LABORATORY METHODS
OF
ORGANIC CHEMISTRY

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LABORATORY METHODS
OF
ORGANIC CHEMISTRY

BY
L. GATTERMANN

COMPLETELY REVISED BY
HEINRICH WIELAND

TRANSLATED FROM
THE TWENTY-SECOND GERMAN EDITION
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WITH 55 ILLUSTRATIONS IN THE TEXT

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PREFACE TO THE FIRST EDITION

THIS book was primarily written in order to satisfy the author's private requirements. When a large class starts practical work in organic chemistry it is, with the best will in the world, often impossible to teach each individual the manipulative details which abound in this work. In order that the student may have some help even in the absence of his teacher when carrying out general operations, the special instructions for the preparations are preceded by a general section on crystallisation, distillation, drying, analyses, etc. In writing this section less attention has been given to the complete enumeration of the numerous modifications of individual operations than to an attempt to describe the most important operations in such a way that the beginner can carry them out independently in the absence of the demonstrator.

In the second, special part each separate preparation is followed by general considerations which concern the nature and the significance of the reactions involved and aim at imparting to the student, already during his practical work, the widest possible range of theoretical knowledge. As is well known, the knowledge acquired under these conditions is more firmly fixed than when it is exclusively derived from a purely theoretical book. Thus the author hopes that, along with the excellent manuals of E. Fischer and Levy, his book also may meet with some acceptance. He will always be grateful to colleagues who point out defects.

L. GATTERMANN

HEIDELBERG, *August* 1894.

PREFACE TO THE REVISED (NINETEENTH) EDITION

It is rather more than thirty years ago since Ludwig Gattermann published the first edition of his *Anleitung für das organisch-chemische Praktikum*. The plan of providing the preparative directions with theoretical explanations has certainly proved satisfactory. That is already shown by the wide circulation of the book, of which eighteen editions have appeared. Methodology and technique are undoubtedly the chief objects of the practical course, but aiming merely at culinary art and technical achievement such a course does not accomplish enough. A command of methods implies above all an understanding of their rationale and a power of adapting their numerous modifications to particular requirements; the architect is more important than the mason. We demand that the student should be conversant with the theory of the transformations which he carries out practically. The comments made on the individual preparations are intended to facilitate a survey of the subject in hand, and to encourage the use of text-books and journals by further reading. Now that a knowledge of the principles of organic chemistry may be assumed during the preparative work in German universities, the danger of such comments becoming a *pons asinorum* is remote.

In rewriting the book the theoretical and practical requirements have been deliberately increased. The equipment which sufficed during the last three decades has now become insufficient for those who desire to work at present-day problems, where difficulties have been accentuated alike in pure science and in technology.

The idea of making the preparative work at once an explanation and a living experience of the science has demanded a rearrangement

of the subject matter in accordance with systematic relationships. It will be seen that the new arrangement does not depart seriously from the path which ascends from the more simple to the more difficult. In any case a considerable educational advantage may be expected to result from the rounding off of successive subjects.

The general part as well as the analytical have been completely revised and greatly shortened in order to make more space for the preparative part. The increase in the number of preparations is intended to provide variety, and to counteract a tendency towards stereotyped routine in the organic practical course.

I am greatly indebted to my assistants, especially to Drs. Franz Bergel and F. Gottwalt Fischer, for untiring co-operation in carrying out numerous experiments. Dr. Fischer has, moreover, drawn the new diagrams for this edition and has prepared the index.

HEINRICH WIELAND

FREIBURG I. B., *Easter* 1925.

PREFACE TO THE TWENTY-SECOND EDITION

THE new edition, which has become necessary after two years, shows greater changes than do the two preceding ones. In the course of laboratory instruction new experience is constantly being gained, which leads to improvements in the directions and the explanations. On this occasion an opportunity occurred to make such changes in many parts of the book. The theoretical discussions have been made more complete by taking account of important new researches (*e.g.* Diels' diene synthesis, polyenes, haemin).

With a view to stimulating the interest of the student in biochemistry, the most important branch of the subject, two enzymic processes have been included. The saccharification of potato-starch is carried out, with reference to the quantitative aspects, and the mash is subsequently fermented. In addition, the preparation of invertase from yeast and the polarimetric observation of the inversion of cane sugar are described.

Alkaloids have, so far, not been represented. Now nicotine has been admitted because the starting material is readily obtainable everywhere.

It seems desirable to point out here that the preparations given in this book are intended to provide a selection, and that the inclusion of all of them in the course is by no means contemplated. In the Munich laboratory a suitable selection is made by the assistants, and, according to his capacity, the student carries out fifty to sixty preparations to which are added six to eight preparations from the original literature. The organic elementary analysis can be conveniently completed in one to two weeks, so that the practical work of the chemistry student in the organic laboratory requires less than

one academic year. In our opinion a further limitation would be fatal to chemical education in our universities.

We also consider it unadvisable to reduce the requirements for those students who intend later to graduate in inorganic or physical chemistry; rather do we think that the thorough study of the varied methods peculiar to preparative organic chemistry provides a basis of experimental skill which should not be withheld from those who have aptitude for the other divisions of the subject. I have to thank sincerely Prof. G. Fischer, Freiburg, and Dr. A. Bertho, Munich, for their active co-operation. My thanks are also due to several other colleagues for many hints.

HEINRICH WIELAND

MUNICH, *July* 1930.

NOTE ON THE TRANSLATION

THE present translation has been prepared by Dr. McCartney while working in a German laboratory. I have read both the manuscript and the proofs. Although here and there the text may still savour of the German, I am confident that it is substantially free from error, and trust that it avoids obscurity. Colleagues and students who point out defects will earn my gratitude. The labour expended on the translation will be fully repaid if it enables English-speaking students to attain the standard of practical work demanded in the Munich laboratory.

G. BARGER

EDINBURGH, *April* 1932.

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ABBREVIATIONS

The abbreviations of the titles of journals are those employed in *British Chemical Abstracts*. The abbreviated title is followed by the year, volume number (in heavy type), and page.

Annalen	= Justus Liebig's Annalen der Chemie.
Ann. Chim.	= Annales de Chimie [et de Physique].
Ber.	= Berichte der Deutschen Chemischen Gesellschaft.
Bull. Soc. chim.	= Bulletin de la Société chimique de France.
Chem. Zentr.	= Chemisches Zentralblatt.
Helv. Chim. Acta	= Helvetica Chimica Acta.
J. Amer. Chem. Soc.	= Journal of the American Chemical Society.
J.C.S.	= Journal of the Chemical Society.
J. pr. Chem.	= Journal für praktische Chemie.
Monatsh.	= Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Rec. trav. chim.	= Recueil des travaux chimiques des Pays-Bas.
Z. angew. Chem.	= Zeitschrift für angewandte Chemie.
Z. physiol. Chem.	= Hoppe Seyler's Zeitschrift für physiologische Chemie.

A. SOME GENERAL LABORATORY RULES

Reaction Velocity and Temperature.—Reactions with organic substances take place much more slowly than those which form the subject matter of a course of practical inorganic and analytical chemistry. The latter are nearly always *ionic reactions*, which proceed with immeasurable rapidity, but organic substances usually react much more slowly and therefore their preparation requires to be accelerated by increased temperature. A rise in the temperature of 10° doubles or trebles the velocity of most reactions. If the velocity at 20° is represented by v, then on the average that at 80° is $v \times 2{\cdot}5^6$. Consequently reactions will proceed in boiling alcohol about 250 times as fast as at room temperature.

For this reason many reactions of organic substances are brought about in heated solvents, usually at the boiling point.

The vapour of the solvent is cooled in a condenser fixed on the reaction vessel in such a way that the evaporated solvent continuously flows back again. Tap water is passed through the condenser.

In order to concentrate a solution the solvent is distilled "through a downward condenser". For this purpose various forms of coil condenser are more convenient than the Liebig pattern. For working "under reflux" such coil condensers are less suitable because of the layers of liquid which form in the coil between the vapour and the external atmosphere. A condenser designed by Dimroth has proved suitable for both types of work. In it the cooling water passes through the coil (Fig. 1). In order to prevent condensation of water vapour on the coil it is advisable to fix a calcium chloride tube into the upper opening of the condenser.

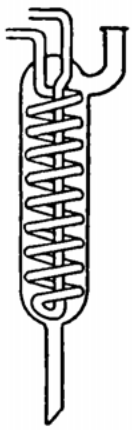

FIG. 1.

If a solvent which boils above 100° is used, the water-cooled condenser can be replaced by a long, wide glass tube (air condenser).

The condenser is attached to the reaction vessel by means of a tightly fitting *cork*, which is softened in a cork-squeezer before being bored. The diameter of the cork-borer chosen should be less than that of the glass tube for which the hole is made. The borer is heated in the flame of a Bunsen burner and is driven in a strictly vertical position through the cork, which stands on the bench with the narrow end upwards. As far as is practicable, collodion should not be used for making stoppers gas-tight. In general, rubber stoppers should not be used in experiments in which they are exposed to the vapours of boiling organic solvents, since they swell greatly and also give off soluble constituents which contaminate the reaction solution.

External Cooling.—Many reactions which occur with great evolution of heat require to be moderated. Further, in the preparation of labile substances which might be damaged by a high temperature, it is often necessary to provide for the cooling of the reaction mixture. The degree of cooling varies and, depending on the amount of heat to be removed and on the reaction temperature necessary, is produced by running tap water (8°–12°), by ice, which is finely crushed and mixed with a little water, by an ice and salt mixture (0° to −20°), or by a mixture of solid carbon dioxide with ether or acetone (down to −80°). Liquid air is generally not required in preparative organic work. To prepare freezing mixtures such as are often required, ice, well crushed in an ice mill or metal mortar, is thoroughly mixed by means of a small wooden shovel with about one third of its weight of rock-salt, preferably in a low, flat-bottomed glass jar or in a low enamelled saucepan.

In order to keep a freezing mixture cold for hours (or even over night) it is transferred to a " thermos " flask in which the contents of test tubes pushed into the freezing mixture can be maintained at low temperatures for a long time. For keeping larger vessels cold in this way, Piccard has indicated an arrangement easily constructed from two filter jars placed one inside the other. The bottom of the outer vessel is covered with kieselguhr until the rim of the centrally placed smaller jar is level with that of the outer jar. Then the annular space between the jars is likewise packed with pressed down

kieselguhr and its upper portion between the rims is tightly closed with pitch.

Too little attention is generally paid to the *concentrations* of the reactants in preparative organic work. With the exception of rare cases (*e.g.* in intramolecular rearrangements) we are concerned with reactions of orders higher than the first, and in these several kinds of molecules—usually two—are involved. Since, according to the kinetic molecular theory, the velocity of bimolecular reactions is proportional to the number of collisions between the various dissolved molecules and therefore to the product of the concentrations,

$$v = C_A.C_B.K \text{ (K = velocity constant)},$$

it is advisable in all cases where there is no special reason to the contrary to choose the highest possible concentration for a reacting solution.

It should always be borne in mind that reduction of the concentration to one-half, one-quarter, or one-tenth makes the reaction four, sixteen, or one hundred times as slow.

Purification of Organic Substances

The substances which form the object of preparative work are usually solid crystalline materials or liquids—occasionally also gases. Because of the multiplicity of reactions in which organic substances can take part, and in pronounced contrast to most reactions of inorganic chemistry, it is rare for an organic reaction to proceed strictly in *one* direction only and to yield a *single* end-product. Almost always secondary reactions occur and greatly complicate the isolation of pure homogeneous substances from a reaction mixture ; this isolation constitutes the chief aim of preparative exercises. Sometimes several well-defined chemical compounds are produced at the same time and must be separated; sometimes it is a question of separating the required substance with as little loss as possible from undesirable products which accompany it—the so-called resins or tars. These terms are used for by-products the origin and nature of which have usually not been investigated ; sometimes they unfortunately become the main product. As regards classical organic chemistry, they have awakened interest only in so far as they are regarded as an unmitigated nuisance.

The substances to be prepared must be freed very carefully from

all these undesirable admixtures. For this purpose two methods are in principle available:

1. **Crystallisation**
2. **Distillation**

1. Crystallisation

General Considerations.—Solid crystallisable substances are usually obtained at the end of a reaction in the form of a crude product which separates in more or less pure form from the solvent on cooling, either directly or after concentration. The rate at which organic substances crystallise varies within very wide limits, and their tendency to form supersaturated solutions is extraordinarily great. But even when supersaturation is counteracted by dropping a crystal into the solution—by "seeding"—the attainment of equilibrium in the cold saturated solution is often exceedingly slow. The cause is indeed the slow rate of crystallisation. Hence the full yield of crude product is often obtained only after the solution has been left for many hours.

The process of recrystallisation is most simply (and most frequently) carried out as follows: A hot saturated solution of the crude product in a suitable solvent is prepared, and from this solution the substance crystallises again in a purer condition. If the procedure is to succeed it is essential that the impurities should be more soluble than the substance itself, and should consequently remain dissolved in the cooled solution (*the mother liquor*).

The principle of differential solubility is also applied conversely, namely, when the by-product can be separated from the just-saturated solution of the substance because of its low solubility in an appropriate solvent. Since, in this case, the solution always remains saturated with respect to the by-product, it is never possible by this method to obtain a substance in *one* operation, as may be possible by the first method.

It is also important for recrystallisation from hot saturated solution that the temperature-solubility curve should rise as steeply as possible, *i.e.* that the dissolving power of the solvent should increase greatly with increasing temperature. In that case only can the amount of substance taken be recovered from the solution in the highest possible yield.

The choice of the right solvent is therefore of great importance

for the process of recrystallisation. The most commonly used solvents are the following: *water, ethyl alcohol, methyl alcohol, ether, acetone, glacial acetic acid, ethyl acetate, benzene, petrol ether, chloroform, carbon bisulphide.*

For quite sparingly soluble substances, formic acid, pyridine, bromobenzene, nitrobenzene, and occasionally also phenol, ethyl benzoate, aniline, and dioxan are used. A distinct relation exists between the constitution of solute and solvent, and is expressed by the old rule: *similia similibus solvuntur.* Thus, as is well known, substances containing hydroxyl (*e.g.* sugars, carboxylic acids) are soluble in water, whereas hydrocarbons are more soluble in benzene and petrol ether than, for example, in alcohols.

The above statements, however, generally hold with some degree of certainty for simple organic compounds only. With complicated substances the conditions are more involved, and unless the worker has long experience he is obliged to test the available solvents *seriatim.* Alcohol is used most, and with this one usually begins; then perhaps water, benzene, and petrol ether. It may be said that, on the whole, of the more usual solvents, benzene, chloroform, and ether have a very great, petrol ether and water a moderate solvent power for organic substances. Although the validity of this rule is contravened by many substances, it nevertheless gives some indication for testing purposes. Thus if the sample is too sparingly soluble in alcohol a solvent from the first group is chosen; if it is too soluble, one from the second. In the case of sparingly soluble substances a higher boiling homologue of the same class is often chosen —in place of the lower alcohol, propyl or amyl alcohol, instead of benzene, toluene or xylene—because the higher boiling point brings about increased solvent power.

It very often happens that the preparation of a substance leads to an *amorphous* crude product, resinous or flocculent, which becomes crystalline on digestion with a suitable solvent or else by direct recrystallisation. It must be remembered that the solubilities of the amorphous and crystalline forms of the same substance are altogether different, and that the amorphous preparation is always much the more soluble.

Salts dissolve quite generally with ease in water, and often also in the alcohols, acetone, and chloroform, but they are not dissolved by ether, benzene, or petrol ether. Consequently organic acids can be extracted by aqueous solutions of alkali, and organic bases by

aqueous solutions of acid, from a mixture of neutral substances in a solvent like ether.

When a substance has not the necessary moderate solubility in any solvent but is either too readily or too sparingly soluble, the combination of different solvents is a useful expedient. The solvents which are used together must be miscible with each other. The following are most frequently used :

Alcohol, glacial acetic acid, acetone with water.

Ether, acetone, benzene, chloroform with petrol ether.

Pyridine with water, ether, or alcohol.

The method of procedure is to add the solvent used as diluent drop by drop to the cold or hot concentrated solution until turbidity is just produced ; crystallisation is then induced by leaving the liquid to stand or by scratching with a sharp-edged glass rod. When crystallisation has begun the solution is cautiously diluted further. It is a mistake to precipitate the dissolved substance at one stroke with large amounts of the diluent.

In the case of all operations which are not yet under control, preliminary test tube experiments should be carried out. The student should acquire the habit of doing this from the very beginning.

Aqueous filtrates should be collected in beakers, but organic solvents in conical flasks, which prevent evaporation and so check the formation of crusts. Already in order to obtain some idea of the degree of purity from the appearance of the crystals, the crystallisation should be left to go on undisturbed so that crystals may separate in the best possible form. It is an error to assume that fine crystals produced by immediate strong cooling of a solution constitute an especially pure substance ; on the contrary, the large surface of the deposit favours the adsorption of by-products. Moreover, with well-formed crystals it is much easier for the organic chemist to meet the imperative requirement that he should check the homogeneity of a substance. The examination of the preparation with a lens or under the microscope should not be neglected ; 50- to 100-fold magnification is sufficient.

If a solution has become saturated at room temperature the yield of crystals can be increased by placing the vessel in ice-water or in a freezing mixture.

Substances of low melting point occasionally separate as oils when their hot saturated solutions are cooled. The solution must then be diluted somewhat. Moreover, in such cases provision is

made for slow cooling by standing the flask containing the solution in a large beaker of water at the same temperature and leaving till cold. Of substances which crystallise with difficulty a small sample should always be retained for use as " seeding " crystals. Separation as an oil may then be obviated by dropping these crystals into the solution before it has become quite cold and rubbing with a glass rod.

Procedure.—In order to prepare a hot saturated solution the substance to be purified is covered, preferably in a short-necked, round-bottomed flask, with a little solvent which is then heated to boiling. More solvent is gradually added in portions until all the substance has dissolved. Since crude substances frequently contain insoluble impurities, the process of dissolution is carefully watched to see exactly if and when the compound to be recrystallised has completely dissolved. On account of the lability of many substances prolonged boiling is to be avoided. Solutions made with solvents which boil under 80° are prepared on the boiling water bath under reflux condenser; the solvent to be added may be poured into the flask through a funnel placed in the top of the condenser. It is better, however, at least when using large quantities, to fit a two-neck attachment (Anschütz tube, Fig. 32, p. 38) to the flask, since in this way it is possible to add the solvent conveniently and, in other cases, to drop in solid substances also. The condenser is fixed in an oblique position to the oblique tube of the attachment, whilst the vertical tube, through which substances are added, is closed with a cork.

Water and other solvents which boil above 80° are most suitably heated on an asbestos support in an air (Babo) oven or on an asbestos-wire gauze. If the boiling point lies considerably above that of water (more than 20°) the danger of cracking the condenser must be avoided by circulating warm water through it, or else the water condenser must be replaced by a long, wide glass tube (air condenser), which may be wrapped in moist filter paper if necessary. For test-tube experiments under reflux the so-called " *cold finger* " is exceedingly convenient. It consists of a glass tube about 15 cm. long and from 6 to 8 mm. wide sealed at one end. About 3 cm. from the other end a narrow tube 3 cm. long is attached at a right angle and bent downwards so that the apparatus can be hung on an iron ring. Cooling water is led away through this side tube to which thin rubber tubing is attached. The water is led into the " cold finger " through a bent glass tube which reaches to the

bottom and is fixed in a small piece of rubber tubing which acts as a stopper. This handy condenser is fitted into the test tube by means of a notched cork.

The very troublesome " bumping " is avoided by adding porous pot, in pieces about half the size of a pea, before the boiling begins. When the pieces of pot become inactive they are replaced by new ones (do not drop them into superheated solutions !). When violent bumping occurs in large volumes of solution the addition of wooden rods is to be recommended.

In order to remove coloured impurities which often adhere tenaciously to a colourless substance, the hot saturated solution is boiled for a short time with a few knife-points of animal charcoal or specially prepared wood charcoal. Since the air which escapes from the charcoal causes copious frothing the adsorbent must be added carefully and with shaking. On account of their colloidal nature the coloured impurities are most easily adsorbed from aqueous solutions.

Filtration.—Solutions from which crystals are to be obtained are not completely clear, even in the absence of charcoal, and they must therefore be filtered. A filter paper in the ordinary conical form is generally to be preferred to the " folded " paper. The angle of glass funnels is usually not quite correct, and allowance can be made for this by making the second fold in such a way that the straight edges of the paper do not quite coincide and then using the larger cone for the filtration.

In preparative organic work readily permeable " grained " filter paper is alone of use.

FIG. 2.

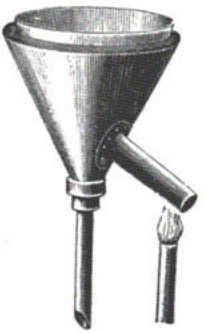

FIG. 3.

FIG 4.

FIG. 5.

The dissolved substance (especially if the solution is very concentrated) often crystallises in the funnel on account of local cooling

and in this way filtration is hindered. This trouble can be partially met by using a funnel (Fig. 2) with the delivery tube cut short (0·5–1·0 cm.). But it is much more satisfactory to use a so-called hot water funnel (Fig. 3) in which the filtering surface of the funnel is heated with boiling water in a metal jacket. When inflammable solvents are used, the flame must be extinguished before filtration. The steam-heated funnel (as in Fig. 4) is likewise very useful. When small amounts of liquid are to be filtered, the empty glass funnel may be heated over a naked flame before use, or the paper may be fixed in the funnel, moistened with alcohol, ignited, and allowed to burn till it begins to char, while the funnel is held in a horizontal position and rotated.

It is often advisable, especially in the case of aqueous solutions which are difficult to filter, to use a porcelain Büchner funnel and apply suction. A well-fitting filter paper is required and the filter flask must be cautiously warmed before use, preferably by standing it in an enamelled pail of warm water and heating to boiling.

If the filter paper becomes choked by crystallisation of the substance, it is best not to push a hole through it. The paper should rather be held upright in a small beaker in which fresh solvent is kept boiling, and the more dilute solution thus obtained is poured through the same paper. In such cases the whole solution must generally be concentrated by evaporation.

If it is desired to produce well-developed crystals when recrystallising, the filtrate, in which separation of crystals often occurs even during filtration, must be reheated till a clear solution is obtained and then allowed to cool slowly without being disturbed.

The **isolation of the crystals** is never accomplished by ordinary filtration, but always by collecting them at the pump on a filter paper, or, in the case of concentrated acids and alkalis, on glass wool, asbestos, or, best of all, on Schott filters of sintered glass. Large amounts of substance are collected on Büchner funnels (Fig. 5) of size appropriate to the quantity of the material to be separated. It is quite wrong to collect a few grammes of substance on a funnel six or more centimetres in diameter. For very large quantities the filter jar (Fig. 6, overleaf) is used. In many cases, especially for small amounts (5 g. or less), the Witt *filter plate* (Fig. 7) is to be preferred. It presents the advantage that its cleanliness can be checked much more readily than that of an opaque porcelain funnel,

and, especially, that much less solvent is required to wash the more compact solid.

In order to prepare the filter paper a small piece of the paper is folded over the upper edge of the filter plate and then a piece having a radius 2–3 mm. greater is cut out with scissors. This piece is moistened with the solvent and fitted closely to the funnel by pressing, rubbing out small folds with a rounded glass rod or, in the case of larger plates, with the finger-nail.

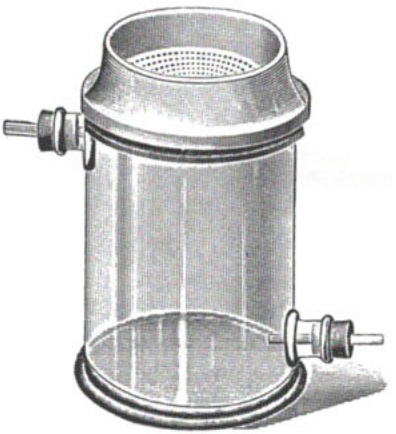

FIG. 6.

When minute amounts of substance (a few hundred milligrammes or less) have to be filtered, small glass plates 0·5–1·0 cm. in diameter are used as supports for the filter paper. These plates are made from thin glass rods by heating one end in the blow-pipe till soft and then pressing out flat on an iron plate (Diepolder). The glass rods must be long enough and thin enough to pass through the delivery tube of a quite small funnel and to project beyond its end. The pieces of filter paper which rest on the glass plates are cut somewhat larger than the plates themselves and are made to fit closely (Fig. 8).

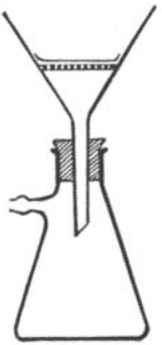

FIG. 7.

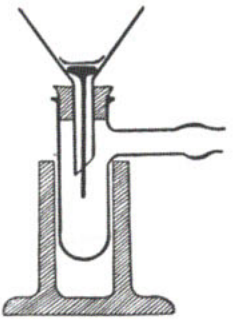

FIG. 8.

In order to remove the substance from the filter plate after filtration

the funnel is inverted over a basin or watch-glass and all the material is transferred to the latter with the help of a thin glass rod or copper wire; the "glass button" is pushed out from its lower end. The plate is removed with forceps, but the paper not before it is dry. The material which adheres to the funnel is removed without loss by scraping with a small, obliquely cut piece of thin cardboard.

The filtrate is collected in a *filter flask* of a size appropriate to the volume of the solution. The very useful *filter tube* (Fig. 8) in its various sizes is also employed when filtering on a small scale. Such tubes stand in a lead support or in a wooden block bored with holes of various diameters.

In view of its great importance as a method for preparing analytically pure substances, the technique of filtration deserves the special attention of the student of practical organic chemistry.

The process of pouring the crystals along with the mother liquor on to porous plate and subsequently washing is emphatically to be rejected. Already in the preparation of organic substances the mind of the beginner should, above all, be directed to working as much as possible in quantitative fashion. It is not the number of preparations which indicates success, but the care and thoroughness with which each separate reaction is carried out.

For these reasons the " mother liquor " must not be treated as waste and neglected. Its importance will indeed only become clear to the research worker, but the beginner at preparative work should extract from it whatever is to be extracted for his purposes.

Filtrates are therefore reconverted into (cold) supersaturated solutions by evaporation of part of the solvent, and so a second crop of crystals is obtained. Occasionally yet another crop may be produced. As a rule the crops so prepared must be recrystallised once again from fresh solvent (check by melting-point determination!).

A few words should be added about the *washing* of crystalline precipitates with the object of freeing them from adherent mother liquor. The same solvent as was used for crystallisation must always be employed and, since its solvent power for the substance, even in the cold, leads to more or less appreciable loss, it must be used in the smallest possible amounts. Suction should not be applied while washing; the precipitate is saturated with the solvent and then the pump is turned on.

It is desirable to provide the Woulf bottle or filter flask, which should

be connected to every water-jet pump, with a regulating cock which not only enables the suction to be cut off conveniently, but also allows of changes in the partial vacuum, which are necessary in many cases.

In the case of substances which are readily soluble even in the cold, the solvent used for washing must previously be cooled in a freezing mixture.

As long as mother liquor adheres to the crystals, although it no longer drains from them, no air should be drawn through the material if volatile solvents are used. Otherwise the impurities in the mother liquor are also deposited, and, especially in the case of easily soluble substances, there is no certainty that these impurities can again be completely removed by washing.

Small amounts of substances are washed with drops of the solvent. A so-called *dropping tube* (Fig. 9), *i.e.* a glass tube drawn out to a not too narrow capillary, is used. Such tubes are also very convenient for carrying out many reactions and they promote cleanliness in working.

FIG. 9.

The practice, which may often be observed, of "purifying" substances by evaporating their solutions to dryness in a crystallising basin, or of leaving them till the solvent has evaporated, naturally does not achieve its purpose because, of course, the impurities are not removed in this way.

Drying of the Substances.—A pure preparation must be completely freed from adherent solvent. Stable substances are most conveniently dried at room temperature by exposure to the air for one or two days between sheets of filter paper laid on a clean support. Substances of high melting point are more rapidly freed from solvent in a drying oven or on the water bath; some care is, however, always indicated.

The method which is most certain, and the sole applicable to analytically pure preparations, consists in drying in a *vacuum desiccator* containing sulphuric acid. The old type of Scheibler is probably the most suitable.

The consistency of the grease used to make the cover of the desiccator air-tight is very important; the most suitable grease is dry lanoline (*adeps lanae anhydricus*) or a mixture of equal parts of beef suet and vaseline. The tube carrying the stop-cock is moistened with glycerol and pushed through the rubber stopper previously fixed in

the opening of the desiccator. Sharp edges on the tube must be rounded off and care taken that an air-tight closure is made. The support inside the desiccator consists of a porcelain plate having three short legs and several circular openings into which small basins, watch-glasses, and the like can be fitted. In order to prevent the support from sliding to and fro, three suitably cut pieces of cork are firmly fixed between the rim and the walls of the desiccator. When air is admitted to the desiccator there is a danger that substances which are being dried may be blown about. To prevent this a stiff strip of cardboard, or similar object, is fixed against the inner opening of the tube. In addition, before the cock is opened, a strip of filter paper is held before the outer opening. This paper is then sucked in against the tube and sufficiently moderates the current of air.

In order to dry the air which enters, a straight calcium chloride tube is attached to the tube of the desiccator. The calcium chloride must be firmly held in position at both ends by means of glass wool or, better, cotton wool. In desiccators which are often carried about, the container for the sulphuric acid is filled to the acid level with pieces of glass —small pieces of broken tube, stoppers, and the like—or with pieces of pumice which have previously been boiled with dilute hydrochloric acid and then dried. Splashing is thus avoided. From time to time the concentrated sulphuric acid is renewed. A special vacuum desiccator must be kept for analytical work.

For intensifying the drying effect, especially in respect of water, a small basin filled with solid technical potassium hydroxide is laid on the support. Most solvents, with the exception of chloroform, benzene, petrol ether, and carbon bisulphide, are absorbed by this combination. In order to free substances from these four solvents, thin slices of paraffin wax in a shallow basin are placed in the desiccator beside the substance, if its properties are such as to preclude drying in the air.

The rule should be adopted that any vacuum desiccator which does not fully keep its vacuum over night (test with a gauge) should be discarded. Thus it is sufficient to evacuate once and to leave over night. To continue suction at the pump for hours is to waste water.

Many substances contain water or other solvent so firmly bound that it cannot be removed in a vacuum at room temperature. These are dried in a vacuum at a higher temperature: they are heated in a small round flask on the water bath or oil bath until they cease to lose weight. The so-called "*drying pistol*" (Fig. 10) is especially convenient for this purpose. The vapours from the liquid boiling in A heat the wide inner tube B, in which the substance is exposed in a porcelain

boat. C contains a drying agent—for water and alcohol, phosphorus pentoxide, for other vapours, paraffin wax. According to the temperature desired, the heating liquid chosen is *chloroform* (66°), *water* (100°), *toluene* (111°), *xylene* (140°). C is connected to the pump.

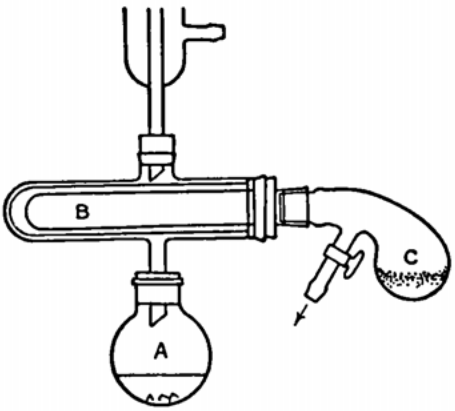

FIG. 10.

If a non-volatile solvent, such as glacial acetic acid, xylene, high-boiling petrol ether, or nitrobenzene, has been used for recrystallisation, it is washed out before drying by means of one which is more easily removed, *e.g.* ether, benzene, petrol. In general a substance which is sparingly soluble in glacial acetic acid or nitrobenzene is so also in ether.

2. DISTILLATION

Purification by distillation consists in transferring the substance in the gaseous state to another place where it is again liquefied or solidified. Where this method of purification is used it is essential that the substance be stable at its boiling point. The latter can be lowered by distillation in a vacuum—at the pressure usually produced by the water-pump (12 mm.) the boiling point is on the average 100°–120° below that at atmospheric pressure. This difference is greater in the case of substances which boil above 250° at ordinary pressure. Very often, therefore, substances which do not distil unchanged at atmospheric pressure can be purified by distillation in a vacuum because they are thus exposed to a much lower temperature.

Simple substances, and in particular those which are also readily volatile, such as hydrocarbons, alcohols, esters, the lower acids and amines, are distilled under atmospheric pressure. All substances which decompose easily, and those which have especially high boiling points, are distilled under reduced pressure. In general solid substances should only be distilled when purification by crystallisation has been unsuccessful on account of too great solu-

bility or for other reasons. Naturally in each case the possibility of distillation (without decomposition) must be established in advance.

Distillation, whether at atmospheric pressure or *in vacuo*, serves not only to separate the product from non-volatile impurities, but also to fractionate mixtures of volatile substances having different boiling points (fractional distillation).

Distillation at Atmospheric Pressure.—The simple distilling flask with side tube sloping downward (Fig. 11) serves exclusively as the distilling vessel. In general the side tube should be attached high in the case of low-boiling liquids and nearer the bulb in that of less volatile liquids.

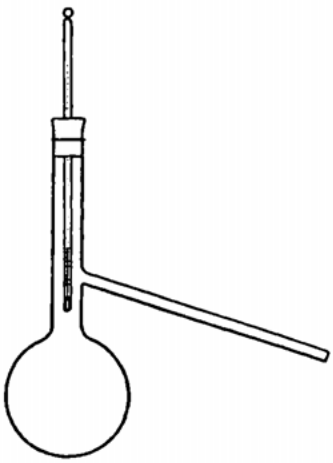

FIG. 11.

The thermometer is held in the flask by means of a clean bored cork; the bulb of the thermometer must be completely immersed in the vapour and hence must be below the junction of neck and side tube.

Since the ordinary laboratory thermometers are often inaccurate, they must be compared with a standard thermometer before use. The most accurate method of standardisation is to hang the two thermometers side by side with the bulbs dipping in concentrated sulphuric acid or paraffin at 250°, and then to observe the temperatures during cooling at intervals of 10° and record the deviations. Thermometers for distillations should have small bulbs so that they record rapidly.

Distilling flasks should be chosen of such a size that the bulb is half or two-thirds full of liquid. In order to avoid bumping and superheating a few pieces of porous plate (pot) half as large as peas are dropped into the flask before each distillation. If boiling is again delayed fresh pieces of pot must be added, not to the superheated liquid, however, but after brief cooling.

The flask is fixed above the side tube in a clamp lined with cork.

Sources of Heat.—Liquids which do not boil above 80° are heated in the water bath (enamelled jar or beaker); the temperature of the bath should be about 20° above the boiling point of the substance. The maintenance of the correct heating temperature is of

the greatest importance, since if it is raised too much the boiling point of the distillate will be found too high in consequence of superheating.

In the case of substances of high boiling point where, for preparative purposes, a margin of a few degrees in the boiling point may be allowed, a naked smoky gas flame may generally be used, which is at first cautiously made to play round the flask. A conical air bath (Babo) or wire gauze may likewise be used. When the substance is valuable, when attention must be paid to analytical purity, or also when, on account of the degree of stability of the substance, superheating should be avoided, it is preferable to use an *oil* or *paraffin bath*. For temperatures greater than 220° a *bath* of Wood's or Rose's *metal* or a molten mixture of equal parts of potassium and sodium nitrates, both in an iron crucible, is to be preferred.

Substances of low boiling point are condensed in a Liebig condenser attached to the side tube of the flask by means of a cork. If it is desired to avoid all loss by volatilisation, the condenser is connected to the filter flask serving as receiver by means of a so-called adapter and the receiver is cooled in ice, or else in a freezing mixture.

For liquids which boil at about 100° a shorter condenser suffices, and when small amounts are being distilled it is especially advisable to use a small cooling jacket slipped firmly over the side tube so that loss of material is minimised. Such a device is illustrated in Figs. 19 and 25.

In the case of boiling points above 120° cooling with running water is generally not practicable, because the condenser tube, being in contact with the hot vapour, may easily crack; instead, the jacket contains as cooling agent standing water which gradually grows warm. When the boiling point exceeds 150° simple air cooling (wide condenser tube without jacket) suffices.

Substances which solidify rapidly after condensation should never be distilled from a flask having a narrow side tube; the distillate in the tube can indeed be reliquefied by warming with the flame, but often it is hardly possible to clear away the material which blocks parts covered by corks or other connections, so that time is lost and annoyance caused.

The *sausage flask* (Fig. 12) is therefore at once chosen. It has a wide side tube from which the product can be removed without trouble when distillation is complete, preferably by melting.

Normally distillation is carried out as follows. After the contents of the flask have been gradually heated, the visible signs of boiling appear, the mercury column of the thermometer rises rapidly and becomes steady at a definite temperature—the boiling point. When this temperature has been attained to within one degree the receiver (a small wide tube or similar vessel) for the first runnings is replaced by one suited to the amount of distillate expected (a conical flask or a narrow-necked bottle in which a small funnel is placed), and heating is continued at such a rate that one drop distils every second or every other second. The thermometer must be watched all the time. In general the boiling point range should not exceed 1°–2°; in the case of analytically pure preparations the limits should be even closer. If a naked flame is used for distillation the boiling point rises a few degrees as a rule towards the end of the process on account of superheating, although pure substance is still passing over. If the boiling point rises even earlier, beyond the limit given, the receiver must be changed again and the distillation continued so that a third fraction, the "last runnings", is collected.

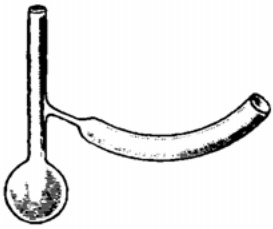

FIG. 12.

It should be borne in mind that both in the first and last runnings there is some of the main product. The vapour pressure of a distillable substance is so considerable even below the boiling point that its vapours already pass over along with the more volatile constituents (usually residues of solvent) of the original material. On the other hand the boiling point of a substance rises when it is mixed with higher boiling substances.

Thus ether, which is very extensively used to take up organic preparations, is not completely removed from a much less volatile substance even on the boiling water bath, although the boiling point of this solvent is 35°. The benzene wash of coke ovens is another well-known example which cannot be discussed in detail here.

Hence it is evident that the last runnings also are not free from the main product, and when first and last runnings form an important amount it is worth while to redistil these two portions separately according to the rules given.

Fractional Distillation.—When several volatile reaction products are to be separated from one another the procedure is not so simple

as described above. In proportion as the boiling points of the various constituents approach each other the separation becomes more difficult, and it is not easy with the help of the usual laboratory apparatus to separate with any degree of precision substances which differ in boiling point by 10°.

The nearest approach to the desired end is attained by repeating the process of distillation. In the case of low-boiling substances it can be done in *one* operation with the help of so-called *fractionating columns*, which are devices introduced into the gaseous phase before final condensation occurs. In the several divisions of these columns, which can be constructed in various forms (Fig. 13), vapours are liquefied by air cooling, and the vapours which are formed later must pass through this liquid which lies in their path. In this way the less volatile constituents of the vapour are condensed, while the more volatile are exposed to the same treatment in the next division. Thus a number of separate distillations corresponding to the number of bulbs in the column occurs, and if the operation is carried out carefully and slowly a far-reaching separation is made possible. Cylindrical columns irregularly filled with glass Raschig rings are especially suitable.

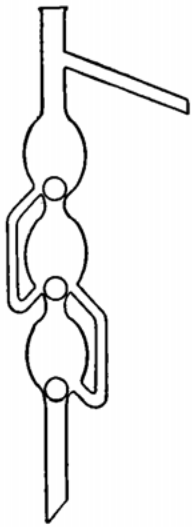

FIG. 13.

If only small amounts of substance are available, glass spirals[1] inserted into the lumen of the distilling flask yield quite excellent results.

Technically the principle of fractional distillation is applied in the manufacture of spirit and in the isolation of aromatic hydrocarbons from the light oil of coal-tar.

Mixtures of liquids of higher boiling point (above 120°) are first separated by distillation into several fractions of about the same boiling-point interval; the separate distillates (in smaller flasks) are again divided by distillation into fractions, and the fractions of adjacent boiling points are then fractionally redistilled, while the boiling-point ranges are continually reduced. If, as is very advisable, the above-mentioned Widmer spiral is also used here, the column in which it is placed must be well lagged with asbestos.

[1] Widmer, *Helv. Chim. Acta*, 1924, 7, 59.

Not all mixtures are separable by distillation; occasionally substances which boil at different temperatures form constant boiling mixtures.

Detailed information about the theory of fractional distillation will be found in Nernst's *Theoretical Chemistry*, 1923, p. 118.

Vacuum Distillation.—The organic chemist must continually bear in mind that almost all substances with which he has to deal are, from the thermodynamical standpoint, metastable. In all cases, however, increased temperature favours the setting up of the true equilibrium—here decomposition—and hence it is appropriate to adopt the rule: Never endanger substances unnecessarily.

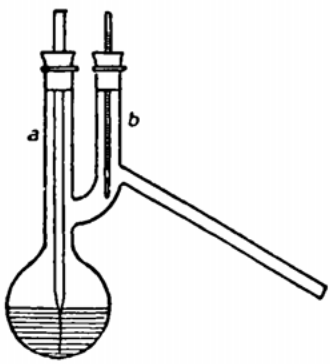

FIG. 14.

Hence distillation under reduced pressure, whereby the boiling point can be reduced by one hundred and more degrees, acquires great importance in organic work. The organic chemist who is doing preparative work must quickly learn how to apply the method, and should early accustom himself to regard vacuum distillation not as in any way extraordinary, but as one of the most elementary operations of laboratory practice.

The appropriate vessel for the distillation is the *Claisen flask* (Fig. 14). The very practical division of the neck into branches minimises the spurting of the boiling liquid, which is especially dangerous in this process. In order that the bumping, which very easily occurs during vacuum distillation, may be avoided, minute bubbles of air, or in the case of substances sensitive to the action of air, bubbles of hydrogen or carbon dioxide, are drawn continuously through the boiling liquid by means of a fine capillary tube.

This tube is drawn out in the flame of a blow-pipe from glass tubing 4–8 mm. wide and is then drawn out again to sufficient fineness in a micro-flame. To make sure before use that the capillary is not closed, the tip is submerged in ether in a small test tube and air is blown in from the mouth. The bubbles should emerge separately and slowly. Capillaries for distillation in a high vacuum should emit air bubbles only on powerful blowing, and then with difficulty.

Occasionally, and especially when liquids which foam are being distilled, it is necessary to regulate the amount of air passing through

the capillary. To do this the capillary must not be too fine, and a small piece of thick-walled rubber tubing is fixed to the upper end of the tube and a screw clip is so attached that its jaws grip the rubber immediately above the glass. It must be borne in mind, however, that if the distillation is interrupted the liquid in the flask will be driven back by the external air pressure into the still evacuated capillary tube, and sometimes into the rubber tubing. This is avoided by cautiously unscrewing the clip before the interruption.

When obstinate foaming occurs, the thermometer is discarded in favour of a second capillary tube in the front neck of the Claisen flask (*b* in Fig. 14). The fine current of air drawn in through this tube bursts the bubbles of foam before they can pass over.[1]

The capillary tube is inserted (with a little glycerol as lubricant), tip first, into a narrow-bored, undamaged rubber stopper which fits tightly into the neck *a* of the Claisen flask. The correct position of the tip is immediately above the deepest part of the bulb of the flask. A thermometer, likewise pushed through a rubber stopper, is inserted into the neck *b*. If it is desired to prevent contact of the substance with rubber, Claisen flasks with

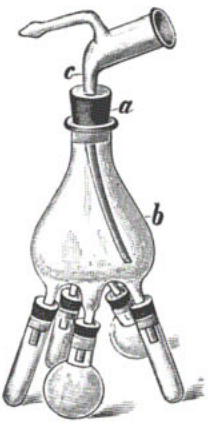

FIG. 15.

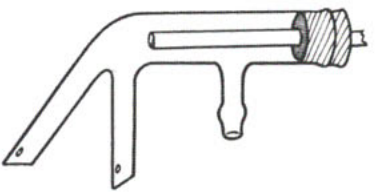

FIG. 16.

constricted necks are used. The capillary tube and thermometer are held in position in these necks by means of small pieces of rubber tubing drawn over each neck and its capillary or thermometer. The proper use of cork stoppers in vacuum distillations requires much practice.

[1] E. Dorrer, *Dissertation*, Munich, 1926.

The vapours are cooled in the way described ; here the use of the small water-cooling jacket drawn over the side tube is especially to be recommended.

Receivers.—When only one or two fractions are expected, small filter tubes of suitable size, as illustrated in Fig. 8, are used (the smallest for the first runnings), or, in the case of larger amounts of substance, small filter flasks. The rubber stoppers for attaching them should be tested in advance as to fit. When the receiver is being changed, the distillation must, naturally, be interrupted.

If this is to be avoided and several fractions are expected, it is preferable to use the so-called *cow's udder*, an apparatus which is illustrated in Fig. 15. By holding the glass tube *c* with one hand and turning the vessel *b* with the other the various receivers can successively be brought under the mouth of the delivery tube. (The tube *c* is lubricated with glycerol.) The form shown in Fig. 16 is handier and more suitable for the distillation of small amounts. According to its shape it is known in laboratory slang as a " spider ", " frog ", or " pigling ".

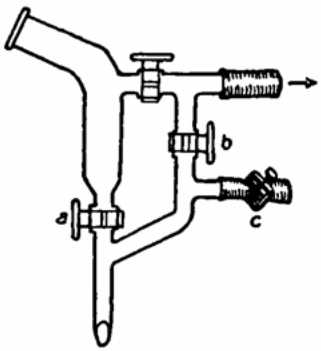

FIG. 17.

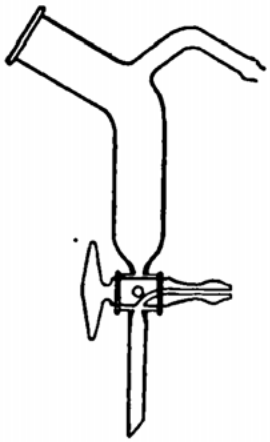

FIG. 18.

Finally, Anschütz and Thiele's adapter with stop-cock (Fig. 17) may be mentioned; it is very useful, in particular in the distillation of large amounts of substance. After the cocks *a* and *b* of this adapter have been closed the pressure in the receiver can be allowed to rise by unscrewing the clip *c* and the receiver can be changed.

Then after *c* has again been closed and a vacuum has been re-

established throughout by opening *b*, the cock *a* may also be opened and distillation continued. The third cock is not required. Of still simpler construction is the adapter (Fig. 18) with a three-way cock. By means of a boring in the cock the receiver can be opened to the atmosphere while the vacuum in the apparatus is maintained. After the receiver has been changed the cock must, however, be turned very cautiously, so that the distillate which has collected above is not blown out by air drawn in from below.

The two pieces of apparatus just described have the great advantage that the various fractions are at once completely isolated and do not come into contact with the vapours; on the other hand, they cannot be used for thick viscous liquids which do not pass through the boring of the cock.

They are therefore of special use for the distillation of relatively low-boiling substances the vapour pressure of which cannot be neglected.

When substances which solidify rapidly are distilled in a vacuum, the side tube of the Claisen flask should be wide, as described for ordinary distillation.

Heating.—Only after much practice can a vacuum distillation be carried out with a naked flame. Indirect heating in a bath is much more reliable. Here also the temperature of the bath should be adjusted with the greatest care to suit the boiling point of the substance (about 20° higher; when the side tube is attached high up, the difference must be increased); when the boiling point of a fraction has been reached, the temperature of the bath should be kept constant.

The flask is immersed in the bath to such a depth that the surface of the material to be distilled lies below that of the heating liquid. The bulb of the flask should not be more than half filled with substance.

When high-boiling substances are distilled, the flask is immersed as deeply as possible and the portion above the bath to the junction with the side tube is wrapped in asbestos paper held in position by a thin wire or by a string.

Sensitive substances which, as such, can be distilled in a vacuum, occasionally decompose when subjected abruptly while hot to large changes of pressure. In such cases the pressure is allowed to rise only after the contents of the flask have cooled. To proceed in this way is quite generally appropriate because thereby the very common oxidising action of hot air is also avoided.

In all distillations under reduced pressure a small gauge (Fig. 19), introduced between pump and apparatus, is indispensable, since the

pressure must be controlled throughout, in view of its effect on the boiling point. Inconstant boiling points are very often due to variations in pressure. In order to hold back vapours which would contaminate the gauge by condensing in it, the cock is kept closed during the distillation, and only opened from time to time to test the pressure.

Before every vacuum distillation the whole apparatus must be tested for tightness with the gauge, i.e. *it must be shown to keep up a satisfactory vacuum.*

The heating of the bath is only begun after the vacuum has been produced. If the pressure over the *already warmed* liquid is reduced,

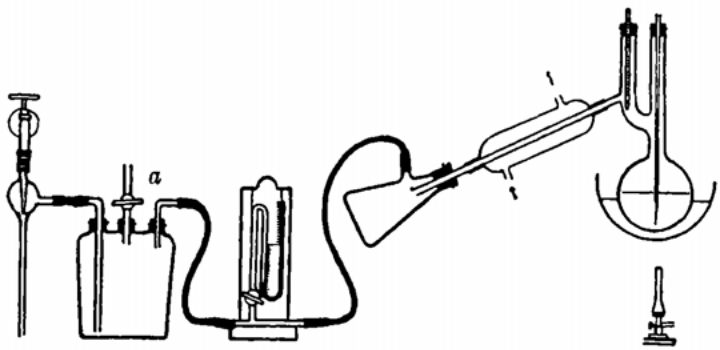

FIG. 19.

it often froths over, owing to superheating. This may happen before the boiling point of the substance is reached: it is enough if the material still contains a little solvent, *e.g.* ether, the removal of which on the water bath is never quite complete because of the greatly reduced vapour pressure.

In many cases when readily volatile low-boiling substances are distilled in a vacuum it is necessary to reduce the volatility by raising the pressure. The full vacuum of the water pump, which, depending on the pressure and temperature of the tap water, amounts to 10-20 mm. of mercury, is then not used, but, instead, pressures of 20–100 mm. Since the action of the pump cannot be regulated, a cock attached to the Woulf bottle (*a*, Fig. 19) is used, so that with the help of the gauge any desired pressure can be obtained. For substances which boil above 150° under atmospheric pressure the maximum effect of the water pump is employed.

The extent to which the reduction of pressure in a vacuum distillation lowers the boiling point can be seen in Fig. 20, in which *nitrobenzene*, boiling point 208°/760 mm. (curve I), and *benzaldehyde* (II), boiling point 179°/760 mm., are the examples chosen. The importance of a " good vacuum " in preparative work is expressed in the steep slope of the curves in the low-pressure region. When the distillation is carried out at 20 mm. the boiling point is about 15° higher than when the pressure is 10 mm. As the pressure rises this effect is reduced, as the curve III in the upper part of the figure makes clear. This curve, which is on a different scale, represents the region of pressure from 760 mm. downwards. At Munich a reduction of the sea-level barometer to 720 mm. only lowers the boiling point of water by 1·5°.

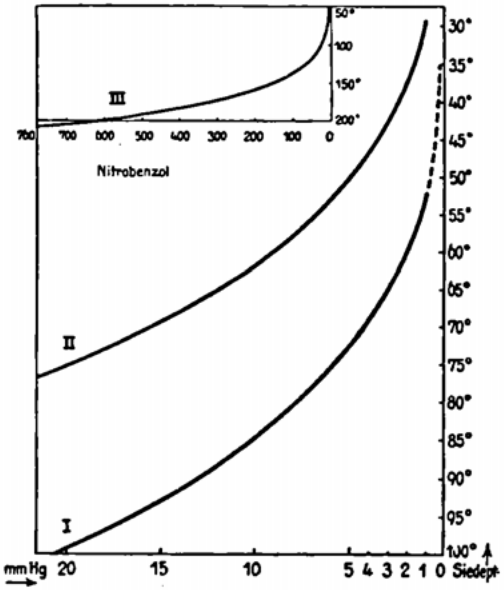

FIG. 20.

The quantitative relations between pressure and boiling point vary from substance to substance, but among organic compounds the variation is not very great, so that the curves here reproduced can in practice very well be used as a guide.

For example, if according to the literature a substance boils at 96°/12 mm., it will boil at 104–105° at 18 mm.

Substances which boil at too high a temperature, even in the vacuum of the water pump, can often be distilled without decomposition in a

high vacuum, *i.e.* at pressures of 1 mm. or less. Reduction of pressure to this limit reduces the boiling point on the average by 150° as compared with the boiling point at atmospheric pressure, and by about 40° as compared with that in the vacuum of the water pump. The dotted continuation of the nitrobenzene curve I illustrates this—it is not based on actual measurements.

Since the introduction of the so-called mercury vapour-jet pumps, which are to-day available in almost every university laboratory, distillation in a high vacuum presents no difficulty, and whoever has mastered ordinary vacuum distillation will also be able to distil in a high vacuum when the occasion arises, possibly when working according to directions from original literature. Because the apparatus is easily damaged, at least in ordinary usage, it has not been applied to the practical exercises in this book, and is not further described. The excellent mercury vapour-jet pump of *Volmer* should be available to-day in every organic teaching laboratory.

Always protect the eyes during a vacuum distillation !

Sublimation

Volatile substances of which the vapours, on cooling, condense directly to crystals without passing through the liquid phase are sometimes advantageously purified by sublimation, particularly when solubility relations render recrystallisation difficult. The purification of iodine is a well-known case in point. In organic chemistry this process is particularly suitable for quinones.

Small amounts of substance are conveniently sublimed between two watch-glasses of equal size. The substance is placed on the lower glass and covered with a round filter paper, having several perforations in the centre, and somewhat larger than the glass. The second watch-glass is laid with its convex side upwards on the lower glass, and the two are fixed together with a watch-glass clip. When now the lower glass is heated as slowly as possible on the sand bath with a small flame the vapour from the substance condenses in crystals on the cold upper glass; and the filter paper prevents the small crystals from falling back into the hot lower glass. The upper watch-glass can be kept cool by covering it with several layers of moist filter paper or with a small piece of wet cloth.

Fig. 21.

If it is desired to sublime larger amounts of substance, the upper

watch-glass of the apparatus just described is replaced by a funnel, of which the diameter is somewhat less than that of the watch-glass (Fig. 21).

Sublimation can also be carried out in crucibles, flasks, beakers, retorts, tubes, etc. If the substance to be purified only sublimes at a high temperature, as is the case, for example, with indigo or alizarin, a vacuum is applied (small round-bottomed flask or retort). When carrying out sublimations the student should always make sure that the apparatus has cooled completely before taking it apart.

Distillation with Steam

This important method of purification is very extensively used, both in the laboratory and on a large scale in chemical industry. It is based on the fact that many substances, the boiling points of which may lie considerably above that of water, are volatilised by injected steam to an extent proportional to their vapour pressure at that temperature, and are then condensed along with the accompanying steam in a condenser. The most suitable and theoretically simplest case (see below) arises when the substance is sparingly soluble or practically insoluble in water.

To test for volatility in steam, heat a small sample of the substance to boiling (porous pot!) in a test tube with about 2 c.c. of water and hold the bottom of a second test tube containing some ice in the issuing vapours until a drop of water has formed on the cold surface. A turbidity in the drop indicates that the substance is volatile with steam.

The substance to be distilled is placed along with a little water in a capacious, long-necked, round-bottomed flask which should not be more than one-third filled, and is heated over a burner until near the boiling point (in order to avoid great increase in volume due to condensation of water). Then after the water has been turned on in the *long* condenser and the receiver has been placed in position, a rather vigorous current of steam is passed in. The wide steam-delivery tube should reach nearly to the bottom of the flask and should be bent slightly, as shown in Fig. 22. If steam is not laid on in the laboratory it is produced in a tin can rather more than half filled and provided with a long vertical safety tube. As a rule distillation is continued until the distillate passes over clear. If the substance crystallises in the condenser the jacket is partly emptied for a short time and the steam then melts the crystals, so that the