiary amines, but with di-alkylated anilines it yields green coloured *p*-nitroso-derivatives (*e.g.* $(CH_3)_2\overset{(1)}{N}\cdot C_6H_4\cdot\overset{(4)}{N}O$), which can be made use of for diagnosing these compounds

Experiment 143 — Preparation of *p*-nitroso-dimethyl-aniline.

2·4 grm. of dimethylaniline, $C_6H_5N(CH_3)_2$, are dissolved in a mixture of 5 c.cm. of concentrated hydrochloric acid and 5 c.cm. of water, and an aqueous solution of 1·4 grm. of sodium nitrite gradually added. The *p*-nitroso-dimethylaniline hydrochloride which is precipitated is filtered off, washed with a little hydrochloric acid, and purified by crystallization from a little hot water. The salt is shaken vigorously with dilute potassium hydroxide solution, and the green nitroso-compound which separates taken up with ether. On removing the ether it is obtained as green plates. Melting-point, 85°.

4. Acetic anhydride readily forms acetyl derivatives with primary and secondary amines (Chap. XIX, A); the majority of these are well-defined crystalline compounds with sharp melting-points, and they are therefore of great use for the determination of the specific amine.

5. Whether a given amine is aromatic or purely aliphatic can usually be determined by an examination of (*a*) its boiling point; the arylamines have relatively high boiling-points (cf S B, p 366) (*b*) The manner in which the substance burns; the arylamines do so with a very smoky flame. (*c*) The strength of the base, the simple alphylamines are more strongly basic than ammonia and give an alkaline reaction with litmus, while the arylamines give a neutral reaction. *N.B.* Aromatic amines, in which the amino-group is in a side chain and not directly attached to the nucleus, *e.g.* benzylamine, $C_6H_5\cdot CH_2\cdot NH_2$, are strongly basic like the alphylamines.

6. If the compound under examination is an aromatic primary amine, the question whether the amino-group is attached directly to the benzene nucleus or to a side chain can be readily determined by seeing whether the compound can yield an azo-dye (cf. Exp. 165). For this purpose a small amount

* B. 1874, 7, 248.

of the amine is dissolved in dilute hydrochloric acid, a few drops of sodium nitrite solution are added, and the *diazo*-solution (cf. Exp. 154) is poured into a solution of β-naphthol in potassium hydroxide. The formation of a brilliant red or reddish-brown dye is a sure indication of the direct attachment of the amino-group to the benzene ring

7. The actual recognition of the specific amine can only be accomplished with certainty by the determination of the physical constants of the amine and of some of its derivatives, *e.g.* the acetyl, benzoyl, bromo- or nitroso-derivatives.

F. Estimation of Amino-Groups in Primary Arylamines

A known weight of the amine is mixed with three times its weight of concentrated hydrochloric acid, and water is added until the solution contains from 0·1 to 0·01 grm. equivalent of the base per litre A standard solution of sodium nitrite (about 0·1 N) is gradually run into a known volume of the amine solution, the temperature being kept at 0°. A drop of the solution is removed from time to time and tested for free nitrous acid with potassium iodide-starch paper, the formation of a blue coloration indicating the completion of the reaction. Each gram molecule of nitrite used corresponds with 16 grm. of amino-radical

N.B.—The sodium nitrite solution may be standardized by the following method *—A solution of 1 part by weight of the nitrite in 300 c.cm. of cold water is prepared, and to this a 0·1 N solution of potassium permanganate is run in, drop by drop, until the liquid has a decided and permanent pink colour, then a few drops of dilute sulphuric acid are added, and immediately afterwards an excess of the permanganate The mixture is made strongly acid with sulphuric acid, heated to boiling, and the excess of permanganate determined by means of 0·1 N oxalic acid. The reaction between the nitrite and permanganate is represented by the equation:

$$K_2Mn_2O_8 + 5HNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

* *Kinnioutt* and *Nef*, Am. 1884, 5, 388.

G. Estimation of Imino-Groups in Secondary Amines*

A weighed quantity of the secondary amine is introduced into a perfectly dry litre flask, which is fitted with a two-holed rubber cork which carries a dropping funnel and a straight glass tube. This glass tube is connected by means of rubber with a second glass tube fitting into the neck of the funnel and reaching practically to the bottom of the body of the funnel. The amine is mixed with 50 c.cm. of a 7 per cent solution of pure acetic anhydride in dry xylene, and after standing for an hour water is added from the dropping funnel, so that the displaced air is made to bubble through the water in the funnel and no anhydride vapour is lost. The acetic acid present is then titrated with standard barium hydroxide (Chap. VI, A), using phenol-phthalein as indicator.

The method may be used for estimating the amount of secondary amine in a solution provided the solvent does not react with acetic anhydride, and also for determining the amount of secondary amine mixed with a primary or with a primary and tertiary, provided the amount of primary amine is first determined by some other method and the quantity of acetic anhydride which reacts with this allowed for in the final calculation.

XIX. ACETYL AND BENZOYL DERIVATIVES

Alcohols of all types, phenols, and primary and secondary amines, yield *acyl-derivatives* by the replacement of the hydrogen of the OH, NH_2, or NH groups by acyl radicals. The commonest acyl derivatives are the *acetyl*, $CO \cdot CH_3 \cdot$, and *benzoyl*, $C_6H_5 \cdot CO \cdot$, and these are of considerable practical importance. The formation of such derivatives is used not merely to indicate the presence of OH, NH_2, or NH groups, but also to determine the individual substance under examination, as the acetyl and benzoyl derivatives crystallize well as a rule, and have definite melting-points.

* *Vaubel*, J. S. C. I. 1893, 12, 954.

A. Acyl Derivatives of Primary and Secondary Amines. (S. B. 180–182.)

The preparation of the anilide, toluidide, &c, of an organic acid can usually be conducted in much the same manner as the preparation of the amide of the acid (Chap XIV, B).

Method I.—By the elimination of water from the salt formed by the union of the acid and amine As examples, we have the formation of acetanilide from aniline and acetic acid, and of benzanilide from aniline and benzoic acid.

$$R\cdot C\overset{O}{\leqslant}ONH_3R' \longrightarrow R\cdot C\overset{O}{\leqslant}NHR' + H_2O.$$

This is often the cheapest method for the preparation of large quantities of an anilide

Experiment 144.—Preparation of acetanilide (acetphenylamide), $CH_3\cdot CO\cdot NH\cdot C_6H_5$, from aniline and acetic acid.*

A mixture of equal weights of pure aniline and glacial acetic acid, with 2–3 per cent of anhydrous zinc chloride, is gently boiled for three hours in a round-bottomed flask fitted with a reflux condenser The hot liquid is then poured into excess of water, filtered, and washed with cold water The crude acetanilide may be crystallized from a mixture of alcohol and water, or from water alone, although it is only sparingly soluble in the latter If the solution is dark coloured it may be boiled with animal charcoal, and filtered by means of a hot-water funnel (fig. 15). As the solution cools, rhombic plates, melting-point 114°, are deposited.

Experiment 145.—Preparation of benzanilide, $C_6H_5\cdot CO\cdot NH\cdot C_6H_5$, from aniline benzoate.

A mixture of 15 grm. of aniline and an equivalent amount of benzoic acid is heated in a retort at 180° and the temperature raised gradually to 225°, a further quantity of aniline is then added and the heating continued The hot mass is poured into a dish, allowed to solidify, powdered, washed in turn with dilute hydrochloric acid, water, dilute sodium hydroxide, and finally washed with water, dried, and recrystallized from alcohol. It forms glistening plates, melting-point 161–162°.

Method II.—By the inter-reaction of an acid chloride, or

**Williams*, J. C. S. 1864, 206; *Häussermann*, J. S. C. I. 1914, 33, 1223.

more frequently an acid anhydride, and the amine* (primary or secondary):

$$C_6H_5\cdot CO\cdot Cl + 2C_6H_5\cdot NH_2 \rightarrow C_6H_5\cdot CO\cdot NH\cdot C_6H_5 + C_6H_5\cdot NH_2, HCl.$$

$$C_6H_5NH_2 + \begin{matrix} CH_3\cdot CO \\ CH_3\cdot CO \end{matrix}\!\!>\!O \rightarrow CH_3\cdot CO\cdot NH\cdot C_6H_5 + CH_3\cdot CO_2H.$$

The acetic anhydride method is extremely convenient when it is desired to prepare a small amount of an acetyl derivative for the identification of an amine.

Experiment 146.—Preparation of acet-*o*-toluidide, $CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3$, from *o*-toluidine and acetic anhydride.

$$CH_3\cdot C_6H_4\cdot NH_2 + (CH_3\cdot CO\cdot)_2O = CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3 + CH_3\cdot CO\cdot OH.$$

5 grm. of *o*-toluidine are warmed for two minutes by means of a free flame with an equal weight of acetic anhydride, and the hot mixture is poured into cold water. When the excess of acetic anhydride has been decomposed the solid is filtered, washed with water, and recrystallized from alcohol. It forms long needles, melting-point 110°. Yield practically theoretical.

If the amine is boiled for some time with an excess of acetic anhydride, a diacetyl derivative, *e.g* $CH_3\cdot C_6H_4\cdot N(CO\cdot CH_3)_2$, is formed together with the monoacetyl derivative The presence of ortho substituents facilitates the formation of diacetyl derivatives.

Experiment 147.—Preparation of diacet-*o*-toluidide, $CH_3\cdot C_6H_4\cdot N(CO\cdot CH_3)_2$.

A mixture of 10 grm. of *o*-toluidine and 38 grm. of acetic anhydride is boiled for an hour in a flask fitted with an upright air condenser and a calcium chloride tube The mixture is then transferred to a distilling flask and distilled under reduced pressure; acetic acid and the excess of acetic anhydride pass over first; then the diacetyl derivative distils over at 152–153° under 20 mm. pressure, and a small amount of monoacetyl derivative (1–2 grm.) is left in the flask. The diacetyl compound is a colourless liquid which solidifies gradually to well-developed pyramids, melting-point, 18°. Yield, 14·5 grm. It is somewhat unstable, and readily gives up one acetyl group in the form of acetic acid.

In order to avoid the formation of a diacetyl derivative in the preparation of a monoacetyl compound an aqueous solu-

* *H. Franzen*, B. 1909, **42**, 2465.

tion of acetic anhydride may be used* — 12·3 grm in 120 c.cm. of water—together with a solution of the base in dilute acetic acid. The yield is practically theoretical.

Amino-derivatives of sulphonic acids cannot, as a rule, yield acetyl derivatives when warmed with acetic anhydride. The simplest method is to use an aqueous solution of a normal salt, *e.g.* sodium or calcium, and add the requisite amount of acetic anhydride

Experiment 148.—Preparation of benzanilide, $C_6H_5 \cdot NH \cdot CO \cdot C_6H_5$

5 grm. of benzoyl chloride are added gradually to 6 grm. of aniline contained in an open dish The mixture becomes quite hot, and is afterwards extracted with hydrochloric acid, sodium hydroxide solution, and water, dried, and finally recrystallized from alcohol (cf Exp 145).

In this reaction only 50 per cent of the amine is transformed into its benzoyl derivative, the remainder forms the hydrochloride (equation, p. 194) and is present in the aqueous filtrate

The method is frequently modified by working in the presence of a free alkali, *e.g.* sodium hydroxide solution, when the whole of the amine is transformed into its benzoyl derivative; this is termed the *Schotten-Baumann*† process of benzoylation.

$$C_6H_5 \cdot CO \cdot Cl + CH_3 \cdot C_6H_4 \cdot NH_2 + NaOH \longrightarrow C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3 + NaCl + H_2O.$$

Experiment 149.—Preparation of benzoyl-*p*-toluidide, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$

2 grm. of *finely-divided p*-toluidine are mixed with 10 c.cm. of a 10 per cent aqueous solution of sodium hydroxide, and excess of benzoyl chloride (2 c.cm.) is added gradually to the warm mixture, which is frequently shaken Thorough shaking is essential, and the simplest method is to cork the flask and agitate as vigorously as possible. If any excess of benzoyl chloride is left, it is destroyed by warming with a further amount of sodium hydroxide solution. The mixture is then poured into water, filtered, the precipitate washed with water, dried, and recrystallized from alcohol. Melting-point, 158°.

* *Lumière* and *Barbier*, Bull. 1905, [iii], **33**, 783.
† B. 1886, **19**, 3219.

B. Aeyl Derivatives of Alcohols and Phenols

Method I.—The acetyl derivatives are usually prepared by heating the hydroxylic compound with an excess of acetic anhydride and *anhydrous* sodium acetate (Exp. 14). Under these conditions the hydric radical of each hydroxyl group present becomes replaced by acetyl.

Experiment 150.—Preparation of pyrogallol triacetate, $C_6H_3(O\cdot CO\cdot CH_3)_3$.

A mixture of 5 grm. of pyrogallol and the same weight of freshly-fused anhydrous sodium acetate is boiled with 15 grm. of acetic anhydride in a small round-bottom flask fitted with a reflux condenser. After thirty minutes the mass is poured into water and left until the oil, which separates at first, solidifies. The solid is then filtered by means of the pump, washed with water, dried, and crystallized from benzene or dilute alcohol. Melting-point, 157°. Yield, 94 per cent of theory.

Experiment 151.—Preparation of the hexa-acetyl derivative of mannitol,* $OAc\cdot CH_2\cdot[CH\cdot OAc]_4\cdot CH_2\cdot OAc$.

5 grm. of mannitol, $OH\cdot CH_2[CH\cdot OH]_4\cdot CH_2\cdot OH$, 20 grm. of acetic anhydride, and a small piece of anhydrous zinc chloride are boiled for an hour. The mass is poured into water, and the solid thus obtained crystallized from alcohol or glacial acetic acid. It forms flat, snow-white prisms, melting-point 119°. Yield nearly theoretical.

Method II.—Benzoates are usually prepared by the *Schotten-Baumann* method.

Experiment 152.—Preparation of glyceryl tribenzoate, $C_3H_5(O\cdot CO\cdot C_6H_5)_3$.†

3 grm. of glycerol are shaken with sodium hydroxide solution (10 per-cent solution) and a considerable excess of benzoyl chloride, as in Exp. 149. The dry product is crystallized from ligroin, and then melts at 76°.

Practically all hydroxylic derivatives can be benzoylated by this method, and other acid chlorides, *e.g.* phenylacetyl chloride, may be substituted for benzoyl chloride.

* B. 1879, 12, 2059. † B. 1886, 19, 3221; M. 1889, 10, 393.

C. Removal of Acyl Radicals

The acetyl and benzoyl derivatives of amines and of alcohols can be hydrolysed by boiling with mineral acids or with alkalis. Since the acyl derivatives of alcohols are esters, this is merely a further example of the readiness with which most esters can be saponified (Chap XII, D). The acyl derivatives of amines are more difficult to hydrolyse, thus acetanilide must be boiled with fairly concentrated potassium hydroxide for some hours before the hydrolysis has proceeded to any appreciable extent. The products in all cases are an amine and an acid or their salts. Benzanilide, and the benzoyl derivatives of amines generally, cannot be hydrolysed by boiling with an alkali solution, but are decomposed when heated with solid potash, or when boiled with concentrated hydrochloric acid.

D Estimation of Acetyl Radicals

The number of hydroxyl radicals contained in a given alcohol or phenol can be ascertained by preparing the acetyl derivative by the method described in Exps. 150 and 151, hydrolysing a known weight of the acetyl derivative with benzene-sulphonic acid and titrating the amount of acetic acid by means of standard barium hydroxide solution.

A solution of pure benzene-sulphonic acid of known strength can be prepared by the following process. 50 grm. of pure barium benzene sulphonate, $(C_6H_5 \cdot SO_3)_2Ba$, are placed in a flask and subjected to steam distillation (p. 10) until the distillate is quite neutral.* The requisite amount (avoid excess) of sulphuric acid, *e.g.* a given volume of acid of known concentration, is added in order to convert the barium salt into the free acid The precipitated barium sulphate is removed, well washed with distilled water, and the distillate and washings made up to a given volume with water, so that the solution is a 10 or 20 per cent solution of the acid.

Experiment 153.—Determine the percentage of acetyl radical present in the hexa-acetyl-mannitol.

About 0·2 grm. of the substance and 100 c.cm. of the

* Small amounts of volatile acid impurities are usually present in the barium salt, and are removed by this treatment.

10 per cent benzene sulphonic acid solution are used. Steam is blown through at such a rate that about 400 c.cm. of distillate are collected per hour. The distillation is continued until the liquid which passes over is neutral (1·5–3 hours), and the whole distillate is titrated with standard barium hydroxide. *N.B.*—The distillation should be conducted in a room fairly free from carbon dioxide, or the distillate should be protected from the atmospheric carbon dioxide by means of a soda-lime tube.

The acetyl radicals in an acetylated amine can be estimated in a similar manner, but the process is more tedious as the acetyl derivatives of amine are hydrolysed but slowly.

XX. DIAZONIUM SALTS AND THEIR USES*

A. The diazo-compounds or diazonium salts are produced by the action of nitrous acid in the cold on primary arylamines or their salts, *e.g.*—

$$C_6H_5NH_2,HCl + HONO \longrightarrow C_6H_5\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\overset{N}{\cdot}Cl + H_2O.$$

The salts may be isolated in solid form by the addition of alcohol and ether to their aqueous solutions, or by the addition of the theoretical amount of amyl nitrite to a solution of a salt of the amine in alcohol and acid †. Since the compounds in the dry state are very explosive, and as they are generally used in aqueous solution, their isolation is not often necessary.

For their constitution, cf. S. B. 384–385; also *Cain*, J. C. S. 1907, **91**, 1049.

Experiment 154.—Preparation of a diazonium salt: phenyl-diazonium chloride, $C_6H_5N_2Cl$.

10 grm. of aniline (1 mol.) are dissolved in 50 c.cm. of a mixture of equal volumes of concentrated hydrochloric acid and water (excess: more than two mol.), and the mixture is well cooled by means of ice. 8–9 grm. of sodium nitrite (more than 1 mol.) dissolved in 20 c.cm. of water are then added slowly from a dropping funnel, the end of which dips under

* *P. Griess*, A. 1860, **113**, 201; 1861, **117**, 1; 1862, **121**, 257; 1866 **137**, 39. † *Knoevenagel*, B. 1895, **28**, 2049.

the solution of amine; the mixture is kept well agitated during the addition and the temperature is not allowed to rise. The addition of the nitrite solution is continued until a drop of the mixture, withdrawn by means of a glass rod, indicates the presence of free nitrous acid by giving a blue coloration with starch-potassium iodide paper.

A solution prepared in this manner may be used for the following experiments.

This process, usually termed *diazotising*, is of very general application, and by its means all aromatic compounds possessing an amino-group directly attached to the benzene nucleus can be converted into diazonium salts, the salt obtained varying with the mineral acid used. Practically all the salts are soluble in water and the solutions are good electrolytes, resembling aqueous solutions of quaternary ammonium salts

The compounds are characterized by a remarkable activity, and can be used for the preparation of numerous groups of compounds, as shown in the experiments described in this chapter. One of the most general properties is the readiness with which nitrogen is eliminated and the $-N_2X$ group replaced by some other univalent group. (S. B 385–387.)

Certain amines do not dissolve readily in dilute mineral acids, either owing to the fact that they do not form salts in dilute aqueous solution or that the salts are sparingly soluble. Under such circumstances the amine or salt in a finely divided state is suspended in the acid and diazotised in the usual manner. When completely diazotised a clear liquid should be obtained; if any insoluble amine remains it can be removed by filtration.

B. Action of Bromine on Diazonium Salts*

Experiment 155. — Preparation of diazo-benzene perbromide, $C_6H_5N_2Br_3$.

$$C_6H_5N_2Cl + KBr + Br_2 \longrightarrow C_6H_5N_2Br_3 + KCl.$$

To a small quantity of a diazonium solution, prepared as in Exp. 154, an equal volume of a strong solution of bromine in concentrated potassium bromide solution is added. A dark oil is formed which is separated and washed with water. On

* *Griess*, A. 1866, 137, 50.

dissolving in a little alcohol and then adding ether it separates as golden yellow plates. (S. B. 388.)

C. Replacement of the Diazo-Group by Iodine

Experiment 156.—Preparation of phenyl iodide,* C_6H_5I, from aniline.

$$C_6H_5N_2Cl + KI \longrightarrow C_6H_5N_2I + KCl$$
$$C_6H_5N_2I \longrightarrow C_6H_5I + N_2.$$

An excess of potassium iodide solution (25 grm. in 50 c.cm. water) is added to a diazo-solution prepared according to Exp. 154, and the mixture heated gradually on a water bath until no more evolution of nitrogen occurs. Phenyl iodide separates as a heavy dark oil, which is steam-distilled. The distillate is extracted with ether, and the ethereal solution washed with water and dilute sodium hydroxide solution until all free iodine is removed, then dried with calcium chloride and distilled. Yield, 18–20 grm. It is a heavy, yellow liquid Boiling-point, 190°; D^{15}, 1·833.

For additive reactions of phenyl iodide (formation of iodoso- and iodoxy-derivatives), see Chap. XXXI.

D. Replacement of the Diazo- by the Hydroxyl-Group

The diazonium salts, more especially the sulphate, decompose when boiled with water, yielding nitrogen and a phenol.

Experiment 157.—Preparation of phenol, $C_6H_5 \cdot OH$, from aniline.

$$C_6H_5N_2 \cdot HSO_4 + H_2O \longrightarrow C_6H_5OH + N_2 + H_2SO_4.$$

10 grm. of aniline are added to the hot solution obtained by pouring 20 grm. of concentrated sulphuric acid into 50 c.cm. of water. The resulting solution is cooled and diazotised as in Exp. 154. The product is heated gently on a water bath for half an hour, and then distilled with steam. The distillate is extracted with ether, the ethereal solution dried with fused sodium sulphate, and fractionated. The phenol distils over at 183°, and solidifies to colourless crystals, melting-point 43°.

* *Griess*, A. 1866, 137, 76.

Yield, 6–8 grm. (For properties of phenols, see Chap. XVII, B.)

E. Replacement of the Diazo-Group by Chloro-, Bromo- and Nitrile Radicals

*(Sandmeyer's Reaction)**

The diazonium halides and cyanides are decomposed by the addition of solutions of the corresponding cuprous salts in acid solution, with the formation of halogen or cyanogen derivatives of benzene and evolution of nitrogen.

$$C_6H_5N_2Cl[+Cu_2Cl_2] \longrightarrow C_6H_5Cl + N_2[+Cu_2Cl_2].$$

Experiment 158. — Preparation of monochlorobenzene, C_6H_5Cl, from aniline.

(*a*) Preparation of a 10 per cent solution of cuprous chloride. The reactions involved are as follows:—

$$CuSO_4 + 2NaCl \longrightarrow CuCl_2 + Na_2SO_4$$
$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$

One-tenth of the gram-molecular quantities should be taken.

25 grm of cupric sulphate crystals ($CuSO_4$, $5H_2O$) and 12 grm. of pure sodium chloride are dissolved in 50 grm. of water in a *tared* flask. The solution is heated to boiling, and then 100 grm. of concentrated hydrochloric acid and 13 grm. of copper filings (excess) are added, and the flask heated until the contents become colourless. During this process 6·4 grm. of copper will dissolve. Concentrated hydrochloric acid is then added, until the total weight is 203·6 grm. The solution, weighing 197 grm., contains 19·7 grm. of cuprous chloride.

(*b*) 20 grm. of aniline are diazotised as described in Exp. 154, and the solution of benzenediazonium chloride thus formed is run gradually into 100 grm. of the cuprous chloride solution, heated to boiling in a flask fitted with a reflux condenser. The yellow precipitate which is formed on the introduction of the diazo-solution disappears almost immediately with evolution of nitrogen. The chlorobenzene formed is distilled with steam, extracted with ether, the ethereal solution dried over calcium chloride, and fractionated. Yield, 18 grm., *i.e.* 75 per cent of theory.

* *Sandmeyer*, B. 1884, 17, 1633, 2650.

It is a colourless liquid with pleasant odour. Boiling-point, 132°; $D^{15°}$, 1·110.

Experiment 159.—Preparation of *m*-nitro-chloro-benzene, $C_6H_4Cl \cdot NO_2(1:3)$, from *m*-nitraniline.

$$C_6H_4\begin{matrix}NH_2\,(1)\\NO_2\,(3)\end{matrix} \longrightarrow C_6H_4\begin{matrix}Cl\,(1)\\NO_2\,(3).\end{matrix}$$

4 grm. of *m*-nitraniline (Exp. 135) are dissolved in a mixture of 7 grm. of concentrated hydrochloric acid and 100 grm. of water, and 20 grm. of the 10 per cent solution of cuprous chloride (Exp. 158) added. The mixture is heated to boiling in a flask, and then decomposed by the addition, through a dropping funnel, of 2·5 grm. of sodium nitrite dissolved in 20 grm. of water. A heavy brown oil separates out, which solidifies on standing in the cold. Melting-point, 44·4°, boiling-point, 235·6° (corr.).

The amino-group can be replaced by bromine in much the same manner. A solution of cuprous bromide is prepared as follows:—

A mixture of 12·5 grm of cupric sulphate crystals (1·5 mol.), 36 grm. of potassium bromide (3 mol.), 80 c.cm. of water, 11 grm. of concentrated sulphuric acid (1 mol.), and 20 grm. of copper turnings is boiled in a flask fitted with a reflux condenser until practically decolorized This solution can then be used in the same manner as the cuprous chloride solution in Exps. 158 and 159.

Experiment 160.—Preparation of benzonitrile, $C_6H_5 \cdot CN$, from aniline.

$$2C_6H_5N_2Cl + 2CuCN, KCN \longrightarrow 2C_6H_5CN + 2N_2 + Cu_2Cl_2 + 2KCN.$$

(*a*) Preparation of potassium cuprous cyanide solution.

N.B.—*Cyanogen is evolved during this reaction; the preparation must therefore be conducted in a fume chamber with a good draught, great care being taken not to breathe the fumes.*

25 grm. of cupric sulphate crystals are dissolved in 150 grm. of water, and 28 grm. of 96 per cent potassium cyanide added to the hot solution. The precipitate at first formed soon redissolves. The product contains 18 grm. of cuprous cyanide, in the form of potassium cuprous cyanide, in 200 grm. of solution.

(*b*) The cuprous cyanide solution is heated to 90°, and a solution of benzene-diazonium chloride, prepared from 10 grm. of aniline, as in Exp. 154, added gradually through a dropping

funnel. The oil which separates is distilled with steam, the distillate extracted with ether, the ethereal solution washed with dilute sodium hydroxide and sulphuric acid solutions, dried with calcium chloride, and fractionated. Yield, 6–7 grm., *i.e.* 60–65 per cent of theory. It is a colourless oil; boiling-point, 191°; $D^{0°}$, 1·023.

This reaction is one of the most important methods for the preparation of aromatic nitriles (cf. Chap. XIV, D).

F Action of finely divided Copper on Diazonium Salts

*(Gattermann's Method)**

Finely divided copper acts similarly to cuprous salts in inducing the decomposition of solutions of diazonium salts.

Experiment 161 —Preparation of *p*-chloro-toluene, $C_6H_4Cl \cdot CH_3(1:4)$, from *p*-toluidine.

$$C_6H_4\begin{matrix}CH_3\ (1)\\NH_2\ (4)\end{matrix} \rightarrow C_6H_4\begin{matrix}CH_3\ (1)\\Cl\ (4).\end{matrix}$$

(*a*) Preparation of finely divided copper.

100 grm of cupric sulphate crystals are dissolved in 350 grm. of water in a porcelain dish, and after cooling, 35 grm. of zinc dust are dusted into the solution from a muslin bag. The liquid is stirred and then allowed to stand until the solution is decolorized, more zinc dust being added if necessary. The precipitated copper is washed several times with water by decantation, and then treated several times with dilute hydrochloric acid to dissolve any residual zinc. It is finally filtered and washed thoroughly on a Buchner funnel. In order to prevent oxidation the powder is preserved in a moist state in a stoppered bottle.

(*b*) 12 grm. of *p*-toluidine are diazotised as described in Exp. 154, and 30 grm. of the moist copper powder are gradually added; the product is distilled with steam, the distillate taken up with ether, the ethereal solution dried with calcium chloride and distilled. The *p*-chlorotoluene passes over at 163°, and forms an oily liquid.

* *Gattermann*, B. 1890, **23**, 1218.

G. Interaction of Diazonium Salts with Primary Arylamines: Formation of Diazo-amino-Compounds. (S. B. 390–392.)

Diazonium salts condense with primary arylamines, yielding diazo-amino-compounds (*Griess*). The same product may be attained in one operation by taking two molecular proportions of the amine, and adding only sufficient acid and nitrite solution to diazotise one molecule. The diazonium salt thus formed reacts with the excess of amine, forming the diazo-amino-compound, *e.g.*:

$$C_6H_5N_2 \cdot HSO_4 + H_2N \cdot C_6H_5 \longrightarrow C_6H_5N{:}N \cdot NH \cdot C_6H_5 + H_2SO_4.$$

Experiment 162.—Preparation of diazo-amino-benzene, $C_6H_5N{:}N \cdot NHC_6H_5$, from aniline *

10 grm. of aniline are dissolved in 3 grm. of concentrated sulphuric acid diluted with 300 c.cm of water. The solution is brought to a temperature of 27° by heating in a water bath, and an aqueous solution of 3·6 grm. of sodium nitrite added. If the temperature rises above 30° the mixture is quickly cooled, ice being added if necessary. (The limits of temperature for obtaining a good yield are 25–35°.) Immediately after the addition of the nitrite solution a yellow precipitate begins to separate, and this separation is complete after thirty minutes The precipitate is removed, washed with cold water, and dried on a porous plate at the ordinary temperature. Yield, 97–98 per cent of theory.

Alternative Method for the preparation of Diazo-amino-benzene. †—A solution of 5·2 grm. of sodium nitrite and 10 grm. of sodium acetate crystals, in 100 c.cm of water, is added to a solution of 15 grm of aniline hydrochloride, in 300 c.cm. of water, which is kept cold by means of running water. The mixture is kept for twenty minutes in cold water, and the diazo-amino-benzene then filtered off.

The substance crystallizes from ligroin in golden-yellow plates. It melts at 98°, but explodes if heated above its melting-point. It is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, ether, and benzene.

* *Staedel* and *Bauer*, B. 1886, 19, 1952.
† *Meyer* and *Jacobson*, II, 1, 838.

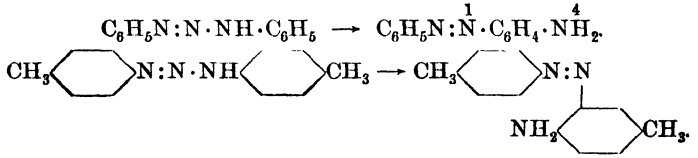
Chemical Properties of the Diazo-amino-compounds.—The hydrogen atom of the :NH group is replaceable by metals, *e.g.* diazo-amino-benzene in ethereal solution reacts with metallic sodium, yielding the compound $C_6H_5N:N\cdot NNa\cdot C_6H_5$, which is readily decomposed by water.

An alcoholic solution of diazo-amino-benzene, treated with silver nitrate solution, deposits reddish crystals of the corresponding silver salt.

In many of their reactions the diazo-amino-compounds resemble diazonium salts, but are not nearly so decomposable

Molecular Rearrangement of Diazo-amino-Compounds: Formation of Amino-azo-Derivatives.

The diazo-amino-compounds in the presence of a small amount of the amine hydrochloride are transformed into the isomeric amino-azo-compounds. The para-derivative is usually obtained, but if the para-position is already occupied by a substituent, an ortho-amino-derivative results.



Experiment 163. — Preparation of *p*-amino-azobenzene, $C_6H_5N:N\cdot C_6H_4\cdot NH_2$, from diazo-amino-benzene.*

5 grm. of diazo-amino-benzene are dissolved in 10–15 grm. of aniline, and 2·5 grm. of aniline hydrochloride are added. The mixture is warmed to 40° for an hour, and then allowed to stand for twenty-four hours, when an excess of fairly strong hydrochloric acid is quickly added (the temperature must not rise above 70°), and the solution allowed to cool Amino-azobenzene hydrochloride separates as fine crystals, which are washed several times with dilute hydrochloric acid. Yield, nearly quantitative. The free base is obtained by treating the hydrochloride with dilute ammonia solution. It crystallizes from dilute alcohol in brownish-yellow needles, melting-point 126°.

Amino-azobenzene is a feebly basic primary arylamine. It does not form stable salts with weak acids like acetic, but does so with strong mineral acids. It can be diazotised, and

* *Staedel* and *Bauer*, B. 1886, 19, 1958.

the resulting diazonium salt "coupled" with phenols, amines, &c. (cf. Exps. 164, 165), when tetrazo-compounds are formed.

$$C_6H_5N{:}N\cdot C_6H_4\cdot N_2Cl + C_6H_5\cdot OH \longrightarrow C_6H_5N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH + HCl.$$

The interaction of diazonium salts with secondary amines is similar to that with the primary amines.

H. Azo-dyes. (S. B. 397–400.)

The diazonium salts "couple" with tertiary amines and also with alkaline solutions of phenols, yielding dialkylamino-azo- and hydroxy-azo- derivatives, many of which are important dyes. The majority of these dyes also contain sulphonic acid groups, as the presence of such groups renders the compound more readily soluble in water. Certain secondary and even primary amines, *e.g* *m*-phenylene-diamine, can also "couple" with diazonium salts.

Experiment 164. — Preparation of helianthine (methyl-orange), $C_6H_4\langle^{SO_3Na}_{N{:}N\cdot C_6H_4\cdot N(CH_3)_2}$, from diazotised sulphanilic acid and dimethylaniline.

$$SO_3Na\cdot C_6H_4\cdot NH_2 \longrightarrow SO_3Na\cdot C_6H_4\cdot N_2OH$$

$$SO_3Na\cdot C_6H_4\cdot N_2\cdot OH + C_6H_5\cdot N(CH_3)_2 \longrightarrow SO_3Na\cdot C_6H_4\cdot N{:}N\langle\rangle N(CH_3)_2.$$

10 grm. of sulphanilic acid (1 mol.) (Exp. 114), dried in a steam oven, are dissolved in a solution of 3·1 grm. of anhydrous sodium carbonate ($\frac{1}{2}$ mol.) in 100 c.cm of water. The mixture is then treated with a solution of 4 grm. of pure sodium nitrite (1 mol.) in 20 c.cm. of water. The mixture is cooled, and gradually treated with a quantity of hydrochloric acid corresponding with 2·1 grm. of the anhydrous acid (1 mol.). For this purpose ordinary concentrated acid should be diluted with an equal volume of water, and the specific gravity of the mixture determined accurately at 15° by means of a hydrometer. The percentage strength of the diluted acid (by weight) is obtained by reference to a table of variation of specific gravity with strength of solution.

A solution of 7 grm. of dimethylaniline, $C_6H_5N(CH_3)_2$, (1 mol.), in the same amount of hydrochloric acid as indicated above (1 mol.), diluted to 20 c.cm., is added to the mixture,

and the liquid made alkaline by the addition of sodium hydroxide solution (excess should be avoided). Separation of methyl orange at once occurs; the quantity of product is increased by "salting out" (about 25 grm. of finely powdered common salt is added to the solution, and stirred well until dissolved). The dye is filtered off, dried on a porous plate, and recrystallized from a little water. Yield, nearly theoretical.

Helianthine is the sodium salt of the sulphonic acid, and the aqueous solution has a yellow colour. On the addition of mineral acid the free sulphonic acid is obtained, which has a red colour in aqueous solution. The use of the dye as an indicator in acidimetry and alkalimetry depends upon this change of colour.

Experiment 165.—"Coupling" of diazotised sulphanilic acid with β-naphthol. Preparation of Orange II.

$$C_6H_4\langle^{SO_3Na}_{N_2Cl} + C_{10}H_7\cdot ONa \rightarrow C_6H_4\langle^{SO_3Na}_{N:N\cdot C_{10}H_6\cdot OH} + NaCl.$$

17·3 grm. of dry sulphanilic acid are dissolved in a solution of the theoretical amount of anhydrous sodium carbonate in 500 c.cm. of water, the mixture cooled with cold water or ice, and 30 c.cm. of concentrated hydrochloric acid added; 100 c.cm of a normal solution of sodium nitrite are then added slowly (apply the starch-potassium iodide paper test to determine the end of the reaction), and part of the diazonium compound settles out as fine crystalline needles.

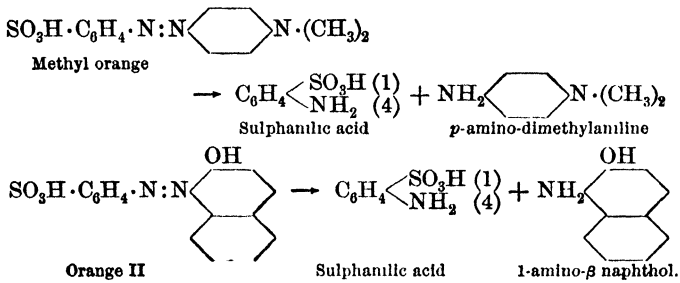
14·4 grm. of β-naphthol are dissolved in 100 c.cm. of normal sodium hydroxide solution, the mixture cooled well, and then the diazonium solution prepared above is added gradually with constant stirring. When the addition is complete the solution should show a slightly alkaline reaction. The solution is allowed to stand overnight, common salt being added to facilitate the separation of the dye. The precipitate is filtered on a Buchner funnel at the pump, washed with a little water, and dried. Yield, 34 grm., *i.e.* 75 per cent of theory.

It is a bright orange powder soluble in water, with an orange colour; it dyes wool orange from an acid bath.

For preparation of other azo-dyes see Cain and Thorpe, *Synthetic Dye-stuffs*, p. 225, *et seq.*

Determination of the Constitution of an Azo-dye by Reduction.—Reducing agents such as zinc dust and water, tin and hydrochloric acid, or stannous chloride, split the azo-

compounds at the point of union of the two nitrogen atoms of the azo-group, yielding (*a*) the base from which the azo-dye was derived, and (*b*) the amino-derivative of the substance with which it was "coupled", the amino-group being in the position previously occupied by the azo-group, *e.g.*:



The best reducing solution* consists of 40 grm. of stannous chloride dissolved in 100 c.cm. of pure hydrochloric acid (sp. gr. 1·19); 1 grm. of the pure recrystallized dye dissolved in the least possible quantity of hot water is treated with 6 c.cm. of the reducing solution.† The reduction usually takes place immediately, frequently with violent ebullition, and the liquid rapidly becomes colourless. The subsequent method of procedure depends on the nature of the azo-compound reduced

Experiment 166.—Reduction of helianthine.

5 grm. of the pure dye are dissolved in the least possible quantity of boiling water to a clear solution (about 50 c.cm.), and treated with 30 c.cm. of a stannous chloride solution prepared as above, until decolorization takes place. The resulting solution is cooled and allowed to stand for some time, when sulphanilic acid (cf. Exp. 114) crystallizes out. This is filtered off, and the filtrate diluted with water and treated with sodium hydroxide solution until the precipitate at first formed is completely redissolved. It is then extracted several times with ether, the ethereal solution dried with sticks of potash, and the ether removed. The residual oil solidifies on cooling and rubbing with a glass rod, and consists of crystals of *p*-amino-dimethylaniline, melting-point 41°.

* *Witt.*, B. 1888, **21**, 3471.

† Another method is to use a solution of 1·3 grm. of tin in 7·5 c.cm concentrated hydrochloric acid for each gram of dye.

Experiment 167.—Determination of the constitution of Orange II, $SO_3H^4 \cdot C_6H_4 \cdot N^1{:}N^1 \cdot C_{10}H_6 \cdot OH^2$.*

Dissolve 20 grm. in 200 c.cm. of water, and add a hot solution of 26 grm. of tin in 150 c.cm. of concentrated HCl. As the solution cools crystals of 1-amino-2-naphthol hydrochloride separate These are removed, washed with dilute hydrochloric acid, dissolved in water containing a little sulphurous acid, and reprecipitated by the addition of concentrated hydrochloric acid. The second reduction product, sulphanilic acid, can be isolated from the mother liquor.

I. Reduction of Diazonium Salts

1. Replacement of the Diazo-group by Hydrogen.

(i) Reduction by means of alkaline stannite solution.

Experiment 168.—Preparation of benzene from aniline.

5 grm. of aniline are diazotised as described in Exp. 154. The diazonium solution is cooled in ice, and then treated gradually with excess of a strong alkaline stannite solution, prepared by dissolving 20 grm. of stannous chloride in 50 c.cm. of water, and adding a strong solution of potassium hydroxide until the precipitate at first formed redissolves. When all the reducing solution has been added, the flask containing the mixture is attached to a condenser and the solution boiled, when benzene distils over. The product is dried with calcium chloride and redistilled Yield, 3-4 grm.; boiling-point, 81°.

(ii) Reduction by means of alcohol.

Experiment 169.—Preparation of 1:3:5-tribromobenzene, $C_6H_3Br_3$, **from sym-tribromaniline.**†

50 grm. of *s*-tribromaniline (Exp. 41) are pulverized and dissolved in about 300 c.cm. of hot rectified spirit mixed with 75 c.cm. of benzene in order to increase its solvent power 20 c.cm. of concentrated sulphuric are run in from a pipette, and if a precipitate forms this is redissolved by longer heating, and, if necessary, by the addition of more of the solvents. 20 grm. of finely powdered sodium nitrite is sifted into the hot liquid as rapidly as the violent reaction will allow, and the whole then heated until effervescence ceases. After standing

* *Grandmougin* and *Michel*, B 1892, **25**, 981.

† *Loring Jackson* and *Bentley*, Am. 1892, **14**, 335.

overnight the precipitate is filtered, washed with hot water to remove the sodium sulphate, and dried. Yield, 45 grm., *i.e.* 95 per cent of theory. It crystallizes from alcohol in colourless prisms; melting-point, 119°.

To make sure that it contains no unaltered tribromaniline, a small amount is dissolved in dry benzene, and dry hydrogen chloride is passed in. If a precipitate of tribromaniline hydrochloride is formed, the whole can be treated in the same manner and the precipitate filtered off. The clear filtrate when evaporated will yield pure tribromobenzene.

2. Reduction of the Diazo-group to the Hydrazo-group in Acid Solution: Aromatic Hydrazines. (S. B. 395–397.)

$$C_6H_5 \cdot N_2Cl + 2SnCl_2 + 4HCl \longrightarrow C_6H_5 \cdot NH \cdot NH_2, HCl + 2SnCl_4.$$

Experiment 170.—Preparation of phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, from aniline

10 grm. of pure aniline are dissolved in a mixture of 30 grm. of concentrated hydrochloric acid and 75 c.cm. of water, and diazotised in the usual manner (Exp. 154). The diazotised solution is saturated with common salt by adding 30 grm. of finely powdered salt, shaking well, and decanting the liquid from any undissolved solid. An ice-cold solution of 60 grm. of stannous chloride in 25 grm of concentrated hydrochloric acid is added, the mixture kept for several hours, and the precipitated phenylhydrazine hydrochloride filtered by means of a Buchner funnel. The hydrochloride is then decomposed with excess of sodium hydroxide solution; the phenylhydrazine separates as an oil and is taken up with ether, the ethereal solution dehydrated with anhydrous potassium carbonate, and the ether removed by distillation. The residue of phenylhydrazine is distilled under diminished pressure. Yield, 10 grm.

It consists of crystalline plates; melting-point, 23°; boiling-point, 120°, under 12 mm. pressure.

The hydrazines are basic substances and yield crystalline salts with acids. They condense with aldehydes, ketones, and their derivatives, with the formation of hydrazones (cf. Exp. 188). In certain cases excess of the hydrazine acts as an oxidizing agent and osazones are formed (cf. Exp. 189).

The hydrazines possess strong reducing properties.

3. To determine the Concentration of a Phenylhydrazine Solution.

(i) By titration with standard iodine solution **(see p. 225).**

(ii) By boiling with Fehling's solution and measuring the volume of nitrogen evolved.*

$$C_6H_5 \cdot NH \cdot NH_2 + O \longrightarrow C_6H_6 + N_2 + H_2O.$$

200 c cm. of Fehling's solution (p. 311) is heated in the flask (fig. 82), and steam † blown through until all the air has been displaced. The phenylhydrazine solution is run in through the tap funnel, the stem of which is drawn out and bent. The funnel is then washed twice with hot water, care being taken that no air is introduced. After boiling for a few minutes the whole is decomposed, and the nitrogen evolved collected in a measuring tube. The tube is removed to a cylinder of cold water, and the volume, temperature, and pressure read off

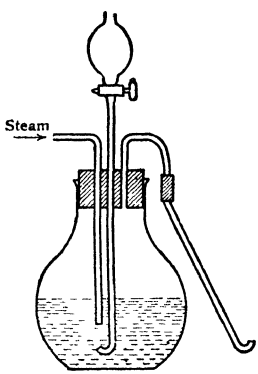


Fig 82

N.B.—A correction must be made for the pressure due to water and benzene vapour. The value of the pressure is as follows:—

Temperature...	15°	16°	17°	18°	19°	20°
Pressure	72·7	76·8	80·9	85·2	89·3	93·7 mm.

K. Estimation of the Diazo-Group in Aromatic Diazonium Salts and in Diazo-amino-Compounds

A given weight of the substance is heated with sulphuric acid and the volume of nitrogen measured. Every gram molecule of nitrogen evolved corresponds with an N_2 group in the original molecule. A somewhat rough method is that described under the velocity of decomposition of diazonium salts (Chap. XXXVI, D). The mixture is heated, then allowed to cool, and the increase in the gaseous volume measured. A more accurate method ‡ is to displace the air in the apparatus by carbon dioxide and to collect merely the nitrogen in some form of nitrometer. A stout glass tube, 10–12 cm.

* *Strache*, M. 1891, **12**, 524; 1892, **13**, 299; 1893, **14**, 270.

† Steam is used in order to avoid the bumping which occurs when the cuprous oxide is formed.

‡ *Mehner*, J. pr. 1901, [ii], **63**, 305.

long and 3 cm. diameter, is fitted as shown in fig. 83. A weighed quantity of the diazo-compound is placed in the tube, the stem of the dropping funnel is drawn out to a fine point and the stem and stopcock filled with freshly boiled water. The tube *a* is clamped and the apparatus evacuated by means of the water pump. Carbon dioxide is then led in through the three-way cock and the apparatus evacuated, and again filled with carbon dioxide. The operation is repeated, and then all the air will have been removed with the exception of the small amount in the rubber tube *a*. This is got rid of by opening the clamp and passing a stream of carbon dioxide through the apparatus. *a* is then attached to a nitrometer or eudiometer over potash, and the gas tested to make sure that it is free from air. Concentrated hydrochloric acid is run in from the dropping funnel, until the tube is about one-fifth full. The contents are rapidly heated to boiling, and then the gas left driven over by allowing water to enter from the funnel, and finally by passing a current of carbon dioxide

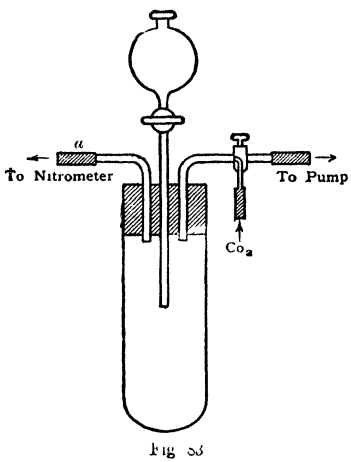


Fig. 83

XXI. ALDEHYDES AND KETONES
(S. B. 121–139, 421–427)

A. Aldehydes, $R\cdot C\lessdot^{O}_{H}$

1. Modes of Formation.—

Method I.—By the regulated oxidation of primary alcohols.

$$R\cdot CH_2OH + O \longrightarrow R\cdot C\lessdot^{O}_{H}$$

(*N.B.*—Secondary and tertiary alcohols do not yield aldehydes on oxidation.)

It is necessary to regulate the amount of oxidizing material somewhat carefully, as the aldehydes themselves are readily oxidized to carboxylic acids.

$$R\cdot C\begin{matrix}O\\H\end{matrix} + O \longrightarrow R\cdot COOH.$$

Experiment 171.—Preparation of acetaldehyde from ethyl alcohol

The reactions involved and the reacting proportions are represented in the following equations:—

$$Na_2Cr_2O_7 + 5H_2SO_4 \longrightarrow 2NaHSO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$3CH_3\cdot CH_2\cdot OH + 3O \longrightarrow 3CH_3\cdot CHO + 3H_2O.$$

To avoid further oxidation of the aldehyde an excess of the alcohol is used.

A round-bottomed flask of 1½ litre capacity, containing a mixture of 120 grm. of concentrated sulphuric acid and 200 grm. of water, is fitted with a cork carrying a dropping funnel and a delivery tube connected with a long condenser. The end of the condenser tube is fitted with an adapter which leads into a receiver surrounded by a freezing mixture of ice and salt

When the contents of the flask have been heated just to boiling, a mixture of a solution of 200 grm. of sodium dichromate in 200 grm. of water and 120 grm. of alcohol (rectified spirit) is added gradually through the tap funnel. Generally the heat developed by the reaction is sufficient to keep the liquid boiling without the aid of external heat, but if this is not so, ebullition is assisted by applying a small flame. The aldehyde formed during the reaction distils over into the receiver, mixed with some water, alcohol, and acetal. Care is taken that the reaction does not proceed too violently, as the aldehyde is extremely volatile, and a portion of the reaction product will then be lost After all the alcohol-bichromate mixture has been added the flask is heated for a short time on a sand tray, in order to drive over the remaining product. Altogether some 150 c.cm. of distillate are collected.

The aldehyde cannot be separated completely from the distillate by fractional distillation, and is therefore purified by conversion into a crystalline derivative, viz. aldehyde-ammonia ($CH_3\cdot CHO$, NH_3). From this the aldehyde can be regenerated by treatment with an acid.

For the preparation of aldehyde-ammonia the apparatus shown in fig. 84 is employed. The flask containing the distillate is attached to a sloping condenser (N.B. *Do not use rubber stoppers*) filled with water at a temperature of 30–35°. A tube leads from the condenser to the absorption vessels; these contain 50 c.cm. of dry ether (Exp. 31), and are cooled by ice. The contents of the flask are heated to boiling; alcohol and aqueous vapour condense in the condenser tube, while the aldehyde passes on and is absorbed by the ether.

The ethereal solution of aldehyde is now saturated with dry ammonia (prepared by gently heating some concentrated (0·880) ammonia solution, and leading the evolved gas through a lime-tower), care being taken that a *wide* tube is used Aldehyde-ammonia separates in the form of colourless crystals, and after standing for a short time the clear liquid is decanted from the crystals, which are filtered with the aid of the pump, washed with a little dry ether, and finally dried in a desiccator. Yield of aldehyde-ammonia, about 30 grm.

To prepare pure aldehyde, a portion of the aldehyde-ammonia is dissolved in an equal weight of water, and distilled in a small distilling flask with a mixture of 1½ part of concentrated sulphuric acid and 2 parts of water The receiver is well cooled in a freezing mixture of ice and salt To dehydrate the product it is redistilled over an equal bulk of granular calcium chloride. The pure aldehyde is a colourless liquid with a characteristic odour, boiling-point, 21°, $D^{0°}_{4°}$, 0·807; it is miscible in all proportions with water, alcohol, and ether.

Method II.—Heating a mixture of the calcium salt of the corresponding monobasic acid with calcium formate, *e.g.*:

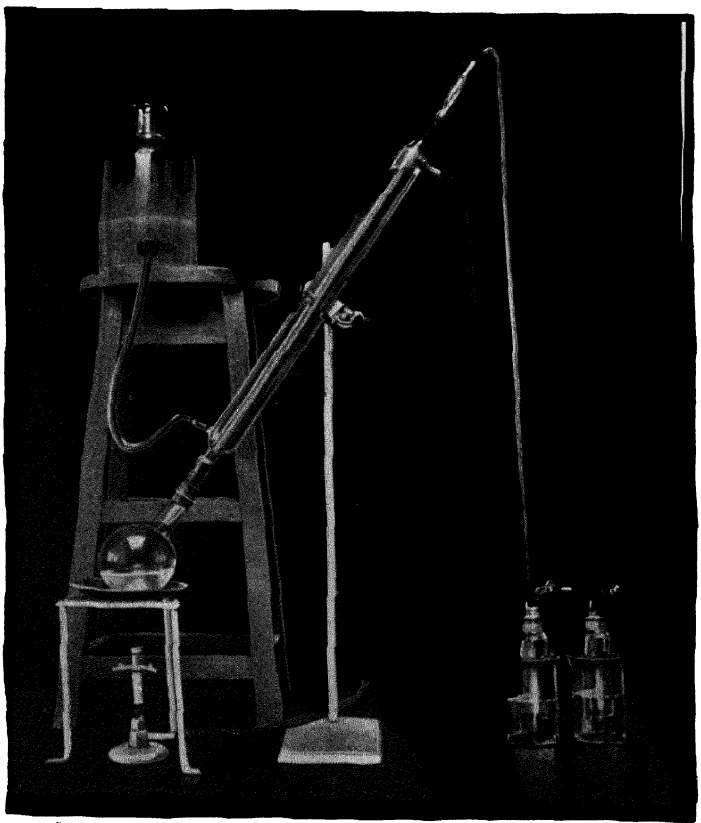
$$CH_3COOca + HCOOca = CaCO_3 + CH_3 \cdot CH{:}O \quad [ca = \tfrac{1}{2}Ca]$$

Experiment 172.—Preparation of acetaldehyde from calcium acetate and calcium formate.

Equal quantities of the two salts are well mixed and heated in a hard glass test tube. Acetaldehyde is evolved, which is detected by its odour. It is tested further by passing into Schiff's reagent (Exp. 178).

The product obtained by this method contains several impurities.

Method III.—By the hydrolysis of dihalogen substitution products of the hydrocarbons, in which the two halogen atoms



B 960

To face p. 214

Fig. 84.

are attached to the same terminal carbon atom, by superheating with water or boiling with milk of lime or calcium carbonate, *e.g.*:

$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} \longrightarrow C_6H_5CH(OH)_2 \longrightarrow \underset{\text{Benzaldehyde.}}{C_6H_5CH{:}O} + H_2O$$

In many cases they may be obtained from the corresponding monohalogen derivatives by a combined process of hydrolysis and oxidation. Cupric or plumbous nitrate is generally used for this purpose.

Experiment 173.—Preparation of benzaldehyde, $C_6H_5 \cdot CH{:}O$, from benzyl chloride.

$$C_6H_5 \cdot CH_2Cl \longrightarrow C_6H_5 \cdot CH_2 \cdot OH \xrightarrow{+O} C_6H_5 \cdot CH{:}O.$$

25 grm. of benzyl chloride (Exp. 39) are heated with a solution of 40 grm. of plumbous nitrate in 250 c.cm. of water in a reflux apparatus, until a test portion of the oily layer, after washing well with water, no longer gives the reaction for halogens (p 38), about five to six hours boiling will be necessary. Half the liquid is then distilled off, the benzaldehyde passing over with the steam and separating as an oil. The distillate is mixed with a concentrated solution of sodium bisulphite until after prolonged shaking the greater part of the oil has gone into solution. The additive compound of benzaldehyde with sodium bisulphite is formed; should crystals separate out, water is added until they are again dissolved. The solution is then separated from any oil remaining undissolved, and treated with solid sodium carbonate until it shows a strongly alkaline reaction. The mixture is then distilled with steam (fig. 10), and pure benzaldehyde which passes over is taken up with ether. The ethereal solution is dried, and after removal of the solvent the residue is distilled. Yield, 15 grm.

Benzaldehyde is a colourless highly refractive liquid, with a pleasant bitter-almond odour; it is sparingly soluble in water, but dissolves readily in alcohol and ether. Boiling-point, 179°; $D_{4°}^{15°}$, 1·050.

*Method IV.—Etard's reaction.** (S. B. 422.)

Aromatic aldehydes may be prepared directly from methyl derivatives of benzene. An additive compound of the hydro-

* *Bornemann*, B. 1884, 17, 1462.

carbon with chromyl chloride is first prepared, which is subsequently decomposed with water.

$$C_6H_5\cdot CH_3 + 2CrO_2Cl_2 = C_6H_5CH_3,(CrO_2Cl_2)_2$$
$$3C_6H_5CH_3(CrO_2Cl_2)_2 + 3H_2O = 3C_6H_5\cdot CHO + 4CrCl_3 + 2H_2CrO_4 + 4H_2O$$

Experiment 174. — Preparation of benzaldehyde from toluene.*

9 grm. of toluene (1 mol.) and 30 grm. of chromyl chloride † (less than 2 mol.) are separately dissolved in dry carbon disulphide to 15 per cent solutions. The toluene solution is placed in a 500 c.cm. flask fitted with a long reflux condenser, and the solution of chromyl chloride added gradually in quantities of from 10 to 15 c.cm at a time. Should no reaction occur at the first addition of chromyl chloride solution, the mixture is allowed to stand for some time before further addition Great heat is developed during the reaction, and the flask should be cooled by immersing in a bath of cold water. Under no condition should the temperature of the mixture rise above 47°. When all the reagent has been added, the mixture is allowed to stand for two hours. The double compound, which separates as a dark-coloured precipitate, is removed by means of a Buchner funnel and the pump, washed well with small amounts of dry carbon disulphide, and when dry is decomposed by adding, little by little, to excess of cold water contained in a large beaker The chromic acid formed is reduced by passing in sulphur dioxide gas, and the resulting product distilled with steam (fig. 10). The benzaldehyde which distils over is taken up with ether, the ethereal solution separated from the aqueous liquid, dried with calcium chloride, the ether removed, and the residue distilled. Yield, about 10 grm., *i e* 95 per cent of theory.

Method V.—Tiemann-Reimer Synthesis.‡ (S. B. 428.)

Hydroxy-aldehydes of the aromatic series are readily obtained from phenols by this method, which consists in condensing the phenol with chloroform in the presence of concentrated sodium hydroxide solution. A dichloro-derivative is

* As there is a possibility that the reaction may become very vigorous and the carbon disulphide boil over, it is advisable to carry out the preparation in a room in which flames are not allowed.

† For preparation see Chap. XXXIX.

‡ *Reimer* and *Tiemann*, B. 1876, 9, 423, 824.

probably first formed, but is immediately hydrolysed to the aldehyde (cf. Method III).

$$OH \cdot C_6H_4 \cdot H + Cl \cdot CHCl_2 \longrightarrow OH \cdot C_6H_4 \cdot CHCl_2 + HCl$$
$$OH \cdot C_6H_4 \cdot CHCl_2 + H_2O \longrightarrow OH \cdot C_6H_4 \cdot CHO + 2HCl.$$

The aldehydic group introduced takes up the *ortho*- and to some extent the *para*-position with respect to the hydroxyl group

Experiment 175.—Preparation of salicylaldehyde, $C_6H_4(OH) \cdot CHO$, from phenol, C_6H_5OH, and chloroform

40 grm of phenol are treated with a solution of 40 grm. of sodium hydroxide in 120 c.cm. of water in a litre flask fitted with a reflux condenser. The mixture is heated to a temperature of 50–60° by immersion in a hot-water bath, while 60 grm of chloroform are added gradually in small portions of 10 c.cm. At the beginning of the operation the yellow-coloured liquid changes to violet, and later assumes a deep-red colour After each addition of chloroform the flask is well shaken, and when all has been added the contents of the flask are boiled for half an hour to complete the reaction.

The excess of chloroform is then removed by heating on a water bath, and the residue is acidified with dilute hydrochloric or sulphuric acid A thick red oil separates, this is steam-distilled (fig 10), the distillation being continued as long as oily drops pass over. The yellow oily distillate contains phenol and salicylic acid in addition to salicylaldehyde It is extracted with ether, and the ethereal solution shaken up with a nearly saturated solution of sodium bisulphite (freshly prepared) The bisulphite additive compound (cf Exp 179) separates in the form of fine crystals, which are filtered off and decomposed by heating with dilute acid The product is extracted with ether, the ethereal solution washed with water and dried over calcium chloride The ether is removed and the aldehyde distilled. It is a colourless oil with pleasant odour. Boiling-point, 196°, $D^{15°}$, 1 172. Yield, 8–10 grm.

The mixture left in the flask after the steam distillation contains a small quantity of *p*-hydroxy-benzaldehyde, which is not volatile with steam. The mixture, which consists of a reddish-yellow liquid and a dark-red resinous substance, is filtered while still hot through a folded filter, and the filtrate when cold extracted with ether. The ethereal extract is dried

over calcium chloride and the solvent removed The residue is recrystallized from a little hot water, and forms colourless crystals, melting-point 116°. Yield, about 2 grm.

2. **Chemical Characteristics of Aldehydes.**

(*a*) The aldehydes show considerable chemical reactivity, thus, they are readily oxidized to the corresponding acids, *e.g*

$$CH_3 \cdot CH{:}O + O \longrightarrow CH_3 \cdot CO \cdot OH.$$

Consequently, they are good reducing agents, *e.g* they reduce alkaline solutions of silver salts and often alkaline cupric solutions (Fehling's solution, p 311)

Experiment 176.—Prepare an ammoniacal silver solution by taking 2 c.cm of dilute silver nitrate solution in a *clean* test tube, and adding dilute ammonia solution drop by drop, until the precipitate at first formed just redissolves (Excess of ammonia must be avoided.) Then add a few drops of acetaldehyde (or benzaldehyde), and after shaking warm the solution in a water bath Reduction takes place to metallic silver, which is deposited as a silver mirror on the sides of the tube. If the latter is not thoroughly clean, a black precipitate of the metal results.

Filter the solution, and test it for an acetate (or benzoate) (pp. 124 or 122)

Experiment 177 —A few drops of acetaldehyde are added to a little Fehling's solution and warmed gradually A reddish-yellow precipitate of cuprous oxide results.

Aromatic aldehydes do not give this reduction.

(*b*) A general reaction of aldehydes is their behaviour towards Schiff's reagent (a dilute solution of fuchsine decolorized by sulphurous acid)

Experiment 178 —A few drops of an aldehyde are added to about 5 c.cm of Schiff's reagent and the mixture well shaken. The red colour of the dye is restored

Additive Reactions —

(*c*) Aldehydes form additive compounds with many reagents.

1. Compounds with ammonia—aldehyde ammonias.

An example has been given in the preparation of acetaldehyde (Exp. 171) The compounds are generally crystalline substances which are soluble in water but insoluble in ether. Treated with acids, they regenerate the aldehyde. Benzaldehyde and other aromatic aldehydes do not form simple additive compounds with ammonia, but yield complex condensation products (cf. also Ketones, p. 223).

2. Aldehydes yield crystalline additive compounds with sodium bisulphite, $NaHSO_3$. For many years the additive compounds were regarded as the sodium salts of sulphonic acids, *e.g.* $CH_3 \cdot CH<^{OH}_{SO_3Na}$, but the readiness with which they are hydrolysed has led chemists to regard them as containing the S atom attached to oxygen and not directly to carbon, *e.g* $CH_3 \cdot CH<^{OH}_{O \cdot SO \cdot ONa}$. See Chap. XVI, B, II.

Experiment 179 —Make a fresh, almost saturated solution of sodium bisulphite in distilled water, and to about 5 c.cm of the solution add 1 c.cm. of benzaldehyde, and shake vigorously. A white crystalline additive compound separates. Filter off the crystals, and treat them with dilute acid; the aldehyde is regenerated.

The bisulphite compounds, like the aldehyde-ammonias, are largely employed in the separation of aldehydes from mixtures (cf Exps 173, 175)

3 The aldehydes also yield additive compounds with hydrogen cyanide, *e.g.*:

$$C_6H_5 \cdot CH{:}O + HCN = C_6H_5 \cdot CH<^{OH}_{CN}.$$

Mandelic nitrile.

(Cf. Exp 271.)

(*d*) **Polymerisation of Aldehydes.**

1. The aldehydes show a great tendency to polymerise.

Experiment 180.—A few drops of concentrated sulphuric acid are added to about 1 c.cm. of acetaldehyde. The mixture becomes hot, and on the addition of water an oil (paraldehyde, $(C_2H_4O)_3$, boiling-point 124°) separates

2. An alcoholic solution of potassium cyanide causes the polymerisation of aromatic aldehydes of the type of benzaldehyde with the production of a hydroxy-ketone (benzoin condensation).*—

$$C_6H_5CHO + O{:}CH \cdot C_6H_5 \rightarrow C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5.$$

Experiment 181.—Preparation of benzoin, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$, from benzaldehyde.†

20 grm. of pure benzaldehyde and a solution of 2 grm. of pure potassium cyanide (94–100 per cent) in 80 c.cm. of 50 per

* *Nef*, A. 1895, 287, 342; 1897, 298, 312.

† *Zinin*, A. 1840, 34, 187; *Zincke*, A. 1879, 198, 150, footnote.

cent alcohol are heated in a reflux apparatus for an hour on a water bath On allowing to cool, crystals of benzoin separate. These are filtered off, and the filtrate is again heated with another quantity of potassium cyanide; on cooling, a second yield of crystals is obtained The product is recrystallized from hot alcohol and obtained in the form of colourless needles, melting-point 137°. Yield, 90–95 per cent of theory.

It contains both a secondary alcohol grouping (cf. Chap. X) and a ketonic grouping (cf. Chap. XXI, B) It is readily oxidized to the α-diketone, benzil (Exp. 229), and yields condensation products with hydroxylamine, &c. (cf. Chap. XXII, A)

(*e*) **Action of Alkalis on Aldehydes**

Various aldehydes behave differently towards alkalis Acetaldehyde and several of its homologues are transformed into a reddish-brown aldehyde-resin, a substance insoluble in water but soluble in alcohol. The majority of the aliphatic aldehydes undergo the aldol condensation (S B, p. 131) The aromatic aldehydes are transformed by alkalis into a mixture of equivalent amounts of the corresponding alcohol and acid (see Exp 28).

The reactivity of the aldehydes is analogous to the reactivity of the olefines (Chap IX, B), and the reactions of the two groups of compounds are somewhat analogous, *e g* both are readily oxidized, both can be reduced, both form additive compounds, and both polymerise readily This similarity in chemical properties is due to a similarity in chemical constitution. The olefines contain a double bond between two carbon atoms, and the aldehydes a double bond between a carbon and an oxygen atom

$$CH_3 \cdot CH{:}CH_2 \text{ and } CH_3 \cdot CH{:}O.$$

B. Ketones (R·CO·R or R·CO·R′)

Modes of Formation.

Method I.—By the distillation of the dry calcium or barium salts of monobasic acids.

$$\begin{matrix} R\cdot COO \\ R\cdot COO \end{matrix}\!\!>\!Ca = CaCO_3 + R\cdot CO\cdot R.$$

Experiment 182.—Preparation of acetone, $CH_3 \cdot CO \cdot CH_3$, from calcium acetate.

100 grm. of dried calcium acetate are heated, by means of a large luminous flame kept in constant motion, in a retort attached to a long condenser. The distillate, which contains some tarry matter, is treated with an equal volume of water which dissolves the acetone, and then filtered through a fluted filter paper to remove insoluble matter The filtrate is allowed to stand for several hours over lumps of quicklime in a flask attached to a reflux condenser, and the acetone is then distilled off. It is further dried by standing over calcium chloride, and forms a colourless liquid with a peculiar odour, boiling-point, 56°, $D^{0°}$, 0 81. It is soluble in water, but may be salted out from its aqueous solutions, and is miscible in all proportions with alcohol and ether

Special Tests for Acetone.

1. Acetone gives the iodoform reaction (cf Exp 47).

2. A solution of acetone in sodium hydroxide gives a blue coloration of indigo when warmed with *o*-nitro-benzaldehyde.

Method II—Friedel and Crafts' Synthesis (S B. 345, 425.)

Friedel and Crafts' general reaction consists in condensing a benzene hydrocarbon with an alkyl or acyl halide in the presence of anhydrous aluminium chloride, hydrogen halide being evolved.

$$C_6H_5\ H + Cl\cdot R = HCl + C_6H_5\cdot R.$$

The reaction is useful for the preparation of hydrocarbons, especially of the triphenyl-methane series (Exp 254*a*). When an acyl chloride is used, the product is a ketone, *e g* .

$$C_6H_5\ H + Cl\cdot CO\cdot CH_3 = HCl + C_6H_5\cdot CO\cdot CH_3$$

The aluminium chloride first forms an additive compound with the acyl chloride (*e.g.* $CH_3\cdot COCl$, $AlCl_3$), which then reacts with the hydrocarbon producing hydrogen chloride and a compound, *e g.* $C_6H_5\cdot CO\cdot CH_3$, $AlCl_3$, and this, when decomposed by water, yields the ketone

Since the reaction takes place vigorously, it is advisable to dilute the reacting substances by solution in a suitable solvent. Generally carbon disulphide is used, but large excess of the reacting hydrocarbon may often be employed.

Experiment 183 —Preparation of benzophenone, $(C_6H_5)_2C{:}O$, from benzene and benzoyl chloride.

20 grm. of freshly prepared and finely divided aluminium chloride (Chap. XXXIX) are added gradually to a mixture

of pure benzene (20 grm.), benzoyl chloride (20 grm.) (Exp. 36), and carbon disulphide (100 grm), contained in a round-bottom flask attached to a reflux condenser. The flask is shaken during the addition of the metallic chloride, and is afterwards heated gently on a water or steam bath (no flame) until hydrogen chloride is no longer evolved (2–3 hours). The carbon disulphide is then distilled off, washed with water, dried, and recovered. The residue left after the removal of the carbon disulphide is cooled, and then poured gradually into ice cold water; concentrated hydrochloric acid is added (about 7 c cm), and the whole subjected to steam distillation in order to remove any benzene. The residue in the flask is extracted with ether when cold, the ethereal solution washed with dilute sodium hydroxide solution, then with water, is finally dried, and after removal of the ether is distilled. The ketone is a colourless liquid, boiling-point 297°, and solidifies to a crystalline mass, melting-point 48°. Yield, 20 grm.

If the benzoyl chloride is replaced by an equivalent quantity of acetyl chloride (Exp. 35), *acetophenone*, $C_6H_5 \cdot CO \cdot CH_3$, melting-point 20·5°, boiling-point 202°, is obtained

Experiment 184.—Preparation of aceto-mesitylene, $C_6H_2(CH_3)_3 \cdot CO \cdot CH_3$, from mesitylene and acetyl chloride

A mixture of mesitylene (*s*-trimethylbenzene) (25 grm.), carbon disulphide (75 grm), and freshly distilled acetyl chloride (30 grm.) is placed in a flask provided with a reflux condenser, and 33 grm of aluminium chloride are added gradually as in Exp 183. The mixture is finally warmed for 15 minutes and the ketone isolated as in Exp 183, the only difference being that the ketone will distil over with the steam. It is a colourless liquid, boiling-point 237°. Yield, 25 grm.

N B.—If a large excess of acetyl chloride is used and the temperature kept low, two acetyl groups can be introduced, *e.g.* use 5 grm. of hydrocarbon, 12 5 of acetyl chloride, 75 of carbon disulphide, and 30 of aluminium chloride, and keep cold. The diketone, $C_6H(CH_3)_3(CO \cdot CH_3)_2$, crystallizes from ligroin in colourless crystals, melting-point 46°.* It is in exceptional cases only that two acyl groups can be thus introduced.

General Chemical Characteristics of Ketones.

(*a*) The ketones are not oxidized as readily as the aldehydes,

* *V. Meyer*, B. 1896, 29, 1413.

and do not reduce alkaline silver and cupric solutions. Oxidizing agents, such as potassium bichromate and dilute sulphuric acid, slowly convert them into acids or ketones possessing a smaller number of carbon atoms to the molecule.

Experiment 185.—Boil 5 c.cm. of acetone for about an hour in a reflux apparatus with dilute sulphuric acid and potassium bichromate solution. Distil the product and test the distillate for acetic acid (p. 124).

$$CH_3 \cdot CO \cdot CH_3 + 4O \rightarrow CH_3CO \cdot OH + CO_2 + H_2O.$$

Only a few ketones restore the colour to Schiff's reagent.

(*b*) **Additive Reactions.**—When reduced they add on hydrogen and yield secondary alcohols.

The ketones do not yield crystalline compounds with ammonia of the type of aldehyde-ammonia. The reaction is more complicated, two or more molecules of the ketone combining with one of ammonia, with elimination of water.

The simpler ketones, *e.g.* dimethyl ketone and methyl-ethyl ketone, yield crystalline compounds with sodium bisulphite (cf. Aldehydes)

Experiment 186.—Shake about 1 c.cm. of acetone with 5 c.cm. of a nearly saturated solution of sodium bisulphite. A crystalline derivative settles out. Filter off and warm the crystalline compound with dilute sodium carbonate solution. Acetone is regenerated, and can be detected by its odour.

Ketones in which the carbonyl group is directly attached to a benzene ring (*e.g.* acetophenone) do not yield bisulphite compounds.

The ketones yield additive derivatives with hydrogen cyanide. They do not polymerise like the aldehydes, but yield an important series of condensation derivatives (see Chap. XXVIII).

C. Recognition of Aldehydes and Ketones

1. The majority of aldehydes and ketones are colourless liquids; a few only are solid. The less complex members are soluble in water, all dissolve in alcohol and ether. All the aldehydes and the ketones with the exception of the more complex ones dissolve in sodium bisulphite solution (p. 219), and if the solution is concentrated, crystals of the additive compound are deposited after some time.

2. **Colour Test for both Aldehydes and Ketones.**

A few c.cm. of an aqueous or alcoholic solution of a ketone or aldehyde mixed with a few drops of a 10 per cent aqueous solution of *m*-phenylenediamine hydrochloride produce in the course of a few minutes a bright-green fluorescence, which reaches its maximum intensity at the end of two hours. The coloration is destroyed by free alkalis

All aldehydes give the coloration, but mixed ketones and ketonic acids do not.

3. **Tollens' Aldehyde Test.***

Two separate solutions are prepared, the one containing 3 grm. of silver nitrate in 30 grm. of water, and the other 3 grm. of sodium hydroxide in 30 grm of water. These can be bottled and used when required In making the test, equal volumes of the two solutions are mixed in a *perfectly clean* test tube, ammonia solution (sp. gr 0 923) is added drop by drop until the precipitate of silver oxide just dissolves. The addition of this ammoniacal solution to a dilute aldehyde solution produces a silver mirror in the cold.

N.B.—*Do not heat the solution, as explosive fulminates are then formed.*

4. **Schiff's Reagent** (Exp. 178).

Most aldehydes restore the colour to a magenta solution which has been decolorized by sulphurous acid. A few ketones give the same reaction when present in large quantities.

5. Aromatic aldehydes form condensation products (Schiff's bases, Exp. 233) with aniline.

6. The aliphatic aldehydes, when warmed with alkali, turn yellow, and ultimately form a brown resin. Benzaldehyde and its substitution products when shaken with concentrated potassium hydroxide solution yield the corresponding acids and alcohols (Exp. 28).

7. To determine the specific aldehyde or ketone present, the physical constants of the original compound and of certain crystalline derivatives must be determined. The simplest crystalline compounds to prepare are usually the phenylhydrazone (Exp. 188), and the semicarbazone (Exps. 190, 191, 192). The oximes are frequently oily and readily soluble in water.

Further Reactions for Specific Aldehydes and Ketones.

Formaldehyde.—When boiled with a small amount of β-

* B. 1881, 14, 1950; 1882, 15, 1635, 1828.

naphthol, dilute alcohol (1:2), and a few drops of concentrated hydrochloric acid, a formaldehyde solution (10 per cent) yields colourless needles of methylene-di-β-naphthol; melting-point, after crystallizing from dilute alcohol, 189–192° (decomp.). The polymeric forms give the same reactions.

Acetone gives the iodoform reaction (p. 102).

All the aldehydes are readily oxidized by alkaline permanganate to the corresponding acids, and the melting-points of these can be determined

Estimation of the Carbonyl Group by means of Phenylhydrazine Solution.*—A given weight of the carbonyl compound is mixed with an excess of dilute aqueous phenylhydrazine solution,† and kept for some time, after which an excess of 0·1 N iodine potassium iodide solution is added. The iodine reacts with the free phenylhydrazine, but not with the hydrazone, according to the equation.

$$C_6H_5NH \cdot NH_2 + 2I_2 \longrightarrow 3HI + N_2 + C_6H_5I.$$

The excess of iodine can then be titrated with standard sulphurous acid, using starch as indicator.

The carbonyl group can also be estimated by means of hydroxylamine Free hydroxylamine is prepared just before use by adding an equivalent of barium hydroxide solution to hydroxylamine sulphate. 0·1 N solutions of the carbonyl derivative and of hydroxylamine in 50 per cent alcohol are used, and after the oxime formation is completed the excess of hydroxylamine is titrated with standard acid, using methyl orange as indicator.

XXII. OXIMES, PHENYLHYDRAZONES, AND SEMICARBAZONES

The aldehydes and ketones are extremely reactive, and enter into a large number of condensations, especially with compounds containing two atoms of hydrogen attached to a carbon or nitrogen atom. The reaction with hydroxylamine, $H_2N \cdot OH$, phenylhydrazine, $C_6H_5NH \cdot NH_2$, and semicarbazide,

* *E. v. Meyer*, J. pr. 1887 [2], **36**, 115. † The base must be pure.

$NH_2 \cdot CO \cdot NH \cdot NH_2$, are especially interesting. These are all of the type—

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C\!:\, O + H_2\, NX \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C\!:\!NX + H_2O.$$

As the derivatives so formed are usually crystalline substances which can be readily purified, they are of use for the characterization of the different aldehydes and ketones.

A. Condensation with Hydroxylamine; Formation of Oximes *

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C\!:\!O + H_2N \cdot OH \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C\!:\!N \cdot OH + H_2O.$$

The carbonyl group in both aldehydes and ketones readily condenses with hydroxylamine, with the formation of aldoximes and ketoximes respectively. The reagent is generally used in the form of its hydrochloride, $HO \cdot NH_2$, HCl. The free base is usually liberated by the addition of the theoretical amount of potassium hydroxide. The conditions best adapted for the preparation of an oxime vary with the specific aldehyde or ketone; sometimes the hydrochloride reacts, and in other cases a large excess of alkali is used.

Experiment 187.—Preparation of an oxime

(*a*) **Acetophenone oxime:**†

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!C\!:\!O + H_2N \cdot OH, HCl + KOH \longrightarrow \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!C\!:\!N \cdot OH + KCl + 2H_2O.$$

8 grm of acetophenone (1 mol.) are added to a solution of 5 grm. of hydroxylamine hydrochloride (1 mol.) in 10 c.cm. of water. 3 grm. of potassium hydroxide (less than 1 mol.) dissolved in 5 c.cm. of water are added, and the mixture warmed, hot alcohol being gradually added until the solution becomes clear when shaken. The mixture is heated in a reflux apparatus on a boiling water bath for two to three hours, and then poured into 100 c.cm. of water. The oxime

* *V. Meyer* and *Janny*, B. 1882, **15**, 1324.
† *Janny*, B. 1882, **15**, 2781.

separates, and is extracted with ether, the ethereal solution dried, and the ether removed. The residue crystallizes from a little petroleum ether in colourless needles, melting-point 59°. Yield, 8 grm.

(*b*) **Benzophenone oxime**, $(C_6H_5)_2C{:}N{\cdot}OH$.* Cold solutions of 1·5 grm. hydroxylamine hydrochloride in water (5 c.cm.) and of 3·5 grm. of potassium hydroxide in water (6 c.cm.) are added to a solution of 2 grm of benzophenone (Exp. 183) in alcohol (15 c.cm.). During the addition the mixture is kept cool, and is ultimately heated for two hours on the water bath. The solution is then poured into water (50 c.cm.), filtered from any unaltered ketone, and the filtrate made faintly acid by the addition of dilute sulphuric acid. The precipitated oxime crystallizes from alcohol in colourless crystals, melting-point 140°.

Aldoximes, and the ketoximes derived from unsymmetrical ketones, may exist in two stereoisomeric forms (S. B. 138–139) represented by the formulæ—

$$\begin{array}{ccc} R{\cdot}C{\cdot}R' & \text{and} & R{-}C{-}R' \\ \ddot{N}{-}OH & & HO{-}\ddot{N} \end{array}$$

Cf. Chap. XXXIII, B.

B Condensation with Phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$; Preparation of Phenylhydrazones and Phenylosazones

I. Phenylhydrazones.

Most ketones and aldehydes react with hydrazine and its derivatives, yielding hydrazones. Phenylhydrazine is the common reagent (see preparation, Exp. 170), but *p*-bromophenylhydrazine, *as*-diphenylhydrazine and methyl-phenylhydrazine are also used. The reaction is of the type—

$$C_6H_5CH{:}O + H_2N{\cdot}NH{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O.$$

As phenylhydrazine when kept turns brown owing to oxidation, it is often better to use a solution obtained by dissolving phenylhydrazine hydrochloride (1 part) and crystallized sodium

* *Gattermann.*

acetate (1·5 part) in water (10 parts). On the addition of the aldehyde or ketone a precipitate of the phenylhydrazone is obtained.

Experiment 188. — Preparation of benzylidine-phenylhydrazone from benzaldehyde.*

1 c.cm. of phenylhydrazine is shaken with the same volume of 50 per cent acetic acid, 5 c.cm. of water are added, and the mixture shaken until a clear solution is obtained. 0 5 c.cm. of benzaldehyde are added, and the mixture is gently warmed and vigorously shaken. After standing for a short time, the yellow flocculent precipitate which settles out is filtered, washed with a small amount of dilute acetic acid, and dried on a porous plate It crystallizes from dilute alcohol in prisms, melting-point 157°.

II. **Phenylosazones**

1:2-diketones, *e.g.* $CH_3 \cdot CO \cdot CO \cdot CH_3$, and 1:2-keto-aldehydes, *e.g.* $CH_3 \cdot CH_2 \cdot CO \cdot CHO$, can react with excess of phenylhydrazine, so that two $:N \cdot NH \cdot C_6H_5$ residues are introduced, and compounds containing the grouping:

$$—C:N \cdot NH \cdot C_6H_5$$
$$—\dot{C}:N \cdot NH \cdot C_6H_5$$

are obtained. Such compounds are termed phenylosazones, and, like the hydrazones, crystallize well and have definite melting-points.

Hydroxy-aldehydes and hydroxy-ketones, which contain the hydroxyl group in the α-position with respect to the carbonyl group, also yield osazones in addition to hydrazones. Many of the simpler sugars, *e.g.* *d*-glucose and *d*-fructose, &c, yield osazones of this type. The osazone is produced as the result of three distinct reactions (S. B. 301–302)—

1. The formation of the phenylhydrazone.
2. The oxidation of the α-$>$CHOH group to a $:C:O$ group at the expense of the excess of phenylhydrazine.
3. The introduction of a second hydrazino-group by condensation of this carbonyl group with a third molecule of the hydrazine.

The osazones derived from the sugars are used largely for their identification.

Experiment 189. — Preparation of phenylglucosazone.

* *E. Fischer*, A. 1878, 190, 184.

$CH_2OH \cdot (CHOH)_3 \cdot C(:N \cdot NH \cdot C_6H_5) \cdot CH:N \cdot NH \cdot C_6H_5$, **from** *d*-**glucose**,* $CH_2OH \cdot (CHOH)_3 \cdot CHOH \cdot CHO$.

2 grm. of phenylhydrazine are treated with 2 c.cm. of 50 per cent acetic acid and 10 c.cm of water, and the mixture shaken until a clear solution is obtained.† A solution of 1 grm. of glucose in 5 c.cm. of water is then added, and the mixture warmed on a water bath for an hour. Yellow crystals of the phenylosazone settle out, these are filtered off and washed with a little dilute acetic acid. The substance is further purified by dissolving in a little hot pyridine with addition of hot alcohol and a little water, from which it is deposited as yellow crystals, melting-point 205°.

The same osazone is obtained from fructose and *d*-mannose. Osazones of other sugars are prepared in a similar manner.

C. Condensation with Semicarbazide; Formation of Semicarbazones¶

Semicarbazide, $NH_2 \cdot CO \cdot NH \cdot NH_2$, condenses readily with compounds containing the carbonyl grouping with the formation of semicarbazones:

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C:O + H_2\,N \cdot NH \cdot CO \cdot NH_2 \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C:N \cdot NH \cdot CO \cdot NH_2 + H_2O$$

The reagent is generally used in the form of its hydrochloride. This is dissolved in water and mixed with an excess of concentrated sodium acetate solution. The aldehyde or ketone is then added, with sufficient alcohol to render the solution clear.

Experiment 190.—Preparation of acetone semicarbazone, $(CH_3)_2 \cdot C:N \cdot NH \cdot CO \cdot NH_2$.

0·5 grm. of semicarbazide hydrochloride is dissolved in 2 c.cm. of a strong solution of sodium acetate and 1 c.cm. of acetone added. The mixture is shaken well, and allowed to stand for several hours. The condensation product crystallizes in the form of needles, and is recrystallized from a small quantity of alcohol. Melting-point, 187° (with decomposition).

* *E. Fischer*, B. 1884, **17**, 579; 1887, **20**, 821.

† A solution of the hydrochloride (2 grm.) of the base and sodium acetate (3 grm.) in water (15 c.cm.) may be substituted for the above solution.

¶ *Thiele* and *Stange*, A. 1894, **283**, 1.

Experiment 191.—Preparation of benzaldehyde semicarbazone,* $C_6H_5 \diagdown H \diagup C{:}N \cdot NH \cdot CO \cdot NH_2$.

A few drops of benzaldehyde are shaken with a solution of 0·5 grm. of semicarbazide hydrochloride in water. A complete separation of the condensation product occurs. Melting-point, 214° (decomp.).

Experiment 192.—Preparation of aceto-acetic ester semicarbazone.

$$COOC_2H_5 \cdot CH_2 \diagdown CH_3 \diagup C{:}\ O + H_2\ N \cdot NH \cdot CO \cdot NH_2$$
$$\rightarrow COOC_2H_5 \cdot CH_2 \diagdown CH_3 \diagup C{:}N \cdot NH \cdot CO \cdot NH_2 + H_2O.$$

1 grm. of semicarbazide hydrochloride and 1 5 grm of sodium acetate crystals are dissolved in the smallest possible quantity of water. 1 grm. of aceto-acetic ester (cf. Exp 198) is added, and sufficient alcohol to dissolve the ester completely. The mixture is warmed gently, then shaken vigorously and allowed to stand for some time The semicarbazone separates in the form of white crystalline needles, which are filtered off and recrystallized from ether. Melting-point, 129°

Diorthosubstituted ketones in many cases do not yield oximes, phenyl-hydrazones,† &c. (S B. 448).

The oximino, :N·OH, phenylhydrazino, :N·NHPh, and semicarbazino, :N·NH·CO·NH_2, groups can be removed from these condensation products, and the aldehyde or ketone regenerated by means of the following reactions —

(*a*) Boiling with 30 per cent sulphuric acid; (*b*) osazones and hydrazones derived from sugars are decomposed when a boiling aqueous solution of the compound is shaken with benzaldehyde.‡

* *Thiele*, B 1894, 27, 32.

† *Baum*, B. 1895, 28, 3209; *V. Meyer*, B. 1896, 29, 830, 836.

‡ *Fischer* and *Armstrong*, B. 1902, 35, 3141; *Herzfeld*, B. 1895, 28, 442

XXIII. QUINONES. (S. B. 428–433.)

Quinones are compounds derived from aromatic hydrocarbons and their derivatives by the replacement of two atoms of hydrogen by two of oxygen, *e.g.* $C_6H_4O_2$. These are divided into para-quinones and ortho-quinones, the oxygen atoms being in the para- and ortho- positions in the respective groups.

Modes of Formation —

Method I.—Para-quinones are readily obtained by the oxidation of many aniline and phenol derivatives belonging to the para-series, or of the amino-compounds themselves, *e.g.*:

$$C_6H_5NH_2 \longrightarrow C_6H_4\begin{matrix}O\,(1)\\ \diagup\!\diagdown\\ O\,(4)\end{matrix}$$

$$(1)\,CH_3\cdot C_6H_4\cdot NH_2\,(2) \longrightarrow (1)\,CH_3\cdot C_6H_3\begin{matrix}O\,(2)\\ \diagup\!\diagdown\\ O\,(5)\end{matrix}.$$

Experiment 193 — Preparation of *p*-benzoquinone, $C_6H_4\begin{matrix}O\,(1)\\ \diagup\!\diagdown\\ O\,(4)\end{matrix}$, from aniline.*

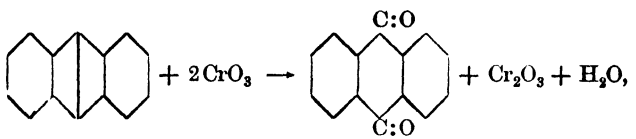
A solution of 20 grm. of aniline in a mixture of water (600 grm.) and concentrated sulphuric acid (160 grm.) is placed in a stout beaker immersed in ice-cold water, and is kept automatically agitated by means of a stirrer worked by a water turbine During the course of an hour 20 grm. of finely powdered potassium dichromate are added in portions of about 1 grm at a time, care being taken that the temperature does not rise above 10°. An even better method is to add a solution of 20 grm of sodium dichromate in 100 c.cm of water from a dropping funnel. In either case the mixture is left in a cool spot overnight, and then a further quantity of potassium dichromate (33 grm), or a solution of sodium dichromate (40 grm. in 200 c.cm. of water), added under conditions similar to the above. After four or five hours the mass extracted three times with ether, the ethereal solution dried with calcium chloride, and the ether removed in the usual manner. The crude quinone is purified by distillation in steam, or by sublimation, and forms orange-yellow needles with a characteristic pungent odour. Melting-point, 116°. Yield, 19 grm., *i.e.* 82 per cent.

Experiment 194.—Preparation of toluquinone, $CH_3\ C_6H_3O_2$ [CH_3:O:O = 1:2:5], from *o*-toluidine.

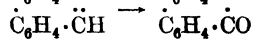
* *Schniter*, B. 1887, 20, 2289.

Similar to previous preparation, except that *o*-toluidine is substituted for aniline. Yield, 19 grm.; melting-point, 67°.

Hydrocarbons with condensed benzene nuclei (S. B. 492) are in many cases readily oxidized to the corresponding quinones, thus anthracene to anthraquinone (S. B. 506)—



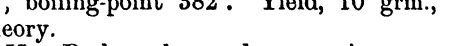
and phenanthrene to phenanthraquinone (S. B 510)—



Experiment 195.—Oxidation of anthracene to anthraquinone.*

A solution of 20 grm of chromic anhydride (Chap. XXXIX) in 10 c.cm. of water and 90 c.cm. of glacial acetic acid is added very gradually through a dropping funnel to a boiling solution of 10 grm. of anthracene in 120 c.cm. of glacial acetic acid contained in a round-bottomed flask fitted with a reflux condenser, the mixture being meanwhile kept in vigorous ebullition When the addition, which should take about an hour, is completed, the mixture, which is of a deep green colour, is allowed to cool, and then poured into a large excess of cold water The anthraquinone separates as a dark powder, which is filtered off on a porcelain funnel, washed with dilute alkali and water, and dried on a porous plate It is purified by sublimation (fig. 19), and forms yellow needles, melting-point 285°, boiling-point 382°. Yield, 10 grm., *i.e.* 80 per cent of theory.

Method II.—Both ortho- and para-quinones may be prepared by the oxidation of the corresponding dihydroxy-compounds. Thus *o*-benzoquinone is obtained by oxidizing an ethereal solution of catechol with silver oxide.†



p-Quinones are readily obtained from *p*-dihydroxy-deriva

* *Graebe* and *Liebermann*, A. Sup. 1870, 7, 285.

† *Willstätter* and *Pfannenstiel*, B. 1904, 37, 4744; 1908, 41, 2580.

tives of benzene and its homologues by oxidation with ordinary oxidizing agents, *e.g.* quinone from quinol (p. 171).

Experiment 196.—Oxidation of catechol, $C_6H_4(OH)_2$ (1:2), to ortho-benzoquinone.

A solution of 2·5 grm. of catechol in 250 c.cm. of pure *dry* ether is treated with 10·5 grm. of freshly precipitated silver oxide, which has been washed well with water, acetone, and dry ether. 8 grm. of anhydrous sodium sulphate are added, and the mixture shaken in a shaking machine for an hour. The silver salt of catechol is formed, and decomposes quickly with separation of the metal. The product is filtered, and the ethereal solution when evaporated deposits deep-red transparent crystalline plates.

Ortho-quinone has no definite melting-point, but begins to decompose between 60° and 70°. It is soluble in hot ether and benzene, and can be recrystallized from these solvents. When kept for any length of time it decomposes.

General Characteristics of Quinones

The quinones as a group are characterized by their yellow (or red) colour, and by the ease with which they are reduced to the corresponding dihydric phenols (cf. Exp. 122).

They form mono- and di-oximes (cf. Exp. 187), and readily form additive compounds with bromine, *e.g.* $C_6H_4O_2 \cdot Br_2$, and $C_6H_4O_2 \cdot Br_4$. They also form additive products with phenols, *e.g.* quinhydrone, $C_6H_4O_2$, $C_6H_4(OH)_2$, the intermediate compound between hydroquinone and quinone. This compound is precipitated as an intermediate product in the reduction of quinone or the oxidation of hydroquinone (cf. Exp 122).

Experiment 197.—Preparation of pheno-quinone, $2C_6H_5OH$, $C_6H_4O_2$, from phenol and quinone *

2 molecular proportions of phenol and 1 of quinone are dissolved in separate amounts of hot ligroin and the warm solutions mixed. On cooling, brilliant deep-red crystals of the additive compound separate. The compound has melting-point 71°, and is decomposed into its components by both acids and alkalis.

* *Nietzki*, A. 1882, 215, 134.

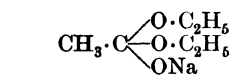
XXIV CLAISEN'S CONDENSATION; ETHYL ACETOACETATE: ITS REACTIONS AND CONDENSATIONS. (S. B. 224, 226–230.)

A. Claisen's Condensation *

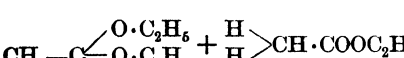
The condensation of two molecules of an ester (*e g.* ethyl acetate, Exp. 198), or of two molecules of different esters (Exp. 201), or of one molecule of an ester with one molecule of a ketone (Exp. 202), under the influence of sodium or sodium ethoxide, is termed Claisen's reaction, and is one of the best methods for preparing β-ketonic esters and β-diketones.

Experiment 198. — Preparation of ethyl acetoacetate, $CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$, from ethyl acetate and sodium

According to Claisen, the ethyl acetate is first converted by sodium ethoxide into the additive compound—



which then reacts with another molecule of ethyl acetate—



$$= CH_3 \cdot C(ONa):CH \cdot COOC_2H_5 + 2C_2H_5OH$$

The sodium derivative when treated with acetic acid yields the corresponding hydroxy compound, but this undergoes immediate transformation into the ketonic ester—

$$CH_3 \cdot C(\cdot OH):CH \cdot COOC_2H_5 \longrightarrow CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5.$$

For the purpose of the preparation the ethyl acetate must be carefully purified and freed from traces of acetic acid and water, and *most of* the alcohol. The latter must not be completely removed, for then the reaction proceeds very slowly.

Purification of Ethyl Acetate.†

* B. 1905, 38, 709.

† *Inglis* and *Knight* (P. 1907, 23, 198) recommend the following method of purification: The ester is dried over anhydrous potassium carbonate and then treated with phosphoric anhydride (10 grm for 100 grm. of ester), and boiled in a reflux apparatus for ½ hour. It is distilled off, using a

The ester purified as described in Exp. 74 reacts too vigorously with sodium, and gives a poor yield of the product. It is therefore allowed to stand for a day over freshly heated granular calcium chloride in a well-stoppered bottle, filtered into a dry distilling flask and redistilled, care being taken that all parts of the apparatus are perfectly dry.

30 grm. of *clean* sodium are cut into thin strips, or better, pressed into wire by means of a sodium press (fig 92), and introduced into a clean, dry, round-bottomed flask. The latter is attached to a long reflux condenser inclined obliquely, and fixed on a water bath. 300 grm. of the purified ethyl acetate are introduced through the condenser tube, which is then fitted with a drying tube, and after some 15 minutes the water bath is gradually warmed, the temperature being regulated so that gentle ebullition takes place within the flask The heating is continued for 3 hours, or until all the sodium is dissolved, when a mixture of 100 grm of glacial acetic acid with an equal quantity of water is added gradually until the contents of the flask show an acid reaction. If any solid is deposited, it is redissolved by vigorously shaking the flask. The liquid is then poured into a separating funnel containing an equal volume of saturated common salt solution, the mixture shaken, and the lower aqueous layer removed. The upper layer, consisting of ethyl acetate and ethyl acetoacetate, is fractionally distilled. For this purpose the whole is placed in a large distilling flask, one or two pieces of porous pot are added, and the flask heated in a rapidly boiling water bath until the thermometer indicates a temperature of 90–95°, when the residue in the flask is subjected to distillation under diminished pressure (fig. 9). Small amounts of impurities first pass over,

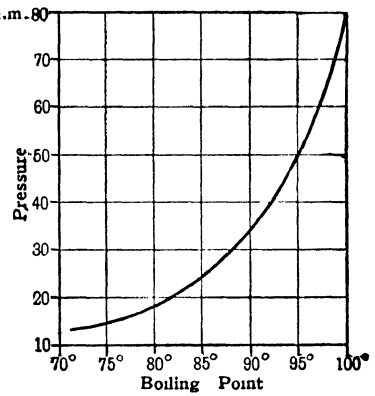


Fig 85

fractionating column, the portion boiling between 76·7° and 77·2° (corr.) being collected. This process gives an approximately pure substance which gives good yields of ethyl acetoacetate.

and when the temperature rises to the value indicated by the curve for the given pressure (fig 85), the receiver is changed, and the acetoacetic ester collected. Should a large amount of liquid distil over before the correct temperature for the given pressure is attained, the first fraction is redistilled and a further yield of the ester thereby obtained. Yield, 45–50 grm.

N.B.—The yield is considerably lowered if the whole experiment is not completed in one day.

The ester is a colourless mobile liquid with a pleasant fruity odour. Boiling-point (at 760 mm.) 181°, but it undergoes slight decomposition under these conditions; it is very sparingly soluble in water, but dissolves in alcohol and ether

Chemical Reactions of Ethyl Acetoacetate

Hydrolysis. — Under varying conditions the ester yields different products of hydrolysis. With dilute alkalis in the cold, the process is normal:

$$CH_3\cdot CO\cdot CH_2\cdot COOEt + KOH \longrightarrow CH_3\cdot CO\cdot CH_2\cdot COOK + EtOH,$$

but it is impossible to isolate the pure acid, as it decomposes rapidly into acetone and carbon dioxide.

Ketonic Hydrolysis. — When warmed with dilute acids or alkalis (baryta water is generally used), the ester decomposes, yielding acetone and ethyl alcohol:

$$\underset{H}{CH_3\cdot CO\cdot CH_2\cdot COO}\ \underset{OH}{C_2H_5} = CH_3\cdot CO\cdot CH_3 + CO_2 + C_2H_5OH.$$

Experiment 199.—Heat 5 grm. of ethyl acetoacetate in a reflux apparatus with 100 c.c.m. of baryta water (saturated solution) for an hour. Distil the product, and test the distillate for acetone (Exp 182) and ethyl alcohol (p. 102).

See also Exps. 205 and 207.

Acid Hydrolysis.—With concentrated alkalis (concentrated alcoholic potash is generally used) the ester decomposes, yielding an acetate and alcohol:

$$\underset{KO\,H}{CH_3\cdot CO\cdot CH_2\cdot COO}\ \underset{K\,OH}{C_2H_5} = 2CH_3COOK + C_2H_5OH.$$

Experiment 200.—Warm 5 grm. of the ester with 20 c.c.m. of concentrated alcoholic potash for a few minutes. Distil off the alcohol, neutralize the contents of the flask with hydrochloric acid, and test for an acetate (p. 124).

Acetoacetic ester gives the reactions characteristic of carbonyl compounds (Chap. XXII). For the preparation of its semicarbazone and phenylhydrazone see Exps 192 and 210.

The aqueous solution of the ester gives a reddish-violet coloration with ferric chloride, usually attributed to the presence of the hydroxy-group.

Other examples of Claisen's condensation

Experiment 201. — Preparation of oxal - acetic ester,* $CO_2Et \cdot CO \cdot CH_2 \cdot CO_2Et$.

$$CO_2Et \cdot CO_2Et + EtONa \longrightarrow CO_2Et \cdot C\langle^{ONa}_{(OEt)_2}$$

$$CO_2Et \cdot C\langle^{ONa}_{(OEt)_2} + H_2CH \cdot CO_2Et \longrightarrow 2EtOH + CO_2Et \cdot C(ONa):CH \cdot CO_2Et$$

$$CO_2Et \cdot C(ONa):CH \cdot CO_2Et \longrightarrow CO_2Et \cdot CO \cdot CH_2 \cdot CO_2Et.$$

2·3 grm. of sodium wire are placed in a flask and covered with 60 c.cm. of anhydrous ether. 14·6 grm. of pure ethyl oxalate (1 mol.) are added, and then 8·8 grm. of pure ethyl acetate (1 mol.) are gradually introduced. The mixture is warmed gently on a water bath in a reflux apparatus until the sodium completely dissolves, care being taken to prevent overheating On standing for several hours the product solidifies to a yellow crystalline mass, which is washed several times with dry ether. The solid product is the sodio-derivative of oxal-acetic ester, this is decomposed with dilute sulphuric acid, the flask being kept well cooled during the process. The oily ester which separates is extracted with ether, the ethereal extract washed with dilute sodium hydroxide solution, and filtered through a dry filter paper in order to remove water as much as possible. It is then fractionated under diminished pressure, the pure ester distilling over at 131–132°, under 24 mm. pressure. Yield, 70–80 per cent of theory.

It is a colourless liquid which decomposes during distillation under ordinary pressure. $D_4^{23.5°}$, 1·159.

The ester undergoes the *acid* hydrolysis into oxalic and acetic acids when warmed with concentrated alcoholic potash, and reacts with phenylhydrazine yielding a hydrazone.

The alcoholic solution of the ester gives an intense dark red coloration with ferric chloride.

* *Widicenus*, A. 1888, **246**, **317**.

Experiment 202.—Preparation of benzoylacetone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$, from ethyl acetate and acetophenone.*

$$CH_3 \cdot COOEt + NaOEt \longrightarrow CH_3C\begin{matrix}(OEt)_2\\ ONa\end{matrix}$$

$$CH_3C\begin{matrix}(OEt)_2\\ ONa\end{matrix} + H_2CH \cdot CO \cdot C_6H_5 \longrightarrow CH_3C(ONa):CH \cdot CO \cdot C_6H_5 + 2EtOH.$$

Sodium ethoxide free from alcohol (1 mol., cf. Chap. XXXIX, is treated with pure ethyl acetate (2 mol.), and the mixture cooled with ice. Acetophenone (1 mol.) is added gradually, and the mixture solidifies to a finely crystalline yellow mass of the sodio-derivative of benzoylacetone. This is washed with ether, then dissolved in water and decomposed with acetic acid, when benzoylacetone crystallizes as fine white prisms. Melting-point, 60–61°. Boiling point, 260–261°. Yield, 80–90 per cent of theory.

In addition to the sodio-derivative, the compound yields a copper derivative which can be prepared readily by adding a solution of cupric acetate to an alcoholic solution of benzoyl acetone. The precipitate is insoluble in water, but crystallizes from benzene in the form of deep-green needles.

B. Alkyl derivatives of Ethyl Acetoacetate

The most important property of ethyl acetoacetate and other β-ketonic esters is their ability to react with sodium, one molecule of the ester taking up an atom of the metal with displacement of hydrogen. The sodio-compound ($CH_3 \cdot CO \cdot CHNa \cdot COOEt$, or probably $CH_3 \cdot C(ONa):CH \cdot CO_2Et$) reacts with various halogen compounds forming sodium halide and an alkyl derivative of the ester, *e.g.*:

$$CH_3 \cdot CO \cdot CHNa \cdot COOEt + C_2H_5I \longrightarrow \underset{\text{Ethylacetoacetic ester}}{CH_3 \cdot CO \cdot CH(C_2H_5) \cdot COOEt} + NaI$$

The product of this reaction can also react with metallic sodium forming a sodio-derivative, which can be decomposed in a similar manner by halogen compounds.

* *Baeyer* and *Claisen*, B. 1887, **20**, 2180.

Experiment 203.—Preparation of ethylacetoacetic ester from acetoacetic ester * (see equation above).

5·7 grm. of clean sodium (1 atom) are dissolved in 70 grm. of absolute alcohol in a reflux apparatus, and the solution treated with 32·5 grm. (1 mol.) of acetoacetic ester. 40 grm. of ethyl iodide are added, and the mixture heated on a water bath until it shows a neutral reaction (about 2 hours). The alcohol is distilled off, the residual oil shaken with water and then extracted with ether. The ethereal solution is dried with anhydrous potassium carbonate, the ether removed, and the residue fractionally distilled. The portion which boils at 190–198° is collected separately. Yield, 80 per cent of theory. The ester is a colourless oil, boiling-point 198°. $D_4^{16°}$, 0·9834.

It reacts with metallic sodium, and gives a blue coloration with ferric chloride.

Experiment 204.—Preparation of methylethylacetoacetic ester from ethylacetoacetic ester.

$$CH_3\cdot CO\cdot CHEt\cdot CO_2Et \longrightarrow CH_3CO\cdot CEt(Na)\cdot CO_2Et \xrightarrow{CH_3I} CH_3\cdot CO\cdot CEtMe\cdot CO_2Et.$$

The method of Conrad and Limpach (Exp. 203) is applied, theoretical amounts of the reacting substances being taken. Yield, 75–80 per cent of theory. The product is a colourless oil, boiling-point 200–201°. $D^{22°}$, 0·947. It does not react with metallic sodium, but gives a violet coloration with ferric chloride.

These alkyl derivatives of acetoacetic ester can undergo ketonic or acid hydrolysis in the same manner as ethyl-acetoacetate itself.

Experiment 205.—Preparation of methyl β-butyl ketone from methylethylacetoacetic ester. †

$$CH_3\cdot CO\cdot \underset{H}{CMeEt}\cdot \underset{OH}{CO_2Et} \longrightarrow CH_3\cdot CO\cdot CHMeEt + CO_2 + EtOH.$$

20 grm. of methylethylacetoacetic ester are boiled in a reflux apparatus with 100 c.cm. of 10 per cent aqueous potassium hydroxide solution for 5 hours. At the end of this time the reaction is completed and the product is distilled. A colourless oil passes over together with water, and is extracted with

* *Conrad* and *Limpach*, A. 1878, **192**, 155.
† *Wislicenus*, A. 1883, **219**, 308.

ether. The ethereal solution is dried with calcium chloride, the ether removed and the residue distilled, when the ketone passes over as a light colourless oil, with an odour of pepper mint. Boiling-point, 118°. $D_{4^\circ}^{14.5^\circ}$, 0·8181.

C. Condensations of Ethyl Acetoacetate

Experiment 206.—Preparation of ethyl diacetosuccinate by the action of iodine on ethyl sodio-acetoacetate.*

$$\begin{matrix} CH_3\cdot CO\cdot CHNa\cdot COOEt \\ CH_3\cdot CO\cdot CHNa\cdot COOEt \end{matrix} + I_2 = \begin{matrix} CH_3\cdot CO\cdot CH\cdot COOEt \\ CH_3\cdot CO\cdot \dot{C}H\cdot COOEt \end{matrix} + 2NaI.$$

450 c.cm. of *anhydrous* ether (Exp. 31) are placed in a 1500 c.cm. flask and 13·8 grm. of clean sodium in the form of wire added. The flask is fitted to a reflux condenser, and 78 grm. of ethyl acetoacetate are added gradually. The vessel is shaken occasionally to assist the solution of the sodium, and when this is complete, 76·5 grm. of iodine dissolved in 300 c.cm. of anhydrous ether are added gradually, the addition being continued only so long as the colour disappears after each addition; sodium iodide separates out and is removed by filtration. The ether is removed from the filtrate, and the residue of ethyl diaceto-succinate recrystallized from glacial acetic acid. It forms colourless thin plates, melting-point 88°. Yield about 30 grm., *i.e.* 40 per cent of theory.

Like ethyl acetoacetate and other ketonic esters, the compound exists in tautomeric forms, of the thirteen possible forms, five have been isolated.†

This substance is a γ-diketone, and as such readily undergoes transformation into closed-chain derivatives. When shaken with dilute alkalis, it undergoes ketonic hydrolysis with the formation of the simple γ-diketone, acetonyl-acetone:

$$\begin{matrix} CH_3\cdot CO\cdot \overset{H}{\underset{H}{C}}\cdot COO\,Et \\ CH_3\cdot CO\cdot \dot{C}H\cdot COO\,Et \end{matrix} = \begin{matrix} CH_3\cdot CO\cdot CH_2 \\ CH_3\cdot CO\cdot \dot{C}H_2 \end{matrix} + 2CO_2 + 2EtOH.$$

* *Knorr* and *Haber*, B. 1894, **27**, 1155.
† *Knorr*, A. 1896, **293**, 101; 1899, **306**, 332.

Experiment 207.—Preparation of acetonyl-acetone from ethyl diacetosuccinate *

A solution of ethyl diacetosuccinate (Exp. 206) is obtained by vigorously shaking 15 grm. of the ester with rather more than the theoretical amount of a 5 per cent aqueous solution of sodium hydroxide (1 mol of ester requires 4 mol. of alkali). The solution is allowed to stand at the room temperature for several days until diacetosuccinic ester no longer separates, when a test portion is acidified with hydrochloric acid. The alkaline solution is then saturated with potassium carbonate; the acetonyl-acetone separates as an oil, which is extracted with ether. The ethereal solution is shaken with saturated salt solution, separated, dried, and distilled. Yield, 5–6 grm., *i.e.* 80–85 per cent of theory.

The diketone is a liquid with an agreeable odour, boiling-point 194°; D^{15^8}, 0·995. It is miscible with water, alcohol, and ether.

The γ (1·4) diketones readily condense with the formation of closed-ring compounds Thus, acetonyl-acetone when heated in a sealed tube with dehydrating agents (*e.g.* zinc chloride) yields dimethylfurane:

$$\begin{matrix}CH_2\cdot CO\cdot CH_3\\ CH_2\cdot CO\cdot CH_3\end{matrix} \rightarrow \begin{matrix}CH{:}C(CH_3)\\ CH{:}C(CH_3)\end{matrix}\!\!>\!O.$$

With alcoholic ammonia under similar conditions it forms dimethylpyrrole:

$$\begin{matrix}CH_2\cdot CO\cdot CH_3\\ CH_2\cdot CO\cdot CH_3\end{matrix} + NH_3 = \begin{matrix}CH{:}C(CH_3)\\ CH{:}C(CH_3)\end{matrix}\!\!>\!NH;$$

and with phosphorus pentasulphide a thiophene derivative is formed:

$$\begin{matrix}CH_2\cdot CO\cdot CH_3\\ CH_2\cdot CO\cdot CH_3\end{matrix} + P_2S_5 \rightarrow \begin{matrix}CH{:}C(CH_3)\\ CH{:}C(CH_3)\end{matrix}\!\!>\!S.$$

Thioxene.

Experiment 208.—Preparation of thioxene (1:4-dimethyl-thiophene) from acetonyl-acetone.† (S. B. 517, 518)

Three parts of acetonyl-acetone (Exp. 207) are heated with two parts of finely powdered phosphorus pentasulphide in a sealed tube at 140–150° for an hour. On cooling, a colourless liquid and a solid are obtained; the former is poured off and

* *Knorr*, B. 1889, **22**, 169. † *Paal*, B. 1885, **18**, 2251.

fractionally distilled. The distillation is repeated over metallic sodium, when the thioxene is obtained as a colourless mobile liquid, boiling-point 134–135°. Yield, 50–60 per cent of theory.

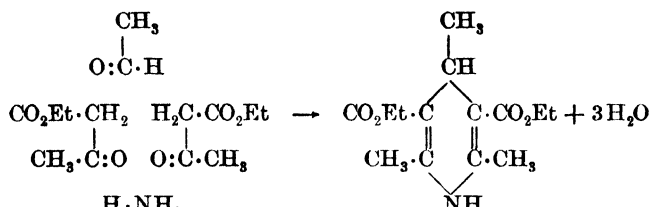
Colour reaction for thiophene derivatives.—Thiophene compounds give intense colorations with solutions of isatin in concentrated sulphuric acid, *e.g.* thioxene gives a cherry-red colour, which changes to reddish-brown on warming.

Experiment 209.—Hantzsch's synthesis of pyridine derivatives: Condensation of ethyl acetoacetate with aldehyde-ammonia

(*a*) **Preparation of ethyl dihydro-collidine-dicarboxylate** *

$$2CH_3\cdot CO\cdot CH_2\cdot CO_2Et + CH_3\cdot CHO, NH_3 = C_5H_2N(CH_3)_3(CO_2Et)_2 + 3H_2O;$$

or represented structurally:



(*To be conducted in a fume chamber.*)

26 grm. of ethyl acetoacetate are mixed with 6·75 grm. of aldehyde-ammonia (Exp. 171) in a beaker, and warmed gently for about three minutes at 100–110° (stir with a thermometer). To the product is added an equal volume of dilute hydrochloric acid, and the mixture is stirred until it sets into a hard solid mass. The mass is powdered, filtered, and washed with dilute hydrochloric acid and water. A small portion is recrystallized from hot alcohol, and then forms colourless plates with a bluish fluorescence, melting-point 131°. It is insoluble in water, sparingly soluble in alcohol, ether, and carbon disulphide, but is readily soluble in benzene.

(*b*) **Oxidation of ethyl dihydro-collidine-dicarboxylate to ethyl collidine-dicarboxylate.**

$$C_5H_2N(CH_3)_3(CO_2Et)_2 + O \longrightarrow C_5N(CH_3)_3(CO_2Et)_2 + H_2O.$$

(*To be conducted in a fume chamber.*)

* *Hantzsch*, A. 1882, **215**, 1.

Nitrous acid is generally used as the oxidizing agent. This is prepared by the action of concentrated nitric acid on *small lumps* of arsenious oxide. On warming gradually a steady stream of nitrous fumes is generated, these are passed through an empty wash bottle and thence into the solution.

The crude dihydro-ester from (*a*) is treated with an equal weight of alcohol in a small flask; complete solution does not take place. Nitrous fumes are led into the flask until a test portion treated with hydrochloric acid becomes clear. Heat is developed during the oxidation and all the ester goes into solution, if necessary, the flask is cooled by immersing in water. The alcohol is evaporated off on a water bath and the residue neutralized by the addition of sodium carbonate solution The oil which separates is extracted with ether, the extract dried by the addition of a small stick of caustic potash, the ether removed and the residue distilled. The fraction passing over between 290° and 310° is collected separately and redistilled.

The pure ester is a yellow oil, boiling-point 308–310°.

(*c*) **Hydrolysis of ethyl collidine-dicarboxylate: Preparation of potassium collidine-dicarboxylate.**

$$C_5N(CH_3)_3(CO_2Et)_2 + 2KOH = C_5N(CH_3)_3(CO_2K)_2 + 2EtOH.$$

The ester is treated with about 10 times its volume of alcoholic potash (2–3 times normal strength), and warmed in a reflux apparatus on a water bath for about four hours. The potassium salt is deposited as white crystalline crusts, and is separated from the alcoholic solution by decantation. It is washed with alcohol, then with ether, and dried A further yield of the salt is obtained by adding ether to the alcoholic solution.

(*d*) **Removal of carboxylic groups from a closed-ring compound by distillation with lime: Preparation of collidine from potassium collidine-dicarboxylate.**

$$C_5N(CH_3)_3(CO_2K)_2 + 2Ca(OH)_2 = 2CaCO_3 + 2KOH + C_5NH_2(CH_3)_3.$$

The potassium salt is powdered and mixed with about twice its weight of slaked lime. The mixture is placed in a piece of combustion tubing about 50 cm. long, sealed at one end, the other end being fitted with an adapter leading into a small receiver. The tube is heated in a combustion furnace, the

rear end of which is slightly elevated. The flames at the closed end are first ignited and the others gradually, and finally the whole tube is heated as strongly as possible. The distillate is shaken with ether, the solution dried with solid potassium hydroxide, the ether removed (a very small flask is used; see p. 3 and fig. 2), and the residue distilled.

It is a greenish-yellow liquid with an obnoxious odour, boiling-point 172°, and possesses the chemical properties of a tertiary base (see Chap. XVIII, E).

Experiment 210.—Formation of 1-phenyl-3-methyl-pyrazolone by condensation of ethyl acetoacetate with phenylhydrazine.*

$$CH_3\cdot CO\cdot CH_2\cdot CO_2Et + H_2N\cdot NH\cdot C_6H_5 = CH_3\overset{\displaystyle N-NH\cdot C_6H_5}{\overset{\|}{C}}\cdot CH_2\cdot CO_2Et + H_2O$$

Ethyl acetoacetate phenylhydrazone

$$CH_3\cdot\overset{\displaystyle N\text{——}NH\cdot C_6H_5}{\overset{\|}{C}}\cdot CH_2\cdot CO\cdot OEt = CH_3\cdot\overset{\displaystyle N-N(C_6H_5)}{\overset{\|}{C}}\!\!>\!CO + EtOH.$$

$$\qquad\qquad\qquad

XXV. ETHYL MALONATE AND ITS USE AS A SYNTHETICAL REAGENT

(S. B. 237, 238)

Experiment 211.—Preparation of ethyl malonate, $CH_2(CO_2Et)_2$, from chloracetic acid.*

$$CH_2Cl\cdot CO_2Na + KCN = CN\cdot CH_2\cdot CO_2Na + KCl$$
$$2CN\cdot CH_2\cdot CO_2Na + 4EtOH + 2H_2SO_4 = 2CH_2(CO_2Et)_2 + Na_2SO_4 + (NH_4)_2SO_4.$$

(*To be conducted in a fume chamber.*)

A solution of 50 grm. of chloracetic acid in 100 c.cm. of water is warmed to 50° in a large flask, and neutralized with 45 grm of sodium bicarbonate added in small portions until an alkaline reaction is obtained The temperature is kept at 55–60° until all the carbon dioxide is evolved. Then 40 grm. of potassium cyanide (98 per cent) in small pieces is added with stirring, but without further warming, until the vigorous reaction which occurs has moderated. After heating on a water bath for half an hour the flask is connected with a condenser and receiver (cf. figs. 5 and 9) and the latter with a suction pump, and heated on the water bath under diminished pressure until the whole of the water has been removed and the mass is quite dry † The flask is then attached to a reflux apparatus, and the almost colourless contents gradually treated with a cooled mixture of 100 c cm. of absolute alcohol and 80 c cm. of concentrated sulphuric acid, and heated on the water bath for four hours with occasional shaking. 100 c.cm. of water are then added, the mixture shaken well and filtered, and the undissolved salt washed several times on the filter with ether. More ether is added to the mixed filtrate and washings, and the whole well shaken. The ethereal extract is carefully treated with dilute sodium carbonate solution (carbon dioxide is evolved, therefore shake carefully) until an alkaline reaction is given. It is then dried over fused

* *Claisen* and *Venable*, A. 1883, **218**, 131; *Noyes*, J. A. C. S. 1896, **18**, 1105–6; *Scarborough*, P. 1914, **30**, 306.

† The solution may be evaporated down in an open dish on a sand bath with constant stirring until a thermometer immersed in the dish registers 130–135°. The method described above gives a better yield.

sodium sulphate, the ether removed, and the residue distilled. Yield, 50 grm., *i.e.* 60 per cent of theory.

Ethyl malonate is a colourless liquid, boiling-point 198°, $D_{4°}^{18°}$, 1·068.

Ethyl malonate yields sodio-derivatives in much the same manner as does ethyl acetoacetate (cf. Chap. XXIV, A), and the sodium atoms in these compounds can be replaced by alkyl groups, &c. The mono- and di-alkylated malonic and acetic acids can be synthesised by this process.

Experiment 212.—Introduction of an alkyl group into malonic ester; Preparation of ethylmalonic ester and ethylmalonic acid.*

$$CH_2(CO_2Et)_2 + NaOEt = \underset{\text{Sodio-ethyl malonate}}{CHNa(CO_2Et)_2} + EtOH$$

$$CHNa(CO_2Et)_2 + EtI = \underset{\text{Ethyl-malonic ester}}{CHEt(CO_2Et)_2} + NaI$$

2·3 grm. of sodium are dissolved in 25 grm. of absolute alcohol in a flask fitted with a reflux condenser, and when solution is complete 16 grm. of pure ethyl malonate are added. A white solid which consists of sodio-ethyl malonate separates, 20 grm. of ethyl iodide are then added slowly from a dropping funnel, the flask being shaken well during the operation. The mass dissolves gradually, heat is developed, and a fine precipitate of sodium iodide is deposited. The mixture is finally heated on a water bath until it no longer shows an alkaline reaction (1–2 hours) The alcohol is distilled off on a vigorously boiling water (or brine) bath, the residue treated with water and the ester extracted with ether. After dehydration with calcium chloride, the ether is removed and the residue distilled, when the product is obtained as a colourless liquid with fruity odour. Boiling-point, 206–208°; $D_{4°}^{18°}$, 1·008. Yield, 15 grm.

Experiment 213.—Hydrolysis of ethyl ethyl-malonate; Preparation of ethyl-malonic acid, $CHEt(CO_2H)_2$.

10 grm. of the ester are added gradually to a concentrated (56 per cent) solution of potassium hydroxide (about double the theoretical amount should be used) in a reflux apparatus. The mixture forms an emulsion which soon solidifies to a white mass of ethyl potassium ethyl-malonate; the whole is carefully heated on a water bath until a clear solution is obtained

* *Conrad*, A. 1880, **204**, 134.

(about half an hour is required), when the hydrolysis may be regarded as complete. The product is diluted with water, neutralized with strong hydrochloric acid, and precipitated as the calcium salt by means of a concentrated solution of calcium chloride This salt is filtered, dried, and decomposed with strong hydrochloric acid, and the free ethylmalonic acid extracted by shaking *several times* with ether. The ethereal solution is dried with calcium chloride and the ether removed. The liquid residue solidifies on standing, it is recrystallized from a small quantity of water with the addition of animal charcoal if the crystals are coloured, and forms colourless rhombic prisms, melting-point 111·5°. It is soluble in water, alcohol, and ether.

Malonic acid and its derivatives undergo decomposition when heated to fairly high temperatures, yielding carbon dioxide, and the corresponding mono-carboxylic acid. The process, therefore, provides a means for the synthesis of the higher acids of the acetic series.

Experiment 214.—Preparation of butyric acid from ethylmalonic acid.

$$CH(C_2H_5)(CO_2H)_2 = C_2H_5\cdot CH_2\cdot CO_2H + CO_2$$

The ethylmalonic acid prepared in the last experiment is placed in a small fractionating flask, and fixed in an oil or metal bath at an oblique angle so that the side tube is inclined upwards. The flask is closed with a cork carrying a thermometer, the bulb of which is immersed in the substance. Heating is conducted at a temperature of 180° until no more carbon dioxide is evolved. The residue, consisting of butyric acid, is distilled over in the usual manner, and is obtained as a colourless liquid with a rancid odour. Boiling-point, 162–163°.

Ethyl malonate in the form of its sodio-derivative reacts not merely with alkyl halides but also with acyl halides and halogen derivatives of esters, *e.g.* ethyl chloracetate, ethyl α-bromopropionate.

$$CHNa(CO_2Et)_2 + CH_2Br\cdot CO_2Et \longrightarrow CO_2Et\cdot CH_2\cdot CH(CO_2Et)_2$$
$$\longrightarrow CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H.$$

When an ester of an α-halogen derivative of a fatty acid is used and the product hydrolysed a substituted succinic acid is obtained, *e.g.* from ethyl α-bromopropionate methyl-succinic

acid, $CO_2H \cdot CHMe \cdot CH_2 \cdot CO_2H$. The yield is not very good, as appreciable amounts of isomeric glutaric acid derivatives are formed. The formation of glutaric acid can be almost completely avoided by using ethyl cyanoacetate in place of ethyl malonate.* This is due to the fact that the ethyl acrylate, formed by the elimination of hydrogen bromide from the ethyl α-bromopropionate, condenses with the ethyl malonate yielding the ester of a tricarboxylic acid, and this when hydrolysed yields glutaric acid. When ethyl cyanoacetate is employed its sodio-derivative is practically insoluble in alcohol, the solution is practically neutral, and there is not the same tendency for the elimination of hydrogen bromide and formation of ethyl acrylate.

Experiment 215.—Preparation of methyl-succinic acid from ethyl cyanoacetate and ethyl α-bromopropionate.†

28·5 grm. of ethyl cyanoacetate are added to a solution of 5·75 grm. of sodium in 70 c cm. of absolute alcohol. The insoluble sodio-derivative separates, and to the pasty mass 42 grm. of ethyl α-bromopropionate are added gradually The mixture is heated in a reflux apparatus for an hour on the water bath, when the solution is quite neutral. It is poured into water, extracted with ether, the ethereal solution washed with dilute sodium carbonate, then with water, and finally dried with calcium chloride. After removal of the ether, a yellow oil is obtained which is fractionated under reduced pressure, the fraction boiling at 140–165°/24 mm. is collected and redistilled, and the fraction passing over at 160–165°/17 mm. collected. This consists of ethyl β-methyl-α-cyanosuccinate, $CO_2Et \cdot CH(CN) \cdot CH(CH_3) \cdot CO_2Et$, and the yield is 70 per cent of theoretical. This ester is boiled in a reflux apparatus with 6–8 times its volume of concentrated hydrochloric acid until the oil has disappeared. On cooling, part of the methyl-succinic acid may separate and is collected with the aid of the pump, washed with concentrated hydrochloric acid, and crystallized from this solvent. The filtrate is made alkaline with concentrated ammonia, filtered from any silica which separates, and the clear solution boiled with excess of a 25 per cent solution of calcium chloride ‡ The insoluble calcium methyl-succinate is removed, washed with hot water, decomposed by dissolving in hot concentrated hydrochloric acid, and

* *Bone* and *Sprankling*, J. C. S. 1899, 75, 845. † *Ibid.* 853.

‡ To avoid bumping, the solution may be boiled by blowing steam through.

allowing to crystallize. After recrystallization from benzene it forms colourless needles, melting-point 111°. Yield, 56 per cent of theory, calculated from the cyanoacetate used.

Ethyl α-bromisobutyrate may be substituted for ethyl α-bromopropionate, but the mixture must then be heated at 100° for twenty-four hours in soda-water bottles corked and wired. The final product is *as*-dimethyl-succinic acid, melting-point 140–141°.

Formation of Closed-Ring Derivatives from Ethyl Malonate

Experiment 216.—Preparation of ethyl phloroglucinol-dicarboxylate.*

According to Moore the reaction proceeds as follows:—

$$3CH_2(CO_2Et)_2 + 2Na = \begin{array}{l} CH_2 \\ OC \quad CO \\ CO_2Et\cdot HC \quad CH\cdot CO_2Et \\ CO \end{array} + 4EtOH + Na_2CO_3.$$

3·6 grm. of sodium are dissolved in 50 c.cm. of absolute alcohol in a reflux apparatus, and when nearly cold, 50 grm. of ethyl malonate are added. The mixture is transferred to a soda-water bottle or pressure flask and heated in a brine bath at 105–108° for fifteen hours. A white compound settles out, which consists of the sodium compound of ethyl phloroglucinol-dicarboxylate and sodium carbonate. The product is filtered with the aid of a pump, the precipitate washed with alcohol, then dissolved in water and decomposed by the gradual addition of dilute hydrochloric acid until acid. The precipitated ester solidifies to an almost white crystalline mass, which is filtered off and recrystallized from alcohol. It forms white crystals, melting-point 106–107°.

When hydrolysed with aqueous potassium hydroxide solution it yields phloroglucinol, $C_6H_6O_3$. (Cf. S. B. 418.)

* *Baeyer*, B. 1885, 18, 3457; *Moore*, J. C. S. 1904, 85, 168.

XXVI. REDUCTION. (S. B. 580–593.)

A. Reduction in Acid Solution

The method in which a metal and acid are employed has been described in Exps. 133, 134, and the use of stannous chloride and hydrochloric acid in Exps. 166, 167, 170. Another type of acid reduction is by means of hydriodic acid in the presence of red phosphorus (S. B., p. 585).

Experiment 217.—Reduction of benzylic acid (diphenyl-hydroxyacetic acid) to diphenylacetic acid.*

$$(C_6H_5)_2C\begin{matrix}OH\\CO_2H\end{matrix} + 2H \rightarrow (C_6H_5)_2CH\cdot CO_2H + H_2O$$

A solution of 25 grm. of benzylic acid (Exp. 288) in 100 grm. of glacial acetic acid is boiled with 7 grm. of concentrated hydriodic acid and the same weight of red phosphorus for one hour in a round-bottom flask provided with an upright air condenser. The hot solution is filtered, poured into water, and the precipitated diphenylacetic acid filtered with the aid of the pump, washed with water, and recrystallized from hot water or alcohol. The yield is practically theoretical, and the product forms colourless needles, melting-point 146°.

In many cases the reduction with hydriodic acid and red phosphorus can only be accomplished by heating the mixture in a sealed tube. In this way benzophenone, $C_6H_5\cdot CO\cdot C_6H_5$, is reduced to diphenyl-methane, $(C_6H_5)_2CH_2$, anthraquinone, $C_6H_4\begin{matrix}CO\\CO\end{matrix}C_6H_4$, to dihydro-anthracene, $C_6H_4\begin{matrix}CH_2\\CH_2\end{matrix}C_6H_4$, and many fatty acids to the corresponding paraffins.

The use of sulphurous acid as a reducing agent is described in Exp. 122, in the preparation of quinol from *p*-benzoquinone.

B. Reduction in Alkaline Solution

(*a*) One of the commonest methods of reduction in alkaline solutions is with sodium amalgam (see Chap. XXXIX) and water, or sodium amalgam and sodium hydroxide solution.

Experiment 218.—Reduction of cinnamic acid to β-phenyl-propionic acid (hydrocinnamic acid).

$$C_6H_5\cdot CH{:}CH\cdot CO_2H + 2H \rightarrow C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H.$$

* *Klingemann*, A. 1893, **275**, 84.

15 grm. of cinnamic acid (Exp. 235) are dissolved in the requisite amount of sodium hydroxide solution, and the solution transferred to a separating funnel, which is placed in a bath so that it can be kept at about 30–35°. 200 grams of 2·5 per cent sodium amalgam are added in small portions, and the mixture well shaken after each addition. The whole operation should be completed in about thirty minutes At the beginning the amalgam liquefies rapidly, very little hydrogen is evolved, and the solution becomes warm. Towards the end the amalgam does not liquefy at all readily, and numerous bubbles of hydrogen are evolved. After standing for an hour the mercury is drawn off by means of the tap, and the alkaline liquid poured into an excess of moderately concentrated hydrochloric acid The hydrocinnamic acid separates as an oil, but quickly solidifies. It may be crystallized from a large volume of warm water or from light petroleum (boiling-point 35–40°), but in the latter case must be dried before dissolution in the solvent. It forms colourless needles, melting-point 47·5°. Yield, 90 per cent of theory.

Most $\alpha\beta$ unsaturated acids may be reduced by this method, but $\beta\gamma$ unsaturated acids, *e.g.* $C_6H_5 \cdot CH:CH \cdot CH_2 \cdot CO_2H$, are not reduced readily by sodium amalgam and water.

Acids containing two double bonds, one in the $\alpha\beta$ and the other in the $\gamma\delta$, usually add on hydrogen in the $\alpha\delta$ (1:4) positions, and yield a $\beta\gamma$ unsaturated acid:

$$C_6H_5 \cdot CH:CH \cdot CH:C(CO_2H)_2 \longrightarrow C_6H_5 \cdot CH_2 \cdot CH:CH \cdot CH(CO_2H)_2.$$

Thus both cinnamylidene-acetic and cinnamylidene-malonic acids (Exps 236 and 247) when reduced in this way yield $\beta\gamma$ unsaturated acids.

(*b*) Another method of reducing in alkaline solution is with sulphuretted hydrogen in the presence of alcoholic ammonia (see Exp. 135).

(*c*) A third method is the reduction with metallic zinc, *e.g.* zinc dust in the presence of sodium hydroxide solution.

Experiment 219.—Preparation of sym-diphenyl-hydrazine (hydrazobenzene) from azobenzene.

$$C_6H_5 \cdot N:N \cdot C_6H_5 + 2H \longrightarrow C_6H_5 \cdot NH \cdot NH \cdot C_6H_5.$$

A solution of 10 grm. of azobenzene (Exp. 222) in 100 c.cm. of alcohol is added to 16 grm of sodium hydroxide solution (25 per cent), and the mixture heated in a round-bottom flask

fitted with a reflux condenser. After the addition of 15 grm. of zinc dust in small portions the solution should be colourless, and may then be filtered, as rapidly as possible by means of the pump, into a dilute solution of sulphurous acid. As the solution cools the hydrazobenzene crystallizes in colourless plates. These may be filtered, washed with a little sulphurous acid, dried, and recrystallized from light petroleum. The melting-point is 131°. In the moist state it is readily oxidized in contact with the air, hence care is required in filtering and drying.

(*d*) Another example of reduction in alkaline solution is the conversion of aromatic nitro-derivatives into azoxy-compounds when boiled with sodium methoxide.

$$4R\cdot NO_2 + 3NaOCH_3 \longrightarrow 2RN\cdot NR + 3H\cdot CO_2Na + 3H_2O.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown\!\diagup \quad O$$

Experiment 220.—Preparation of azoxybenzene, $C_6H_5\cdot N_2O\cdot C_6H_5$, from nitrobenzene.*

Sodium methoxide is prepared by dissolving 20 grm. of metallic sodium in 200 grm of methyl alcohol (Kahlbaum's No. 1), contained in a litre round-bottomed flask fitted with a reflux condenser through which a rapid stream of water is passing. The sodium should be quite clean, and may be dropped through the condenser tube in quantities of 2–3 grm. at a time. A vigorous action occurs, and fresh metal is added when the previous lot has dissolved. When all the sodium has been added 30 grm. of nitrobenzene are run in, and the whole is boiled on the water bath for three to four hours. As the reaction proceeds sodium formate crystals are deposited, and may produce bumping The excess of methyl alcohol is removed by distillation, the flask being immersed in boiling water; and the residue is mixed with water in a beaker, when a dark oil separates, which, however, solidifies rapidly in a cool spot to a hard cake. This cake is washed several times with water, and pressed on a porous plate. Yield, 23 grm. When dry it may be crystallized from light petroleum, and is deposited in the form of yellow needles, melting-point 36°

* *Klinger*, B. 1882, **15**, 865.

C. Reduction in Neutral Solution

(*a*) The production of paraffins from alkyl iodides (see Exp. 16) is an example of reduction in practically neutral solution.

(*b*) Another example is the reduction of an aromatic nitro-derivative to the corresponding hydroxylamine.

Experiment 221.—Preparation of phenyl-hydroxylamine from nitrobenzene *

$$C_6H_5 \cdot NO_2 + 4H \longrightarrow C_6H_5 \cdot NH \cdot OH + H_2O.$$

Warning.—Warm solutions of phenyl-hydroxylamine produce wounds, and the dry powder causes violent sneezing. The operations should be conducted in a good fume cupboard.

A mixture of 12 grm. of nitrobenzene (freshly distilled) (Exp. 99) and 250 c.cm of water containing 6 grm. of ammonium chloride is well agitated by an automatic stirrer in a stout glass beaker which is surrounded by cold water, so that the temperature is kept below 15°. 18 grm of zinc dust (75 per cent, or an equivalent amount of a less active dust) are added in four equal parts after intervals of a quarter of an hour. The stirring is continued until the odour of nitrobenzene has disappeared; this should take some 10 minutes after the addition of the last portion of zinc dust. The mixture is then filtered by means of the pump and a Buchner funnel. The precipitate of zinc and hydroxide is washed by adding about 200 c.cm. of water at 45° when the pump is not working; the water is then slowly sucked through by means of the pump, and the precipitate ultimately pressed together and sucked as dry as possible.

It is an advantage to keep the main filtrate separate from the washings. The two solutions are separately saturated with finely powdered pure sodium chloride (about 70 and 55 grm. respectively), and are then cooled to 0°. After some 15 minutes colourless crystals of phenyl-hydroxylamine separate. These are filtered, and dried on a porous plate without washing. Yield, practically theoretical. A small portion is crystallized from benzene, and is obtained as colourless crystals, melting-point 81°. The remainder may be used for the preparation of nitrosobenzene (Exp. 229).

* D. R. P. 89978, also *Gattermann*, Prax. org. Chem. 194

The β-aryl-hydroxylamines are good reducing agents; they readily reduce Fehling's solution and ammoniacal silver nitrate solution, and hence the formation of a hydroxylamine derivative may be used for the detection of NO_2 radicals in aromatic compounds (Chap. XV, C).

β-aryl-hydroxylamines are unstable in the presence of mineral acids, and undergo molecular rearrangement to *p*-aminophenols.

D. Reduction by Heating with a Metal

Oxygen is frequently removed when a compound is heated with a metal, such as zinc or iron.

Experiment 222.—Preparation of azobenzene from azoxybenzene.*

$$C_6H_5 \cdot N_2O \cdot C_6H_5 + Fe \longrightarrow C_6H_5 \cdot N{:}N \cdot C_6H_5 + FeO.$$

15 grm. of iron filings, which have been freed from oil by washing with alcohol and ether, and subsequently dried in the steam oven, are well mixed in a mortar with 5 grm. of crystallized and dried azoxybenzene (Exp. 220), and the mixture transferred to a small non-tubulated retort and then carefully heated, the whole mass being evenly heated by moving the flame. The temperature is gradually raised until no more distillate passes over The distillate is collected in a small porcelain dish, and solidifies to a bright-red crystalline mass. It is well pressed on a porous plate to remove oily impurities, and crystallized from light petroleum (boiling-point 45–50°), in which it is readily soluble. It forms compact red plates, melting-point 68°.

Experiment 222*a*.—Preparation of anthracene from anthraquinone

1 grm. of anthraquinone (Exp. 195) is mixed with 5 grm. of zinc dust and the mixture placed in the end of a hard glass test tube, 15 grm. of zinc dust are added, and the tube is placed in a horizontal position and heated, beginning at the open end. Crystals of anthracene are deposited in the front part of the tube, and may be purified by sublimation; melting-point, 213°. For further recognition prepare a specimen of the additive compound with picric acid.

* *Mitscherlich*, A. 1834, 12, 311.

E. Electrolytic Reduction

As pointed out in S. B. p. 591 the products obtained in the case of electrolytic reduction depend not merely on the original materials, but also to a large extent on the conditions of electrolysis, *e.g.* nature of solvent, nature of electrodes, current density, and temperature.

Experiment 223.—Reduction of nitrobenzene to aniline.*

A mixture of 200 c cm. alcohol, 150 c cm sulphuric acid (25 per cent) and 25 grm. of nitrobenzene contained in a porous cell serves as cathode compartment. It is placed in a beaker containing 25 per cent sulphuric acid. The cathode is a sheet of lead in the form of a cylinder, and has several narrow slots cut in it, a small leaden paddle stirrer is also connected with the negative pole, and serves to keep the solution well agitated. The anode is also a cylinder of lead. An E.M.F. of 3·5–4 volts and a current density † of 4–5 amperes is used.

When the current passes the temperature rises rapidly, and should be kept at 65–80° For 25 grm. of nitrobenzene 33 ampere-hours are required, but as slight loss of hydrogen occurs the current may be passed for 35 ampere hours.‡ The cathode liquid is then removed, the alcohol distilled off, and if there is an odour of nitrobenzene this is removed by steam distillation The liquid is then made alkaline with sodium hydroxide, and the aniline isolated and purified, as in Exp. 133.

Other aromatic compounds may be reduced in the same manner, *e g* *o*-nitrotoluene gives a good yield of the corresponding amine

Experiment 224.—Reduction of nitrobenzene to *p*-aminophenol.§

$$C_6H_5 \cdot NO_2 + 4H \longrightarrow OH \cdot C_6H_4 \cdot NH_2 + H_2O.$$

30 grm. of nitrobenzene, 280 c.cm. of concentrated sulphuric acid, and 4–6 c.cm. of water are placed in a beaker which serves as the cathode compartment. The anode compartment consists of a porous cell containing concentrated sulphuric acid. The anode consists of a coil of stout platinum wire or of a cylinder of platinum foil. The cathode consists of a similar

* For general arrangement of apparatus see Exp. 17.
† In all these experiments the current density, C.D., is given per sq. dm.
‡ See notes in connection with Exp. 17.
§ *Gattermann*, B. 1893, 26, 1846.

coil or cylinder wound round the porous cell. An E.M.F. of 7–8 volts and a C.D.* of 5–6 amperes is employed. The temperature rises to 75–80° during the electrolysis, but should not be allowed to rise beyond 85°, as sulphonation can then occur. After 30 ampere hours the reduction is complete, the current is stopped, and the cathode liquid cooled by means of a freezing mixture. Crystals of *p*-amino-phenol separate, and are filtered at the pump, using a glass funnel and plug of glass wool. They are pressed on a porous plate, and finally recrystallized from alcohol. Yield, 20–30 per cent of the theoretical.

An 80 per cent sulphuric acid may be employed if the cathode is rapidly rotated.

The nitrobenzene is probably first reduced to phenyl-hydroxylamine, but as this is unstable in the presence of acids it is immediately converted into the isomeric *p*-amino-phenol.

$$C_6H_5 \cdot NO \cdot OH \longrightarrow OH \cdot C_6H_4 \cdot NH_2$$

Reduction of Ketones and Carbonyl Derivatives.—*Tafel* † has conducted numerous experiments on the reduction of carbonyl compounds, and has worked out the conditions under which the reduction is most easily effected. The carbonyl group is not readily reduced, and it is necessary that the hydrogen ions should be discharged at a high potential. This is accomplished by using electrodes of *pure* lead coated with a layer of spongy lead. The lead electrode should have a tongue of the same metal, to which a copper wire can be soldered On no account must the copper be soldered directly to the electrode at a point at which it will be immersed in the liquid, as metallic impurities will be introduced, and the high potential of the hydrogen ions will be lowered As a low current density is essential, a large cathode surface should be used. To obtain a deposit of spongy lead the cathode is subjected to the following treatment. The metallic surface is first polished with wet sand, then washed with dilute sodium hydroxide solution, and finally with distilled water. It is then electrolytically oxidized by placing in 20 per cent sulphuric acid, and making it the anode, whilst a current of 2 amperes per sq. dcm. is passed for half an hour. It is then washed with cold water, immersed in boiling water for a few

* See note, p. 255. † B. 1900, 33, 2209.

minutes, and finally washed with alcohol and dried. Both electrodes should be treated in this manner, and can be kept for a long time in this state. When the cathode is first used the layer of peroxide is reduced, and a deposit of spongy metal is formed After having been used, the cathode but not the anode should be again oxidized and washed before being used a second time. In order to remove metallic impurities from the porous cells, they are first soaked in warm dilute sodium hydroxide solution for several hours, then washed with water for one to two days, and finally left in dilute hydrochloric acid (sp. gr 1·02–1·03) for two days, and then well washed by immersing in water for four to five days, and occasionally changing the water.

Experiment 225.—Preparation of iso-propyl alcohol and pinacone from acetone *

The normal reduction product of a ketone is a secondary alcohol—

$$\begin{matrix}R\\R\end{matrix}\!\!>\!C\!:\!O + 2H \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!CH\cdot OH,$$

but in many cases small amounts of dihydric alcohols—*pinacones*—are formed—

$$\begin{matrix}R\\R\end{matrix}\!\!>\!C\!:\!O + 2H + O\!:\!C\!<\!\!\begin{matrix}R\\R\end{matrix} \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!C(OH)\cdot C(OH)\!<\!\!\begin{matrix}R\\R\end{matrix}$$

A mixture of the two compounds is formed when acetone is reduced, using lead electrodes, whereas *iso*-propyl alcohol alone is formed when a mercury cathode is used.

The anode consisting of a piece of sheet lead is placed in 10 per cent sulphuric acid contained in a porous cell. The cathode is a sheet of lead in the form of a cylinder placed in a beaker,† and surrounding the porous pot. The cathode liquid is a solution of 20 grm. of acetone in 100 c.cm. of 40 per cent sulphuric acid. The solution is kept cool by means of running water, and a C.D. of 4 amperes is employed. As soon as hydrogen is evolved rapidly at the cathode the reaction is complete. The cathode liquid is neutralized with potassium hydroxide, and then saturated with potassium carbonate. The oily layer which separates is removed by means of a separating funnel, dried with solid potassium carbonate, and fractionally

* *Merck*, D. R. P. 113,719 (1893).

† If the vessel itself is made of lead this can be used as the cathode if previously treated as described on p. 256.

distilled. Iso-propyl alcohol boils at 80–81°, and pinacone at 171–172°. Pinacone melts at 33°, and its hydrate, $C_6H_{14}O_2$, $6H_2O$, at 42°.

Experiment 226.—Reduction of camphor to borneol.

$$C_{10}H_{16}O \longrightarrow C_{10}H_{17}\cdot OH.$$

When **camphor** (S. B., p. 566) is reduced in a similar manner the corresponding alcohol **borneol** is formed. The conditions are: a mixture of a 10 per cent solution of camphor in alcohol, with half its volume of 75 per cent sulphuric acid as cathode liquid, 70 per cent acid as anode liquid, a C.D. of 3–12 amp., and E.M.F. 10–15 volts. The temperature must not rise above 20–24°. With C.D. 12 amp. five hours are required. The product is poured into water, the solid filtered, dried, and crystallized from light petroleum. Melting-point, 204–205°. Yield, 40 per cent.

XXVII. OXIDATION

A. With Potassium Permanganate. (S. B. 595.)

(*a*) **In Alkaline Solution.**—In the presence of alkali a molecule of potassium permanganate can yield three atoms of oxygen for oxidation purposes according to the equation—

$$K_2Mn_2O_8 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O.$$

An example of its action has already been given in Exp. 50. An important application is due to *Fittig*, who showed that in dilute solution the reagent oxidizes a compound containing an ethylene linkage to a dihydroxy-derivative, *e.g.*:

$$C_6H_5\cdot CH{:}CH\cdot CO_2H + H_2O + O \longrightarrow C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot CO_2H.$$

N.B.—If a stronger solution is used the molecule of the unsaturated compound is ruptured, and acids containing a smaller number of carbon atoms are formed. An examination of such oxidation products affords valuable evidence as to the position of the double bond in the original ethylene compound (S. B. 162).

Experiment 227.—Preparation of phenyl-dihydroxy-propionic acid (phenyl-glyceric acid),* $C_6H_5 \cdot (CH \cdot OH)_2 \cdot CO_2H$, from cinnamic acid.

10 grm. of cinnamic acid (Exp. 235) are dissolved in dilute sodium hydroxide, and the solution made up to 1 litre. The solution is placed in a vessel surrounded by ice, and vigorously agitated by means of a mechanical stirrer, while a solution of 15 grm of potassium permanganate in 750 c.cm. of water is added gradually by means of a tap funnel. When the addition is completed the liquid is filtered from the precipitated hydrated manganese dioxide and concentrated to half its volume. Any benzaldehyde present is carried away with the steam. The residue is neutralized by the addition of concentrated hydrochloric acid, and evaporated on a water bath until the dissolved salts begin to separate. More concentrated hydrochloric acid is added, and the product extracted several times with large quantities of ether. This is necessary because the chief product of oxidation (phenyl-glyceric acid) is only sparingly soluble in ether while readily soluble in water. The ethereal solution is evaporated, and the residue recrystallized from hot benzene or ether.

It consists of white glistening needles, melting-point 141–142°, is readily soluble in water, sparingly in ether, insoluble in cold but sparingly soluble in hot benzene.

(*b*) **In Neutral Solution**.—The permanganate is sometimes used in neutral solution; in order to remove the potassium hydroxide formed during its decomposition excess of magnesium sulphate is added at the beginning.

Experiment 228.—Preparation of acetanthranilic acid,† $CO_2H \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$, from acet-*o*-toluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

10 grm. of acet-*o*-toluidide (Exp. 146) and 20·6 grm. of magnesium sulphate crystals are dissolved in 1200 c.cm. of water in a large beaker fitted with a mechanical stirrer and thermometer. The mixture is heated to 75–80°, and then 29·2 grm. of potassium permanganate are added. The liquid is stirred vigorously until all the permanganate has disappeared, the temperature during this process being maintained at 85°; this takes about one and a half hours. The hot solution is then filtered, and the clear filtrate acidified with dilute sulphuric acid. A colourless precipitate is obtained, which is

* *Fittig* and *Ruer*, A. 1892, 268, 27. † D. R. P. 94,629.

filtered off and washed with a little water. Yield, 75 per cent of theory. Melting-point, 185°.

(*c*) **In Acid Solution.**—In the presence of mineral acid, a molecule of potassium permanganate can yield five atoms of oxygen for oxidation purposes. The mixture is a powerful oxidizing agent, and is only used for the preparation of very stable organic compounds (cf. S. B. 596).

B. Chromic Acid Derivatives

Chromic anhydride, CrO_3, is generally used in acetic acid solution (cf. Exp. 195).

Chromyl chloride, CrO_2Cl_2, oxidizes benzene hydrocarbons to aldehydes (Etard's reaction) (cf Exp 174).

The usual method of using chromic acid is in the form of a mixture of a dichromate and sulphuric acid. Examples of its use have been met with in Exps 58 and 171.

A further example is the oxidation of phenylhydroxylamine to nitrosobenzene.

$$C_6H_5\cdot NH\cdot OH + O \longrightarrow C_6H_5\cdot N{:}O + H_2O.$$

Experiment 229.—Oxidation of phenylhydroxylamine to nitrosobenzene.*

An ice-cold solution of 4·6 grm. of potassium dichromate in 200 c.cm. of water is added rapidly to a freshly prepared mixture of finely divided phenylhydroxylamine (4 grm), concentrated sulphuric acid (30 grm.), and water (270 grm.), also cooled by ice water. Nitrosobenzene separates, and is removed by immediately subjecting the mixture to steam distillation, when the nitrosobenzene passes over as green oily drops which solidify in the condenser to colourless crystals. These are removed, pressed on a porous plate, and washed with a little low-boiling ligroin. It melts at 67·5–68° to a deep-green liquid.

C. Nitric Acid

One of the chief drawbacks to the use of this reagent for oxidation is that it is also a nitrating agent (cf. Chap. XV). An example of its oxidizing power has been given in Exp. 59; the following experiment illustrates its use in oxidizing a secondary alcoholic group to a ketonic group.

* D. R. P. 89,978, *Wohl* and *Bamberger*.

Experiment 230.—Preparation of benzil,* $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$, from benzoin, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$.

15 grm. of benzoin (Exp. 181) are heated with 35 grm. of concentrated nitric acid (sp. gr. 1·4) in a small flask on a boiling-water bath for 1½–2 hours. The product is poured into cold water, and the mass which solidifies is washed several times with cold water, dried on a porous plate, and recrystallized from alcohol. Yield, 90 per cent of theory.

Benzil crystallizes in well-developed yellow prisms, melting point 95°. It is a diketone and yields two monoximes and three dioximes. (S. B. 477.)

D. Sulphuric Acid

An example of commercial importance is the oxidation of naphthalene by means of sulphuric acid to phthalic acid (Exp. 51).

E. Peroxides

Manganese dioxide in the presence of sulphuric acid is now largely used for the oxidation of benzene homologues to aldehydes, *e.g.* toluene to benzaldehyde. An excess of the hydrocarbon must always be present, and the mixture is kept vigorously stirred

Lactic acid when oxidized with manganese dioxide and sulphuric acid is first hydrolysed to acetaldehyde and formic acid,

$$CH_3 \cdot CHOH \cdot CO_2H \longrightarrow CH_3CH{:}O + H \cdot CO_2H;$$

and the latter is oxidized to carbonic acid The reaction may be used for the quantitative estimation of lactic acid.

Experiment 231 — Determination of the strength of a solution of lactic acid

The solution of lactic acid is diluted to a strength of about 0·5 per cent 5 c cm of the diluted solution are treated with 5 c.cm. of pure concentrated sulphuric acid, the whole diluted with water to 50 c cm., a small quantity of manganese dioxide added, and the mixture distilled from a small distilling flask. The distillate, which contains the aldehyde, is titrated with 0·1 N iodine solution, using starch solution as indicator.

For other examples of oxidizing reactions, see Exps. 51, 173, 232.

* *Zinin*, A. 1840, 34, 188.

F. Electrolytic Oxidation. (S. B. 602.)

The method is not so general in application as electrolytic reduction, as it is difficult to gauge the end of the reaction.

Experiment 232. — Preparation of bromoform, $CHBr_3$, from acetone.*

60 grm. of potassium bromide and 0·3 grm. of potassium chromate are dissolved in 150 c.cm. of water, and 20 c.cm. of acetone are added to the solution.

The electrolysing cell is a beaker of 200 c.cm. capacity, the anode, consisting of a sheet of platinum of 50 sq. cm. area, bent so as to fit closely to the wall of the beaker. The cathode, consisting of a stout platinum wire in the form of a spiral, is fixed in the centre of the cell.

A current of 3 amperes is passed through the solution (E.M.F. 4–4·2 volts) for 4–5 hours. In order that the temperature shall not rise above 20° the beaker is placed in a bath of cold water. To remove the potassium hydroxide formed at the cathode, a rapid current of carbon dioxide from a Kipp's generator is bubbled through the liquid.

The bromoform, which settles at the bottom of the beaker, is strongly coloured with bromine. The oily bromoform is removed with the aid of a separating funnel, and is then shaken with a mixture of dilute sodium carbonate solution and acetone until the brown colour disappears. It is finally washed with water, dried over calcium chloride, and distilled. Melting-point, 7·6°; boiling-point, 151°.

Experiment 233.—Preparation of *p*-nitro-benzyl alcohol, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OH$, from *p*-nitro-toluene, $NO_2 \cdot C_6H_4 \cdot CH_3$ (1:4).

The electrolysis is carried out in a divided cell, the anode compartment consisting of a porous cell in which is placed an anode of platinum foil or gauze. The anode liquid consists of a mixture of 80 c.cm. of glacial acetic acid, 8 c.cm. of concentrated sulphuric acid, and 15 grm. of *p*-nitro-toluene.

The porous cell is surrounded with a cylindrical cathode of sheet lead, the electrolyte being sulphuric acid of sp. gr. 1·6–1·7. The whole apparatus is fixed in a water bath, which is kept at the boiling temperature during the experiment. A current density of 1 to 1·5 ampere and an E.M.F. of 4 to 4·5

* *Muller* and *Loebe*, Z. E. 1904, 10, 409.

volts is used, and the current is passed through for 20 ampere-hours.

The product is distilled with steam to remove any unchanged *p*-nitro-toluene. The remaining hot solution is filtered through a fluted filter paper in order to remove resinous matter, the latter being washed a few times with hot water. On cooling the filtrate and washings, *p*-nitro-benzyl alcohol separates in the form of long yellow needles. These are filtered off and the mother liquor extracted with ether. The extract contains *p*-nitro-benzyl alcohol and its acetyl derivative, the ether is evaporated and the residue extracted with small quantities of alcohol. The solution contains the *p*-nitro-benzyl alcohol only, which may be recovered by evaporating the solution. The product is crystallized from water after boiling with animal charcoal, and consists of long yellow needles, melting-point 93°. Yield, 35–40 per cent of theory.

XXVIII. CONDENSATION

By condensation is meant the formation of a new compound by the interaction of two others, generally with the separation of water, alcohol, hydrogen chloride, hydrogen sulphide, ammonia, &c The new substance is not readily reconverted into the original compounds in a simple manner, so that the definition excludes such reactions as the formation of esters, &c.

Various examples of condensation have already been described.

The action may take place without the influence of any condensing agent, *e.g.* the formation of oximes, hydrazones, &c. (cf. Chap XXII; also Exps. 210, 234). In most cases, however, the condensation is facilitated by the addition of suitable agents. Some of the most important condensing agents are: acetic anhydride (Exps. 235–237), aluminium chloride (Exps. 183, 184), phosphoric anhydride, phosphorus trichloride, potassium hydroxide (Exp 238), plumbous oxide (Exp. 242), sodium acetate (Exp. 150), sodium ethoxide (Exps. 198, &c.), sulphuric acid (Exps. 243 and 244), zinc chloride (Exp. 256), &c. Certain amines, *e.g.* diethylamine (Exp. 245) and quinoline (Exp. 247), are useful in some cases, while sunlight has a great effect in promoting certain condensations.

As a rule, one condensing agent cannot be substituted for

another; such substitution generally produces divergent results in the yield, if not in the actual product.

A. Condensation without the Aid of Condensing Agents

Aromatic aldehydes condense readily with primary amines with the production of benzylidene-anilines (Schiff's Bases, S. B. 423), *e.g.*:

$$C_6H_5\cdot CH{:}\overset{\cdots}{O} + H_2\,N\cdot C_6H_5 \longrightarrow H_2O + C_6H_5\cdot CH = N\cdot C_6H_5.$$

No condensing agent is necessary in this case.

Experiment 234. — Preparation of benzylidene-aniline, $C_6H_5\cdot CH{:}N\cdot C_6H_5$, from benzaldehyde and aniline.*

Equivalent proportions of benzaldehyde (Exps. 173 or 174) and aniline (Exp. 133) are warmed together in a dish on a water bath with continual stirring. A solid product is obtained, which is dried by means of the filter pump and on a porous plate, and recrystallized from carbon disulphide (see warning, Introduction)

It crystallizes in yellow needles, melts at 54°, boils at 300°, is insoluble in water, but dissolves readily in alcohol and ether

As examples of the use of various condensing agents the following reactions may be studied.

B. Acetic Anhydride

The most important example of the use of this reagent for producing condensation is *Perkin's* synthesis of unsaturated acids † (S. B. 439). Aromatic aldehydes when heated with a salt of a carboxylic acid in the presence of acetic anhydride yield unsaturated acids, provided the acid contain two hydrogen atoms in the α-position, *e.g.*:

$$C_6H_5CH\,O + H_2{:}CH\cdot CO_2Na \longrightarrow C_6H_5CH{:}CH\cdot CO_2H$$

$$C_6H_5CH{:}CH\cdot CH\,O + H_2\,CH\cdot CO_2Na \longrightarrow C_6H_5CH{:}CH\cdot CH{:}CH\cdot CO_2H.$$

Experiment 235.—Preparation of cinnamic acid, $C_6H_5CH{:}CH\cdot CO_2H$, from benzaldehyde and sodium acetate

* *Laurent* and *Gerhardt*, A. 1850, **76**, 304.
† *Perkin*, J. C. S. 1868, **21**, 53; 1877, **31**, 389.

2 parts by weight of benzaldehyde, 3 of acetic anhydride, and 1 of *anhydrous* finely powdered sodium acetate (p. 88), are heated in a flask provided with a long and wide air condenser in an oil or metal bath at 180° for 8 hours. The product is poured while hot into excess of water, and the residual benzaldehyde removed by distilling with steam. The amount of water being large the cinnamic acid dissolves, with the exception of a small quantity of an oily impurity. If the solution is coloured, animal charcoal is added and the liquid boiled for some time, then filtered and allowed to cool. The cinnamic acid separates as lustrous plates, melting-point 133°. Yield, 70 per cent of theory

Experiment 236.—Preparation of cinnamylidene-acetic acid, $C_6H_5CH:CH\cdot CH:CH\cdot CO_2H$, from cinnamic aldehyde and sodium acetate.*

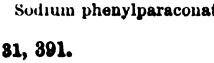
2 parts by weight of cinnamic aldehyde and 3 parts of acetic anhydride (both freshly distilled) and 1 part of freshly fused sodium acetate are placed in a round-bottom flask fitted with a reflux condenser, and heated in an oil bath at 160–170° for 8 hours. The product is poured into water, the precipitate extracted with sodium carbonate solution, filtered, and the filtrate acidified with hydrochloric acid. The precipitated acid is filtered and recrystallized from alcohol or ligroin. Yield, 25 per cent of theory. Melting-point, 165–166°.

The sodium salts of certain dibasic acids of the type of succinic acid also react with aromatic aldehydes in the presence of acetic anhydride. With sodium succinate and benzaldehyde a lactonic acid, phenylparaconic acid, is obtained, together with a certain amount of the $\beta\ \gamma$ unsaturated acid phenylisocrotonic acid, $C_6H_5\cdot CH:CH\cdot CH_2\cdot CO_2Na$. The reaction probably proceeds in the following stages:—

1. $C_6H_5\cdot CH:O + CH_2(CO_2Na)\cdot CH_2\cdot CO_2Na \longrightarrow C_6H_5\cdot CH(OH)\cdot CH(CO_2Na)\cdot CH_2\cdot CO_2Na.$

The acetic anhydride liberates the acid salt from the normal salt, and then water is eliminated from the acid salt.

2. $C_6H_5\cdot CH(OH)\cdot CH(CO_2Na)\cdot CH_2\cdot CO\cdot OH \longrightarrow H_2O + C_6H_5\cdot CH\cdot CH(CO_2Na)\cdot CH_2$



Sodium phenylparaconate.

* *Perkin*, J. C. S. 1877, **31**, 391.

Experiment 237.—Preparation of phenylparaconic acid from benzaldehyde and sodium succinate.*

Equimolecular quantities of anhydrous sodium succinate, pure benzaldehyde, and acetic anhydride are heated at 100–110° for 10 hours. When cold the mixture is extracted twice with ether, and the ethereal solution shaken with sodium carbonate solution so long as acid is extracted. The alkaline solution is warmed gently to remove ether and then acidified with hydrochloric acid, when the phenylparaconic acid is precipitated together with a small amount of phenylisocrotonic acid, $C_6H_5 \cdot CH:CH \cdot CH_2 \cdot CO_2H$. When dry the mixture is extracted with warm carbon disulphide, in which the unsaturated acid is readily soluble. The insoluble paraconic acid crystallizes from hot water in glistening needles, melting-point 99°. When the dry acid is heated at 100° it loses in weight to the extent of 2 per cent, and then melts at 109°. A further amount of the acid is obtained by acidifying the aqueous solution which has been extracted with ether.

C. Potassium Hydroxide

Potassium hydroxide facilitates the condensation of substances which combine with the elimination of one or more molecules of an acidic compound, thus primary amines condense readily with carbon disulphide in the presence of this reagent yielding substituted thiocarbamides,† *e.g.*:

$$S{:}C{:}\,S\cdot\overset{\cdots}{\underset{H}{H}}{:}NH\cdot C_6H_5 \;\rightarrow\; C{:}S \;+\; H_2S.$$
$$\qquad\quad H\ NH\cdot C_6H_5 \qquad\quad NH\cdot C_6H_5$$

Experiment 238.—Preparation of thiocarbanilide, $CS(NH \cdot C_6H_5)_2$, from aniline and carbon disulphide.

40 grm. of aniline and 50 grm. of carbon disulphide (excess) are added to 60 c.cm. of alcohol, and 10 grm. of powdered potassium hydroxide in a flask attached to a very long reflux condenser (or better, a double surface condenser). The mixture is heated on a boiling-water bath for 3–4 hours. The excess of carbon disulphide and alcohol is then distilled off, the residue washed with water, then with dilute hydrochloric

* *Jayne* A. 1883, 216, 100; *Sudborough* and *Thomas*, J. C. S. 1907, 91 1034.

† *Hofmann*, A. 1849, 70, 144.

acid in order to remove any unchanged aniline, and again with water. The substance is filtered and dried in a steam oven. Yield, 35 grm., *i.e.* 70 per cent of theory.

A portion of the crude product is recrystallized from alcohol, and is deposited as large colourless plates, melting-point 151°, which are sparingly soluble in water but readily soluble in hot alcohol

When boiled with mineral acids the substituted thioureas decompose, yielding isothiocyanates (thiocarbimides or mustard oils).

$$\begin{matrix} \diagup \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{CS} \\ \diagdown \text{N H}\cdot\text{C}_6\text{H}_5 \end{matrix} + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\cdot\text{N:C:S} + \text{C}_6\text{H}_5\text{NH}_2,\ \text{HCl}.$$

At the same time a portion of the unchanged thiourea condenses with the aniline set free in the above reaction, yielding a guanidine derivative.

$$(\text{C}_6\text{H}_5\cdot\text{NH})_2\text{C:S} + \text{H}_2\text{N}\cdot\text{C}_6\text{H}_5 \longrightarrow \begin{matrix} \diagup \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{C:N}\cdot\text{C}_6\text{H}_5 \\ \diagdown \text{NH}\cdot\text{C}_6\text{H}_5 \end{matrix} + \text{H}_2\text{S}.$$

Experiment 239.—Preparation of phenyl isothiocyanate (phenyl mustard oil), $\text{C}_6\text{H}_5\cdot\text{N:C:S}$, from thiocarbanilide.*

(*To be conducted in a fume chamber.*)

25 grm. of the crude product obtained in the last experiment are distilled with 100 grm of concentrated hydrochloric acid from a large flask attached to a condenser. The mixture is heated on a sand bath until only about 20 c.cm. of liquid remain in the flask. The distillate is diluted with water, and the oil, which can be separated by means of a tap funnel, dried over calcium chloride, and redistilled, using an air condenser.

The product is a colourless liquid with a pungent odour resembling that of mustard oil. Boiling-point, 222°; $D_4^{15°}$, 1·135.

The residue in the flask contains the by-product triphenylguanidine (cf. Exp. 242).

Isolation of the by-product triphenylguanidine,

$$\text{C}\begin{matrix} \diagup \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{:N}\cdot\text{C}_6\text{H}_5 \\ \diagdown \text{NH}\cdot\text{C}_6\text{H}_5 \end{matrix}.$$

The residue in the flask after distillation of the phenyl mustard oil is diluted with 75 c.cm. of water, and allowed

* *Hofmann*, J. 1858, 349; *Weith* and *Merz*, Beil. II, 388.

to stand for several hours. The crystals of triphenylguanidine hydrochloride are filtered off, and the free base isolated by warming the hydrochloride with a little dilute alkali. It is filtered off and recrystallized from a little alcohol.

Characteristic Reactions of the Mustard Oils.

(i) The mustard oils form additive compounds (substituted thioureas) with ammonia,* hydroxylamine, and amino compounds, *e.g.*:

$$C_6H_5N{:}C{:}S + NH_3 \longrightarrow C_6H_5NH{\cdot}CS{\cdot}NH_2.$$

Experiment 240.—Heat a small quantity of phenyl isothiocyanate with a little alcohol and concentrated ammonia solution for a few minutes. On cooling, crystals of phenyl thiocarbamide separate. Melting-point, 154°.

Treated similarly with aniline, diphenyl-thiocarbamide is formed:

$$C_6H_5N{:}C{:}S + H_2N{\cdot}C_6H_5 \longrightarrow (C_6H_5NH)_2{:}C{:}S.$$

(ii) When boiled with alcohols the mustard oils yield esters of thiocarbanilic acid,† *e.g.*:

$$C_6H_5N{:}C{:}S + HO{\cdot}Et \longrightarrow C_6H_5NH{\cdot}CS{\cdot}OEt.$$

Experiment 241.—5 grm of phenyl mustard oil are boiled with 15 c.cm. of absolute alcohol in a reflux apparatus on a water bath for three hours. The product is poured into cold water, and the solid which separates is recrystallized from alcohol. Melting-point, 67°.

(iii) When heated with yellow mercuric oxide the isothiocyanates are converted into the corresponding oxygen compounds.

$$C_6H_5N{:}C{:}S + HgO \longrightarrow C_6H_5N{:}C{:}O + HgS.$$

The mercuric oxide blackens owing to formation of the sulphide. The phenyl isocyanate is detected by its characteristic irritating odour.

Triphenylguanidine is obtained in larger amount by the condensation of thiocarbanilide with aniline through the agency of *lead oxide* or *mercuric oxide* (cf. equation above).

Experiment 242.—Preparation of triphenylguanidine.‡

10 grm. of thiocarbanilide (Exp. 238) and 5 grm. of aniline dissolved in 50 c.cm. of alcohol are heated in a beaker on

* *Hofmann*, J. 1858, 349. † *Ibid.*, B 1870, **3**, 772.
‡ *Ibid.*, B. 1869, **2**, 458.

a water bath. 15 grm. of litharge are gradually added, the mixture being frequently stirred. The product is filtered while hot, and the residue is washed several times with hot alcohol. On cooling, triphenylguanidine separates as crystals These are filtered off and the mother liquor poured into water, whereby the remaining substance is precipitated. The yield is almost quantitative, and the product crystallizes from alcohol in colourless needles, melting point 143°.

D. Sulphuric Acid

Experiment 243. — Condensation of benzyl alcohol and benzene to diphenylmethane.*

$$C_6H_5\cdot CH_2\cdot OH + H\cdot C_6H_5 \rightarrow C_6H_5\cdot CH_2\cdot C_6H_5 + H_2O.$$

A mixture of equal parts by weight of concentrated sulphuric and glacial acetic acids is run into a mixture of 12 grm. of benzyl alcohol (Exp. 28), 30 grm. of benzene, and 100 grm. of glacial acetic acid, until the benzene has separated to a large extent as an oily layer floating on the surface. The whole is left until next morning, when 500 grm. of concentrated sulphuric acid are added, whilst the mixture is kept well cooled. After several hours the mass is poured into water, extracted with ether, the ethereal solution dried with calcium chloride, the ether removed, and the residue fractionated.

It is a colourless oil, boiling-point 261–262°, solidifies to needle-shaped crystals, melting-point 23°, and has an odour of oranges.

Substituted benzyl alcohols and mandelic acid react in much the same manner as benzyl alcohol itself, and the benzene may be replaced by various nitro-derivatives, amines, or phenols.

As a further example of the condensing action of this reagent, **Skraup's quinoline synthesis**† may be given (S. B 540). This consists in the condensation of an amino-compound with glycerol and an oxidizing agent in the presence of concentrated sulphuric acid, *e.g.*:

$$\begin{array}{l} CH{:}CH\cdot CH \\ \dot{C}H{:}CH\cdot\ddot{C}\cdot NH_2 \end{array} + \begin{array}{l} OH\cdot CH_2\cdot CH\cdot OH \\ \quad\quad\dot{C}H_2\cdot OH \end{array} + O \rightarrow \begin{array}{l} CH{:}CH\cdot C\cdot CH{:}CH \\ \dot{C}H{:}CH\cdot\ddot{C}\cdot N{=}\dot{C}H \end{array} + 4H_2O.$$

* *V. Meyer* and *Würster*, B. 1873, **6**, 964.
† M. 1881, **2**, 139; B. 1881, **14**, 1002.

Nitrobenzene is generally used as oxidizing agent, but arsenic acid gives better results.

Experiment 244.—Preparation of quinoline, C_9H_7N, from aniline and glycerol.

36 grm. of aniline, 24 grm. of nitrobenzene,* and 100 grm. of glycerol are mixed in a large flask, and 100 grm. of concentrated sulphuric acid added gradually, with shaking. The flask is then fitted to a *long and wide reflux condenser*, and heated on a sand bath until the reaction commences, as shown by the sudden evolution of bubbles of white vapour throughout the liquid. The source of heat is removed immediately, and the vigorous reaction allowed to continue without the further aid of external heat. When the reaction has moderated, the contents of the flask are further heated for two to three hours. The product is diluted with water and steam-distilled in order to remove unchanged nitrobenzene. The residue in the flask is then made alkaline by the gradual addition of strong sodium hydroxide solution, and again distilled with steam The distillate contains both quinoline and aniline. To remove the aniline, the distillate is treated with dilute sulphuric acid until the oil is completely dissolved and an excess of acid is present. The solution is cooled, and then treated gradually with a solution of sodium nitrite, until a drop of the liquid gives a blue coloration with potassium iodide-starch paper By this means the aniline is diazotised, while the tertiary amine, quinoline, is unchanged. The product is boiled for some time on a water bath to convert the diazo-compound into phenol, again made alkaline, and distilled with steam. The quinoline now passes over in a pure condition, and is taken up with ether; the ethereal solution is dried with solid potassium hydroxide, the ether removed, and the residue distilled, when the base is obtained as a colourless liquid with a characteristic odour. Boiling-point, 237°. $D^{0°}_{4°}$, 1·108. It has the properties of a tertiary base (cf. Chap. XVIII, E). Yield, 35 grm., *i.e.* 70 per cent of theory.

E. Amines

Compounds of the type of ethyl acetoacetate (Chap. XXIV), or ethyl malonate (Chap. XXV), condense readily with aldehydes, &c., under the influence of primary or secondary amines as condensing agents. A small quantity only of the amine is generally sufficient to produce large quantities of the conden-

* Or 55 grm. of arsenic acid. Knüppel, B, 1896, 29, 704.

sation product. The reaction is a continuous one, an intermediate product of the amine with the aldehyde being probably formed.

$$R\cdot CH{:}O + H_2N\cdot R' \longrightarrow R\cdot CH{:}N\cdot R' + H_2O;$$

$$\text{or, } R\cdot CH{:}O + \begin{matrix}H\\H\end{matrix}\!\!\begin{matrix}NR'_2\\NR'_2\end{matrix} \longrightarrow R\cdot CH\!\!\begin{matrix}NR'_2\\NR'_2\end{matrix}.$$

These compounds are then decomposed by interaction with the ester, regenerating the amine

Experiment 245.—Condensation of ethyl malonate with formaldehyde by the agency of diethylaniline; Preparation of methylene-dimalonic ester.*

$$CH_2{:}O + \begin{matrix}H\cdot\\H\cdot\end{matrix}\!\!\begin{matrix}CH(CO_2Et)_2\\CH(CO_2Et)_2\end{matrix} \longrightarrow CH_2\!\!\begin{matrix}CH(CO_2Et)_2\\CH(CO_2Et)_2\end{matrix} + H_2O.$$

32 grm of ethyl malonate (Exp. 211) are mixed with 8 grm. of a 40 per cent aqueous solution of formaldehyde, and, after cooling with ice, 0·5 grm of diethylamine added. The mixture is allowed to stand in a well-stoppered flask for twelve hours at the ordinary temperature, and then, in order to complete the reaction, is heated on a water bath for several hours. The water formed is separated off, and the remaining oil fractionally distilled under reduced pressure (cf fig. 9). A previous drying of the oil is unnecessary if the temperature during the distillation is kept below 50° until all the water passes over. The product boiling at 190–200° under 12 mm. pressure is pure methylene-dimalonic ester. Yield 30 grm., *i.e.* 90 per cent of theory. Boiling-point, 197–198° at 12 mm. pressure.

The gram-molecule of the above condensation product on hydrolysis with concentrated acids loses two gram-molecules of carbon dioxide, and is converted into glutaric acid.

$$CH_2\!\!\begin{matrix}CH(CO_2Et)_2\\CH(CO_2Et)_2\end{matrix} \longrightarrow CH_2\!\!\begin{matrix}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}.$$

Experiment 246.—Preparation of glutaric acid.

20 grm of methylene-dimalonic ester are warmed with a mixture of 20 grm. of concentrated hydrochloric acid and 20 c.cm. of water, for six hours, in a reflux apparatus. The product is evaporated to dryness, and the remaining glutaric acid distilled *in vacuo*, when it passes over at 185–195° under

* *Knoevenagel*, B. 1894, 27, 2346.

10 mm. pressure. A small amount of the anhydride which is produced during the distillation is got rid of by warming the distillate with a few drops of water. The product is crystallized from benzene. Yield 6 grm., *i.e.* 75 per cent of theory. Melting-point, 97–98°.

Experiment 247.—Condensation of cinnamic aldehyde and malonic acid to cinnamylidene-malonic acid, $C_6H_5 \cdot CH:CH \cdot CH:C(CO_2H)_2$.*

Equal weights of cinnamaldehyde (pure), malonic acid, and quinoline are mixed and kept at the ordinary temperature for twenty-one days in a corked flask. The mixture is then made alkaline with potassium hydroxide solution, the quinoline extracted by shaking with ether, and the alkaline aqueous liquid acidified with sulphuric acid An almost theoretical yield of cinnamylidene-malonic acid is precipitated, and is removed by means of the pump, washed with water, dried, and recrystallized from alcohol. It forms bright yellow needles, melting-point 206°, and when heated above its melting-point loses carbon dioxide and yields the corresponding monobasic acid, melting at 165–166°. When reduced, as in Exp. 218, at 30° it yields 1:4-dihydrocinnamylidene-malonic acid, $C_6H_5 \cdot CH_2 \cdot CH:CH \cdot CH(CO_2H)_2$, melting-point 112°.

F. Condensation in the Electrolytic Cell

In the electrolysis of salts of organic acids the complex residue which separates at the anode is generally incapable of independent existence, and consequently undergoes decomposition or condensation (cf. page 89). The electrolysis of the alkali salts of the mono-ethyl esters of dicarboxylic acids affords a means for the preparation of higher acids of the same series, *e.g.* potassium ethyl succinate, $CO_2Et \cdot CH_2 \cdot CH_2 \cdot CO_2K$, on electrolysis yields the monovalent residue, $CO_2Et \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot$, which when released at the anode decomposes according to the equation—

$$2CO_2Et \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot \longrightarrow \begin{matrix} CH_2 \cdot CH_2 \cdot CO_2Et \\ | \\ CH_2 \cdot CH_2 \cdot CO_2Et \end{matrix} + 2CO_2.$$

Experiment 248.—Preparation of ethyl adipate, $CO_2Et \cdot (CH_2)_4 \cdot CO_2Et$, from potassium ethyl succinate.†

* *Riiber*, B. 1904, **37**, 2274.

† *Crum Brown*, and *Walker*, T. R. S. E. 1891, **36**, 211; or A. 1891, **261**, 117.

50 c.cm. of a concentrated aqueous solution of potassium ethyl succinate (1·5 part of the salt to 1 part of water; cf. Exp. 83) are placed in a narrow beaker. The latter should not be more than half full, and should be cooled by standing in ice water. A platinum spiral is introduced as anode, the cathode being a platinum sheet, and the current used should be 50–100 amperes per square decimeter of anode surface. The arrangement of the apparatus should be as shown in fig. 73.

The electrolyte froths considerably during the experiment, gas is evolved, and an oily layer of adipic ester appears on the surface of the aqueous solution. At least fifteen ampere-hours should be employed. The oil is separated from the solution, washed with water, dried with calcium chloride, and distilled under diminished pressure. The lower boiling fraction contains ethyl acrylate, the higher fraction is collected separately and redistilled under atmospheric pressure, when it passes over at 245°. Yield, 30–35 per cent of theory.

XXIX. GRIGNARD'S REAGENTS

(For summary see *A. M'Kenzie*, B A. Rep. 1907; cf. S. B. 72, 120, 126, 143, 355, 438, 479.)

Practically all halogen derivatives, with the exception of acyl halides, react with metallic magnesium, forming additive compounds of the type R·Mg·X (R = alkyl, X = halogen), which are usually termed Grignard's reagents.* These substances are of enormous value as synthetical reagents, as by means of them the following groups of compounds can be synthesised· Paraffins, olefines, benzene homologues, primary, secondary, and tertiary alcohols, aldehydes, ketones, acids, phenols, sulphinic acids, and organo-metallic compounds. The reagents are usually prepared in the presence of perfectly dry ether, but they may also be obtained in dimethylaniline solution, or in benzene solution containing a small amount of ether, or of a tertiary base, or even by heating the metal and alkyl iodide.

When ether is used as solvent a compound of the type $CH_3 \cdot Mg \cdot I$, $(C_2H_5)_2O$, or $CH_3 \cdot Mg \cdot I$, $2(C_2H_5)_2O$, is formed

* *Grignard*, C. R. 1900, 130, 1322.

These compounds are comparatively stable, and react in the same manner as the simple compound, $CH_3 \cdot Mg \cdot I$. When aryl halides are used it is often necessary to add a crystal of iodine or a drop or two of methyl iodide to start the reaction.

A. Preparation of a Grignard Reagent

Experiment 249.—Preparation of phenyl magnesium bromide, $C_6H_5 \cdot Mg \cdot Br$.

For success in this preparation the reagents must be thoroughly dry. Magnesium in the form of clean ribbon or powder is dried in an oven at 110–120° for several hours. The phenyl bromide is allowed to stand for some time over fused calcium chloride and then redistilled. The ether is purified and dehydrated, as in Exp. 31.

2·4 grm. of magnesium are placed in a dry flask of 250 c.cm. capacity, together with about 50 c.cm. of ether and 15·7 grm of monobrombenzene. The flask is attached to a reflux condenser, the inner tube of which has been thoroughly dried, and is heated gently on a water bath. If the reaction does not commence soon it is facilitated by the addition of a fragment of iodine, and the heating is continued until all (or nearly all) the magnesium has dissolved. Access of moisture into the flask is prevented by fitting a calcium chloride tube to the upper end of the condenser.

In the preparation of Grignard's reagents small amounts of hydrocarbons are usually formed, *e.g.* in the above reaction, diphenyl:

$$2C_6H_5Br + Mg = C_6H_5 \cdot C_6H_5 + MgBr_2.$$

This secondary reaction is especially noticeable with alkyl halides of high molecular weight.

B. Preparation of a Benzene Homologue

Experiment 250.—Preparation of *p*-xylene from *p*-bromotoluene.*

$$C_6H_4\begin{matrix}CH_3 & (1)\\ Mg \cdot Br & (4)\end{matrix} \rightarrow C_6H_4\begin{matrix}CH_3 & (1)\\ CH_3 & (4)\end{matrix}.$$

50 grm. of *p*-bromotoluene, 7·4 grm. of magnesium, and

* *Werner* and *Zilkins*, B. 1903, **36**, 2116.

150 c.cm. of anhydrous ether are heated as in Exp 249. When practically all the magnesium is dissolved a solution of 37 grm. of methyl sulphate in dry ether is added. After the vigorous reaction has ceased the product is poured on to ice, the ether distilled off, and the residue subjected to steam distillation. The oil which passes over is separated and fractionated. Yield 30 grm., *i.e.* 74 per cent of theory. It is a colourless oil, boiling-point 137–139°.

A small amount of solid *p*-ditolyl is deposited in the condenser when all the *p*-xylene has been driven over by the steam.

C Synthesis of Secondary Alcohols

Experiment 251 —Preparation of benzhydrol, $(C_6H_5)_2CH \cdot OH$, from benzaldehyde.

$$C_6H_5 \cdot Mg \cdot Br + C_6H_5 \cdot CHO \longrightarrow (C_6H_5)_2CH \cdot O \cdot MgBr$$
$$(C_6H_5)_2CH \cdot O \cdot MgBr + HCl \longrightarrow (C_6H_5)_2CH \cdot OH + Mg(Br)Cl.$$

A solution of 10·6 grm of freshly distilled benzaldehyde in 25 c.cm. of dry ether is placed in a dry flask fitted with a reflux condenser, and the Grignard reagent, prepared as in Exp 249, gradually added A vigorous reaction occurs, and a precipitate of the intermediate compound (cf. equation) separates. The reaction is completed by heating the mixture on a water bath for fifteen to thirty minutes; it is then cooled, and poured gradually into excess of dilute hydrochloric acid, with continual shaking and cooling, until all the precipitate has dissolved. The aqueous layer is separated and extracted with ether, the extract added to the original ethereal solution, and the whole shaken with a dilute solution of sodium bisulphite to remove any unchanged benzaldehyde; it is then dried over anhydrous potassium carbonate, and the ether distilled off. The oily residue solidifies on standing, and the crystals are dried on a porous plate and recrystallized from ligroin, when the benzhydrol is obtained as colourless needles, melting-point 68°, boiling-point 298° (with decomposition). Yield 13 grm., 70 per cent of theory.

D. Synthesis of Tertiary Alcohols

Experiment 252. — Preparation of triphenyl-carbinol, $(C_6H_5)_3C\cdot OH$, from methyl benzoate.*

$$C_6H_5C\langle^{O}_{OMe} \rightarrow (C_6H_5)_2C\langle^{O\cdot MgBr}_{OMe} \rightarrow (C_6H_5)_3C\cdot O\cdot MgBr \rightarrow (C_6H_5)_3C\cdot OH.$$

The Grignard reagent, prepared as in Exp. 249, is added to a solution of 7 grm. of methyl benzoate in 10 c.cm. of dry ether. After the reaction has moderated the mixture is heated on a water bath for an hour to render it complete. It is then treated with hydrochloric acid, as in Exp. 251. The ether is removed, and the residue steam-distilled in order to remove unchanged bromobenzene and a little diphenyl. The carbinol which is not volatile with steam is recrystallized from alcohol, and is deposited as colourless crystals, melting-point 159°, boiling-point above 360°.

Tertiary alcohols can also be prepared by the action of Grignard's compounds on ketones and on acid chlorides. The initial magnesium products yield the alcohols when treated with dilute mineral acids.

$$C_6H_5\cdot Mg\cdot Br + (C_6H_5)_2C{:}O = (C_6H_5)_3C\cdot O\cdot MgBr$$
$$(C_6H_5)_3C\cdot O\cdot MgBr + HCl = (C_6H_5)_3C\cdot OH + MgBrCl.$$

The yield is practically quantitative.

E. Preparation of Olefine Hydrocarbons

In attempting to prepare certain secondary and tertiary alcohols by means of Grignard's reagents, olefines are frequently obtained, especially when the ether is removed and the residue heated, thus, when phenyl magnesium bromide reacts with acetyl chloride the product is not diphenyl-methyl carbinol, $(C_6H_5)_2C\langle^{OH}_{CH_3}$, but diphenyl-ethylene, $(C_6H_5)_2C{:}CH_2$.† These olefines are undoubtedly formed by the elimination of basic magnesium halides, *e.g.* Mg(OH)I, from the original product.

Experiment 253. — Preparation of diphenyl-propene,

* *Ullmann* and *Munzhuber*, B. 1903, **36**, 406.
† *Tissier* and *Grignard*, C. R. 1901, **132**, 1182.

$(C_6H_5)_2CH{:}CH{\cdot}CH_3$, from benzophenone and magnesium ethyl iodide.*

$$(C_6H_5)_2C{:}O \longrightarrow (C_6H_5)_2C\begin{matrix}O{\cdot}MgBr\\ CH_2{\cdot}CH_3\end{matrix} \longrightarrow (C_6H_5)_2C{:}CH{\cdot}CH_3.$$

18 grm. of finely divided and dry benzophenone are added to the Grignard compound obtained by dissolving 5 grm. of dry magnesium and 32 grm. of ethyl iodide in 50 c.cm. of anhydrous ether The reaction is vigorous and the flask may require cooling. The mixture is ultimately heated for five hours on the water bath. It is then treated with dilute acid, extracted with ether, and the residue left after removal of the ether distilled under reduced pressure. The hydrocarbon distils at 169–170° under 18 mm pressure. It solidifies on cooling to crystals, melting-point 52°, and may be crystallized from alcohol or ligroin.

F Synthesis of Carboxylic Acids

Carboxylic acids can be synthesised by passing carbon dioxide into ethereal solutions of Grignard's compounds and then decomposing with water.

$$R{\cdot}MgI \longrightarrow R{\cdot}CO{\cdot}OMgI \longrightarrow R{\cdot}CO{\cdot}OH.$$

The yields are not always good, and tertiary alcohols are sometimes formed.

Another method of synthesising acids in the form of their esters, is by the action of ethyl chloroformate, $Cl{\cdot}CO_2Et$, on the ethereal solution of the Grignard compound.†

$$R{\cdot}Mg{\cdot}Cl + Cl{\cdot}CO_2Et \longrightarrow R{\cdot}CO_2Et + MgCl_2.$$

If excess of the Grignard compound is used, appreciable amounts of tertiary alcohols are formed.

Experiment 254.—Preparation of triphenylacetic acid, $(C_6H_5)_3C{\cdot}CO_2H$, from triphenylchloromethane.‡

(*a*) Preparation of triphenylchloromethane from carbon tetrachloride and benzene. (Application of *Friedel* and *Craft's* reaction, Chap. XXI, B.)

$$CCl_4 + 3\,C_6H_6 \longrightarrow Cl{\cdot}C(C_6H_5)_3 + 3HCl.$$

* *Klages*, B. 1902, **35**, 2647. † *Houben*, B. 1903, **36**, 3087.
‡ *Schmidlin*, B. 1906, **39**, 634.

10 grm. of dry carbon tetrachloride and 35 grm. of pure dry benzene are placed in a flask fitted with a long reflux condenser, 12·5 grm. of freshly prepared and powdered aluminium chloride (Chap. XXXIX) are added in two or three portions. When the vigorous reaction has ceased, the mixture is heated for an hour on the water bath, then cooled and carefully poured on to ice, surrounded by a freezing mixture. The addition must be carried out very slowly and the mixture well stirred, benzene being added to dissolve the triphenylchloromethane as it separates The benzene solution is removed, washed with dilute hydrochloric acid, then rapidly with a little water, dried over calcium chloride, and concentrated on the water bath. About 50 per cent of the chloro-compound crystallizes on cooling, and a further quantity is obtained by removing the benzene from the filtrate under diminished pressure and washing the residue with ether.

It forms colourless crystals, melting-point 108–112°. Yield 70–85 per cent.

(*b*) Preparation of triphenylacetic acid

A mixture of 10 grm. of triphenylchloromethane, 0·05 grm. of iodine, 50 c.cm. of dry ether, and 2 grm of magnesium powder is heated in a reflux apparatus to boiling, and a stream of dry carbon dioxide led into the boiling solution for some three hours, or until the red colour disappears and the liquid is filled with a lemon-yellow precipitate. The mixture is shaken from time to time, and ether is periodically added as it is removed by the carbon dioxide When the reaction is complete, 60 c.cm. of water are added to the flask, the mixture well shaken, poured into a dish, and gradually treated with 40 c cm. of concentrated hydrochloric acid. The whole is boiled for five minutes and well stirred. When cold, the crude acid is filtered off, washed, and then boiled in a dish with 200 c.cm. of 10 per cent sodium hydroxide solution and 100 c.cm. of water. After dilution with 300 c.cm. of water, and allowing to cool, the mixture is filtered and the clear filtrate precipitated with 100 c.cm. of concentrated hydrochloric acid. To render the precipitated acid more granular the mixture is heated for some time, then cooled, filtered, and the precipitate washed and dried. Yield 8·5 grm., *i.e.* 83 per cent of theory.

It crystallizes from glacial acetic acid in long, glistening prisms, melting-point 264–265°.

G. Reformatsky's Synthesis

In many cases it is not necessary to prepare the Grignard compound separately, but it suffices to introduce magnesium (or usually zinc) and the halogen derivative directly into the other reacting substance. (*Reformatsky's* condensation *)

Experiment 255.—Preparation of ethyl β-hydroxy-αβ-dimethylbutyrate from acetone, zinc, and ethyl α-bromopropionate. †

$$(CH_3)_2C{:}O + CH_3{\cdot}CHBr{\cdot}CO_2Et + Zn \longrightarrow$$

$$(CH_3)_2C\!\!<\!\!\begin{matrix}OZnBr\\ CH(CH_3){\cdot}CO_2Et\end{matrix} \longrightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!\!C(OH){\cdot}CH(CH_3){\cdot}CO_2Et.$$

To a mixture of 90 grm. of pure dry acetone and 182 grm. of ethyl α-bromopropionate ‡ contained in a large flask fitted with a wide reflux condenser, a small amount of dry and carefully cleaned zinc § is added. On warming gently on a water bath a reaction commences and usually proceeds very briskly, the flask sometimes requiring to be cooled. When the reaction subsides more zinc is added, and this is repeated until there is some zinc left undissolved (about 45 grm. of the metal are required). After the mixture has been heated for 2–3 hours on a boiling-water bath, the syrupy product is poured off as far as possible from the residual zinc and treated with water. The mixture sets to a thick white paste, owing to the formation of the basic zinc bromide, which can be dissolved by addition of dilute sulphuric acid. The thick oily ester which separates is taken up with ether, the ethereal solution is washed three times with dilute sulphuric acid and finally with water, and dried over calcium chloride. The ether is removed and the residue distilled under reduced pressure (30 mm, fig. 9), a considerable portion distils over below 100° at this pressure, but about 50 per cent of the oil distils at 105°, and is the pure ester.

* J. R. C. S. 1890, **22**, 49. † *W. H. Perkin*, J. C. S. 1896, **69**, 1482.

‡ Prepared from propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$, by application of the reactions illustrated by Exps 43, 44, and 79.

§ Zinc filings are washed successively with hot alkali, then dilute acid, water, alcohol and ether, and finally dried in an air oven.

XXX. DYES

A. The Azo Dyes

(S. B. 397. Cf. Chap. XX, H.)

B. The Triphenylmethane Dyes. (S. B. 480–491.)

The hydrocarbon, triphenylmethane, $H \cdot C(C_6H_5)_3$, is the mother substance of a series of important dyes which may be considered as anhydro-derivatives of the salts of amino- or hydroxy-derivatives of triphenyl-carbinol, $HO \cdot C(C_6H_5)_3$. The entrance of three amino- or hydroxy-groups converts compounds of this type into dyes. Two amino-groups suffice for the development of the dyeing power only when the amino-hydrogen atoms are replaced by alkyl radicals.

The following are the chief groups:—

1. The Derivatives of Diamino-triphenylmethane: the Malachite-green Series (S. B. 481.)

An aromatic aldehyde is condensed with a tertiary amine in the presence of zinc chloride.

$$C_6H_5 \cdot CH{:}O + \begin{matrix} H \cdot C_6H_4 \cdot NMe_2 \\ H \cdot C_6H_4 \cdot NMe_2 \end{matrix} \longrightarrow H_2O + C_6H_5 \cdot CH(C_6H_4 \cdot NMe_2)_2$$

The leuco-base, which is a derivative of diamino-triphenylmethane, is then oxidized to the corresponding carbinol, $C_6H_5 \cdot C(OH)(C_6H_4 \cdot NMe_2)_2$, the dye base, which reacts with acids forming salts, and these immediately give up water and form the dye itself.

Experiment 256.—Preparation of malachite green from benzaldehyde and dimethylaniline.*

The dye is isolated in the form of its double salt with zinc chloride.

$$3\left(C\begin{matrix} C_6H_5 \\ C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 : N(CH_3)_2Cl \end{matrix}\right), ZnCl_2, H_2O.$$

(*a*) Preparation of the Leuco-base, Tetramethyldiamino-triphenylmethane.

* *Otto Fischer*, A. 1877, 206, 122.

50 grm. of dimethylaniline, 20 grm. of benzaldehyde, and 20 grm. of freshly fused zinc chloride are heated for four hours in a porcelain dish on a water bath, care being taken that the mixture is frequently stirred. The product is melted by heating with water, and transferred while hot into a $\frac{1}{2}$ litre flask, and subjected to steam distillation in order to remove any unchanged dimethyl-aniline. The leuco-base remains in the flask, and adheres to the glass; when cold the liquid is removed, the solid residue washed with water, and then dissolved in hot alcohol. After filtering, the solution is allowed to stand overnight in a cool place, when the base separates as colourless needles, which are filtered off and dried on filter paper. By concentrating the mother-liquor a second crop of crystals may be obtained Should the base separate in the form of an oil, the alcoholic solution is too concentrated, in such a case more alcohol is added, the whole is redissolved, and the crystallization repeated.

(*b*) **Oxidation of the Leuco-base**

$$C_6H_5\cdot CH[C_6H_4\cdot N(CH_3)_2]_2 + O \longrightarrow \underset{\text{Dye-base (carbinol)}}{C_6H_5\cdot C(OH)[C_6H_4\cdot N(CH_3)_2]_2}$$

$$C_6H_5\cdot C(OH)[C_6H_4\cdot N(CH_3)_2]_2 + HCl \longrightarrow \underset{\text{Malachite-green hydrochloride}}{C_6H_5C\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4:N(CH_3)_2Cl\end{matrix}} + H_2O$$

10 parts by weight of the leuco-base are dissolved in dilute hydrochloric acid containing exactly 2·7 parts of the anhydrous acid. The solution is diluted with 800 parts of water in a large flask, and treated with a 30–40 per cent solution of acetic acid containing 4 parts of anhydrous acid. The mixture is well cooled by adding pieces of ice, and is then oxidized by adding gradually a thin paste containing 7·5 parts of pure lead dioxide,* the whole being well shaken during the addition. After standing for five minutes, the solution is treated with a solution of 10 parts of sodium sulphate crystals in 50 parts of water, and filtered off from the precipitate of lead sulphate, &c. The filtrate is then treated with a filtered solution of 8 parts of zinc chloride in the least possible amount of water. On addition of excess of a saturated solution of common salt, the zinc chloride double salt of the dye separates, is filtered with the aid of the pump, and purified by redissolving in water and again salting out. It is finally dried on porous

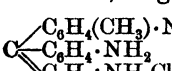
* For preparation, see Chap. XXXIX.

plate, and consists of bright-green crystals. The solution dyes silk, wool, &c., bluish-green.

Substituted benzaldehydes react in much the same manner as benzaldehyde, and various tertiary amines can be used instead of dimethylaniline.

2. **Dyes derived from Triamino-triphenyl-methane. The Rosaniline-group.** (S. B 482.)

As an example of this class, magenta (fuchsine)



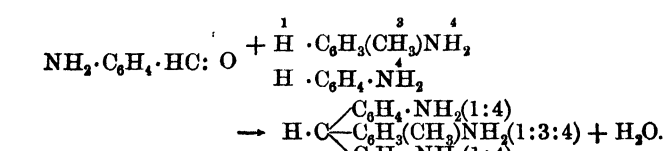
may be cited. The dye is prepared by oxidizing a mixture of equimolecular proportions of *o*-toluidine, *p*-toluidine, and aniline (the mixture of bases is described as "aniline oil for red") by means of arsenic acid or nitrobenzene. When the latter oxidizing agent is used, a solution of iron in hydrochloric acid is also added, this serves to start the process, the ferrous chloride being oxidized by the nitrobenzene to ferric chloride, which then effects the oxidation of the mixture of bases. The nitrobenzene does not appear to take any part in the formation of the dye beyond acting as an oxidizing agent.

The reactions are as follows:—

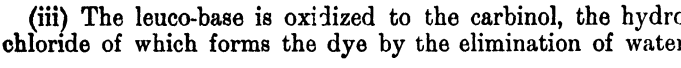
(i) *p*-toluidine is converted into the corresponding aldehyde:

$$CH_3 \cdot C_6H_4 \cdot NH_2(1:4) \longrightarrow CHO \cdot C_6H_4 \cdot NH_2(1:4).$$

(ii) The aldehyde condenses with one molecule of *o*-toluidine and one of aniline to form the leuco-base.



(iii) The leuco-base is oxidized to the carbinol, the hydrochloride of which forms the dye by the elimination of water.



Experiment 257.—Preparation of magenta.

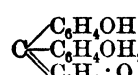
10 grm. of aniline and 40 grm. of commercial toluidine (a

mixture of 64 per cent of *o*-toluidine with 36 per cent of *p*-toluidine) are treated with 33 grm. of concentrated hydrochloric acid in a round flask of 250 c.cm. capacity, 28 grm. of nitrobenzene are added, and the mixture is heated to 100° in an oil bath. When this temperature is attained a solution of 1·5 grm. of iron powder, in just sufficient hydrochloric acid to dissolve it, is added gradually. The flask is then fitted with an air condenser, and the temperature raised gradually to 180°, at which point it is maintained until a sample of the melt, withdrawn by means of a glass rod, solidifies on cooling This requires four to six hours. The product is distilled with steam to remove nitrobenzene, &c., after which it is treated with 250 c.cm. of boiling water, and concentrated hydrochloric acid added until an acid reaction is obtained. 12 grm. of common salt are added, and the whole boiled for a few minutes. The aqueous solution which contains the hydrochlorides of aniline and toluidine is then poured off, the residue on cooling sets to a green brittle mass, which is broken up and extracted with 750 c.cm. of boiling water to which 6 c.cm. of concentrated hydrochloric acid have been added. The magenta dissolves, and is filtered off from any insoluble matter; after cooling to 60° it is again filtered. Salt is added, and after cooling and standing for some time, the magenta is filtered off and recrystallized from water containing a little hydrochloric acid.

The dye forms greenish glistening crystals which dissolve in water to a red solution. It dyes silk and wool bluish-red.

3. **The Derivatives of Trihydroxy-triphenylmethane. The Aurine-group.** (S. B. 488.)

Aurine,



is prepared by heating a mixture of phenol, oxalic acid, and sulphuric acid, the oxalic acid providing the "methane carbon atom".

Experiment 258.—Preparation of aurine.*

6 parts of phenol, 3 parts of concentrated sulphuric acid, and 4 parts of *anhydrous* oxalic acid (Exp. 75) are heated, at 120–130°, by means of an oil bath in a round flask fitted with an air condenser for twenty-four hours. The melt is extracted

* *Kolbe* and *Schmitt*, 1859.

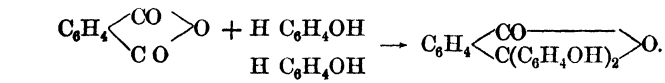
with water, and the residue dissolved in hot alcohol. Ammonia gas is passed into the solution, and the precipitate formed is boiled with hydrochloric acid. The product is filtered and recrystallized from a mixture of alcohol and acetic acid.

It consists of brilliant green needles with a metallic lustre, dissolves in alkalis with a red colour, and is thrown down again on the addition of acids.

4. **The Phthaleïns or Eosin-group.*** (S. B. 489.)

These may be regarded, on the one hand, as derivatives of triphenylmethane, and on the other as derivatives of phthalic acid. They are prepared by the action of phenols on phthalic anhydride (cf. p. 173).

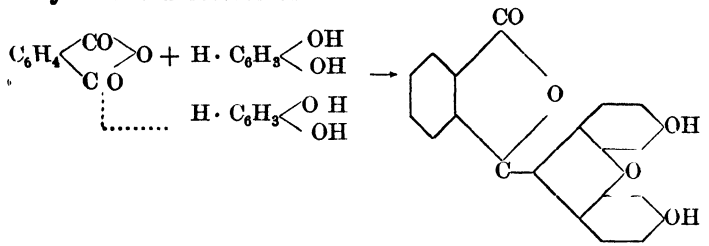
Experiment 259.—Preparation of phenolphthaleïn from phenol and phthalic anhydride.



5 grm. of phthalic anhydride (Exp 85) and 10 grm. of phenol are mixed with 4 grm. of concentrated sulphuric acid in a boiling tube, and heated in an oil bath at 115–120° for eight hours. The mass which assumes a dark-red colour is poured while hot into excess of cold water, and boiled to remove excess of phenol. The undissolved yellow powder is filtered off, washed with water, and extracted with dilute potassium hydroxide solution The solution is filtered from any undissolved residue, and the filtrate acidified with acetic acid and a few drops of hydrochloric acid. The phthalein is reprecipitated, filtered off, and dried. For further purification it is boiled for an hour on a water bath with about six times its weight of absolute alcohol and a little animal charcoal (use a reflux apparatus), filtered, and the residue washed thoroughly with hot absolute alcohol. The solution is treated with about eight times its volume of cold water, and after stirring is filtered through a previously wetted filter paper in order to remove the resinous oil which separates. On heating the filtrate on a water bath for some time, the alcohol is evaporated and the phenol phthalein separates out as a white crystalline powder, melting-point 250–253°. It is only very sparingly soluble in water, more soluble in alcohol, readily in hot alcohol, and dissolves in alkalis, yielding a crimson solution.

* *Baeyer*, A. 1876, **183**, 1; 1880, **202**, 36.

Experiment 260.—Preparation of fluoresceïn from phthalic anhydride and resorcinol.*

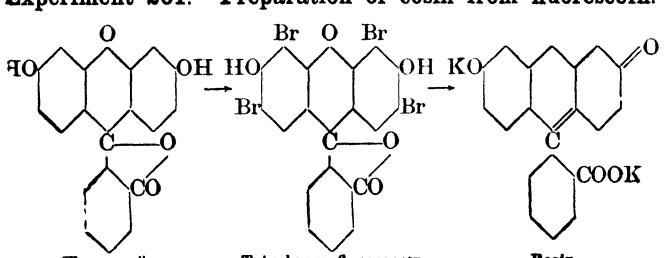


An intimate mixture of 10 grm. of phthalic anhydride (Exp. 85) and 15 grm. of resorcinol is heated in a nickel crucible or porcelain dish in an oil bath to 180°. When this temperature is attained 5 grm. of powdered fused zinc chloride are added gradually during ten minutes, the mixture being stirred with a glass rod. The temperature is then raised to 210°, and kept at this point until the mass becomes solid, for which one to two hours are required. After cooling, the solid mass is broken out with a chisel, powdered, and boiled for ten minutes with 200 c.cm. of water and 10 c.cm. of concentrated hydrochloric acid. The solution is filtered from the insoluble fluorescein, which is washed thoroughly with water and dried. Yield almost quantitative.

It is a dark-red crystalline powder, which dissolves in alcohol with a yellow-red colour and in alkalis with a red colour and splendid green fluorescence.

When treated with bromine, fluorescein yields red crystals of tetrabromofluorescein, the potassium salt of which is the dye eosin.

Experiment 261.—Preparation of eosin from fluoresceïn.



* *Baeyer*, A 1876, **183**, 3.

15 grm. of fluorescein are added to 60 grm. of alcohol in a small flask, and 33 grm. of bromine (11 c.cm.) are gradually added from a dropping funnel or burette. When half the bromine has been added, the dibromo-derivative which is formed has dissolved; on further addition of bromine the tetrabromo-derivative separates. After standing for two hours, the precipitate is filtered, washed with alcohol and then with water It is converted into the potassium salt by mixing with a little hot water, carefully adding the exact amount of potassium hydroxide solution (two equivalents), and evaporating to dryness on the water bath.

It forms brownish-red crystals, and dyes wool or silk yellowish-red.

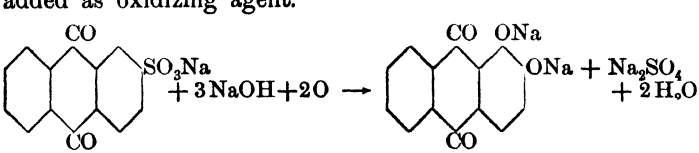
C. Anthraquinone Dyes—Alizarine (S. B. 507)

This important dye was originally obtained from madder root, in which it occurs in the form of a glucoside, ruberytheric acid, $C_{26}H_{28}O_{14}$ ($= HO \cdot C_{14}H_6O_2 \cdot O \cdot C_{12}H_{14}O_8(OH)_7$), which yields alizarine and glucose when boiled with hydrochloric acid.*

$$HO \cdot C_{14}H_6O_2 \cdot O \cdot C_{12}H_{14}O_3(OH)_7 + 2H_2O = C_{14}H_6O_2(OH)_2 + 2C_6H_{12}O_6.$$

Alizarine is a derivative of anthracene, for on distillation with zinc dust (cf. Exp 222*a*) it yields the latter compound.†

The dye is now prepared artificially by fusing anthraquinonesulphonic acid with sodium hydroxide, potassium chlorate being added as oxidizing agent.



Experiment 262.—Preparation of alizarine.‡

60 grm. of sodium hydroxide are dissolved in 60 c.cm. of water, and 20 grm. of sodium anthraquinonesulphonate (Exp. 116) added. 4 grm. of potassium chlorate dissolved in 20 c.cm

* *Liebermann* and *Bergami*, B. 1887, **20**, 2244.
† *Graebe* and *Liebermann*, B. 1868, **1**, 49.
‡ *Caro, Graebe*, and *Liebermann*, B. 1870, **3**, 359.

of hot water are mixed with the mass, which is placed in an autoclave,* the lid of which is firmly screwed on, and heated for twenty hours at 170°. After cooling, the melt is extracted several times with boiling water, and the solution acidified with hydrochloric acid. The alizarine which separates is filtered with the aid of the pump, and dried on porous plate in a steam oven.

It is a yellow powder, which is only sparingly soluble in hot water, but readily soluble in alcohol and ether; when sublimed it forms long red needles, melting-point 290°. It dissolves in alkalis, yielding a purple-red colour, and from such solutions the calcium and barium salts may be obtained as blue precipitates It dyes cotton mordanted with alumina (the fabric is immersed in aluminium acetate, and then heated) a scarlet-red colour, with ferric oxide, a dark-violet colour.

D. Indigo Blue (Indigotin)

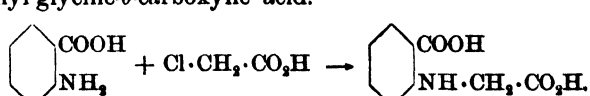
$$C_6H_4\langle\begin{matrix}CO\\NH\end{matrix}\rangle C{:}C\langle\begin{matrix}CO\\NH\end{matrix}\rangle C_6H_4. \quad \text{(S. B. 523.)}$$

This substance occurs in nature, especially in the indigo plant and in woad, as the glucoside indican, which yields indigo and glucose when hydrolysed with dilute acid.

The dye is now manufactured artificially on a large scale by an application of Heumann's synthesis, which consists of the following steps:—

Naphthalene → Phthalic acid (Exp. 51) → Phthalic anhydride (Exp. 85) → Phthalimide (Exp. 94) → Anthranilic acid (Exp. 132).

Anthranilic acid condenses with chloracetic acid, yielding phenyl-glycine-*o*-carboxylic acid.



* An autoclave is a stout metal vessel, frequently enamelled inside, and in it substances can be heated under pressure. The vessel is provided with a metal lid, which can be screwed on and the whole made air-tight. A safety-valve and a manometer are attached to the autoclave, and by means of the latter the pressure inside the vessel is registered. In all cases the pressure must be kept well below that to which the special autoclave has been tested. The temperature is registered by means of a thermometer dipping into mercury contained in a depression of the lid.

The latter on fusion with potassium hydroxide yields indoxyl,

$$C_6H_4\langle\begin{matrix}COOH\\NH\cdot CH_2\cdot CO\cdot OH\end{matrix} \rightarrow C_6H_4\langle\begin{matrix}C(OH)\\NH\end{matrix}\rangle CH + H_2O + CO_2,$$

which can be oxidized to indigo blue.

$$C_6H_4\langle\begin{matrix}C(OH)\\NH\end{matrix}\rangle CH + CH\langle\begin{matrix}C(OH)\\NH\end{matrix}\rangle C_6H_4 + O_2$$
$$\rightarrow C_6H_4\langle\begin{matrix}CO\\NH\end{matrix}\rangle C:C\langle\begin{matrix}CO\\NH\end{matrix}\rangle C_6H_4 + 2H_2O.$$

Experiment 263.—Preparation of phenylglycine-*o*-carboxylic acid from anthranilic acid and chloracetic acid.*

13·6 grm. of anthranilic acid (Exp. 132) and 9·4 of chloracetic acid are dissolved in 100 c.cm. of water containing 11·2 grm. of potassium hydroxide in solution, and warmed in a reflux apparatus in a water bath at 60–80° for two hours. The product is neutralized with hydrochloric acid and allowed to stand, and the precipitated phenylglycine-*o*-carboxylic acid is filtered off and dried; a further yield is obtained by evaporating and cooling the filtrate. The acid is recrystallized from hot water, and is obtained as colourless crystals, melting-point (with decomposition) 200°. It is only sparingly soluble in water, and the alcoholic solution shows a blue fluorescence.

Experiment 264.—Preparation of indigo blue from phenylglycine-*o*-carboxylic acid.†

A mixture of 1 part of phenylglycine-*o*-carboxylic acid and 3 parts of potassium hydroxide is fused in a nickel crucible, the mass being well stirred by means of a thermometer.‡ At 180–200° the mass becomes yellow coloured, and subsequently reddish-yellow, and the heating is continued until the depth of the colour no longer increases. The cooled melt is added to about 200 parts of water, and a current of air led through the solution until a test-portion, withdrawn for the purpose, no longer produces a bluish precipitate when air is drawn through. When the oxidation is completed the precipitate of indigo is filtered, washed successively with water, dilute hydrochloric acid, and alcohol, and finally dried.

Indigo forms a dark-blue powder with coppery lustre. It is insoluble in most solvents (including alkalis and acids), but dissolves to a blue solution in hot aniline, and to a red one in paraffin, from either of which it may be crystallized.

* *Heumann*, B. 1890, **23**, 3432. † *Ibid.* 3434.

‡ Or, better, a short iron tube containing a thermometer.

It is converted by reducing agents, *e.g.* grape sugar and sodium hydroxide, into the leuco-compound *indigo white*, $C_{16}H_{12}O_2N_2$, a white crystalline substance, soluble in alcohol, ether, and alkalis The alkaline solution is oxidized rapidly by atmospheric oxygen, and indigo is deposited. In dyeing with indigo the fabric is impregnated with indigo white, which is then oxidized on the fabric.

XXXI. IODINE COMPOUNDS CONTAINING A POLYVALENT IODINE ATOM. (S. B. 357–358.)

A. Iodide Chlorides

Iodine atoms attached directly to a benzene nucleus may in many cases unite with other atoms, yielding compounds in which iodine exercises a higher valency than one. Thus phenyl iodide and its homologues combine readily with chlorine, yielding dichlorides, *e.g.*:

$$C_6H_5I + Cl_2 \longrightarrow C_6H_5 \cdot I{:}Cl_2.$$

Experiment 265.—Preparation of phenyl-iodide dichloride, $C_6H_5ICl_2$, from phenyl iodide.*

Chlorine dried by bubbling through two wash bottles containing concentrated sulphuric acid is led through a *wide* delivery tube into a solution of phenyl iodide (10 grm.) (Exp. 156) in dry chloroform (20 c.cm.). During the passage of the gas, the solution is cooled by ice water, and when no more gas is absorbed the yellow crystals are filtered off, washed with chloroform, and allowed to dry in a desiccator. Yield, nearly quantitative.

B. Iodoso-compounds

The chloride is very unstable, and is decomposed slowly by moist air, also by warming and by treatment with potassium iodide solution. Treated with alkalis, the chlorine atoms are exchanged for oxygen:

$$C_6H_5I{:}Cl_2 + 2H_2O \longrightarrow C_6H_5I{:}(OH)_2 + 2HCl,$$

or

$$C_6H_5I{:}Cl_2 + H_2O \longrightarrow C_6H_5I{:}O + 2HCl.$$

* *Willgerodt*, J. pr. 1886, **33**, 154; B. 1892, **25**, 3494.

The product obtained after drying in air is iodoso-benzene, $C_6H_5I{:}O$.

In addition to the above a secondary reaction occurs, resulting in the formation of an iodonium base. A small portion of the iodoso-benzene, $C_6H_5I{:}O$, is probably oxidized to iodoxybenzene, $C_6H_5IO_2$ (cf. Exp. 268), which reacts with the hypothetical hydroxide, $C_6H_5I(OH)_2$, probably present in the solution, forming diphenyl-iodonium hydroxide.

$$C_6H_5I\langle^{OH}_{OH} + IO_2\cdot C_6H_5 \rightarrow C_6H_5{-}I(OH){-}C_6H_5 + HIO_3.$$

This base is present in the alkaline filtrate after removal of the iodoso-benzene, and can be precipitated in the form of an insoluble iodide by saturating the solution with sulphur dioxide gas, which reduces the iodic acid to hydriodic acid, and at the same time neutralizes the excess of alkali (cf Exp 269).

Experiment 266.—Preparation of iodoso-benzene, $C_6H_5I{:}O$, from phenyl-iodide dichloride: Isolation of diphenyl-iodonium iodide, $(C_6H_5)_2{:}I\cdot I$.

10 grm. of phenyl-iodide dichloride are rubbed with excess of a 5 per cent solution of sodium hydroxide in a mortar, and allowed to stand for at least five hours. The iodoso-benzene, which forms a white amorphous substance, is filtered off, washed well with water, and air-dried.

The alkaline filtrate is saturated with sulphur dioxide gas, and the precipitated diphenyl-iodonium iodide removed and crystallized from a small quantity of hot water.

Iodoso-benzene puffs up and decomposes when heated to about 210°. It dissolves in water, yielding a neutral solution.

The iodoso-compounds are quantitatively decomposed by hydriodic acid (an acidified solution of potassium iodide), *e.g.*:

$$C_6H_5I{:}O + 2HI \rightarrow C_6H_5I + I_2 + H_2O,$$

but form salts with all acids that are not readily oxidized, *e.g.*:

$$C_6H_5IO + 2CH_3\cdot CO_2H \rightarrow C_6H_5I\langle^{O\cdot CO\cdot CH_3}_{O\cdot CO\cdot CH_3} + H_2O.$$

Experiment 267.—Prepare crystals of **iodoso-benzene acetate** by dissolving a few grams of iodoso-benzene in the smallest possible quantity of glacial acetic acid, evaporating to dryness on a water bath, and recrystallizing the residue from a little benzene. It forms colourless prisms, melting-point 156–157°.

C. Iodoxy-compounds

The iodoso-compounds when heated carefully to 90–100° change into iodoxy-compounds and aryl iodides.

$$2C_6H_5I{:}O \longrightarrow C_6H_5IO_2 + C_6H_5I.$$

The change also takes place when the iodoso-compound is distilled with steam.

Experiment 268.—Preparation of iodoxy-benzene, $C_6H_5IO_2$, from iodoso-benzene.

The iodoso-benzene is mixed in a flask with sufficient water to form a thin paste and distilled with steam (fig. 10), the distillation being continued until no more phenyl iodide passes over. The residue, which is a clear liquid, is concentrated on a water bath and then allowed to cool, when crystals of iodoxy-benzene are deposited.

Iodoxy-benzene is a snow-white powder which decomposes suddenly on heating to 210–230°. It is decomposed quantitatively by acidified potassium iodide solution,

$$C_6H_5IO_2 + 4HI \longrightarrow C_6H_5I + 2H_2O + 2I_2,$$

and does not form salts with acids.

D. Iodonium Bases*

These are best obtained by the action of moist silver oxide on equivalent proportions of iodoso- and iodoxy-compounds, *e.g.*:

$$C_6H_5{\cdot}I{:}O + C_6H_5{\cdot}IO_2 + Ag{\cdot}OH \longrightarrow (C_6H_5)_2I{\cdot}OH + AgIO_3.$$

Experiment 269.—Preparation of diphenyl-iodonium-hydroxide, $(C_6H_5)_2I{\cdot}OH$.

Equivalent amounts of iodoso-benzene and iodoxy-benzene are treated with water and excess of freshly precipitated silver oxide in a stout well-stoppered bottle, and shaken for three or four hours by means of a shaking machine. The product is filtered.

The filtrate, which contains the free base, has a strongly alkaline reaction.† The base has not been prepared in the pure form, but its salts are readily prepared from the solution.

* *Hartmann* and *V. Meyer*, B. 1894, 27, 502, 1592.

† Test the solution for an *iodate*.

Experiment 270. — Preparation of diphenyl-iodonium iodide, $(C_6H_5)_2I \cdot I$.

The solution contains part of the base in the form of its iodate, and is therefore reduced with sulphur dioxide. It is then treated with excess of potassium iodide solution, when the iodide separates out completely. Yield, 93 per cent of theory.

It crystallizes from alcohol in long yellow needles, melts at 175–176°, but is at the same time completely decomposed into iodobenzene.

XXXII. STEREOISOMERIC ACIDS

(S. B. 154–157, 214–215, 243–247, 250–252).

When acids and other compounds containing one or more asymmetric carbon atoms (S. B. 154) occur naturally they are almost invariably optically active, and in the form of liquids or solutions rotate the plane of polarization to the right or left. When compounds of the same composition are synthesised in the laboratory from inactive materials they are invariably found to be optically inactive. This is due to the fact that in the synthetical formation the dextro and lævo modifications of the compound have been formed in equal amount, and the final product is thus a mixture of 50 per cent of *d* and 50 per cent of *l* acid, usually denoted by *d-l* (lactic) acid, or a definite compound of the *d* and *l* acids, when it is known as a racemic compound, and denoted by *r*-acid. In either case it is possible to resolve such substances into their optically active components by Pasteur's methods (S. B. 254–257).

A. Synthesis of Racemic Acids

Method I.—Racemic acids may often be prepared from aldehydes or unsymmetrical ketones by the addition of hydrogen cyanide (the cyanhydrin synthesis) and subsequent hydrolysis.

These cyanhydrins, and also the acids obtained on hydrolysis, contain an asymmetric carbon atom, *e.g.*:

$$C_6H_5 \cdot CH{:}O + HCN \longrightarrow C_6H_5 \cdot \underline{C}H(OH) \cdot CN$$

$$C_6H_5 \cdot \underline{C}H(OH) \cdot CN + 2H_2O \longrightarrow C_6H_5 \cdot \underline{C}H(OH) \cdot CO_2H + NH_3$$

Experiment 271.—Preparation of mandelo-nitrile and mandelic acid.

(*a*) The nitrile of mandelic acid can be prepared by the direct addition of hydrogen cyanide to benzaldehyde,* but a more convenient method is to use the additive compound of the aldehyde and sodium bisulphite.† 15 grm. of benzaldehyde (freshly distilled) are stirred in a stout beaker with about 50 c.cm. of a nearly saturated solution of the bisulphite. After some time the crystals are removed with the aid of the filter pump, washed with a little water, then with alcohol and ether. The crystals are then suspended in a small amount of water and a solution of 12 grm. of potassium cyanide (98–99 per cent) in 25 c.cm of water is added. If the mixture is stirred the crystals disappear, and the nitrile separates as an oil, which can be removed with the aid of a separating funnel and washed with water. Yield, 10–15 grm.

(*b*) The nitrile may be hydrolysed by heating it on a water bath with four times its weight of concentrated hydrochloric acid, until the mandelic acid begins to crystallize The mixture is then left overnight, and the crystals removed next morning A further quantity of acid is obtained by extracting the filtrate with ether. It separates from benzene in colourless rhombic crystals, melting-point 118°. Yield, about 80 per cent of theory.

Method II.—Racemic acids containing *two* asymmetric carbon atoms are often formed by the saturation of an acid containing an ethylene linkage by the addition of groups not already represented in the molecule, *e.g.*:

$$C_6H_5\cdot CH{:}CH\cdot CO_2H + Br_2 \longrightarrow C_6H_5\cdot \underline{C}HBr\cdot \underline{C}HBr\cdot CO_2H.$$

Experiment 272.—Preparation of cinnamic acid dibromide (β-phenyl-$\alpha\beta$-dibromo-propionic acid), $C_6H_5\cdot \underline{C}HBr\cdot \underline{C}HBr\cdot CO_2H$, from cinnamic acid.‡

40 grm. of finely divided cinnamic acid (Exp. 235) are spread out on a large clock-glass and placed in a desiccator over concentrated sulphuric acid. A dish containing slightly more than the theoretical amount of dry bromine is supported on a glass tripod above the cinnamic acid, the desiccator is closed and allowed to stand until all the bromine has evaporated from the dish and been absorbed by the acid; this

* B. 1881, **14**, 239. † D. R. P. 85.230.

‡ *Sudborough* and *Thompson*, J. C. S. 1903, **83**, 669.

occurs in about three days. The clock-glass is removed, the product exposed to the air for several hours, and then weighed in order to make sure that the theoretical amount of bromine has been absorbed. A portion of the product is then crystallized from alcohol, and is deposited as colourless needles, melting-point 197° (with decomposition). Yield, theoretical.

B. Resolution of Racemic Acids into the Optically Active Antipodes

Method I.—The biochemical method.

Experiment 273.—The action of Penicillium glaucum (ordinary green mould) on inactive mandelic acid.*

3 grm. of mandelic acid in the form of its ammonium salt, and 1·25 grm. of a mixture of various inorganic salts (potassium hydrogen phosphate, ammonium nitrate, and common salt), are dissolved in a litre of water. The solution is made distinctly acid with sulphuric or phosphoric acid, and is sterilized by boiling for half an hour in a flask closed with sterilized cotton-wool. When cold a small amount of a pure culture of *Penicillium glaucum* is introduced by means of a sterilized platinum wire, the flask is immediately closed by reinserting the plug of sterilized cotton-wool, and allowed to stand in a warm room at constant temperature. When the increase of the fungus is ended—which occurs in about six weeks—the solution is concentrated by evaporation, acidified, and the mandelic acid extracted with ether. The residue left after removal of the ether is crystallized from water, when *d*-mandelic acid separates as colourless crystals, melting at 133°, and having $[\alpha]_D^{20^\circ} = +156{\cdot}5$.

Method II.—Resolution by means of optically active bases.

The racemic acid is dissolved in a suitable solvent and treated with the equivalent amount of the active base, and the two salts formed are separated by fractional crystallization. In the majority of cases, it is better to use two equivalents of the acid and one of the base; under these circumstances the less soluble salt is formed and crystallizes out and the mother liquor contains the other active component in the form of the free acid. The optically active acid can be separated from the salt by treatment with a mineral acid.

* *Lewkowitsch*, B. 1883, **16**, 1569.

Experiment 274.—Resolution of cinnamic acid dibromide $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2H$, into its optically active components.*

(a) *Preparation of* d-*acid by means of brucine.*

26·4 grm. of cinnamic acid dibromide (Exp. 272) (two equivalents) and 20 grm. of *l*-brucine, $C_{23}H_{26}N_2O_4 + 4H_2O$ (one equivalent), are dissolved in 560 c.cm. of *absolute* alcohol and allowed to stand in a large beaker. After about twenty-four hours, 20–25 grm. of the brucine salt of the dextro acid (*d*-acid *l*-base) have crystallized out. The mother liquor is removed and the salt recrystallized *at least* three times from absolute alcohol. The product of the last crystallization is decomposed by treatment with dilute hydrochloric acid and the precipitated acid washed repeatedly with dilute hydrochloric acid until the filtrate no longer gives the reactions for brucine.

(b) *Preparation of the* l-*acid by means of cinchonidine.*

23 grm. of cinnamic acid dibromide (1 mol.) and 23 grm. cinchonidine, $C_{20}H_{24}N_2O_2$ (1 mol.), are dissolved in 500 c.cm. of benzene. The salt which separates is extracted at least five times by boiling with 100 c.cm. of benzene and filtering while hot. The residual salt is decomposed by treatment with dilute hydrochloric acid, and the product washed with acid until free from cinchonidine

To obtain an acid of maximum rotation the above process should be repeated.

For determination of its rotatory power see Exp. 276.

Determination of Rotatory Power: The Polarimeter

A ray of ordinary light consists of ether vibrations in all directions in a plane at right angles to the axis of the ray. When it passes through a Nicol's prism (a crystal of Iceland spar cut in a certain manner, cf. text-books of physics), the emergent ether vibrations are all in the same direction and the light is said to be plane polarized. If this polarized light be examined through another Nicol's prism, it is found that the light is transmitted through the second prism when the principal planes of the two prisms are parallel; when the planes are at right angles to one another no light passes

* *Hirsch*, B. 1894, **27**, 887.

through, while at intermediate positions a portion only of the light is transmitted, the amount depending on the angle which the two prisms make with one another. The position of maximum brightness is followed at an interval of 90° by a position of total darkness, and at an interval of 180° by a second position of maximum brightness, &c. The Nicol's prism by which the light is polarized is called the polarizer, the one by which it is subsequently examined, the analyser.

If a tube containing a solution of cane sugar is placed between the two prisms when they are in the position of maximum darkness (*i.e.* at right angles to one another), the field of view becomes more or less bright. To attain the position of maximum darkness again, it is necessary to rotate the analyser through a certain angle. This indicates that the plane of polarization of the light falling on the analyser has been rotated by the solution, the degree of rotation being indicated by the angle through which the analyser must be turned in order to attain the position of maximum darkness again.

Substances, such as cane sugar (in the pure form or in solution), which rotate the plane of polarization in this manner are said to be *optically active*, when the analyser must be rotated to the right in order to attain the position of darkness, the substance is *dextro-rotatory*; if to the left, *lævo-rotatory*. It is obvious that positions of darkness may be found on either side of the zero point, because in a complete revolution of 360° there are two positions each of maximum brightness and maximum darkness, but on one side the rotation will be greater than 90°. In determining the optical activity of a substance the sign of the rotation is taken as that in which it is less than 90°.

The angle of rotation produced in such a case as the above is found to depend on the following factors:—

(i) The nature of the substance; if the substance is in solution this includes the concentration of the solution and the nature of the solvent.

(ii) The length of the layer of optically active substance through which the light passes.

(iii) The wave length of the light used.

(iv) The temperature.

These factors must be taken into account in determining the specific rotatory power of a substance, which is defined as the rotation produced by 1 grm. of the active substance in

1 c.cm. by a layer 1 dcm. in length. This for sodium light (the D line) and temperature t is denoted by $[\alpha]^t_D$.

For a homogeneous optically active liquid (*e.g.* ethyl tartrate, Exp. 78), if α be the rotation produced for sodium light at a temperature t by a layer of the liquid l dcm. long, the density of the liquid being d; then

$$[\alpha]^t_D = \frac{\alpha}{ld}.$$

For a solution of the optically active substance in an inactive liquid the term d must be replaced by the number of grams of the substance in 1 c.cm. of solution. If c represent the concentration of the solution, *i.e.* the number of grams of substance in 100 c.cm of solution,

$$[\alpha]^t_D = \frac{100\alpha}{lc}.$$

For purposes of comparison between different optically active substances the quantity termed *molecular rotation* is used. This consists of the above quantity multiplied by the molecular weight of the substance and divided by 100 in order to avoid unwieldy numbers. It is denoted by $[M]^t_D$, and

$$[M]^t_D = \frac{[\alpha]^t_D \times M}{100}.$$

By comparison with the definition of specific rotatory power, this is seen to denote the angle of rotation produced by a layer of active substance 1 mm. thick containing 1 grm. molecular weight in 1 c.cm.

The simple arrangement of two Nicol's prisms described above is not sufficient for accurate work, for the analyser, when adjusted to intercept the light transmitted through the solution, can be rotated through a small angle in either direction without allowing any appreciable amount of light to pass. Various forms of polarimeter have been invented to overcome this difficulty; the ones in general use are the Laurent and Lippich half-shadow polarimeters.

The arrangement of the optical parts of the Laurent polarimeter is shown diagrammatically in fig. 85*a*. Monochromatic light from a sodium burner M passes through a thin plate

or cell of potassium bichromate P, which absorbs blue or violet rays, and then through the collimating arrangement of lenses A; the parallel rays of light fall on the polarizing Nicol's prism B, and then pass through the observation tube T, which contains the liquid under examination, to the analyser D, which is observed by the Galilean telescope E. At C a com-

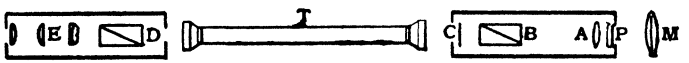


Fig. 85*a*

bination of glass and quartz semicircles termed a *half-shade* is introduced. The theory of this will be understood from the following considerations. Let ACB (fig. 86) represent a semicircular plate of quartz cut so that the optic axis is in the plane of the paper and parallel to AB. Plane-polarized light falling normally on the plate will be resolved into two sets of waves travelling along the same path but polarized in planes perpendicular to one another. Thus, if the plane of polarization at incidence is parallel to OP, the incident ray is polarized in the direction OP and the resolved vibrations will be parallel to and can be represented by OX and OY respectively. The former is termed the ordinary, the latter the extraordinary ray. These traverse the quartz with different velocities, and if the thickness of the quartz is so chosen that the retardation of one ray with respect to the other is just half a wave length (a *half-wave* plate), the emerging rays can be represented by OY and OX′ (instead of OX). These will combine on emerging into a ray polarized in the direction OQ, where the angle AOQ = the angle AOP. The direction of polarization of the light passing through the glass portion of the half-shade is unchanged, so that the angle POQ represents the angle between the directions of polarization of the light passing through the two halves of the half-shade.

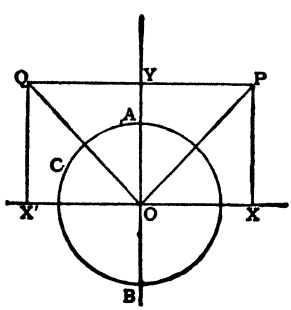
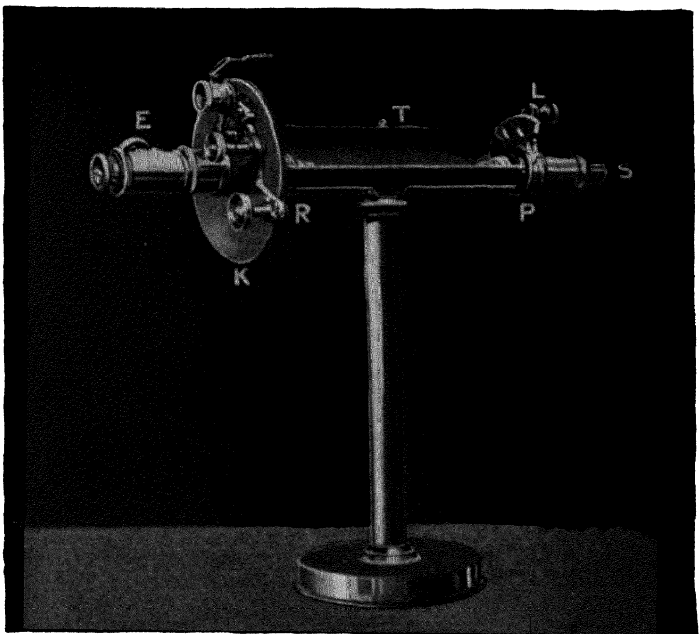


Fig 86

If now, the polarizing prism being parallel to OP, the analyser is also placed parallel to OP, the two halves of the half-shade



To face p 298.

Fig. 87.

will appear unequally bright, for whereas in the glass half the whole of the light is transmitted, in the quartz half only the component of OQ along OP will pass through. If the analyser be rotated until it occupies a position parallel to OQ, the quartz half will be fully illuminated, while the glass half will only be partially so. Between these two positions there will necessarily exist a point at which the illumination is equally bright. By diminishing the angle YOP (*i.e.* the angle which the polarizer makes with the optic axis of the quartz), the transition can be made more abrupt, and thus more easily detected; but at the same time the illumination diminishes with the diminution of this angle. Consequently in practice the size of the angle must be chosen so as to give the best results. For clear colourless liquids the angle is made comparatively small, but in the case of coloured liquids it is necessary to increase it, and so obtain increased illumination at the cost of sensitiveness.

When a tube containing an optically active substance is introduced between the polarizer and analyser it will cause a rotation of the plane of polarization of the rays OP and OQ in the same sense and by equal amounts, and a measure of this rotation is obtained by observing the rotation of the position of equal illumination of the two portions of the half-shade.

The Lippich polarimeter differs from the above only in the method of producing the half-shadow. The half-shade plate is replaced by a small Nicol prism, which covers half the opening of the polarizer tube. This produces the same effect as the quartz plate. Moreover, in the more accurate type of instrument it enables the division of the field into three portions by the use of two small Nicols in this position. The instrument also possesses the advantage that it can be used with light of any wave length.

The complete polarimeter is shown in fig. 87. At S is placed a sodium lamp consisting of a Bunsen burner fed with common salt or borax. P is the polarizer, which can be rotated (thus altering the half-shadow angle) by means of the lever L. The case T contains the observation tube. The analyser is at A, and can be rotated by means of a screw, independently of the graduated circular disc K; this allows for the correction of the zero-point. The analyser and the telescope E can be made to rotate simultaneously by means of the rack-and-pinion arrangement R. Accurate readings are taken by means of verniers attached to the disc.

In working with the instrument reliance should not be placed on one reading only, but at least six observations should be made, which with a good instrument should not vary beyond 0·1°.

Experiment 275.—Determination of the rotatory power of ethyl tartrate (Exp. 78).

A 200 mm. observation tube is filled with ethyl tartrate and allowed to stand for some time in order that any suspended particles present may settle. Meanwhile the zero of the polarimeter is determined, an observation tube filled with water being placed in position. The half-shade angle is fixed by means of the lever L, so that the transition is as sharp as possible consistent with a sufficiency of illumination, and the position of equal illumination of the two semicircles determined as accurately as possible, several separate readings being taken. The tube containing ethyl tartrate is then placed in position, and the position of equal illumination again determined, the mean of several readings being taken. Hence the specific rotatory power and molecular rotation of the substance is calculated from the formulæ given above.

For ethyl tartrate $[\alpha]_D^{20°} = +7\ 66$.

Experiment 276.—Determination of the specific rotatory power of the resolved cinnamic acid dibromide.

The acids separated from the brucine and cinchonidine salts in Exp. 274 are dissolved in absolute alcohol. For this purpose 2 grm. of the dry substance is dissolved in the alcohol, and the solution made up to 20 c cm. The solution is placed in a 200 mm. tube, and the rotation determined as in the above experiment.

Specific rotatory power of cinnamic acid dibromide = ±64°.

Temperature has a considerable effect on the specific rotation of optically active substances, the molecular rotation gradually increasing with rise of temperature.

Experiment 277*a*.—Determine the specific rotatory power of ethyl tartrate at several different temperatures, and plot the results on a curve.

In the case of solutions of solid substances the rotation varies both with the concentration and also with the solvent.

Experiment 277*b*.—Determine the variation of the specific rotatory power of tartaric acid at several different concentrations, *e.g.* 20, 10, and 5 per cent solutions.

C. Stereoisomeric Unsaturated Compounds

An essentially different type of stereoisomerism is met with in the case of certain unsaturated compounds. This isomerism occurs when the two monovalent radicals attached to the two carbon atoms between which a double linkage exists are different, *e.g.* abC:Cab, or abC:Ccd, or abC:Cac. For examples see fumaric and maleic acids (S. B. 243–247), oleic and elaidic, erucic and brassidic acids (*ibid.* 165–166), cinnamic acids (*ibid.* 452–454).

A pair of such stereoisomerides is usually formed when hydrogen bromide (chloride) is eliminated from compounds of the type of crotonic acid dibromide (chloride), or cinnamic acid dibromide (chloride). Cf. Exp. 278.

The two isomerides differ entirely as regards physical properties, and to a certain extent as regards chemical properties. As a rule, they can be separated by the differences in the solubilities of the compounds themselves or of their derivatives.

Experiment 278. — Preparation of α-bromoallocinnamic acid and α-bromocinnamic acid from cinnamic acid dibromide.* (αβ-dibromo-β-phenyl-butyric acid.)

$$C_6H_5\cdot CHBr\cdot CHBr\cdot CO_2H \longrightarrow C_6H_5\cdot CH{:}CBr\cdot CO_2H + HBr.$$

20 grm. of cinnamic acid dibromide (Exp. 272) (1 mol.) are covered with alcohol, and the theoretical amount (2 mol.) of alcoholic potash solution (10–15 per cent) is added. The mixture is heated for about fifteen minutes, and is finally evaporated to dryness on a water bath.

The two stereoisomeric α-bromocinnamic acids are most readily separated by means of their barium salts, as barium α-bromocinnamate is practically insoluble in cold water, whereas barium α-bromallocinnamate is readily soluble. The residue is mixed with water (it is not necessary to dissolve the potassium salts present completely), and excess of a 10 per cent barium chloride solution is added. The precipitated barium α-bromocinnamate is removed with the aid of a porcelain funnel and washed several times with dilute barium chloride solution. The two acids are obtained by treating the precipitate and the filtrate separately with hydrochloric acid; the precipitated acids are filtered off, washed with water, and dried on porous

* J. C. S. 1903, 83, 673.

plate. Yield of α-bromo acid, 1·5 grm., of α-bromo-allo acid 11–12 grm.

The α-bromocinnamic acid is crystallized from benzene, when it is obtained as colourless prismatic needles, melting-point 131°. The allo-acid crystallizes from ligroin, or from a mixture of chloroform and carbon disulphide, as yellowish transparent prisms, melting-point 120°.

Almost invariably one of the two stereoisomers is less stable than the other; this is frequently termed the allo-compound, and may be transformed into the more stable compound by one or more of the following methods: (1) Exposure to sunlight for some weeks; (2) exposure to moderately high temperature; (3) treatment with small amounts of certain chemicals.

An example of the last method has been met with in Exp. 57, namely, the conversion of oleic acid, $CH_3(CH_2)_7 \cdot CH : CH(CH_2)_7 \cdot CO_2H$, into its stereoisomer elaidic acid by the action of nitrous acid.

α-Bromoallocinnamic acid may be transformed into the more stable α-bromo acid by either the first or second of the above methods.

Experiment 279.—Transformation of α-bromoallocinnamic acid into α-bromocinnamic acid.*

10 grm. of α-bromoallocinnamic acid are placed in a boiling tube, a thermometer being immersed in the substance. The tube is heated in a bath of sulphuric acid until the thermometer indicates a temperature of 200–210°, and is kept at this point for about twenty minutes. The product after cooling is dissolved in dilute alkali, and after neutralization of excess of alkali the solution is treated with excess of barium chloride solution; the separation of the α-bromo acid from any residual allo-acid is carried out as indicated in the last experiment. Yield of α-bromocinnamic acid, 8–9 grm.

Both of the bromo-acids lose hydrogen bromide when heated with alkaline solutions, and yield the acetylene derivative, phenylpropiolic acid, $C_6H_5 \cdot C : C \cdot CO_2H$ (cf. Exp. 21). It is found, however, that the α-bromo-acid reacts with alkali much more readily than the allo-acid.

Experiment 279*a*.—Elimination of hydrogen bromide from α-bromocinnamic acid: Preparation of phenyl-propiolic acid.

10 grm. of the α-bromo acid is heated for two hours on a

* *Sudborough* and *Thompson*, J. C. S. 1903, 83, 686.

boiling water bath with 20 per cent aqueous potassium hydroxide solution (2·5 mol.). When cold the solution is filtered, if not quite clear, and then acidified with hydrochloric acid. The precipitate is removed, washed, dried, and recrystallized from a mixture of chloroform and ligroin, when the phenyl-propiolic acid, $C_6H_5 \cdot C \vdots C \cdot CO_2H$, is obtained as colourless prismatic needles, melting-point 137°.

XXXIII. MOLECULAR REARRANGEMENT

Many organic compounds are changed under certain conditions into isomerides, *i.e.* substances possessing the same molecular but different structural formulæ. In many cases an attempted synthesis of a certain compound results in the production of an isomeride. The following are important cases of such transformations.

A. The Urea Transformations

Experiment 280.—Transformation of ammonium cyanate to urea (carbamide).

$$NH_4O \cdot C \vdots N \rightleftharpoons NH_2 \cdot CO \cdot NH_2$$

This change occurs when a solution of ammonium cyanate is boiled. The cyanate is prepared by oxidizing potassium cyanide or ferrocyanide to the cyanate by fusing with an oxidizing agent (usually a peroxide), and treating the extracted product with an ammonium salt.

20 grm. of dry potassium ferrocyanide are mixed with 7 grm. of anhydrous potassium carbonate in an iron crucible or ladle, and fused in a blowpipe flame or fire. 36 grm. of red lead are added gradually, and the mixture kept well stirred. When the whole of the red lead has been added, the fused mass is poured on to an iron tray, and after cooling is extracted with boiling water. The solution is filtered, and the filtrate treated with 20 grm. of ammonium sulphate and evaporated to dryness on a water bath. The solid residue is broken up and extracted with hot alcohol, which dissolves the urea. When the alcoholic solution is evaporated crystals of urea are ob-

tained. It may be purified by recrystallization from water, when it is deposited as colourless prisms, melting-point 132°.

The transformation in this case is not complete, but when the point of equilibrium is reached only a small amount of cyanate remains unchanged.

Urea is the diamide of carbonic acid, and as such shows the general properties of amides (Chap IV, B). In addition, it possesses feebly basic properties; thus it forms a sparingly soluble nitrate, $CO(NH_2)_2$, HNO_3, and oxalate, $CO(NH_2)_2$, $H_2C_2O_4$, $2H_2O$.

A similar transformation occurs in the case of ammonium thiocyanate with the production of thiourea (thiocarbamide):

$$NH_4 \cdot S \cdot C{:}N \rightleftharpoons CS(NH_2)_2$$

In this case the transformation is only partial, as equilibrium is attained after 45 minutes at 170°, and the mixture then contains only 25 per cent of thiourea. When thiocarbamide is fused it is partially converted into ammonium thiocyanate.

Experiment 281.—Transformation of ammonium thiocyanate to thiocarbamide.*

30 grm. of ammonium thiocyanate are placed in a boiling tube, and a thermometer immersed in the substance, which is heated by means of an oil bath. The salt fuses at 147° to a yellowish liquid. The temperature is raised to 170°, at which point it is maintained for an hour. The melt is allowed to cool, and is then extracted with 50 c cm of hot water. The solution is filtered and allowed to cool, when crystals of thiocarbamide separate. These are removed and recrystallized from a little hot water, when the thioamide is obtained as flat needles, melting-point 172°. It dissolves fairly readily in cold water, very readily in hot water and in alcohol, but is almost insoluble in ether or benzene. It forms a sparingly soluble nitrate, $CS(NH_2)_2HNO_3$.

B. Beckmann's Transformation of Oximes†

(S. B. 137, 139, 427.)

Oximes (Chap. XXII, A) derived from aldehydes and from unsymmetrical ketones frequently exist in two stereoisomeric forms represented by the formulæ:

* *Reynolds*, J. C. S. 1869, **22**, 1; *Reynolds* and *Werner*, *ibid.* 1903, **83**, 1

† *Beckmann*, B. 1886, **19**, 989; 1887, **20**, 1507.

$$\text{Syn } \begin{matrix} R\cdot C\cdot H \\ \| \\ N\cdot OH \end{matrix} \quad \text{anti } \begin{matrix} R\cdot C\cdot H \\ \| \\ HO\cdot N \end{matrix}$$

$$(1)\ \begin{matrix} R\cdot C\cdot R' \\ \| \\ N\cdot OH \end{matrix} \quad \text{and} \quad (2)\ \begin{matrix} R\cdot C\cdot R' \\ \| \\ HO\cdot N \end{matrix}$$

The configuration of the oxime of an unsymmetrical ketone can be determined from the nature of the product obtained by the action of phosphorus pentachloride or sulphuric acid on the oxime (the Beckmann transformation). Under the influence of the dehydrating agent the hydroxyl group of the :N·OH radical exchanges place with the alkyl radical in the *syn* position. The products thus obtained from the oximes (1) and (2) would be:

$$\begin{matrix} R\cdot C\cdot OH \\ \| \\ NR' \end{matrix} \quad \text{and} \quad \begin{matrix} HO\cdot C\cdot R' \\ \| \\ RN \end{matrix}$$

which are immediately transformed into the tautomeric forms:

$$R\cdot CO\cdot NHR' \text{ and } R'\cdot CO\cdot NHR.$$

If R' = C_6H_5 and R = C_6H_4Cl, the final products would be

$C_6H_4Cl\cdot CO\cdot NH\cdot C_6H_5$, chlorobenzoylanilide,
and $C_6H_5\cdot CO\cdot NH\cdot C_6H_4Cl$, benzoylchloranilide.

Experiment 282.—Beckmann's transformation of acetophenone oxime.

A weighed amount of acetophenone oxime (Exp. 187*a*) is dissolved in anhydrous ether and treated gradually with one and a half times its weight of phosphorus pentachloride. The ether is distilled off and the residue treated with water; the insoluble product is removed and recrystallized from alcohol.

Determine the melting-point of the product and hence derive the molecular configuration of acetophenone oxime.

C. Transformations under the Influence of Alkalis

Treatment of unsaturated acids with dilute alkalis (S. B. 162), and Fusion of benzene-disulphonic acids with potash (S. B. 416) are examples of this transformation.

A further example is met with in the action of alkalis on monosaccharoses* (S. B. 312), a reaction which can be represented as

glucose ⇄ fructose ⇄ mannose.

The conversion of glucose (or invert sugar) into *dl*-lactic acid, $CH_3 \cdot CH(OH) \cdot CO_2H$, may also be regarded as a type of molecular rearrangement by alkalis.

$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot C\overset{O}{\underset{H}{<}} \longrightarrow 2OH \cdot CH(CH_3) \cdot C\overset{O}{\underset{OH}{<}}$$

Experiment 283.—Preparation of lactic acid.†

500 grm. of cane sugar, 250 grm. of water, and 10 c.cm. of sulphuric acid (3 parts of acid to 4 of water) are shaken in a stoppered bottle for three hours at 50°. When cold, 400 c.cm. of sodium hydroxide solution (1 part of NaOH to 1 of water) are added in portions of 50 grm. at a time, care being taken that the liquid is well shaken after each addition and that the flask is cooled by means of water. The whole is finally heated to 60–70° until a test portion no longer gives a red precipitate when warmed with Fehling's solution. When the liquid is cold the theoretical amount of sulphuric acid (3 parts acid to 4 of water) required to neutralize the alkali used is added. A crystal of Glauber's salt is added, and the mass well shaken and cooled until a crystalline crust is no longer formed. After the mixture has stood for twelve to twenty-four hours, 93 per cent alcohol is added until no further precipitate is obtained. The crystals are removed with the aid of the pump, washed with a little alcohol, and the alcoholic filtrate divided into two equal parts. One of these is neutralized by heating with zinc carbonate on the water bath; it is filtered hot and mixed with the remaining half. After some thirty-six hours the deposition of zinc lactate is complete, and the salt can be obtained pure by one recrystallization. Yield 30–40 per cent of the weight of sugar used.

D. The "Wandering" of Radicals. (S. B. 393–394.)

1. Many examples are known in which radicals—sometimes relatively complex—shift, under certain conditions, from one

* *Lobry de Bruyn*, B. 1895, 28, 3078. † *Kiliani*, B. 1882, 15, 699.

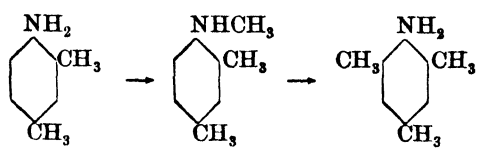
position in a molecule to another, *e.g.* from the side chain of a benzene derivative into the ring. Thus, in the Hofmann reaction * (S. B. 368) the alphyl radical of a secondary alphyl-arylamine replaces a hydrogen atom of the benzene nucleus, when the hydrochloride is heated to a high temperature, *e.g.*:

$$C_6H_5 \cdot NH \cdot CH_3, HCl \longrightarrow CH_3 \cdot C_6H_4 \cdot NH_2, HCl.$$

The methyl groups invariably take up the *o*- or *p*- and not the *m*-position with respect to the amino-group.

Experiment 284.—The Hofmann reaction: Transformation of methyl-*m*-xylidine, $C_6H_3Me_2 \cdot NHMe$, to mesidine, $C_6H_2Me_3 \cdot NH_2$.

Molecular proportions of *m*-xylidine hydrochloride (2:4-dimethyl-aniline hydrochloride) and methyl alcohol are heated in a sealed tube at 300° for twenty-four hours. When cold the product is dissolved in water, made alkaline with sodium hydroxide and extracted with ether. The ethereal solution is dried with solid potash, the ether removed, and the base distilled. Mesidine is a colourless oil, boiling-point 229–230°.



2. Nitrosamines are transformed into the isomeric *p*-nitroso-compounds on treatment with alcoholic hydrogen chloride.† (S. B. 376.)

Experiment 285.—Preparation of *p*-nitroso-methyl-aniline from methylphenylnitrosamine.

$$C_6H_5 \cdot N\begin{matrix}<^{NO}\\ _{CH_3}\end{matrix} \longrightarrow NO \cdot C_6H_4 \cdot NH \cdot CH_3.$$

1 part of methylphenylnitrosamine (Exp. 136*a*) is dissolved in 2 parts by weight of ether, and 4 parts by weight of absolute alcohol saturated with hydrogen chloride are added. After some time a mass of crystalline needles separates. These are filtered and washed with a mixture of alcohol and ether, and then melt at 118°. The yield is theoretical.

* *Hofmann*, B. 1872, **5**, 704.
† *Fischer* and *Hepp*, B. 1886, **19**, 2991; 1887, **20**, 1247.

Similar transformations are:

The formation of aminoazo-compounds from diazoamino-compounds under the influence of an amine hydrochloride (Exp. 163).

The transformation of β-phenyl hydroxylamine to *p*-amino-phenol in the presence of mineral acids (Exp. 224).

The transformation of hydrazo-compounds into diphenyl derivatives under the influence of hydrochloric acid (S. B. 393).

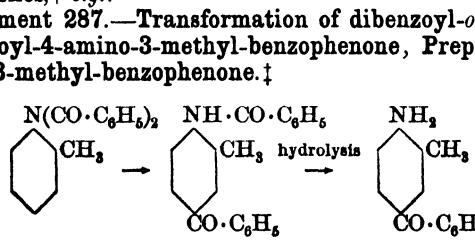
$$C_6H_5\cdot NH\cdot NH\cdot C_6H_5 \longrightarrow NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2.$$

Experiment 286.—Conversion of hydrazobenzene into benzidine.*

2 grm. of hydrazobenzene (Exp. 219) are mixed with concentrated hydrochloric acid, and kept for five minutes at the ordinary temperature. Water is then added, and the mixture made alkaline by the addition of sodium hydroxide solution. The benzidine may be extracted with ether and crystallized from water, when it forms glistening plates, melting-point 127·5–128°.

3. The isomeric change of diacylanilides into acyl-aminoketones,† *e.g.*:

Experiment 287.—Transformation of dibenzoyl-*o*-toluidine into benzoyl-4-amino-3-methyl-benzophenone, Preparation of 4-amino-3-methyl-benzophenone.‡



o-Toluidine (1 mol.) is added gradually to the equivalent quantity of benzoyl chloride (2 mol.), and the whole gradually heated in an oil bath to 220–230°, this temperature being maintained for about fifteen hours. A brown viscid liquid is produced which solidifies on cooling to a hard resinous mass. The benzoyl-4-amino-3-methyl-benzophenone can only be isolated from this product with some difficulty, so it is best to hydrolyse it, as the corresponding base is more readily separated. The whole mass is dissolved in excess of alcohol,

* *Meyer* and *Jacobson*. † *Chattaway*, J. C. S. 1904, 85, 386.
‡ *Chattaway* and *Lewis*, *ibid.* 591.

containing half its bulk of concentrated hydrochloric acid, and heated to boiling for fourteen hours. A rapid current of steam is blown through the product thus obtained, when alcohol and ethyl benzoate distil over successively. The strongly acid residue is boiled for some time with water, and the hot solution containing the hydrochloride of the base filtered from the brown tarry matter, which is always formed in considerable amount during the transformation. The filtrate is then made slightly alkaline, and again distilled with steam to remove any *o*-toluidine derived from untransformed dibenzoyl-*o*-toluidine. After cooling, the solid separating from the alkaline liquid in the distillation flask is filtered off and extracted with alcohol. This alcoholic solution is evaporated to a small bulk, and a few drops of strong sulphuric acid added; on diluting with a little ether, the almost pure base crystallizes in colourless needles After recrystallization from water slightly acidified with sulphuric acid, it forms pale yellow prisms, melting-point 112°. Yield, 50 per cent of the weight of *o*-toluidine used

4. **The wandering of halogen from a side chain into the ring,*** *e g* :

$$C_6H_5N\langle^{Cl}_{CO\cdot CH_3} \longrightarrow Cl\cdot C_6H_4N\langle^{H}_{CO\cdot CH_3} (1:4).$$

Experiment 288.—(*a*) **Preparation of acetchloranilide,** $C_6H_5\cdot N(Cl)CO\cdot CH_3$, **from acetanilide.**

$$C_6H_5NH\cdot CO\cdot CH_3 + Cl_2 \longrightarrow C_6H_5NCl\cdot CO\cdot CH_3 + HCl.$$

Acetanilide (Exp. 144) is suspended in excess of a solution of potassium bicarbonate, and the calculated quantity of bleaching powder solution added.† The product is extracted with chloroform, and after recrystallization from a mixture of chloroform and ligroin consists of large transparent plates, melting-point 91°. Yield, 96 per cent of theory.

The substance liberates iodine from an acid solution of potassium iodide.

$$C_6H_5N\langle^{Cl}_{CO\cdot CH_3} + 2HI \longrightarrow C_6H_5NH\cdot CO\cdot CH_3 + HCl + I_2.$$

* *Chattaway* and *Orton*, J. C. S. 1899, 75, 1046; 1900, 77, 134, 152, 789, 797; *Raper*, *Thompson*, and *Cohen*, J. C. S. 1904, 85, 371.

† The solution should be standardized by means of standard thiosulphate solution.

(*b*) Determine the amount of iodine liberated by a known weight of the substance by dissolving in chloroform and shaking the solution with a solution of potassium iodide acidified with acetic acid; titrate the liberated iodine with 0·1 N sodic thiosulphate solution.

(*c*) **Transformation of acetchloranilide to *p*-chloracetanilide.**

This change occurs slowly on keeping the substance, and is complete in two or three weeks; it may be accelerated by the addition of acid.

The acetochloranilide is dissolved in warm dilute acetic acid, and crystals of *p*-chloracetanilide separate as the liquid cools. Melting-point, 172·5°.

5. The transformation of benzil into benzilic acid.

Under the influence of potassium hydroxide, the α-diketone benzil is transformed, with the addition of the elements of water, into the potassium salt of benzilic acid.

$$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5 + KOH \longrightarrow (C_6H_5)_2C(OH) \cdot CO_2K.$$

Experiment 289.—Preparation of benzilic acid.*

50 grm. of potassium hydroxide and 100 grm. of water are introduced into a flask containing 50 grm. of benzil (Exp. 229), and after the alkali has dissolved 100 grm. of alcohol are added. The mixture is boiled on a water bath for not more than ten minutes, and the contents then poured into a beaker. After some hours the crystals are removed on a hardened filter-paper, washed with alcohol, and then well stirred with 75 to 100 grm. of cold alcohol. The crystals are removed, dissolved in from 0·5 to 1 litre of water, and the solution filtered and made up to 1 litre. The solution is then boiled, and boiling dilute sulphuric acid added, when a 90–95 per cent yield of acid is deposited. The crude acid can be recrystallized from boiling benzene, when it separates as colourless needles, melting-point 150°.

* *H. von Liebig*, B. 1908, **41**, 1644

XXXIV. QUANTITATIVE EXPERIMENTS WITH CARBOHYDRATES

A. Estimation of the Concentration of a Glucose Solution by means of its Cupric Reducing Power.

Experiment 290.—When a solution of glucose is warmed with Fehling's solution a precipitate of cuprous oxide is obtained, and on this reaction is based a quantitative method for estimating the amount of glucose, viz. by observing the exact volume of the sugar solution required to decolorize 10 c.cm. of the Fehling's solution of known concentration.

Fehling's Solution.*—Two distinct solutions are prepared, and equal volumes of these are mixed just before use. *Solution 1.*—69·28 grm. of pure copper sulphate crystals are dissolved in water, 1 c.cm. of pure sulphuric acid added, and the whole made up to 1 litre. *Solution 2.*—350 grm. of sodium potassium tartrate (Rochelle salt) are dissolved in about 700 c.cm. of water, the solution is filtered if necessary, mixed with a solution of 100 grm. of pure sodium hydroxide (purified by alcohol), and the whole made up to 1 litre. Each c.cm. of the mixed solutions (equal volumes) should contain 0·03464 grm of cupric sulphate, and is equivalent to 0·005 grm. of pure anhydrous glucose. The two solutions may be kept for some time without deteriorating, but it is advisable to standardize occasionally by means of pure sucrose (cane sugar). For this purpose a solution of 0·95 grm. of pure sucrose in 50 c.cm. of water and 2 c.cm. of concentrated hydrochloric acid is heated at 70° for ten minutes, then neutralized with sodium carbonate and made up to 1 litre with distilled water. By this process the cane sugar is hydrolysed to a mixture of equal quantities of glucose and fructose, both of which reduce Fehling's solution. The standardizing by means of this solution is accomplished in the same manner as the glucose estimations.

Titration of Glucose Solution with Fehling's Solution.—5 c.cm. of each of the Fehling's solutions are measured by means of a calibrated pipette and placed in a small porcelain dish, 40 c.cm. of water are added, and the solution quickly heated to boiling. With good solutions no change in colour should occur; if any change is observed a second experiment

* See Addenda, p. 374.

is made by adding a little more sodium hydroxide solution before boiling.

Small amounts of the glucose solution are then run in from a burette, the mixture boiled, and the operations repeated until the blue colour of the solution is just discharged. The end point is most readily observed by tilting the dish slightly, so that the colour of the clear liquid free from the precipitate can be observed. This first titration can only be performed somewhat roughly, *e.g.* 1 c.cm. of sugar solution can be run in each time. The titration will give a rough idea of the concentration 10 c.cm. of the Fehling's solution are equivalent to 0·05 grm. of glucose, since each c.cm. of Fehling's solution contains 0·11 grm. CuO, and 5 grm. mol. of CuO oxidise 1 grm. mol. of $C_6H_{12}O_6$. If it is found that the solution contains more than 1 per cent of glucose it must be diluted until the concentration is between 0·5 and 1 0 per cent, as reliable and comparable results can be obtained with solutions of such concentrations only. Several titrations are made and the mean taken.

Points to notice are:

1. The Fehling's solution must not be exposed for a long time to the air, and must not be unnecessarily heated, hence the need for making a preliminary rough titration in order to determine approximately the right amount of sugar solution required. In the subsequent titrations nearly the correct amount of sugar solution is added at first, the solution boiled, and then more sugar solution added drop by drop.

2. The concentration of the sugar solution is an important factor, and comparable results can only be obtained by using solutions of about the same concentration, *e.g.* 0·5–1 per cent, as recommended above.

Alternative Method.*

The hot solution of sugar is mixed with excess of Fehling's solution and immersed in a boiling water bath for fourteen minutes. The solution is then filtered, using a Hirsch porcelain funnel (fig. 13*b*), the plate of which is covered with a layer of fine asbestos. The liquid is sucked through with the aid of the pump, and the precipitated cuprous oxide washed with hot water until free from alkali. The oxide is then dissolved in a known volume of acidified standard permanganate solution, *e.g.* 25 c.cm. of 0·2 N permanganate and 100 c.cm. of

* *Caven and Hill*, J. S. C. I. 1897, 16, 981; 1898, 17, 124.

25 per cent sulphuric acid, if the amount of oxide does not exceed 0·2 grm Boiling water is added to raise the temperature to 45–50°, an excess of 0·2 N oxalic acid is run in and the excess titrated by means of the standard permanganate.

For a 0·2 N solution of permanganate each c.cm. used corresponds with 0·01426 grm. of cuprous oxide, since $Cu_2O + O \longrightarrow 2\ CuO$ or with 0·01426 × 0·5045 grm. of glucose.

The cuprous oxide may also be estimated by filtration, washing, and oxidizing to cupric oxide or reducing to metallic copper, and weighing as such.

B Sucrose (Cane Sugar)

Experiment 291 —Sucrose may be estimated by the above process after it has been hydrolysed or "inverted" by acids to the mixture of glucose and fructose known as invert sugar. Each c cm of *Fehling's* solution is equivalent to 0·00475 grm. of sucrose.

A mixture of glucose and sucrose may be analysed by first determining the glucose, then hydrolysing another portion and determining the glucose and invert sugar.

Other sugars may be estimated by a similar method. 1 c.cm. of *Fehling's* solution is equivalent to 0·005 grm. of glucose, fructose, or galactose, 0 00678 grm. of milk sugar, or 0·00807 grm. of maltose.

C. Polarimetric Estimation of Sugars

Experiment 292.—Estimation of Glucose.

Glucose has a specific rotatory power * $[\alpha]_D = +52{\cdot}7$. Since $[\alpha]_D = \frac{100\alpha}{l \cdot c}$, where c = number of grm. of glucose in 100 c.cm. of solution, α = the rotation observed for such a solution, and l = length of tube, *i.e.* length of layer of liquid used in decimetres, it is easy to calculate c when all the other factors are known.

10 grm. of the crude glucose are made up to 100 c.cm. with water, the solution heated,† then cooled, and the rotation observed in a 200 mm. tube.

* See p. 296.

† This is essential, as glucose exhibits the property of mutarotation (S. B. 629), and a constant value for the rotation can only be obtained after heating or treatment with alkali.

Experiment 293.—Sucrose has a value $[\alpha]_D = +66{\cdot}5°$, and the concentration of a solution can be determined in the same manner as with glucose.

Experiment 294.—A mixture of both glucose and sucrose can also be determined polarimetrically. The method consists in taking a polarimetric reading of the solution before inversion, and again after inversion (hydrolysis).*

The sucrose can be calculated from the formula:

$$P = \frac{\alpha - 2\alpha'}{m}$$

Where α is the number of divisions indicated by the polarimeter scale for 200 mm. of the original solution, α' is the same factor for the inverted solution, and m = the number of divisions of the polarimeter scale which 200 mm. of a solution containing 1 grm. of cane sugar per 100 c.cm. alters on inversion, and P = number of grm. of cane sugar present in the original solution.

The rotation due to this amount of cane sugar is subtracted from the initial rotation, and the difference gives the rotation due to the glucose present.

The specific rotatory powers of some of the commoner carbohydrates are:

Sucrose	+ 66·5	*d*-Fructose	− 95·5
Maltose	+ 139	Invert sugar	− 21·5
Lactose	+ 52·5	*d*-Galactose	+ 80·3
d-Glucose	+ 52·7		

XXXV. QUANTITATIVE EXPERIMENTS WITH ACIDS, ESTERS, AMINES, ETC.

A. Estimation of the Amount of Free Acid and of Ester in a Mixture

Experiment 295.—A small amount of the mixture is weighed, dissolved in water or alcohol, and carefully titrated with standard alkali, preferably barium hydroxide, using phenol phthalein as indicator. The end point is usually very sharp, but if the

* See page 311.

ester present is readily hydrolysed the pink coloration will disappear after a minute or two. From the results of several titrations the percentage of acid in the mixture can be calculated, provided it is known what particular acid is present. To determine the ester a known weight of the mixture is boiled for some time with an excess of standard alkali solution in a flask * provided with a reflux condenser, care being taken that atmospheric carbon dioxide is excluded. When the hydrolysis is complete the excess of alkali is titrated with standard acid (hydrochloric or oxalic). The total volume of alkali taken—alkali left after hydrolysis = alkali required to neutralize the free acid and to hydrolyse the ester. The amount required to neutralize the acid in a given weight of mixture is already known, the amount of alkali required to hydrolyse the ester in the given weight of mixture is determined by difference, and hence the weight of ester in the mixture can be calculated, provided it is known what particular ester is present.

A mixture containing acid, ester, and alcohol can be analysed in a similar manner; the amounts of acid and ester are determined, and the amount of alcohol calculated by difference.

B. Estimation of the Amounts of each of Two Acids Present in a Mixture when One is Volatile in Steam and the Other Not

Experiment 296.—A given weight of the mixture is steam-distilled until the distillate is no longer acid. The distillate and the residue in the flask are separately titrated with standard barium hydroxide, using phenol phthalein as indicator.

C. Estimation of the Amounts of a Primary and Tertiary Amine in a Mixture of the Two

Experiment 297.—(*a*) The primary amine may be estimated by adding an excess of acetic anhydride gradually to a known weight (about 10 grm.) of the mixture, warming for a few minutes and then distilling under reduced pressure. The excess of acetic anhydride, the acetic acid, and tertiary amine distil over and the temperature then rises suddenly. The

* Resistance flasks are best for this purpose as the glass is practically unacted upon, whereas ordinary glass is readily attacked by caustic alkalis

distillation is stopped, and the acetyl derivative of the primary amine weighed; this is readily accomplished if the weight of the distilling flask is known.

(*b*) If the primary amine is an arylamine it may be titrated with standard sodium nitrite (cf. p. 191), or may be diazotized and the nitrogen evolved by heating the diazonium salt measured (XXXVI, D).

D. Estimation of a Mixture of two Acids by Indirect Analysis

Experiment 298.—(*a*) *By titration.* A given weight of the mixture or a given volume of solution containing a known weight of the mixed acids is titrated with standard barium hydroxide.

(*b*) By determination of the percentage of one constituent, *e.g.* in a mixture of pure mono- and tri-chloracetic acids, a chlorine determination will suffice for calculating the amounts of the two acids by indirect analysis

E. Estimation of a Mixture of an Acid and an Acid Anhydride, *e.g.* Acetic Acid and Acetic Anhydride

Experiment 299.—Both acid and anhydride react with the alkali according to the equations—

$$CH_3 \cdot COOH + NaOH \longrightarrow CH_3 \cdot COONa + H_2O,$$

and

$$(CH_3 \cdot CO)_2O + 2NaOH \longrightarrow 2CH_3 \cdot COONa + H_2O.$$

The amount of standard alkali required to neutralize a given weight of the mixture is determined when phenol phthalein is used as indicator, and the percentages of the two calculated by indirect analysis.

F. Estimation of a Mixture of an Acid and an Acid Amide, *e.g.* Oxalic Acid and Oxamide

Experiment 300.—The free acid is estimated by titration, using an alcoholic solution. The acid amide can be estimated by hydrolysing with potash, collecting the ammonia in a given volume of standard acid, and titrating the excess of acid as in the ordinary estimation of ammonium salts. (Cf. p. 148.)

G. Estimation of a Mixture of an Acid and an Amine, *e.g.* Benzoic Acid and *p*-Toluidine

Experiment 301.—The acid may be determined by dissolving a given weight of the mixture in alcohol and titrating with standard barium hydroxide, using phenol phthalein as indicator.

To estimate the amine a given weight of the mixture (5–10 grm.) is dissolved in ether, the acid removed by shaking the ethereal solution with sodium carbonate solution, and the amine transformed into its acetyl derivative by adding an excess of acetic anhydride to the ethereal solution. The ether is distilled over, and then the acetic acid and excess of acetic anhydride under reduced pressure, and the weight of the residual acetyl derivative determined.

H. Estimation of a Mixture of an Acid and an Aldehyde, *e.g.* Acetic Acid and Acetaldehyde

Experiment 302.—The free acid is estimated by direct titration with standard alkali (preferably sodium hydroxide), the neutralized solution is then diluted to a known volume until it is approximately 0·5 per cent.* 25 c.cm. of this solution is added gradually to 50 c.cm. of a solution of potassium bisulphite (12 grm. $KHSO_3$ per litre). The flask is corked and kept for about 0·25 hour, and then titrated with 0 1 N iodine solution. This gives the amount of sulphite which has not combined with the aldehyde.† 50 c.cm. of the original sulphite are titrated, and the difference gives the amount which has combined according to the equation—

$$R{\cdot}CHO + KHSO_3 \longrightarrow RCH(OH)(OSO_2K).$$

If the aldehyde is insoluble in water a small amount of alcohol may be added, but care must be taken that too large a quantity of solvent is not used, as the blue coloration of iodide of starch is not obtained in the presence of much alcohol.

* The solution must be dilute, otherwise in the subsequent titrations the hydriodic acid formed will interfere.

† *Ripper*, M. 1900, **21**, 1079; *Rocques*, C. N. 1900, **79**, 119.

XXXVI. VELOCITY OF SOME TYPICAL ORGANIC REACTIONS

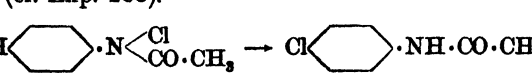
Numerous organic reactions proceed comparatively slowly, and it is an easy matter in many of these cases to actually determine the velocity constant of the reaction. The determination of the constant is based on Guldberg and Waage's Law of Mass Action. According to this law, the rate at which a reaction proceeds at a given temperature (*i.e.* the amount transformed in unit time) depends upon the concentration (in gram molecules per litre), and upon a constant K which is characteristic of that reaction. Thus if a chemical reaction takes place between three substances, A, B, and C, in a given solvent, one molecule of each reacting and forming two new compounds, D and E.

$$A + B + C \rightarrow D + E.$$

Then if the initial concentrations be a, b, and c respectively, the rate at the beginning is denoted by $K \cdot a \cdot b \cdot c$. After the lapse of time t, if x gram molecules of A, B, and C have reacted, the concentrations will be $a - x$, $b - x$, and $c - x$, and the rate will then be $K(a - x)(b - x)(c - x)$.

In this chapter a description is given of the methods used to determine K in the cases of some fairly simple organic reactions.

The simplest type of reaction is that in which one molecule only is involved, and one of the best examples of this is the conversion of acetochloranilide into the isomeric *p*-chloracetanilide (cf. Exp. 288).*



Starting with a solution containing a gram molecules of the chloranilide per litre, the velocity at the beginning is $K \cdot a$. After time t, when x gram molecules have become transformed, the concentration is $a - x$, and the reaction then proceeds at the rate $K(a - x)$, assuming that the temperature remains constant. The differential equation is thus—

$$\frac{dx}{dt} = K(a - x),$$

* *Blanksma*, Rec. 1902, 21, 366; 1908, 22, 290.

and when this is integrated we obtain the equation—

$$K = \frac{1}{t} \log_e \frac{a}{a - x}$$

$$\text{or } K = \frac{2{\cdot}302}{t} \log_{10} \frac{a}{a - x} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This equation may be written in the form

$$K = \frac{2{\cdot}302}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where x_1 and x_2 denote the number of gram molecules transformed at the end of the intervals of time t_1 and t_2.

Such a reaction as the above is termed a *unimolecular* or *monomolecular* reaction, or a reaction of the *first order*. The above equation holds good for all such reactions, and the only difficulty is the determination of the concentration of the solution at the beginning and after given intervals of time. In the above example this is extremely simple, as the original acetochloranilide liberates iodine from a solution of potassium iodide, whereas the transformed product does not. The concentration is thus determined by adding an excess of potassium iodide to known volumes of the solution after given intervals of time, and titrating the liberated iodine by means of standard sodium thiosulphate, using starch solution as indicator.

It is not necessary to introduce the actual concentrations in gram molecules into the equations 1 and 2; as we are dealing with the ratio $\log \frac{a}{a - x}$, we may simply substitute for a the number of c.cm. of thiosulphate required at the beginning of the reaction, and for $a - x$ the number of c.cm. required after time t (in hours). The results are usually tabulated as follows:—

t (hours).	$a - x$ (c.cm of thiosulphate).	$K = \frac{1}{t} \log \frac{a}{a - x}$.
0	49·30	—
1	35·60	0·139
2	25·75	0·140
3	18·50	0·140

In the determination of the velocity constant it is essential that the temperature should remain constant, as a slight rise or fall in temperature affects the rate to a considerable extent;

in certain reactions a rise of 5° will double the velocity. In order to attain a constant temperature the vessels in which the reaction is proceeding are placed in a thermostat. The commonest form is a large water bath kept automatically stirred by means of a small water turbine, hot-air motor, or electric motor. The water is heated to the required temperature, and is kept at this temperature by means of a regulator. One of the best is an Ostwald toluene regulator (fig 88).

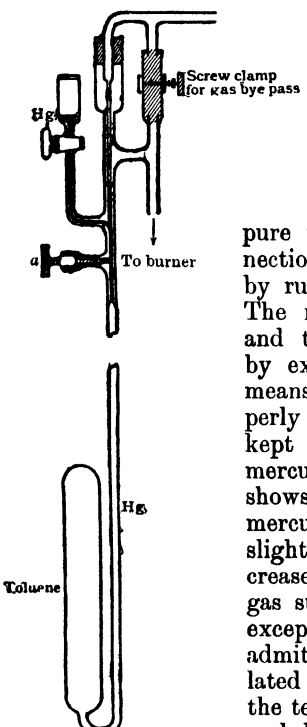


Fig 88

This is filled with pure toluene, pure mercury is added, and the connections with the gas and burner made by rubber tubing, which is wired on. The regulator is placed in the bath and the correct temperature obtained by exactly adjusting the mercury by means of the screw *a*. When properly adjusted the temperature can be kept constant for weeks. If impure mercury or toluene is used the toluene shows a tendency to creep through the mercury. If the temperature rises slightly the volume of the toluene increases and the mercury shuts off the gas supply from the burner, with the exception of a small amount which is admitted by means of the by-pass regulated by the screw clamp. As soon as the temperature falls, the mercury drops and lets through a larger gas supply. *Lowry* * recommends placing the toluene in a glass tube, which is wound in a spiral round the upright tube containing the mercury. As thus arranged the regulator is much more sensitive.

Various reactions in which several molecules are involved can be regarded as unimolecular, provided large excesses of all the reacting substances but one are used. Thus, in the hydrolysis of cane sugar by mineral acids, the reaction con-

* J. C. S. 1905, 87, 1080.

sists in the addition of water to the cane sugar molecules, and the acid acts as a catalyser.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

If a very dilute solution of sugar is used, then the alteration in the amount of water present is so extremely small that we may regard the concentration of the water as remaining constant, and the only alteration is the concentration of the cane sugar.

Equation (1) or (2) may then be used for the determination of K, the concentrations $a - x$ at different intervals of time being determined polarimetrically (see Chap. XXXIV). It is not necessary to determine the absolute concentration of the cane sugar. If r_0 is the rotation at the beginning and r_∞ the rotation after complete hydrolysis, then $r_0 - r_\infty$ can be substituted for a and $r_t - r_\infty$ for $a - x$, where r_t is the rotation at end of time t.

Other examples of the same type are given in Sections A and D.

When two molecules are involved in the reaction, then the alteration in concentration of each has to be taken into account. One of the simplest cases is where the initial concentrations of the two substances are the same. In the reaction,

$$CH_3 \cdot CO \cdot OC_2H_5 + KOH \longrightarrow CH_3 \cdot CO \cdot OK + C_2H_5OH,$$

we start with a gram-molecules of ester and a gram-molecules of potassium hydroxide in 1 litre of solution. After time t, x gram-molecules of each will have disappeared, and the concentration will then be $a - x$ for each.

The rate of reaction is then $K(a - x)(a - x)$ or $K(a - x)^2$.

The differential equation is $\frac{dx}{dt} = K(a - x)^2$, and this on integration gives—

$$K = \frac{1}{t} \cdot \frac{x}{(a - x)a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The concentrations corresponding with a, x and $a - x$ are determined after given intervals of time t and substituted in the equation, and practically constant values for K are obtained. If equimolecular quantities are not taken the equation is somewhat different. In the hydrolysis of ethyl acetate

if the concentration of the ester be a grams per litre and that of the potassium hydroxide be b grams per litre, then after time t the respective concentrations are $(a - x)$ $(b - x)$, the differential equation is $\frac{dx}{dt} = K(a - x)(b - x)$, and this on integration gives—

$$K = \frac{1}{t(a - b)} \log_e \frac{b(a - x)}{a(b - x)},$$

$$\text{or } K = \frac{2\,302}{t(a - b)} \log_{10} \frac{b(a - x)}{a(b - x)} \quad \ldots\ldots\ldots\ldots (4)$$

The constants cannot be calculated by means of the simple formulæ (1) to (4) when the action is reversible.

A. Determination of the Rate of Esterification of an Organic Acid in presence of Hydrogen Chloride

Pure methyl or ethyl alcohol is required. (For Purification, cf. Exp. 26.)

Some 250 c.cm. of a standard solution of hydrogen chloride in the alcohol is prepared by passing the dry gas (cf. Chap. XXXIX, A) into a given weight of the alcohol until it has increased in weight to the required extent, taking care that moisture is excluded. One of the best methods of conducting this operation is to make use of a chlorinating vessel. The solution is afterwards carefully standardized by means of barium hydroxide solution (p. 71). If too concentrated the solution can be diluted with pure methyl alcohol. Usually a 0·1 N or 0 025 N solution is required.

A 0·1 N solution of the organic acid is prepared by weighing out the theoretical amount of the pure dry acid, and making up to 100 c.cm. with pure methyl alcohol. This solution is also carefully titrated with the standard barium hydroxide solution, using phenol phthalein as indicator. The two solutions are kept at 15°, and then 70 c.cm. of the hydrogen chloride solution is mixed with 70 c.cm. of the organic acid solution, and the time carefully noted. Four separate lots of 30 c.cm. each of the mixture are run into four small stoppered bottles, which are immediately placed in the thermostat; the contents are titrated, after given intervals of time, by means of the standard barium hydroxide. The reaction may

be regarded as a monomolecular one, since the alcohol is present in very large excess.

$$R{\cdot}OH + R'{\cdot}CO_2H \rightarrow R'{\cdot}CO_2R + H_2O$$

The reaction is practically non-reversible, and the concentration of the alcohol may be regarded as remaining constant. The amount of water produced is comparatively small, and affects the constant to a very slight extent only.

The equation number 1 is made use of for calculating the constant. The concentrations, a and $a - x$, may be represented by the number of c cm. of standard barium hydroxide required to neutralize the organic acid present in 30 c.cm of the solution immediately after mixing, and after the lapse of t hours respectively. The value a is obtained by titrating 15 c.cm. of the original solution of the organic acid, and the value $a - x$ by taking the total number of c.cm of baryta required to neutralize the 30 c.cm. of mixture after time t, and subtracting the amount required for the hydrogen chloride present. The hydrogen chloride at 15° or 20° reacts so slowly with the methyl alcohol that for all practical purposes its concentration may be regarded as remaining constant throughout the experiment.

The results are best tabulated in the following form:—

t in hours.	f total no. of c cm of baryta required for the HCl and organic acid.	g. c cm of baryta required for the HCl.	$a - x$ $(= f - g)$ c cm. of baryta required for the organic acid.	$K = \frac{1}{t} \log \frac{a}{a - x}$.

As the rate of esterification in the presence of pure alcohol is directly proportional to the concentration of the hydrogen chloride, the constant obtained should be divided by the concentration (normality) of the hydrogen chloride, and the constant thus obtained will give the esterification constant for normal hydrogen chloride.

Some general points of interest are:

1. The velocity increases rapidly with the temperature; a rise of 5° nearly doubles the constant.

2. The constant for ethyl alcohol is always less than for methyl; the two values stand in about the ratio 1:25.

3. The constant is very different for different types of acids The fatty acids are esterified very readily. When methyl alcohol and a temperature of 15° are used the concentration of the hydrogen chloride should be about 0·01 N, and the titrations should be made about every six to ten minutes

Benzoic acid and its derivatives are esterified extremely slowly, and titrations may be made every twenty-four hours, using 0·1 N hydrogen chloride. An unsaturated acid with a double bond in the $\alpha\beta$-position is esterified much less readily than the corresponding saturated acid, *e.g.* crotonic, $CH_3 \cdot CH : CH \cdot CO_2H$, and cinnamic acid, $C_6H_5 \cdot CH : CH \cdot CO_2H$, can be titrated every two or three hours, using 0 05 N hydrogen chloride.

Substituents in the α- or ortho-positions with respect to the carboxylic group retard the esterification to an appreciable extent.

Experiment 303 — Determine the esterification constants of phenylacetic and cinnamic acids at 15° C., using methyl alcohol.

B. Determination of the Rate of Addition of Bromine to an Unsaturated Acid

One of the best media to use is carbon tetrachloride, as most of the acids dissolve in this, and it is not attacked by the bromine. The carbon tetrachloride should be washed with acid and alkali if necessary, and then with water, and dried first over granular calcium chloride, and finally distilled over phosphoric anhydride. The bromine should be pure, as certain impurities, *e.g.* iodine, affect the rate of addition to an appreciable extent. The bromine may be shaken up with concentrated sulphuric acid in a separating funnel, the lower layer of bromine run off and placed in a freezing mixture of ice and calcium chloride. The bromine solidifies, and liquid impurities can be decanted off; the operation is repeated until the melting-point of the bromine is −7°.

Solutions of the bromine and of the organic acid in carbon tetrachloride are prepared and accurately standardized, the bromine solution by adding an excess of aqueous potassium iodide solution, and titration of the liberated iodine by means of standard sodium thiosulphate, using starch as an indicator, and the acid solution by means of standard barium hydroxide solution, using phenol phthalein as indicator. It will facilitate

the calculation if the two solutions are of exactly the same strength, *e.g.* $\frac{1}{30}$ of a gram-molecule per litre.

Definite volumes (20 c.cm.) of the bromine solution are run out by means of a burette into small dry bottles, say six. To each of these is added an equivalent volume of the unsaturated acid solution *in the dark.** The time of mixing is carefully noted in each case, and the bottles (carefully stoppered) are placed in a thermostat at 15° or 20° and kept in the dark. After given intervals of time, the contents of the bottles are mixed with an excess of aqueous potassium iodide solution and titrated with the thiosulphate. The time allowed varies with different acids, but with an $\alpha\beta$-unsaturated acid such as crotonic, $CH_3 \cdot CH:CH \cdot CO_2H$, or cinnamic, $C_6H_5 \cdot CH:CH \cdot CO_2H$, one titration every twenty-four hours will suffice.

The reaction,

$$C_6H_5 \cdot CH:CH \cdot CO_2H + Br_2 = C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2H,$$

is a bimolecular one, and the velocity of the reaction can be calculated by means of the equation (3) (p. 321), if equimolecular solutions are employed, or equation (4) if the concentrations of the two solutions are different.

The concentration of the solution as regards bromine at time t is determined by the addition of a slight excess of potassium iodide solution and titration with the standard thiosulphate, and as one molecule of bromine reacts with one of the acid the concentration of the acid solution will diminish at the same rate as that of the bromine. If only a relative and not the actual constant is required, the number of c.cm. of standard thiosulphate can be used to denote the concentrations.

It is advisable that the thiosulphate solution should be freshly standardized before use, and it is best kept from contact with atmospheric carbon dioxide in the same way as barium hydroxide solution.

Experiment 304. — Determine the rate of addition of bromine to cinnamic and erucic acids at 20°.

N.B.—In the latter acid the double bond is not in the $\alpha\beta$-position, and bromine is added very readily even in the dark, so that the titrations should be made every thirty seconds. The experimental error in reading the time at all accurately

* If a dark room is not available, amber brown bottles may be used, and the solution transferred to a colourless bottle for titration.

is so great that with acids of this type the values for K do not agree well.

C. Determination of the Rate of Addition of Iodine to an Acetylenic Acid in Aqueous Solution *

Experiment 305.—Pure phenylpropiolic acid is transformed into its potassium salt by dissolving in water containing the theoretical amount of potassium carbonate, the solution is then diluted until it contains 0·1 gram-molecule per litre. A 0·2 N solution of iodine in potassium iodide is also prepared and accurately standardized by means of sodium thiosulphate. The two solutions are kept at 15° for a short time, and then equal volumes (75 c.cm. of each) mixed in the dark,† and the time noted. 20 c.cm. of the mixture is placed in each of six small bottles placed in a thermostat (15°) in a dark room and the contents titrated with the thiosulphate after several hours, *e.g.* after 2, 6, 10, 20, 24, 42 hours.

The constant is calculated by means of the ordinary equation for a bimolecular reaction.

D. Determination of the Rate of Decomposition of a Diazonium Salt in Aqueous Solution ‡

The decomposition of a diazonium salt, *e.g.* benzene diazonium chloride, when warmed with water may be represented by the equation

$$C_6H_5 \cdot N_2Cl + H \cdot OH \longrightarrow C_6H_5OH + HCl + N_2.$$

When a dilute aqueous solution is employed, the reaction should be unimolecular.

The concentrations of the solution at time t and at the beginning are best represented in terms of the volume of nitrogen evolved. The total number of c.cm. of nitrogen evolved will represent the original concentration a, and the number of c.cm. collected after time t will give the value for x at time t.

* *James* and *Sudborough*, J. C. S. 1907, **91**, 1042.

† See note, p. 325.

‡ *Hantzsch* and *Osswald*, B. 1900, **33**, 2528; *Cain* and *Nicoll*, J. C. S. 1902, **81**, 1412; *Lamplugh*, P. 1906, **22**, 280.

The apparatus generally employed is a wide test tube provided with a side tube (1 mm. bore) placed near the top. This side tube is connected with a Hempel gas burette, so that the volume of gas which escapes can be measured after given intervals of time. It is necessary to keep the solution rapidly stirred, as otherwise the nitrogen forms supersaturated solutions. The stirring is accomplished by means of a stirrer worked by a turbine and furnished with a mercury trap so that gas cannot escape through the stirring arrangement. One of the simplest forms of mercury trap is represented in fig. 89. The tube *a*, which should be slightly wider than the axle *s* of the stirrer, passes right through the cork, but the wide tube *b* passes only halfway into the cork and so forms with *a* a cup into which mercury can be poured. The top part of the stem of the stirrer fits air-tight into the two tubes *c* and *d*; *c* is of the same diameter as *a*, and the edges of both *a* and *c* are made as straight as possible and then rounded off. The wider tube *d* dips below the surface of the mercury, and thus forms a trap which will not allow gas to escape unless the pressure in the flask reaches a high value. Friction can be diminished by coating the stem of the stirrer with vaseline.

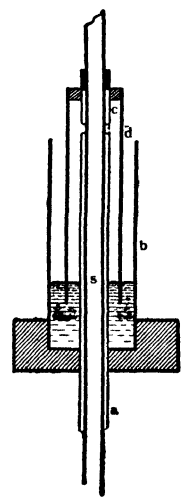


Fig 89

Experiment 306.— Decomposition of benzene diazonium chloride.

A solution containing 10 grm. of the diazonium chloride per litre is prepared by dissolving 6·64 grm. (1 mol.) of pure aniline in 21·5 c.cm. (3 mols.) of hydrochloric acid (sp. gr. 1·16), cooling with ice, and diazotizing with a solution of 4·93 grm. of sodium nitrite in 75 c.cm. of water (see Exp. 154), and the whole then made up to 1 litre. Sufficient of the solution is introduced into the tube so as to fill it nearly to the level of the capillary side tube. The tube is fitted with a cork and stirrer and immersed in a thermostat at 20° or 25°, so that the whole of the liquid can be kept at the same temperature. The stirrer is started, and after some seven minutes the side tube is connected with the measuring apparatus and the time noted. This is the zero point from which the sub-

sequent times are reckoned. The first reading may be taken after two hours and subsequent readings every forty-five to sixty minutes. If the mixture is not stirred, the flask should be tapped before each reading is taken, and the level of the water in the two tubes of the Hempel burette are brought to the same level when the reading is taken. The experiment should be conducted in a room the temperature of which remains constant, or the measuring tube should be surrounded by a jacket of cold water, or otherwise the volumes of gas measured will need to be corrected for variations of temperature.

The value of a is obtained by heating the tube by means of hot water, cooling, and repeating the experiment several times until no more gas is evolved, and taking the final reading.

E. Rate of Hydrolysis of an Ester by means of Potassium Hydroxide

The reaction

$$R{\cdot}COOR' + KOH \longrightarrow R{\cdot}COOK + R'OH$$

is a typical bimolecular reaction, and its velocity constant may be determined in alcoholic or in aqueous solution if the ester is sufficiently soluble.

If solutions of ester and alkali of the same concentration are employed, equation (3) may be used for calculating the constant, otherwise equation (4).

Experiment 307.—Determine the velocity constant for the hydrolysis of ethyl acetate by potassium hydroxide in aqueous solution at 20°. Use perfectly clean vessels, and solutions of ester and alkali of 0·025 N strength. *N.B.*—The alkali should be free from carbonate and the ester should be quite pure. The original concentration of the ester solution can be determined from the weight of *pure* ester used, or by hydrolysing a given volume of the ester solution by boiling with an excess of the alkali, and determining the amount of alkali required for complete hydrolysis by estimating the excess of alkali with standard acid, using phenol phthalein as indicator.

Equal volumes of the two solutions are mixed at the given temperature, and then 30 to 50 c.cm. of the mixture placed in small bottles in the thermostat. The contents of a bottle are titrated after 5, 10, 20, 30 minutes. The titration is accom-

plished by adding an excess of standard hydrochloric acid (0·025 N) and titrating the excess by means of barium hydroxide solution. For a may be substituted the number of c.cm of HCl required to neutralize the potash originally present, and for $a - x$ the number of c.cm. of HCl required to neutralize the potash after time t.

If it is desired to compare the constants for different esters or different alkalis, these should all refer to normal solutions. The value for such can be obtained by taking the constant as calculated above and multiplying by $\frac{v}{N}$, where v represents the number of c.cm. of the reaction mixture taken in each experiment, and N represents the normality of the acid used for titrating.

The velocity constant varies with the alkali employed, with the temperature, and with the ester. This last factor is of considerable interest, and depends both upon the alcohol and the acid from which the ester is derived. The more complex the alkyl radical R′ the less readily is the ester hydrolysed. Similarly, the more complex the acyl group R·CO the less readily is the ester hydrolysed, but another important factor appears to be the strength (activity) of the acid from which the ester is derived.

Further examples of determinations of velocity constants of organic reactions are: Conversion of synaldoximes into antialdoximes (*Ley*, Z. 1895, **18**, 376); Hydrolysis of esters with dilute hydrochloric acid; Hydrolysis of acetamide by acids (*Ostwald*, J. pr. 1883 (1), **27**, 1, The formation of anilides (*Goldschmidt* and *Wach* Z. 1897, **24**, 353); Action of bromine on fatty acids; Formation of ethers (*Conrad*, Z. 1889, **3**, 273, 450, 631; 1890, **5**, 289; 1891, **7**, 274, 283); Reduction of nitro-derivatives with stannous chloride (*H. Goldschmidt*, Z. 1904, **48**, 435; 1906, **56**, 1), Conversion of diazoamino- into amino-azo-compounds (*Goldschmidt* and *Reinders*, B. 1896, **29**, 1369, 1899); Action of chlorine on benzene (*Slator*, J. C. S. 1903, **83**, 729); The formation of olefines from alphyl iodides (*Brussoff*, Z. 1900, **34**, 129).

XXXVII. ELECTRICAL CONDUCTIVITY

The power of conducting the electric current in solution is dependent on the dissociation of the dissolved substance into ions. Substances which, when dissolved in a suitable solvent, possess this property, are termed electrolytes, and those which do not, non-electrolytes. The great majority of organic compounds are non-electrolytes, the power of conducting the current being limited to solutions of acids, bases, and salts.

The electrical resistance between two parallel faces of a regular cube of 1 cm. edge is termed the *specific resistance* of the material, and the reciprocal of this is the *specific conductance* or *conductivity*.* In the case of solutions of electrolytes, since the conductivity of the solvent (pure water, cf. p. 332) can be practically neglected, the conductivity depends on the solute alone. It is therefore expressed as *equivalent* or *molecular conductivity*. These terms express the conductivity possessed by one equivalent weight (expressed in grams) or gram-molecular weight respectively of the electrolyte when dissolved in the solvent and brought between two electrodes of sufficiently large area, 1 cm. apart. Thus if 1 gram-molecule of an electrolyte is dissolved in v c.cm. of solvent, and the specific conductance of the resulting solution is found to be l, then—

$$\text{Molecular conductivity } (\mu) = lv \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This quantity will depend on the degree of ionization of the solute under the conditions of the experiment, and this varies with (i) the solvent, (ii) the temperature, and (iii) the dilution. Pure water is almost always used as the solvent; to express the other factors, the molecular conductivity is usually denoted by

$$\mu_v^t$$

i.e. the molecular conductivity at temperature t and dilution v.

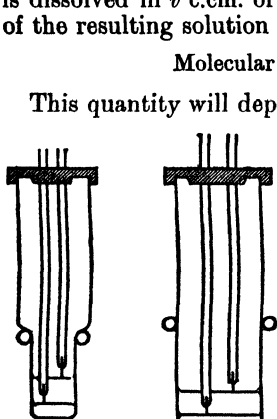


Fig. 90

Determinations of conductivity are carried out in *conductivity cells* (fig. 90), which consist essentially of two platinum elec-

* The unit of conductivity is the *mho*, *i.e.* the reciprocal ohm.

trodes, insulated from one another, and fixed at a definite distance apart in a glass vessel which contains the solution. If the electrodes were exactly 1 sq. cm. in area, and were fixed 1 cm. apart, the determination of the electrical resistance of the cell when the space between the electrodes is filled with a certain solution, would afford the value of the molecular conductivity of that solution by equation (1) above. This is, however, not generally the case, and it is therefore necessary to make a preliminary determination of the *cell constant, i.e.* the factor by which the observed conductivity must be multiplied in order to yield the specific conductivity of the substance under examination (cf. p. 333).

For the purpose of determining the resistance of the con-

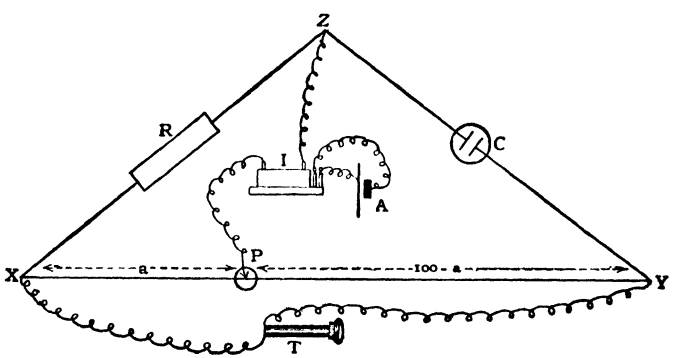


Fig. 91

ductivity cell containing a solution, a modification of the Wheatstone's bridge arrangement due to Kohlrausch is adopted. Since the use of a direct current would cause gases to be evolved in the conductivity vessel, and thus give rise to polarization effects, the current through the cell must be alternating. This can be effected in one of two ways.

(*a*) In Kohlrausch's method (fig. 91) the current is obtained from the secondary circuit of a small toy induction coil of few turns I, worked by a single accumulator cell A. The current is detected by means of the telephone T. The contact-breaker of the induction coil should be small and light, so that it has a high vibration frequency, and consequently produces a high-pitched and audible note in the telephone. The current is

regulated so that the sound of the alternate contact and break of the hammer is just distinctly audible; this can be effected by introducing a suitable resistance into the primary circuit of the induction coil.

XY represents the wire bridge, consisting of a fine wire of platinum-iridium (or other metal possessing a high resistance) stretched on a scale of length 1 metre and graduated in mm. A sliding-contact piece P makes contact with the wire. R is a resistance box of ordinary type, while C represents the conductivity vessel. This is usually of the type shown in fig. 90, and is mounted on a suitable stand, and fixed in a thermostat kept at 15°, 20°, or 25°.

(*b*) *Whetham's Method.**—The resistance is determined by the method of Wheatstone's bridge. By the use of a special commutator an alternating current is obtained, and at the same time a moving-coil galvanometer is used for testing the balance.

A. Preliminary Operations

1. *Preparation of Pure Water.*†—The water used as solvent in conductivity determinations must be of a high degree of purity, for the presence of even a very slight amount of dissolved substance causes a great increase in its conductivity. The chief causes of impurity in ordinary distilled water are ammonia and carbon dioxide, and in a redistillation special precautions should be taken to exclude these. If they are only present in minute quantity one redistillation of ordinary distilled water should suffice. The condenser should consist of a block-tin tube or of a length of *resistance* glass tubing, and the receiver a flask of the same material. The latter should communicate with the air through a U tube containing soda lime. Only the middle third of the distillate should be collected.

A poor sample of water, especially if containing much ammonia, should be distilled with a mixture of potassium permanganate and sulphuric acid, and again redistilled with baryta water.

The purest water that has yet been obtained had a specific conductance of $0{\cdot}4 \times 10^{-7}$ mhos at 18°. For experiments

* Trans. 1900, 259, 321.

† See *Hartley, Campbell,* and *Poole,* J. C. S. 1908, 93, 428.

such as are described below water having a conductivity of $2 - 3 \times 10^{-6}$ is sufficiently pure.

2. *Platinizing the Electrodes.*—The clearness of the sound emitted by the telephone depends largely on the surface of the electrodes, and is increased by coating them with a fine layer of platinum black. For this purpose the electrodes are chemically cleaned with chromic acid solution, the cell is filled with a platinizing solution consisting of 3 grm. of platinic chloride and 0·02 to 0·03 grm. of lead acetate in 100 c.cm. of water, and a current from an accumulator is passed through for ten to fifteen minutes, the direction of the current being changed at intervals of half a minute by means of a reversing key. The electrodes are then withdrawn and washed thoroughly, the last washings being done with water purified as above. To ascertain whether the washing is complete a series of blank experiments should be carried out as detailed below, the cell containing pure water only. The series is continued until two successive determinations give equal values for the conductivity of the cell contents.

3. *Determination of the Cell Constant.*—A 0·02 N solution of potassium chloride in pure water is prepared. The conductivity of this solution is expressed in the following table:—

Temperature.	Conductivity.
10°	$1{\cdot}996 \times 10^{-3}$ mhos.
18°	$2{\cdot}399 \times 10^{-3}$ „
25°	$2{\cdot}768 \times 10^{-3}$ „

The conductivity cell is well washed with quantities of this solution, and is then filled with the solution and placed in the thermostat. The apparatus is joined up as indicated in fig. 91. When the temperature has become constant a resistance (say 500 ohms) is introduced into the arm XZ by withdrawing plugs in the resistance box. The position of P when the sound in the telephone is a minimum is determined as accurately as possible (to 0·5 mm.). Several determinations are made by withdrawing different resistances from the box; to diminish errors, these should be so arranged that the position of P should fall between the 40 and 60 cm. graduations of the scale.

If R ohms is the resistance introduced into the arm XZ, and a represents XP, then $PY = 100 - a$.

Let R′ ohms represent the resistance of the arm ZY (*i.e.* of the cell).

Then when no current passes through the telephone—

$$\frac{R}{a} = \frac{R'}{100 - a}$$

$$\text{and } R' = \frac{(100 - a)R}{a}.$$

$$\text{The conductivity of the cell} = \frac{1}{R'} = \frac{a}{(100 - a)R} \text{ mhos.}$$

If C represent the cell constant, and x the molecular conductivity of the potassium chloride solution, as given in the above table—

$$\frac{1}{R'} \times C = x$$

$$\therefore C = R'x = \frac{xR(100 - a)}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

B. Determination of Molecular Conductivity

To determine the molecular conductivity of a given substance in solution, a sample of the solution is examined as above. Thus if 1 grm.-mol. of the substance is dissolved in v of the solvent (usually expressed in litres), and the resistance of the cell is found by experiment to be R ohms (C = cell constant)—

$$\mu_v = \frac{1}{R} \times C \times v \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

C. Dissociation Constant

Moderately dissociated binary electrolytes, such as the organic acids, show a variation of their molecular conductivity with the concentration. The molecular conductivity depends on the degree of ionization; thus, if a represents the proportion of molecules dissociated at dilution v, it follows from the law of mass action that—

$$\frac{a^2}{v(1 - a)} = \text{a constant } k.$$

But if μ_∞ represents the conductivity of the solution at infinite dilution, *i.e.* when all the molecules are dissociated.

$$a = \frac{\mu_v}{\mu_\infty};$$

whence it follows that

$$\frac{\mu_v^2}{v\mu_\infty(\mu_\infty - \mu_v)} = k \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

k is the *dissociation* or *ionization* constant, or in the case of acids and bases the so-called *affinity* constant. Since this value is very small, the constant $K = 100\,k$ is usually taken. This is a constant of great importance, which is used as a measure of the strengths or activities of all feeble acids such as the organic acids. The above equation suggests a method for its determination.

Experiment 308.—Determination of the affinity constant of acetic acid.

100 c cm. of a $\frac{1}{16}$ N solution of acetic acid are made, and its strength determined accurately by titration with standard 0·1 N baryta solution. Two pipettes are obtained, one to deliver, the other to take up, 10 c.cm. of water; when not in use these should be placed in an upright position with their ends resting on filter paper.

20 c.cm. of the acid solution are introduced into the conductivity cell which is fixed in position in the thermostat, and the resistance of the solution determined as described above. (Make at least three separate determinations.) Then 10 c.cm. of the acid solution are withdrawn from the cell and 10 c.cm. of pure water (100 c.cm. are previously allowed to stand for some time in a bottle in the thermostat in order to gain its temperature) are added. After mixing thoroughly, the resistance of this second solution is determined. The process is repeated several times until the dilution has reached 1024 litres. Values for μ_{16}, μ_{32}, μ_{64} . . . μ_{1024} can be calculated from the results by means of equation (3).

Determination of μ_∞.

The limiting value of μ, *i.e.* the molecular conductivity at infinite dilution, can only be determined experimentally for strong monobasic acids, *e.g.* hydrochloric acid, by a determination of the conductivity of the acid itself in very dilute solution. The method cannot be applied in the case of weak acids such as the organic acids, but the value μ_∞ for such acids can be obtained indirectly from the value μ_∞ for the corresponding sodium salt. The limiting value for the sodium salt can be obtained directly, as the sodium salts of feeble acids are much more readily ionized than the acids from which they are derived

μ_∞ for weak monobasic acids is determined from the limiting value of μ for their sodium salts by subtracting the conductivity due to the sodion (43·5 at 18°, 51·0 at 25°), and adding the conductivity of hydrion (314·0 at 18°; 347 at 25°). For weak polybasic acids this rule cannot be applied. In such cases, especially in the case of organic acids, the only method is to apply Ostwald's rule connecting the conductivity with the number of atoms in the molecule.

Acetic	acid has	μ_∞	.....	.....	389
Propionic	„	„	.....	.....	384
Benzoic	„	„	.....	.....	381
For acids containing		12	atoms in the molecule	μ_∞	= 383
„	„	15	„	„	= 380
„	„	18	„	„	= 378
„	„	22	„	„	= 376
„	„	25	„	„	= 375
„	„	30	„	„	= 374

D. Determination of the Basicity of an Organic Acid

Pure sodium hydroxide, free from carbonate, is made by placing metallic sodium freed from the crust of oxide in a platinum or silver basin under a bell jar over water. The basin is supported on a glass tripod stand well above the level of the water, and the entrance of carbon dioxide is prevented by means of a soda-lime tube. In a few days the sodium is transformed into sodium hydroxide, which is dissolved in pure water and brought up to $\frac{N}{32}$ strength.

About 20 c.cm. of this solution is coloured pink with a few drops of phenol phthalein and then treated with the dry acid until the colour just vanishes It is then filtered, the first few drops of the filtrate being discarded, and the remainder is exactly neutralized by the careful addition of more of the sodium hydroxide solution from a burette. This provides a $\frac{N}{32}$ solution of the sodium salt of the acid.

The conductivity of this solution is then determined, after which it is diluted to $\frac{N}{1024}$ as described in Exp. 308. The conductivity of this diluted solution is similarly determined

Then—

$$\text{Basicity of the acid } (n) = \frac{\mu_{1024} - \mu_{32}}{10}.$$

This rule has been tested and confirmed as far as the pentabasic acids. It is not quite strict, but the nearest whole value of n is taken.

If the acid is a very feeble acid and the sodium salt is appreciably hydrolysed by water, the values for n are only approximate

Experiment 309.—Determine the basicity of succinic or of citric acid by the above method.

E. Pseudo-acids.* (S. B. 363, &c.)

Certain organic compounds, especially open-chain nitro-compounds possessing a hydrogen atom attached to the same carbon atom as the nitro-group, though in the free state possessing no acidic properties, are able to neutralize alkalis gradually. The substances as such are not acidic and do not neutralize the base, but are gradually transformed into isomeric true acids which then neutralize the alkali.

$$\underset{\text{(non-ionized)}}{CH_3\cdot CH_2\cdot NO_2} \longrightarrow \underset{\text{(ionized)}}{CH_3\cdot CH{:}N(=O)\cdot O\cdot H} \longrightarrow \underset{\text{(ionized)}}{CH_3\cdot CH{:}N(=O)\cdot ONa}$$

If to a solution of the salt derived from the pseudo-acid, the equivalent amount of hydrochloric acid is added, the converse process to the above takes place, and can be followed by measuring the electrical conductivity of the solution.

Experiment 310.—Examination of the electrical conductivity of a solution of the baric salt of nitro-ethane on treatment with an equivalent amount of hydrochloric acid.†

$$\underset{\text{(ionized)}}{CH_3\cdot CH{:}NOOba} + \underset{\text{(ionized)}}{HCl} \longrightarrow \underset{\text{(ionized)}}{CH_3\cdot CH{:}NO\cdot OH} + \underset{\text{(ionized)}}{baCl}\ddagger$$

and

$$\underset{\text{(ionized)}}{CH_3\cdot CH{:}CO\cdot OH} \longrightarrow \underset{\text{(non-ionized)}}{CH_3\cdot CH_2\cdot NO_2}$$

$\frac{N}{36}$ solutions of barium hydroxide and hydrochloric acid are

* *Hantzsch*, B. 1899, **32**, 575. † *Hantzsch* and *Veit*, ibid. 617–619.

‡ ba = ½ Ba.

prepared and a solution of the barium salt of iso-nitro-ethane is made by dissolving the calculated weight of nitro-ethane (Exp. 104) in 100 c.cm. of the baryta solution (protect from atmospheric carbon dioxide). The solutions of the salt and of hydrochloric acid are cooled to 0° and then 10 c.cm. of each are introduced into the conductivity cell, which is also kept at 0°, and the electrical conductivity of the mixture determined at definite intervals of time. It is found to fall and finally attain a constant value.

The following values are given by *Hantzsch* and *Veit* for v_{72} at 0°:—

Time in minutes		μ.		Time in hours		μ.
1	.....	72·1	.....	1	.....	67·1
2	.....	71 5	.....	3·5	.....	65·5
5	.....	70·1	.....	5·5	.....	64·2
15	.....	69·0	.....	48	.....	60·2
30	.....	68·4	.....	—	.....	constant.

The last value represents the electricity conductivity of a $\frac{N}{72}$ solution of barium chloride.

XXXVIII. RECOGNITION OF TYPICAL CARBON COMPOUNDS

A. Simple or Complex

One of the first points to be settled when an organic material is provided for examination is whether it is a single chemical individual or a mixture.

(*a*) If the substance is a liquid, a small amount is heated in order to determine whether it is volatile, and if so it is distilled. If all passes over at a constant temperature, then, in the majority of cases the conclusion may be drawn that one compound only is present. As a certain number of mixtures of constant boiling-point are known, the possibility of the presence of these should be borne in mind, and the solubilities of the liquid in different solvents should be examined.

If the boiling-point is not constant then probably the material is a mixture, and in many cases it will be possible to separate the constituents of the mixture by fractional distilla-

tion, *e.g.* a solution of aniline in alcohol or of nitrobenzene in benzene. In certain cases when the liquid of low boiling-point has been removed the residue will solidify and may be purified by crystallization, *e.g.* a solution of dinitrobenzene in benzene.

If the boiling-points of the different constituents of the mixture are too close to one another for separation by fractional distillation, the components must be separated by chemical methods. Thus a mixture of aniline (boiling-point 182°) and nitrobenzene (boiling-point 206°) is readily separated by dissolving the aniline in dilute hydrochloric acid, when the oily nitrobenzene would form a separate layer.

If the substance decomposes when heated under atmospheric pressure, an attempt may be made to distil under reduced pressure (fig. 9).

(*b*) If the substance is a solid, its appearance to the naked eye and also under the microscope or lens should be noted. If it is possible under any of these conditions to detect different types of particles, the material is probably a mixture.

The melting-point of the substance may also throw light upon this question. If, when heated, part of the material melts and leaves a number of particles which remain solid even at a much higher temperature, the material is undoubtedly a mixture, or, again, if the actual melting-point covers a wide range of temperature, *i.e.* it begins to melt at a fixed temperature but is not completely molten until a temperature several degrees higher is attained, the conclusion that we are dealing with a mixture may, as a rule, be drawn. On the other hand, if the substance has a well-defined sharp melting-point, the probability is that it is a single compound.

Further light on this point may be obtained by attempting to fractionally crystallize the substance from a suitable solvent (p. 19). If the melting-points of the different fractions are the same, the only conclusion to be drawn is that the substance is a single compound, or that it is a mixture of two closely allied compounds which form mixed crystals (solid solutions). If, on the other hand, the different crystalline fractions have quite different melting-points, then the original material must have been a mixture of two or more compounds.

The action of common chemical reagents, such as dilute hydrochloric acid, dilute sodium carbonate, or sodium hydroxide, may be studied. If part of the substance dissolves readily in the cold solvent, leaving an insoluble residue even in the presence of an excess of the solvent, the conclusion is obvious.

If the substance appears to be a single compound, then it may be tested for its elements, and experiments made in order to determine to which characteristic group of carbon compounds it belongs.

B. Separation of Mixture into Components

If the material is a mixture it is usually an advantage to separate it into its constituents before a detailed investigation of the chemical nature of these is made. The method of separation to be adopted will, in all probability, have been indicated in the previous investigation as to its complex nature.

The commoner methods adopted are:

1. Fractional distillation.
2. Fractional crystallization.
3. Fractional solution, when one of the constituents is readily soluble and the other practically insoluble in a given solvent, *e.g.* cold water would readily extract acetic acid from a mixture of acetic and benzoic acids, and cold benzene benzoic acid from a mixture of the acid and benzanilide.
4. Use of a reagent with which the one compound will react and give a soluble derivative, whereas the other will not, *e.g.* the separation of an acid from an ester or from an amine, when the ester or amine is insoluble in water, by shaking the mixture with sodium carbonate solution. A very good method is to use two liquids, *e.g.* in the above case ether and sodium carbonate solution. The mixture of acid and ester is dissolved in ether, and the ethereal solution then shaken with dilute sodium hydroxide or sodium carbonate solution. The ether retains the ester, whereas the acid is extracted by the dilute alkali and will be present in the aqueous solution as a sodium salt. The two solutions are separated by means of a tap funnel and each worked up separately. The acid, if insoluble in water, may be precipitated by acidifying the alkaline liquid with a mineral acid, and the ester is obtained when the ethereal solution is dried and the ether removed.
5. A method which can be adopted when one of the constituents of the mixture is readily volatile, is to subject the mixture to a process of sublimation (fig. 19). A mixture of naphthalene and acetanilide could be separated quite readily by this method.

C. Determination of Elements Present

The next step is to determine the elements present in each compound isolated.

For C and H, see p. 36.

For N, the sodium test (p. 37) or *Castellana's* test (p. 38) is usually employed.

For halogens, the copper oxide wire, sodium, or lime test (p. 38).

For sulphur, the nitro-prusside test (p. 39).

Simple physical constants such as boiling-point or melting-point are also determined.

D. Examination of some Simple Reactions of the Compound

A considerable amount of useful information with respect to the nature of the chemical compound under examination may often be obtained by performing a few preliminary experiments. Some of the simpler are as follows:—

(*a*) Ignite a small amount of the substance on platinum* and notice if any mineral residue is left. Examine this residue in the ordinary manner for metallic and acid radicals. As a rule it will be a metal, metallic oxide, or carbonate. Occasionally a sulphite, sulphate, or halide.

The formation of a metallic residue indicates the presence of the metallic salts of an acid (sulphonic or carboxylic), or the metallic derivative of a phenol, alcohol, mercaptan, ketone, or aldehyde.

(*b*) Burn a small amount of the substance on a glass rod, or notice how the substance burns in (*a*), also observe odour during burning. All aromatic compounds produce an intensely smoky flame, and, as a rule, give rise to characteristic odours. Very simple aliphatic compounds burn with a non-luminous flame, but an increase in molecular complexity is accompanied by an increase in the luminosity of the flame.

Many carbohydrates when heated char and produce an odour of burning sugar.

(*c*) *Behaviour with water.*—If soluble, test solution and ob-

* Make sure that lead, mercury, and arsenic compounds are absent.

serve if neutral, acid, or alkaline to litmus. A strongly alkaline solution may be due to the presence of a soluble amine, such as trimethylamine, or may be due to the hydrolysis of the sodium or potassium salt of a very feeble acid or acidic compound, *e.g.* sodium carbonate, potassium cyanide, sodium ethoxide, potassium phenate, &c. If an acid reaction is obtained it does not necessarily mean that the original compound is a free acid; it may be an acid derivative, *e.g.* anhydride, chloride, or ester, which has been decomposed by the water yielding an acid. It may also be the salt of a very feeble base, *e.g.* aniline hydrochloride. All such salts when dissolved in water are largely hydrolysed (p. 131), and the acid reaction is due to the free mineral or organic acid thus formed. If nitrogen has not been found when testing for the elements the substance cannot, obviously, be a compound of this type.

If the substance is practically insoluble in cold, but dissolves in hot water, and the solution deposits crystals as the solution cools, it is advisable to examine these crystals in order to see whether they are identical with the original compound or not. A melting-point determination, after the crystals are dry, will usually settle this point. The melting-point of a mixture of the crystals and the original compound should also be taken. If succinic anhydride (melting-point 120°) is boiled with water, crystals of succinic acid (melting-point 185°) will separate as the solution cools, if this be sufficiently concentrated, again, if crystals of methyl oxalate are boiled with water, crystals of oxalic acid can be obtained.

(*d*) *With dilute mineral acid, preferably hydrochloric acid.*—If the compound is sparingly soluble in cold water but dissolves readily in cold dilute hydrochloric acid, the presence of an amine or an amino-derivative, *e.g.* an amino-acid such as *o*-amino-benzoic acid, may be inferred, and experiments may then be made in order to determine the nature of the amine, *e.g.* primary, secondary, tertiary; aromatic or aliphatic; see p. 188 *et seq.*

If the original substance dissolves readily in cold water and the aqueous solution yields a precipitate on the addition of hydrochloric acid, the substance is undoubtedly the metallic salt of an acid, insoluble in water, probably an aromatic acid. The precipitate can be removed, crystallized, and its physical and chemical characteristics investigated. If the original compound is the salt of a simple aliphatic acid, *e.g.* ammonium acetate, no change will be observed on the addition of hydro-

chloric acid. If a silver or lead salt is present a precipitate of the metallic chloride will be produced on the addition of hydrochloric acid, the majority of silver and lead salts of organic acids, however, are insoluble or only very sparingly soluble in water.

If the compound is insoluble in water and in cold dilute hydrochloric acid, but dissolves in the latter on warming and crystallizes as the solution cools, it is advisable to examine the crystals which separate in order to find out whether they are identical with the original compound or not. α-Naphthylamine is very sparingly soluble in water and also in cold hydrochloric acid, as its hydrochloride is not readily soluble in water. When the base is warmed with excess of dilute hydrochloric acid, a clear solution is obtained and, on cooling, crystals of α-naphthylamine hydrochloride separate, and it will be found that the chemical and physical properties (*e.g.* melting-point, solubility, &c.) of the crystals are quite different from those of the original substance, indicating that the compound must have reacted with the acid, *e.g.* formed a salt, thus pointing to the basic nature of the compound under investigation.

(*e*) *With a strong alkali*, e.g. *potassium hydroxide solution*.—If the compound is insoluble or only sparingly soluble in water, but dissolves readily in dilute caustic potash solution, it must be an acid (carboxylic, sulphonic, or pseudo-acid) or a phenol. The behaviour of the compound towards sodium carbonate solution can be investigated; if insoluble in water but soluble in both sodium carbonate and potassium hydroxide solutions it is undoubtedly an acid, if insoluble in water and in sodium carbonate solution it is a phenol. *Note.*—Many nitro-phenols are so strongly acidic that they dissolve in sodium carbonate solution yielding the corresponding sodium derivatives. Many acids and phenols are fairly readily soluble in water, and it will always be found that an acid, whether soluble or insoluble in water, will completely dissolve in dilute sodium carbonate solution, and that carbon dioxide will be evolved if the carbonate solution is warmed. If the compound is soluble in water but yields an oil or a precipitate on the addition of alkali, the probability is that the substance is the salt of a base, *e.g.* of a simple amine or an alkaloid.

Both chloral and bromal and their hydrates are decomposed by alkalis and colourless oils with pleasant sweet odours are formed; these oils are chloroform and bromoform respectively,

and their boiling-points may be determined. The alkaline solution can also be tested for a formate:

$$CCl_3 \cdot CHO + KOH = CHCl_3 + H \cdot COOK.$$

If ammonia* is evolved when the substance is heated with potassium hydroxide solution it may be accepted as an indication of the presence of an ammonium salt, an acid amide, imide, or a nitrile. As a rule the ammonium salts are readily soluble in water (exception, ammonium urate), whereas the acid imides, amides, and nitriles are not, with the exception of those derived from the lower fatty acids. Ammonium salts give up their ammonia, as a rule, more readily than amides or nitriles, *e.g.* when treated with cold alkali, or, even better, when rubbed with slaked lime and a little water. The only reliable method of determining whether the compound is the amide, ammonium salt, or nitrile of a given acid, is to determine the special acid from which it is derived, and then from an examination of the physical constants of the original compound to determine whether these agree with those of the ammonium salt, amide, or nitrile.

If the substance has a pleasant fruity odour, is insoluble in water, but dissolves gradually when boiled with alkalis (use reflux condenser), then it is probably an ester. The hydrolysis can be completed and the liquid examined for both alcohol and acid.

It is necessary to bear in mind that a given compound may give the reactions characteristic of two or more different types of compounds. This is due to the fact that the compound in question contains two or more characteristic atomic groupings or radicals in the molecule. Thus succinamic acid, $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot OH$, as a free acid, dissolves readily in sodium carbonate or potassium hydroxide solution, although only sparingly soluble in water; but it also possesses the properties of an acid amide, and evolves ammonia when boiled with potash. The fact that it yields succinic acid when hydrolysed, indicates that it must be a derivative of this acid, its solubility in sodium carbonate solution shows that it must be an acid, and the evolution of ammonia indicates that it must be an ammonium salt, acid amide, or nitrile. An examination of its solubility

* Methylamine may easily be confused with ammonia, as it is strongly alkaline and has a similar odour; it can be distinguished from ammonia by its inflammability.

in water, of its melting-point, and of certain derivatives will decide which of these it is.

Certain compounds when boiled for some time with concentrated potash are decomposed, and yield oils or solids of low melting-point which have odours characteristic of aromatic amines. Such behaviour points to the presence of an acyl derivative of an arylamine (an anilide, toluidide, &c.), and the compound should be completely hydrolysed with concentrated potash, or concentrated hydrochloric acid, and the product examined for the organic acid and for the amine.

(*f*) Another simple preliminary test is to determine whether the substance has strong reducing properties or not. The simplest method of doing this is to warm an aqueous solution of the compound with Fehling's solution (Exp. 290) or with ammoniacal silver nitrate (Exp. 176). Strong reducing properties are characteristic of practically all aldehydes, including the commoner monosaccharoses, such as glucose and fructose (a hydroxy-ketone), and even disaccharoses such as maltose. Formic acid and its salts are also strongly reducing compounds, and even a few simple ketones and alcohols. Certain complex compounds do not reduce directly, but have strong reducing properties after hydrolysis with mineral acids. To this category belong disaccharoses of the type of cane sugar, polysaccharoses such as starch, dextrin, and practically all glucosides (S. B. 572, and this chapter, p. 363).

E. More Important Groups of Compounds

The preliminary investigation thus outlined, including the determination of the elements present and the solubilities of the compound in the commoner organic solvents, *e.g.* alcohol, ether, benzene, will, as a rule, give some clear indication of the probable nature of the substance, and a more detailed investigation may be made as described under the following headings:—

Hydrocarbons, p. 96. For physical constants, see S. B. 30, 43, 344, 352.

Alcohols, p. 101. For physical constants, see this chapter, pp. 347, 348.

Halogen derivatives, p. 119. For physical constants, see S. B. 56, 353, 357.

Acids, p. 131; acid derivatives: salts, p. 141; esters, p. 142,

anhydrides, p. 145; amides, p. 148; imides, p 150; nitriles, p. 151. For physical constants, see this chapter, pp. 349–351.

Sulphonic acids, p. 167.

Nitro-derivatives, p. 157. For physical constants, see S. B. 94, 359.

Phenols, p. 172. For physical constants, see this chapter, pp. 347–348.

Amines, p. 118 *et seq.* For physical constants, see this chapter, pp. 353, 354.

Acetyl and benzoyl derivatives, p. 197, and this chapter, pp. 353, 354.

Diazo compounds, &c., p. 198.

Aldehydes and ketones, p. 223. For physical constants, see this chapter, p. 357.

The two most difficult classes of compounds to characterize are probably hydrocarbons and ethers (alcoholic or phenolic). As a rule the other groups of compounds must be eliminated. The ethers react when warmed with PCl_5, whereas the hydrocarbons do not. If other compounds have been shown to be absent and it is thought that a benzene hydrocarbon is present the specific hydrocarbon can be identified by—(*a*) physical constants of the compound; (*b*) oxidation to an aromatic acid usually by chromic anhydride and recognition of this acid; (*c*) preparation of a solid nitro or other substituted derivative; (*d*) in certain cases, *e.g.* naphthalene or anthracene, the crystalline picrates can be prepared. Naphthalene picrate forms golden-yellow crystals, melting-point 149°; anthracene picrate, red crystals, melting-point 170°; phenanthrene picrate, golden-yellow crystals, melting-point 145°.

If an ether is thought to be present it can be hydrolysed (p. 177) and the alcohol or phenol tested for.

For reference purposes the physical constants of the commoner members of the more important groups are given in the following tables, together with the melting-point or boiling-point of characteristic derivatives.

These lists are by no means exhaustive, and compounds not mentioned in these lists can be found by reference to Richter's *Lexicon der Kohlenstoff Verbindungen.*

ALCOHOLS AND PHENOLS

THEIR METHYL AND ETHYL ETHERS, ACETYL AND BENZOYL DERIVATIVES

			Ethers				Esters.			
			Methyl		Ethyl.		Acetate.		Benzoate.	
	M.-pt.	B.-pt.	M.-pt.	B.-pt.	M.-pt.	B.-pt.	M.-pt.	B.-pt.	M.-pt.	B.-pt.
Alcohols—										
Methyl	—	67°	gas		gas		—	57·5°	—	195°
Ethyl	—	78·3	"		—	35°	—	77	—	211
Propyl	—	97·4	—	39°	—	63·6	—	101	—	230
iso-Amyl	—	131	—	92	—	112	—	140	—	261
Benzyl	—	206	—	167	—	185	—	216	20°	345
Glycol	—	198	— (di)	82	— (di)	124	—	187	—	—
Glycerol	17°	290	— (tri)	102	— (tri)	185	—	258	70·5	—
Mannitol	160	—	—	—	—	—	119°	—	149	—
Phenols—										
Phenol	43	183	—	152	—	172	—	195	69	—
o-Cresol	31	188	—	171	—	181	—	—	—	307
m-Cresol	—	201	—	177	—	192	—	—	54	314
p-Cresol	36	198	—	175	—	190	—	213	71·5	316
Catechol	104	—	32°(mono)*	205	—	—	—	—	—	—
"	—	—	15 (di)	205	44°	—	—	—	84	—

* Monomethyl ether = guaiacol.

ALCOHOLS AND PHENOLS—*Continued.*

			Ethers.				Esters			
			Methyl.		Ethyl.		Acetate		Benzoate.	
	M -pt.	B -pt.	M -pt.	B -pt	M -pt.	B -pt.	M.-pt	B -pt	M -pt.	B -pt.
Phenols—(contd.)										
Resorcinol	118°	276°	—	214°	12·5°	235°	—	278°	117°	—
Quinol	169	—	56°	205	71	—	123°	—	199	—
Orcinol (3:5-dihydroxy-toluene)	107	289	—	244	16	252	25	—	88	—
Pyrogallol	132	—	47	235	39	—	160	—	90	—
Phloroglucinol	218	—	52	—	—	—	105	—	173	—
Thymol	50	232	—	217	—	227	—	245	—	—
Carvacrol	—	236	—	217	—	235	—	246	—	260°
Tribromophenol	92	—	87	—	72	—	82	—	81	—
o-Nitrophenol	44	214	9	276	—	268	41	253	58	—
m- „	96	—	38	258	34	264	—	—	95	—
p- „	114	—	54	260	60	283	81	—	142	—
Trinitrophenol (picric acid)	122	—	65	—	78	—	75	—	—	—
α-Naphthol	94	278	—	258	—	277	49	—	56	—
β- „	122	286	72	274	37	274	70	—	107	—

ALIPHATIC MONOBASIC ACIDS

The majority are soluble in water, except the higher acids.

Acid.	Formula.	M -pt	B -pt	Ethyl Ester B -pt	Methyl Ester M -pt	Methyl Ester B -pt	Anhydride M -pt.	Anhydride B -pt.	Amide. M -pt.	Amide. B -pt.	Anilide M -pt.
Formic	$H \cdot CO_2H$	—	101°	55°	—	32·5°	—	—	—	200–212°	46°
Acetic	$CH_3 \cdot CO_2H$	—	118	78	—	57·5	—	136·5°	82°	—	115
Propionic	$CH_3 \cdot CH_2 \cdot CO_2H$	—	141	99	—	80	—	168·6	79	—	105
n-Butyric	$CH_3 \cdot (CH_2)_2 \cdot CO_2H$	—	162	121	—	102	—	192	115	—	92
iso-Butyric	$(CH_3)_2CH \cdot CO_2H$	—	154	110	—	92	—	182	128	—	102·5
iso-Valerianic	$(CH_3)_2CH \cdot CH_2 \cdot CO_2H$	—	174	134	—	117	—	215	128	—	115
Myristic	$CH_3 \cdot (CH_2)_{12} \cdot CO_2H$	54°	—	295	—	—	51°	—	102	—	84
Palmitic	$CH_3(CH_2)_{14} \cdot CO_2H$	62	—	*	28°	—	64	—	104	—	90·5
Stearic	$CH_3(CH_2)_{16} \cdot CO_2H$	69	—	*	38	—	—	—	109	—	—
Chloracetic	$CH_2Cl \cdot CO_2H$	63	185	145	—	130	—	168 (dec)	119	—	134·5
Dichloracetic	$CHCl_2 \cdot CO_2H$	—	190	158	—	143	—	214 (dec.)	98	—	117
Trichloracetic	$CCl_3 \cdot CO_2H$	55	195	167	—	152	—	224	141	—	82
Bromacetic	$CH_2Br \cdot CO_2H$	50	208	159	—	144	—	245	91	—	131
Tribromacetic	$CBr_3 \cdot CO_2H$	135	dec.	225	—	—	—	—	121	—	—
Unsaturated—											
Crotonic	$CH_3 \cdot CH : CH \cdot CO_2H$	72	182	142	—	121	—	—	149	—	118
Oleic	$C_{18}H_{34}O_2$	14	—	*	—	—	—	—	75	—	—
Elaidic	"	51	—	*	—	—	50	—	93–94	—	—
Erucic	$C_{22}H_{42}O_2$	34	—	*	—	—	—	—	84	—	55

* Decomposes

AROMATIC MONOBASIC ACIDS

Acid.	Formula.	M.-pt.	Ethyl Ester M.-pt.	Ethyl Ester B.-pt.	Methyl Ester M.-pt.	Methyl Ester B.-pt.	Chloride. M.-pt.	Chloride. B.-pt.	Anhydride M.-pt.	Amide. M.-pt.	Anilide. M.-pt.
Benzoic	$C_6H_5 \cdot CO_2H$	121°	—	211°	—	195°	—	198°	42°	128°	163°
o-Toluic	$CH_3 \cdot C_6H_4 \cdot CO_2H$	105	—	220	—	—	—	211	36–38	139	125
p- „	„	179	—	228	32°	217	—	214	—	158	145
Phenyl-acetic	$C_6H_5 \cdot CH_2 \cdot CO_2H$	76	—	226	—	220	—	102·5 (at 17 mm.)	72·5	155	117
o-Chlor-benzoic	$C_6H_4Cl \cdot CO_2H$	138	—	243	—	230	—	235	—	139	114
m- „	„	153	—	245	21	114	—	225	—	133	—
p- „	„	234	—	—	42	—	—	220	—	170	194
o-Brom-benzoic	$C_6H_4Br \cdot CO_2H$	150	—	254	—	246	—	241	—	156	142
m- „	„	155	—	259	32	122	—	239	—	151	137
p- „	„	251	—	262	74	—	42°	245	213	186	197
o-Nitro-benzoic	$NO_2 \cdot C_6H_4 \cdot CO_2H$	148	30°	—	—	—	—	—	135	176	—
m- „	„	141	47	298	70	279	35	184 (at 50 mm.)	—	143	154
p- „	„	240	57	—	96	—	75	202 (at 105 mm.)	—	198	204
Hydrocinnamic	$C_6H_5 \cdot (CH_2)_2 \cdot CO_2H$	48·5	—	249	—	239	—	119 (at 13 mm.)	—	82	92
Unsaturated—											
Cinnamic	$C_6H_5CH{:}CH \cdot CO_2H$	133	12	271	36	260	36	154 (at 25 mm.)	135	147	151
Atropic	$CH_2{:}C(C_6H_5) \cdot CO_2H$	106	—	—	—	—	—	—	—	—	—
Phenyl-propiolic	$C_6H_5C{:}C \cdot CO_2H$	136	—	—	—	—	—	130 (at 25 mm.)	—	100	126

DIBASIC ACIDS, ALIPHATIC AND AROMATIC

Acid.	Formula.	M.-pt	Normal Methyl Ester M.-pt	Normal Methyl Ester B.-pt	Normal Ethyl Ester M.-pt	Normal Ethyl Ester B.-pt	Anhydride M.-pt	Amide M.-pt	Imide M.-pt	Anilide. M.-pt.
Aliphatic—										
Carbonic.....	$CO(OH)_2$	—	—	91°	—	126°	—	132°	—	235°
Oxalic.....	$CO_2H \cdot CO_2H$	98°	54°	163	—	186	—	dec.	—	245
Malonic.....	$CO_2H \cdot CH_2 \cdot CO_2H$	132	—	182	—	198	—	170	—	224
Succinic.....	$CO_2H \cdot (CH_2)_2 \cdot CO_2H$	185	18	195	—	217	119°	242	126°	227
Glutaric.....	$CO_2H \cdot (CH_2)_3 \cdot CO_2H$	97·5	—	—	—	236	56	176 (dec.)	60	224
Malic.....	$CO_2H \cdot CH_2 \cdot CH(OH) \cdot CO_2H$	100	—	122 (10 mm.)	—	128 (10 mm.)	—	—	—	197
Tartaric.....	$CO_2H \cdot (CH \cdot OH)_2 \cdot CO_2H$	168	48	280	—	280	—	—	—	263
Aromatic—										
Phthalic.....	$C_6H_4(CO_2H)_2$ (1:2)	184	—	282	—	295	128	—	233	231 (dec.)
Iso-phthalic.....	„ (1:3)	300	64	dec.	—	285	—	265	—	250
Tere-phthalic...	„ (1:4)	—	140	—	44°	—	—	—	—	—

Characteristic Reactions of Some of the Commoner Acids

Formic acid (cf. p. 125 and S. B. 148).—Reduces ammoniacal silver nitrate and evolves carbon monoxide with cold concentrated sulphuric acid. A neutral solution with mercuric chloride gives a white precipitate of mercuric formate, which yields metallic mercury when warmed. Ferric chloride, similar to acetic acid.

Acetic acid (cf. p. 124 and S. B. 152).—Characteristic odour. The normal ferric salt is soluble in water to blood-red solutions, which yield a brown precipitate of a basic acetate when boiled No reducing properties, with ethyl alcohol and concentrated sulphuric acid it yields ethyl acetate, which has a characteristic odour.

n-**Butyric acid** (p. 247).—Its calcium salt is less soluble in hot than in cold water.

Oxalic acid (pp. 128–129 and S. B. 235).—The calcium salt is insoluble in water and dilute acetic acid. Concentrated sulphuric acid decomposes the acid and its salts at fairly high temperatures, yielding carbon monoxide and dioxide. The acid and its salts are readily oxidized to carbon dioxide with warm acidified permanganate.

Hydrocyanic acid (S. B. 267).—Solutions of cyanides usually smell of hydrocyanic acid, as they are readily decomposed by dilute acids, even by carbonic acid. They show a great tendency to combine with each other, forming complex cyanides (cf. below); thus a cyanide in alkaline solution treated with ferrous sulphate solution and a few drops of ferric chloride yields a precipitate of prussian blue.

With ammonium sulphide solution the cyanides yield thiocyanates (cf. below).

Silver cyanide is precipitated from neutral or acid solutions of cyanides. It is only sparingly soluble in ammonia (cf. chloride), but dissolves readily in potassium cyanide solution and sparingly in concentrated nitric acid.

Hydroferrocyanic acid (S. B. 269).—Ferrocyanides yield with ferric salts the characteristic prussian-blue precipitate, with ferrous salts a light precipitate which soon darkens. The cupric salt is a brownish-red precipitate.

Hydroferricyanic acid (S. B. 269).—Ferricyanides yield no precipitate with ferric chloride, but give a dark-blue precipitate with ferrous salts. The cupric salt is a yellowish-green precipitate, insoluble in dilute hydrochloric acid.

Thiocyanic acid (S. B. 273).—Thiocyanates are distinguished by the blood-red solution of ferric thiocyanate (soluble in ether).

Succinic and **phthalic acids** readily yield anhydrides, and either anhydride when fused with resorcinol yields a fluorescein, which can be recognized by dissolving the melt in sodium hydroxide solution and obtaining a brilliant fluorescent solution (Exp. 260).

Tartaric acid (S. B. 252).—Forms a sparingly soluble potassium bitartrate. The acid chars readily, and is blackened by concentrated sulphuric acid, evolving CO, CO_2, and SO_2. The calcium salt is soluble in acetic acid or sodium hydroxide, but insoluble in water. Solutions of tartrates reduce ammoniacal silver nitrate.

Citric acid (S. B. 262).—Hydrated melting-point 100°, anhydrous melting-point 153°. No blackening with concentrated sulphuric acid. The calcium salt is precipitated when a cold concentrated solution is heated. Citrates also reduce ammoniacal silver nitrate solution at 100°.

COMMON AMINES, THEIR ACETYL AND BENZOYL DERIVATIVES

	Free Base		Acetyl.		Benzoyl	
	M.-pt	B.-pt.	M.-pt.	B.-pt	M.-pt	B. pt
Aniline	—	184°	112°	304°	161°	—
o-Toluidine	—	197	110	296	142	—
p- „	45°	198	153	307	158	—
ψ-Cumidine	68	235	162	—	167	—
Mesidine	—	230	216	—	204	—
m-Nitraniline	114	—	142	—	155	—
p-Bromaniline	66	—	167	—	202	—
Tribromaniline	119	—	232	—	198	—
Methyl aniline	—	192	102–104	—	63	—
Dimethyl „	—	192	—	—	—	—
Ethyl aniline	—	206	54·5	250	60	—
Diethyl „	—	213	—	—	—	—
α-Naphthylamine	50	300	159	—	160	—
β- „	112	294	133	—	157	—
Diphenylamine	54	310	103	—	180	—
Phenyl-hydrazine	—	243	128	—	168	—
Benzylamine	—	183	60	—	105	—
Pyridine	—	115	—	—	—	—
Quinoline	—	239	—	—	—	—
Piperidine	—	106	—	226	48	—

All the amines enumerated above are basic, *i.e.* form salts with mineral acids. The introduction of several nitro- or halogen radicals tends to diminish the basic nature of the amine, and in the case of *s*-tribromaniline this has occurred to such an extent that the amine will form salts with mineral acids only in the absence of water. The salts of diphenylamine are also decomposed by water.

Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$, is a strong base, and although only sparingly soluble in water, the solution has pronounced alkaline properties.

Diamines.—The majority of these are aromatic, and the *o*, *m*, and *p* compounds show distinct reactions. With ferric chloride (10 per cent solution) *o*- and *m*-diamines give red colorations, whereas the *p*-compounds yield an odour of a quinone. The common diamines are:—

	M.-pt.	Diacetyl Derivative. M.-pt.	Dibenzoyl Derivative M.-pt.
o-Phenylene-diamine	102°	185–186°	301°
m- ,, ,,	63°	191°	240°
p- ,, ,,	147°	above 295°	above 300°
2:4-Diamino-toluene	99°	224°	224°
3:4- ,, ,,	88°	210°	263°
Benzidine (p. 308), $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$	122°	317°	sublimes
o-Tolidine, $NH_2 \cdot C_6H_3Me \cdot C_6H_3Me \cdot NH_2$	128°	314° (tetra- 211°)	—

All these compounds yield acetyl and benzoyl derivatives, and form azo-dyes.

The Alkaloids (S. B. 550–557).

General Tests for Alkaloids.—They are characterized as a group by their bitter astringent taste, and by their poisonous properties. The majority are optically active. With the exception of coniine and nicotine they are not readily soluble in water, but dissolve in mineral acids, and may be thrown down from solutions of their salts on the addition of ammonium hydroxide. Precipitates are formed with the following reagents:—

1. A solution of iodine in potassium iodide solution; the precipitates are brown and flocculent.

2. Potassium mercuric iodide; white or yellowish white precipitates.

3. Phosphomolybdic acid; light to brownish-yellow precipitates.

Tests for Specific Alkaloids.

Coniine, $C_8H_{17}N$, boiling-point 167°, sparingly soluble in water; the solution precipitates metallic hydroxides from solutions of their salts like ammonia. Chlorine water gives a copious white precipitate, easily soluble in hydrochloric acid.

Nicotine, $C_{10}H_{14}N_2$, is a colourless lævo-rotatory oily liquid, boiling-point 247°; its aqueous solutions precipitate hydroxides from metallic salt solutions.

By gently warming 1 drop of nicotine with 3 or 4 drops of hydrochloric acid (sp. gr. 1·12) a brownish-red solution is obtained. If after cooling a drop of concentrated nitric acid be added, the solution becomes violet-red, gradually changing to red.

Chlorine water gives only a white turbidity or slight precipitate with an aqueous solution of nicotine, which immediately disappears on the addition of hydrochloric acid.

Morphine, $C_{17}H_{19}O_3N + H_2O$. — Small prisms, sparingly soluble in water.

0·1 grm. of ammonium molybdate dissolved in 1 c.cm. of concentrated sulphuric acid gives a deep violet colour with a trace of morphine, which gradually changes to olive-green, and finally to a deep blue.

1 part of morphine with 6–8 parts of cane sugar and a few drops of concentrated sulphuric acid gives a rose-red to purple-red solution, the intensity of the colour depending on the amount of morphine added.

Quinine, $C_{20}H_{24}O_2N_2 + 3H_2O$, sparingly soluble in water. Melting-point 67°, or anhydrous melting-point 177°. Dilute solutions of its salts exhibit a bluish fluorescence.

The addition of concentrated chlorine water ($\frac{1}{8}$ its volume) to a solution of a quinine salt does not colour the solution, but on adding concentrated ammonia solution to this an intense emerald-green colour is produced.

A quinine salt when dissolved in acetic acid and treated with an alcoholic solution of iodine gives after a short time a black crystalline powder (plates).

Cinchonine, $C_{19}H_{22}ON_2$.—White prisms or needles; almost insoluble in water. The solutions of its salts do not exhibit fluorescence.

Chlorine water gives no reaction, but on addition of ammonia a yellowish-white precipitate is formed.

Strychnine, $C_{21}H_{22}O_2N_2$. — White prisms, melting-point 284°.

A few drops of concentrated sulphuric acid added to a little strychnine in a porcelain dish dissolves it without coloration; addition of a little powdered potassium chromate gives a magnificent blue-violet coloration.

Brucine, $C_{23}H_{26}O_4N_2 + 4H_2O$.—Transparent prisms. The anhydrous base has melting-point 178°.

A solution of a brucine salt mixed with a solution of mercurous nitrate gives a colourless solution, which on gently heating in a water bath gradually gives a beautiful carmine colour. (No coloration is produced by strychnine.)

Chlorine water gives a bright-red solution; addition of ammonia changes this to yellowish-brown.

F. Compounds with Double Functions

A compound may, as has already been pointed out, have the chemical properties characteristic of two distinct groups of compounds, owing to the presence of two different atomic groupings, and the student must be on the lookout for such compounds. A few examples of these types of compounds are:—

1. **Acid** and **Acid Amide.**—Such are the *amic acids* derived from dibasic acids (S. B. 234): Oxamic acid, melting-point 210°; succinamic acid, no definite melting-point; carbamic acid, dec. 60°; phthalamic acid, melting-point 148°.

2. **Acid** and **Amine.**—(*a*) No sulphur present. Aminocarboxylic acids; as a rule, soluble in both dilute acids and dilute alkalis. Examples: Aminoacetic acid (glycine) (S. B. 211); α-aminopropionic acid (alanine), melting-point 255°; aspartic acid or aminosuccinic acid (S. B. 249); *o*-aminobenzoic acid or anthranilic acid, and the isomeric *m* and *p* acids (S. B. 447). Compounds closely related to the above are the corresponding acetyl and benzoyl derivatives; one of the commonest of these is hippuric acid or benzoylglycine (S. B. 445), melting-point 187°.

(*b*) Sulphur present. Aminosulphonic acids—the commonest of these is sulphanilic acid (aniline *p*-sulphonic acid); metanilic acid (aniline-*m*-sulphonic acid); naphthionic acid (1-naphthylamine-4-sulphonic acid); amide, melting-point 206°; R-acid (2-naphthylamine-3:6-disulphonic acid); G-acid (2-naphthylamine-

ALDEHYDES AND KETONES—THEIR PHENYL-HYDRAZONES AND SEMI-CARBAZONES

	Formula	Mt.-pt.	B.-pt.	Phenyl-hydrazone M.-pt.	Semicarbazone. M.-pt.
Aldehydes—					
Formaldehyde	$H \cdot CH:O$	In solution only		146–155°(!)	—
Paraformaldehyde	——	amorphous solid		—	—
Metaformaldehyde	$(H \cdot CHO)_3$	171°	—	—	—
Acetaldehyde	$CH_3 \cdot CH:O$	—	21°	99°	162°
Paraldehyde	$(CH_3 \cdot CHO)_3$	—	124°	—	—
Metaldehyde	$(CH_3 \cdot CHO)$	112° sublimes		—	—
Acrolein	$CH:CH \cdot CH:O$	—	52°	—	—
Crotonaldehyde	$CH_3 \cdot C:CH \cdot CH:O$	—	104°	—	—
Benzaldehyde	$C_6H_5 \cdot CH:O$	—	179°	155°	214° (dec.)
p-Cuminaldehyde	$C_3H_7 \cdot C_6H_4 \cdot CH:O$	—	232°	128°	—
Cinnamaldehyde	$C_6H_5 \cdot CH:CH \cdot CH:O$	—	247°	168°	—
m-Nitrobenzaldehyde	$NO_2 \cdot C_6H_4 \cdot CH:O$	58°	—	120°	246°
Furaldehyde	——	—	162°	97°	—
Ketones—					
Acetone	$(CH_3)_2C:O$	—	56°	42° (anh.)	187° (dec.)
Acetophenone	$C_6H_5 \cdot CO \cdot CH_3$	26·5°	202°	105°	198–200° (dec).
Benzophenone	$(C_6H_5)_2C:O$	48°	—	137°	—
Benzoin	$C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$	134°	—	β 106°, α 155°	—
Deoxybenzoin	$C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_5$	60°	—	116°	—
Benzil	$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$	90°	—	134°(monohy.)	—

6:8-disulphonic acid). Most of these crystallize from water, form soluble alkali salts, and can be diazotised and converted into azo-dyes. As a rule, they have not basic properties, as the acidic sulphonic acid groups more than counterbalance the basic amino-groups. They have no definite melting-points, and can only be further characterized by conversion into derivatives.

(*c*) An interesting example of *ester* and *amine* is ethyl carbamate (urethane) (S. B. 282), which melts at 50°.

3. **Salt** and **Ester.**—The acid esters derived from dibasic acids can form metallic salts, *e.g.* potassium ethyl succinate, $CO_2K \cdot CH_2 \cdot CH_2 \cdot CO_2Et$. Such compounds are recognized by the presence of the metallic radical and by the products of hydrolysis, *e.g.* in the above case ethyl alcohol and succinic acid.

N.B. Similar compounds derived from dibasic mineral acids are also met with, *e.g.* potassium ethyl sulphate, $OK \cdot SO_2 \cdot OEt$, a well-defined crystalline compound. This will give the reactions for the sulphate ion only after hydrolysis.

4. **Acid** (or salt) and **Anilide** (toluidide, &c.), *e.g.* anilic acids derived from dibasic acids. Oxanilic acid (S. B. 381), succinalic acid. On complete hydrolysis, *e.g.* with concentrated hydrochloric acid, they yield the amine (aniline, &c.), and the acid (oxalic, succinic, &c.).

5. **Ketone** and **Acid**, or **Ketone** and Ester.

Examples.	M.-pt. or B pt	Phenyl-hydrazone	Semi-carbazone
Pyruvic acid, $CH_3 \cdot CO \cdot CO_2H$	b. 165–170°	192°	—
Ethyl acetoacetate, $CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$	decomposes	—	129° (dec.)
Levulic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$	m. 33°	—	187° (dec.)
Benzoyl formic acid,* $C_6H_5 \cdot CO \cdot CO_2H$	oil unstable	—	—
Benzoyl acetic acid,† $C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2H$	m. 103°	—	—

* When heated yields carbon monoxide and benzoic acid.

† When heated above melting-point yields carbon dioxide and acetophenone.

6. Phenol and Acid. (S. B. 441.)

	M.-pt	Methyl Ester	Ethyl Ester	Amide M.-pt.	Anilide M.-pt.	Acetyl Derivative. M.-pt.
Salicylic acid	159°	b.-pt. 224°	b.-pt 231°	138°	134°	118°
m-Hydroxy-benzoic acid	200°	—	m.-pt 72°	167°	154°	127°
p- „ „	210°	m.-pt 131°	m.-pt 112°	162°	196°	185°
Gallic (2:3:4 trihydroxy-benzoic) acid	222–240°	192°	m.-pt. 90° or 141° (anhyd.)	243°	207°	151°

7. Phenol and Aldehyde.

	B.-pt	Phenyl-hydrazone M.-pt	Acetyl Derivative M.-pt	Benzoyl Derivative. M.-pt	With $FeCl_3$
Salicylaldehyde or *o*-hydroxy-benzaldehyde	196°	142°	37°	b.-pt above 360°	violet.
Protocatechuic aldehyde, 3:4-dihydroxy-benzaldehyde	150°	—	—	—	green.
Vanillin, 3-methoxy-4-hydroxy-benzaldehyde	m.-pt 80°	105°	77°	75°	blue-violet, and when warmed white precip.

8. **Phenol** and **Alcohol**, or **Phenol** and **Ether**.—Saligenin (*o*-hydroxy-benzyl alcohol), melting-point 82°, gives a deep blue colour with $FeCl_3$. Guaiacol (*o*-hydroxy-anisole), $OH \cdot C_6H_4 \cdot OMe$, boiling-point 220°; has reducing properties, and gives a green coloration with ferric chloride. Eugenol (3-methoxy-4-hydroxyl-cinnamene), $(OH)(OMe) \cdot C_6H_3 \cdot CH : CH_2$, boiling-point 247°, has an odour of cloves, and blue coloration with ferric chloride.

9. **Amine** and **Phenol**.—Examples: *p*-amino-phenol (p. 256), melting-point 184°; *p*-methylamino-phenol, melting-point 87°.

10. **Alcohol** and **Aldehyde**, or **Alcohol** and **Ketone**.—To this category belongs the important group of carbohydrates

Carbohydrates

If the substance is non-volatile and chars when strongly heated, emitting an odour of burnt sugar, it is in all probability a carbohydrate (S. B. 298–319) If soluble in water, yielding a solution with a sweet taste, it will indicate a mono- or di-saccharose, if insoluble in water, a polysaccharose, *e.g.* starch, cellulose.

The following is a general test for soluble carbohydrates:—*Molisch's test.* 2–3 drops of a saturated alcoholic solution of α-naphthol are added to 2 c.cm. of a very dilute aqueous solution of the carbohydrate, and a few c.cm. of concentrated sulphuric acid are poured down the side of the tube, so as to form a separate layer. A deep violet-coloured ring is formed, and this coloration spreads gradually throughout the liquid.*

Monosaccharoses.—The following reactions may be made use of in order to distinguish a *pentose*:—

(*a*) Distil a small amount of the sugar with a mixture of concentrated hydrochloric acid (1 vol.) and water (2 vol.), and test the distillate for furaldehyde (S. B. 515), *e.g.* add a few drops of aniline and hydrochloric acid (concentrated), and observe whether a deep red coloration is produced.

(*b*) A small amount of the sugar solution is warmed with orcinol and sufficient hydrochloric acid (concentrated) to make the final concentration of the acid about 18 per cent. If a pentose is present, a red, then violet, and ultimately a bluish-green coloration is produced. A bluish-green precipitate is

* *Neuberg*, Z. physiol. 1901, 31, 565.

also formed, and this dissolves in amyl alcohol to a blue-green solution.*

Ketoses and **aldoses** may be differentiated by means of the following reactions:—

1. Ketoses (*e.g.* fructose) react with methylphenyl-hydrazine, $C_6H_5N(CH_3)\cdot NH_2$, yielding sparingly soluble *yellow* methylphenyl-osazones. *Preparation*: 0·9 grm. fructose in 5 c.cm. water and 2 grm. of the hydrazine dissolved in alcohol; 50 per cent acetic acid (2 c.cm.) is added, and the whole warmed for five to ten minutes and the osazone allowed to crystallize. Aldoses under similar conditions yield *colourless* methylphenyl hydrazones and not osazones.†

2. Ketoses (1 part) and sugars which yield ketoses, when warmed with resorcinol (0·5 part) and a little water and concentrated hydrochloric acid, give a deep red coloration, and ultimately a brown-red dye, which is soluble in alcohol (*Seliwanoff*).

3. A small amount of the sugar is heated at 60–70° with 10 c.cm. of bromine water, the excess of bromine is removed by boiling, and a little very dilute ferric chloride solution is added If an aldose were originally present a deep yellow coloration due to the presence of a hydroxy-acid is obtained.‡

The specific sugar present can only be decided by determining some of the physical constants The table on p. 362 gives a list of the more important.

As polyhydroxylic compounds, most of the sugars yield acetyl derivatives when heated with acetic anhydride and a little fused zinc chloride (cf. Table, p. 362).

The common **polysaccharoses**, $(C_6H_{10}O_5)_x$, are.—

Starch.—It is soluble in boiling water, and yields with free iodine solution a deep blue coloration, which is destroyed when the solution is boiled. It is hydrolysed to *d*-glucose, or a mixture of *d*-glucose and dextrine, when boiled with dilute hydrochloric acid for some ten minutes, or when digested for some time with malt extract. The solution is then able to reduce Fehling's solution.

Cellulose.—Similar to starch, but is soluble in an ammoniacal solution of cupric sulphate.

Dextrines.—There are a number of these intermediate be

* *Tollens*, A. 1890, **260**, 395.

† *Neuberg*, B. 1902, **35**, 959, 2626.

‡ *Berg*, Bull. 1904 [3], **31**, 1216.

Sugar.	Aldose or Ketose.	M.-pt.	$[\alpha]_D$*	M.-pt. of Osazone.†	Acetyl Derivative.		Reduction of Fehling's Solution.
					Number of Acetyl Groups Present	M.-pt	
Arabinose	A	100°	+ 104 5°	160°	4	liq.	+
Xylose	A	144–145°	+ 18°	160°	4	124°	+
Rhamnose	A	93°	+ 9°	180°	—	—	+
d-Glucose	A	144–146°	+ 52·7°	205°	5	111°	+
d-Galactose	A	163–164°	+ 80·3°	205°	5	142°	+
d-Mannose	A	136°	+ 13°	205°	—	—	+
d-Fructose	K	95°	− 95·5°	205°	5	liq.	+
Sucrose	—	160°	+ 66·5°/20°	—	8	78°	−‡
Maltose + H_2O	A	—	+ 139°	190°	8	158°	+
Lactose + H_2O	A	—	+ 52·5°	200°	8	95–100°	+

* See p. 297. These numbers vary somewhat with temperature and concentration.
† See p. 228. ‡ Reduces after inversion, see p. 313.

tween starch and glucose. They all yield glucose on further hydrolysis, and then reduce Fehling's solution. They are soluble in water, and yield blue, red, or no coloration with iodine.

Glucosides.—Tnese compounds yield glucose together with other products when hydrolysed. The best method is to boil the glucoside with 10 per cent potassium hydroxide solution, or with dilute mineral acid, in a flask fitted with a reflux condenser. The solution may then be tested for glucose and examined for other products of hydrolysis

Some of the commoner glucosides are:—

α-**Methylglucoside**, melting-point 165°; *β*-**methylglucoside**, melting-point 107°, both of which yield glucose and methyl alcohol when hydrolysed.

Amygdalin, $C_{20}H_{22}O_{11}N$.—Melting-point 200°. When hydrolysed with dilute acids it yields *d*-glucose, benzaldehyde, and hydrogen cyanide.

Salicin, $C_{13}H_{18}O_7$.—Melting-point 201°. On hydrolysis it yields *d*-glucose and *o*-hydroxy-benzyl alcohol; with very concentrated potash salicylic acid is formed.

Arbutin, $C_{12}H_{16}O_7$.—Melting-point 157°. When hydrolysed with dilute sulphuric acid it yields glucose and quinol. Its aqueous solution gives a deep blue coloration with ferric chloride.

Myronic acid, $C_{10}H_{17}O_9NS_2$, is hydrolysed to glucose, sulphuric acid, and allyl thiocyanate, allyl mustard oil (S. B. 275).

XXXIX. PREPARATION OF INORGANIC REAGENTS

A. Gases and Solutions of Gases

The most convenient method of obtaining large quantities of the commoner gases is from the compressed gases which are sent out in steel cylinders similar to those used for oxygen. The following gases can be obtained in this form:—Ammonia, carbon dioxide, chlorine, hydrogen, oxygen, nitrous oxide, sulphur dioxide (in glass syphons).

If the compressed gases are not available, the following methods may be adopted:—

1. **Ammonia.**—This is most readily obtained by gently warming concentrated ammonium hydroxide (0·880), and passing the gas through a drying tower containing quicklime.

2. **Carbon dioxide.**—From marble and hydrochloric acid (sp. gr. 1·08), obtained by mixing equal volumes of concentrated acid and water, in a Kipp's generator or other common form of apparatus for generating gases.

3. **Chlorine.**—(*a*) By the action of concentrated hydrochloric acid on lumps of pyrolusite (MnO_2). The pyrolusite is just covered with the acid in a flask fitted with delivery tube and safety funnel, and when very gently warmed over asbestos gauze a regular stream of the gas is obtained, and is purified by passing through two wash bottles, one containing water and the other concentrated sulphuric acid.

(*b*) A regular stream of chlorine can also be obtained by the action of concentrated hydrochloric acid on potassium permanganate or dichromate crystals, 5 parts by weight of acid to 1 of crystals. The mixture requires to be very gently heated, *e.g.* on a water bath.

4. **Hydrogen chloride.**—This is most easily prepared in a Kipp's apparatus by the action of concentrated sulphuric acid on lumps of fused ammonium chloride.

5. **Hydrogen bromide solution (hydrobromic acid).**—(*a*) Such a solution is obtained during processes of bromination (see Exp. 38), and can be purified by distillation. Water passes over first, and the temperature rises gradually to 126°, when a solution of hydrobromic acid of constant boiling-point distils over, and is collected. It has D 1·47, and contains 47·8 per cent hydrogen bromide.

(*b*) A convenient method of preparation is as follows*:—Sulphur dioxide is led into a mixture of 35 c.cm. of bromine and 200 c.cm. of water, the end of the delivery tube being about 1 cm. above the surface of the bromine.

$$SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4.$$

The sulphur dioxide is passed in until the whole is transformed into a pale yellow homogeneous liquid, which is then distilled. The sulphuric acid remains in the flask, and the distillate, which may contain traces of sulphuric acid, is redistilled over barium bromide.

(*c*) See p. 369.

* *Scott*, J. C. S. 1900, **77**, 648.

6. **Hydrogen iodide solution (hydriodic acid).**

$$P + 3I + 3H_2O \rightarrow P(OH)_3 + 3HI.$$

11 parts by weight of crystalline iodine are introduced into a small round-bottom flask, and 1 part of yellow phosphorus is cut into small pieces under water, and after drying with filter paper (care) added gradually to the iodine. The addition of each piece produces a flash of light, and the contents of the flask become liquid. When all the phosphorus has been added the flask is allowed to cool, and 1·5 parts by weight of water are added to the solid phosphorus tri-iodide. If the flask is heated with a very small flame hydrogen iodide is evolved, and is purified by passing through a U tube filled with pieces of glass coated with red phosphorus and a *little* water. The heating can be continued until the contents of the flask are colourless.* If a solution is required the gas is led by means of a very wide delivery tube (as in fig 77) or an inverted funnel into cold water. As the gas is very soluble only a relatively small amount of water should be taken. In this way solutions of varying degrees of concentration may be obtained, even solutions saturated at 0° or −10°. Dilute solution may be concentrated by distillation. At 127° a solution of constant boiling-point passes over which contains 57 per cent HI, and has D 1·70.

7. **Nitrous anhydride.**—A mixture of NO and NO_2, which reacts as if it were N_2O_3, is obtained when *lumps* of arsenious oxide (As_4O_6) are warmed very gently with concentrated nitric acid. To remove nitric acid and moisture the gas is passed through an empty flask.

B. Solids

1. **Aluminium chloride,** $AlCl_3$.—Strips of aluminium foil or aluminium turnings, which have been freed from oil by boiling with alcohol and dried, are placed in a wide combustion tube open at both ends. The tube is placed in a furnace, and one end is attached to an apparatus for generating dry hydrogen chloride (cf. this chap., A. 4), whilst the other just passes through a cork which closes the mouth of a wide-necked bottle or flask. The cork also carries a bent delivery tube which

* If the heating is continued too long phosphine and phosphonium iodide are formed and an explosion may occur.

leads the hydrogen into the air. As soon as the air in the apparatus has been displaced by hydrogen chloride,* the burners are turned on gradually until the whole length of the tube is at a dull red heat. A rapid stream of hydrogen chloride is passed through, and the heating is continued until practically all the aluminium has disappeared. The aluminium chloride is volatilized and carried over into the glass bottle or flask, and is subsequently removed and stored in a dry bottle in a desiccator. If kept in an ordinary stoppered bottle the chloride is attacked by atmospheric moisture, and becomes covered with a layer of basic chloride or of oxide, and is then of very little use for the Friedel-Crafts' synthesis.

2. **Aluminium-mercury couple** (see Exp. 38).

3. **Chromic anhydride**, CrO_3.—One volume of a cold saturated aqueous solution of potassium chromate (K_2CrO_4) is added gradually, and with constant stirring, to 1·5 volumes of concentrated sulphuric acid. The mixture is allowed to cool, when crystals of the anhydride separate. The liquid is decanted, and the crystals washed with a little nitric acid and dried on porous plate in a desiccator. The oxide forms brilliant scarlet crystals, and is hygroscopic.

4. **Chromyl chloride**, CrO_2Cl_2.—(*a*) A mixture of sodium chloride, potassium dichromate, and fuming sulphuric acid, in the proportions required by the equation

$$K_2Cr_2O_7 + 4NaCl + 3H_2S_2O_7 \longrightarrow 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4,$$

is heated in a retort attached to a condenser and receiver, and the heating continued until coloured liquid no longer distils over. The product is purified by distillation.

(*b*)† Chromic anhydride is dissolved in rather more than the theoretical amount of concentrated hydrochloric acid, and to this solution concentrated sulphuric is added gradually, the mixture being cooled between the additions. After standing for about twenty minutes the heavy layer of chromyl chloride is removed by means of a tap funnel, and is purified by aspirating air through it and subsequent distillation. Yield practically theoretical.

* If the air is not displaced the hydrogen formed during the reaction will form an explosive mixture with the air, and a serious explosion will occur.

† *Law* and *Perkin*, P. 1907, **23**, 11.

5. **Cuprous chloride** (see Exp. 158), **Cuprous bromide** (p. 202), **Cuprous cyanide** (Exp. 160).

Cuprous iodide, CuI.

$$CuSO_4 + 2KI \rightarrow CuI + I + K_2SO_4.$$

Equivalent amounts of crystallized cupric sulphate and of potassium iodide are dissolved in small amounts of water, and the cold solutions mixed. After a short time the precipitate is removed with the aid of the pump, washed with water and then with alcohol until free from iodine, and finally dried in a steam oven.

6. **Fehling's solution** (Exp. 290).

7. **Lead peroxide**, PbO_2.—A filtered solution of bleaching powder (2 parts) in water (30 parts) is added gradually to a practically boiling solution of lead acetate crystals (1 part) in water (4–5 parts). The addition is continued until the precipitate turns dark brown, and until a small test portion of the clear liquid no longer forms a precipitate with the bleaching powder solution. The precipitate is allowed to settle and the liquid decanted; it is then washed several times with water, filtered with the aid of the pump, and preserved in the form of a paste.

Determination of the percentage of peroxide in the preparation.

(*a*) A given weight of the peroxide is distilled with concentrated hydrochloric acid, the liberated chlorine is collected in potassium iodide solution, and the free iodine titrated by means of 0·1 N sodium thiosulphate.

(*b*) About 5 grm of the paste is mixed with a solution of potassium iodide (12 grm.), sodium acetate (90–100 grm.), and 50 per cent acetic acid (50 c.cm.) The clear solution is diluted to 250 c.cm. with distilled water, and 25 c.cm. titrated with 0·1 N thiosulphate.

$$PbO_2 + 4HI \rightarrow PbI_2 + 2H_2O + I_2.$$

8. **Phosphorus pentasulphide**, P_2S_5.—The theoretical quantities of sulphur and red phosphorus are mixed in a retort from which the air has been displaced by carbon dioxide, and heated until half the material has distilled over. The distillate consists of phosphorus, sulphur and volatile sulphides of phosphorus, and the residue is the pentasulphide, which is removed from the retort and broken up.

9. **Sodium amalgam.**—This alloy is prepared by gently warming dry mercury, placing in a mortar, and adding the theoretical amount of sodium required to form a 2½ or 4 per cent amalgam. The operation should be conducted in a fume cupboard, and the hand protected by a glove or duster. The sodium is added in small pieces, and produces a vigorous action. It is an advantage to introduce the sodium on the end of a glass rod drawn out to a point, and to press it on the bottom of the mortar if amalgamation does not take place immediately. When prepared it must be protected from atmospheric moisture and carbon dioxide

10. **Sodium wire.**—A piece of thoroughly clean sodium is placed in the cavity *b* of the sodium press (fig. 92), and by turning the handle (*ee*) is forced through a small opening, and forms a continuous wire which is caught by the vessel placed beneath. After use the press must be thoroughly cleaned and oiled. No trace of alkali must be left.

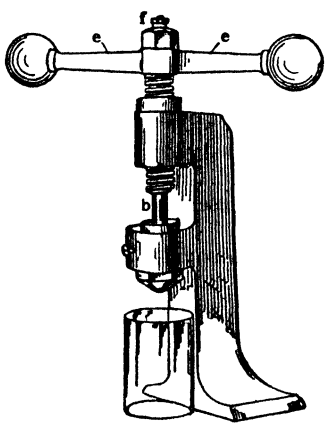


Fig. 92

11. **Sodium Ethoxide** (free from alcohol).*—Sodium dust is prepared by heating metallic sodium with dry xylene in a round-bottomed flask until the hydrocarbon boils vigorously. The flask is then closed with a cork, wrapped in a duster, and vigorously shaken. As much as 50 grm. of sodium may be used in one operation, and after a very few minutes the metal is obtained in the form of a fine powder.

The mixture of xylene and finely divided sodium is diluted with more dry xylene until there is 250 c.cm. of liquid for each 23 grm. of sodium. The flask is then fitted with a cork provided with a stirring arrangement (cf. fig. 89), and also with a reflux condenser, the upper end of which is closed by a cork carrying a dropping funnel and soda-lime tube. The flask is placed in cold water, and the stirrer worked vigorously whilst the theoretical amount (1 mol. for each atom of Na) of

* *Brühl*, B. 1902, 35, 3516; 1904, 37, 2066.

alcohol, mixed with twice its volume of xylene, is added from the dropping funnel. After several hours all the sodium is used up (warm for a few minutes if necessary), and snow-white sodium ethoxide, C_2H_5ONa, is obtained. The xylene can be removed if necessary by rapid filtration with the aid of the pump.

12. **Zinc dust**, evaluation of. The value of zinc dust as a reducing agent depends to a large extent upon the percentage of metallic zinc present. This is most readily determined by measuring the volume of hydrogen evolved when a known weight of the dust is dissolved in dilute acid. The apparatus shown in fig. 80 may be used.

13. **Zinc-copper couple** See Exp. 16. This may be replaced with advantage by the aluminium-mercury couple (Exp. 38).

ADDENDUM

(*c*) Dry hydrogen is bubbled through a bottle containing bromine, and the resulting mixture passed through a hard glass tube containing heated platinized quartz. The issuing gas is passed through a U tube containing moist red phosphorus, and then dissolved in water. A saturated solution may readily be obtained in this manner.*

* *Claisen* and *Eisleb*, A 1913, 401, 28.

APPENDIX

TABLE I.—PRESSURE OR TENSION OF AQUEOUS VAPOUR AT DIFFERENT TEMPERATURES

t° C.		P. in mm	t° C		P in mm
0	.....	4 6	16	.....	13·5
2	.....	5 3	18	.....	15·4
4	.....	6·1	20	.....	17·4
6	.....	7·0	22	.....	19 7
8	.....	8·0	24	.....	22 2
10	.....	9·2	26	.....	25 0
12	.....	10·5	28	.....	28·1
14	.....	11·9	30	.....	31 6

TABLE II.—VAPOUR PRESSURES OF CONCENTRATED POTASSIUM HYDROXIDE SOLUTIONS AT DIFFERENT TEMPERATURES

t° C		40 grm KOH, 100 grm water P in mm		49 grm. KOH, 100 grm water. P in mm
10	.....	6 5	.....	5 6
12	.....	7 5	.....	6·5
14	.....	8·4	.....	7·3
16	.....	9 6	.....	8·3
18	.....	10 9	.....	9·5
20	.....	12 4	.....	10·8
22	.....	13 9	.....	12·1

TABLE III.—TABLE FOR DETERMINING THE PERCENTAGE OF FREE SULPHUR TRIOXIDE IN A FUMING SULPHURIC ACID FROM ITS SPECIFIC GRAVITY AT 20°

Sp. gr.		Per cent Free SO_3.	Sp. gr.		Per cent Free SO_3.
1·840	.....	8·39	1·890	.....	31·67
1·845	.....	16·08	1·895	.....	32·52
1·850	.....	19·04	1·900	.....	33·09
1·855	.....	22·85	1·910	.....	34·10
1·860	.....	26·45	1·920	.....	37·27
1·865	.....	27·57	1·930	.....	41·56
1·870	.....	28·76	1·940	.....	46·46
1·875	.....	29·95	1·950	.....	49·01
1·880	.....	30·38	1·960	.....	52·29
1·885	.....	31·08	1·970	.....	58·81

TABLE IV.—TABLE FOR THE PREPARATION OF A FUMING SULPHURIC ACID OF ANY GIVEN CONCENTRATION *

If a concentrated sulphuric acid and a fuming sulphuric acid of given strength are provided, it is possible by mixing these in suitable proportions to obtain a fuming acid of lower concentration. The simplest method is by means of the formula $x = 100\frac{b-a}{a-c}$, where x = the number of grams of the concentrated acid which must be mixed with 100 grm. of the fuming acid to produce the more dilute fuming acid of required strength. a = the total per cent of SO_3 in the acid required, b the total per cent of SO_3 in the original fuming acid, and c the per cent of SO_3 in the concentrated acid. The values for a, b, c can be obtained from the following tables:—

Fuming Sulphuric Acid			Concentrated Sulphuric Acid.		
Per cent Free SO_3		Total per cent SO_3	Per cent H_2SO_4		Per cent SO_3
0	.....	81·6	90·0	.....	73·4
2	.....	82·0	90·4	.....	73·8
4	.....	82·4	90·8	.....	74·2
6	.....	82·7	91·0	.....	74·3
8	.....	83·1	91·4	.....	74·7
10	.....	83·4	91·8	.....	75·0
12	.....	83·8	92·0	.....	75·1
14	.....	84·2	92·4	.....	75·4
16	.....	84·5	92·8	.....	75·8
18	.....	84·9	93·0	.....	76·0
20	.....	85·3	93·4	.....	76·3
22	.....	85·7	93·8	.....	76·5
24	.....	86·0	94·0	.....	76·6
26	.....	86·4	94·4	.....	77·0
28	.....	86·8	94·8	.....	77·4
30	.....	87·1	95·0	.....	77·5
32	.....	87·5	95·4	.....	77·9
34	.....	87·9	95·8	.....	78·2
36	.....	88·2	96·0	.....	78·3
38	.....	88·6	96·4	.....	78·7
40	.....	89·0	96·8	.....	79·0
42	.....	89·3	97·0	.....	79·2
44	.....	89·7	97·4	.....	79·5
46	.....	90·1	97·8	.....	79·8

* *Gerster*, C. Z. 1887 3; L. C. Spezieller Teil, 1291.

Fuming Sulphuric Acid.			Concentrated Sulphuric Acid		
Per cent Free SO_3		Total per cent SO_3	Per cent H_2SO_4.		Per cent SO_3
48	.....	90·4	98·0	.....	80·0
50	.....	90·8	98·4	.....	80·3
52	.....	91·2	98·8	.....	80·6
54	.....	91·5	99·0	.....	80·8
56	.....	91·9	99·4	.....	81·1
58	.....	92·3	99·8	.....	81·4
60	.....	92·6	100	.....	81·6

If a concentrated acid of 98 2 per cent H_2SO_4, and a fuming acid containing 25·6 per cent SO_3 are provided, and an acid containing 19 per cent SO_3 is required,

$$a = 85{\cdot}1,\ b = 86{\cdot}3,\ c = 80{\cdot}1.$$

$$\text{Then } x = 100\,\frac{86{\cdot}3 - 85{\cdot}1}{85{\cdot}1 - 80{\cdot}1} = 24.$$

So 24 grm. of the concentrated acid must be mixed with 100 grm. of the given fuming acid to yield the fuming acid of required strength.

ADDENDA

Page 55. **Modifications of Dennstedt's Method.**—*Walker* and *Blackadder** recommend a furnace 60 cm. long, and the use of copper oxide in place of the platinum or platinized quartz. Some 30 grm. of granular oxide are used, and this must be carefully dehydrated before use. Part is placed in the combustion tube, and the remainder mixed with a given weight of the substance in a stoppered tube and then transferred to the combustion tube; the stoppered tube being washed out two or three times with dry oxide of copper. Otherwise the method is similar to Dennstedt's, and the time occupied between attaching and removing the absorption tubes need not exceed half an hour.

Marek† uses a similar method. He introduces an oxidized copper coil (5 cm. long) into the tube. The coil is some 2 mm. less in diameter than the tube and is surrounded with asbestos, so that it fits tightly into the tube. The substance is weighed in a porcelain boat, and this is placed in a hard glass tube closed at one end. The open end of this tube is about 4–10 cm. from the copper oxide coil.

Page 258. Chap. XXVI.

F. Catalytic Reduction

Many unsaturated compounds may readily be reduced directly by means of hydrogen under the influence of certain finely divided metals.

Experiment 226*a*.—Reduction of allyl alcohol to propyl alcohol.‡

Pass the vapour of allyl alcohol mixed with excess of hydrogen over finely divided nickel (prepared by reduction of the oxide by means of hydrogen) heated gently (130°–170°) in a hard glass tube. Pass the product through a water condenser and purify by fractional distillation. Boiling-point of propyl alcohol 97·4°.

A further example is afforded by the reduction of phenyl propiolic acid to *allo*cinnamic acid by shaking a solution of the sodium salt of the former, containing colloidal palladium, with the calculated volume of hydrogen.§

* C. N., 1909, **99**, 4.
† J. pr., 1906, **73**, 359.
‡ *Sabatier*, C. R. 1907, **144**, 879.
§ *Paal* and *Hartmann*, B. 1909, **42**, 3930.

Page 311. **Fehling's Solution.**—The following substitute for Fehling's solution has been recommended*: Dissolve 200 grm. of crystallized sodium carbonate, 200 grm. sodium citrate, and 125 grm. potassium thiocyanate in about 800 c.cm. of hot water, and filter. Dissolve exactly 18 grm. pure crystallized copper sulphate in 100 c.cm. of water, add the copper solution to the citrate mixture with constant stirring, add 5 c.cm. of a 5 per cent aqueous solution of potassium ferrocyanide and make up to a litre with water. 25 c.cm. of this reagent is brought into a porcelain dish, 10–20 grm. of crystallized sodium carbonate and a little pumice are added, the whole heated to boiling and then titrated with the sugar solution until the blue colour is completely destroyed. 25 c.cm. of the solution are equivalent to 0·05 grm. of glucose or 0·053 grm. of fructose.

The ferrocyanide prevents the precipitation of cuprous oxide, and the end point is much sharper than with ordinary Fehling's solution.

* *S. R. Benedict*, J. Biol. Chem. 1911, **9**, 57.

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