# LABORATORY MANUAL
# *of* ORGANIC CHEMISTRY

BY

HARRY L. FISHER, Ph.D.

*Instructor in Organic Chemistry, Columbia University*

*FIRST EDITION*

NEW YORK
JOHN WILEY & SONS, Inc.
London: CHAPMAN & HALL, Limited
1920

PRESS OF
BRAUNWORTH & CO.
BOOK MANUFACTURERS
BROOKLYN, N. Y.

# PREFACE

THIS book is the outgrowth of almost ten years of intensive laboratory teaching. Practically all the laboratory experiments, in mimeograph form, have been in the hands of three different classes of students, day, night, and summer, each year for over five years, and during this time have been repeatedly corrected. As our classes grew we found it necessary to keep to a definite list of experiments and all our attention was devoted to these. In order to bridge the gap between the particular reaction studied and allied reactions, many questions were added. These questions have been made the basis of laboratory quizzing and are meant primarily for the student to use for his own advancement in the subject to aid him to become his own teacher. A portion of the questions are on the practical work in the laboratory, that is, on the methods of handling apparatus, etc. Many of them will appear to be perfectly obvious. They are, nevertheless, put in since it has been noticed that it is the most obvious point which is most often overlooked.

The experiments are, in general, the usual ones found in laboratory manuals, changed of course in accordance with our experience, and they were chosen for their teaching value and for the good all-round practical manipulation involved. There are only a few innovations. Menthone and menthone oxime illustrate typical reactions even though their formulas may seem large to the beginner. Glycocoll is prepared by hydrolysis, thus linking up the chemistry of the proteins with that of simpler compounds. Limonene dihydrochloride has tremendous teaching value, and the synthesis of camphor from pinene gives an opportunity for select work in an enticing field. The methods described give good yields in most cases, but the yield was not the prime reason for choosing any experiment.

It will be noticed that there are no directions for preparing such substances as acetacetic ester, malonic ester, etc. These can advantageously be given in connection with special advanced synthetic work, for example, malonic ester can be prepared as the starting-point in the synthesis of veronal (barbital), acetacetic ester and also phenyl hydrazine in the preparation of antipyrine, anthranilic acid for methyl anthranilate or indigo, ethylene chlorhydrin for novocaine (procaine), pyruvic acid for atophan, etc.

In the large classes of to-day the beginning student does not any longer have the opportunity of " rubbing elbows " with the older men and learning from such contact many of the little things about laboratory manipulation which aid materially in the successful outcome of an experiment. For this reason, the first experiments in this book are written up in considerable detail with the hope that after the student has learned how to set up his apparatus in the correct way, he will thereafter follow this practice. For the most part this hope has been realized in this laboratory. All operations are described where they are first used, in the order of the experiments, and afterwards their use only is mentioned, sometimes being cross-referenced, but always fully indexed. Special discussions are included only where it is believed the material cannot be found in the ordinary books which the student has at his disposal.

It is assumed that before beginning organic laboratory work students have been prepared with a long course in general chemistry and a short course in qualitative analysis.

A shortened organic course is mentioned below which has been designed especially for pre-medical students. A good grounding in organic chemistry is, however, absolutely essential for the study of medicine, and the long course should be taken whenever possible. A student gets much more out of his work when he prepares certain compounds and has time to study their characteristics and think over his work, than when he goes through a very great number of test-tube reactions which superficially are very much alike and therefore the more easily forgotten.

The long course consists of two afternoons a week for *two* semesters, and comprises for the first semester, experiments

Nos. 1–7, 9–15, 17–23, and for the second semester, experiments Nos. 24–29 (1), 30–46, 48–49, 51–53, 56, 58, 65, 66. These are arranged in the order of discussion found in Stoddard's "Introduction to Organic Chemistry." The short course consists of two afternoons for *one* semester, and comprises experiments Nos. 1, 2, 3, 4, 28, 5, 10, 6, 24, 12, 25, 29 (1), 16, 19, 22, 30, 8, 9, 26, 27, 34, 37, 33, 38, 43, 45, 46, 51, 53, 49, 13 (optional), in the order given. This different order is in accordance with the discussion in Moore's "Outlines of Organic Chemistry." Since the order of both courses is not the same, some of the experiments in the long course which also occur early in the short course, have been written up in greater detail than would ordinarily be necessary from their position in the list. A list of apparatus furnished to each student and lists of the chemicals used in each course will be found on pages 312–323. In our laboratory each student receives his complete set of chemicals and apparatus for the semester when he starts work, and keeps them in his desk.

Each desk in the organic laboratory at Columbia University is equipped with gas (2), air blast, water (2 outlets including one which can be used for suction pump), steam cup, steam outlet for steam distillation, etc., draft pipe (downward), and electric fixture for extra light and with a 20-ampere connection. It is expected that in addition a special hot-plate will soon be installed having a steam pipe cast in it and also having another pipe cast in it which can be connected with the air blast to give hot air when desired. At the adjacent sink is a goose-neck outlet for water and another one with a steam mixer attached for producing water of any desired temperature. The desks, phich are 6 feet long, contain the Fales type of cupboards, and are arranged for two students to work on alternate afternoons. There are no shelves or racks between the desks and on this account the room is light and it is possible to look across the entire laboratory at any time. The room is of course equipped with fire extinguishers, bottles of dry sodium bicarbonate for burning oil, and blankets, at each end of every aisle, and three needle shower-baths in case one's clothing catches fire.

A book is never a thing by itself. It is always a growth and many factors and influences from other workers contribute largely in the making of it. The author is very glad to make acknowledgment for assistance of various kinds to such works as the following: Barnett, " The Preparation of Organic Compounds"; J. B. Cohen, " Practical Methods of Organic Chemistry"; E. Fischer, " Introduction to the Preparation of Organic Compounds"; Gattermann, " Practical Methods of Organic Chemistry"; Henle, " Anleitung für das organisch präparative Praktikum"; Holleman, "Laboratory Manual of Organic Chemistry for Beginners "; L. W. Jones, " Laboratory Outline of Organic Chemistry"; F. J. Moore, " Experiments in Organic Chemistry "; J. F. Norris, " Experimental Organic Chemistry "; W. A. Noyes, " Organic Chemistry for the Laboratory "; Sudborough and James, " Practical Organic Chemistry "; and Ullmann, " Organisch-chemisches Praktikum." Special references are given here and there largely to induce students to get acquainted with articles in the journal literature and thus to stimulate them toward acquiring a good scientific attitude toward chemistry.

I wish to make most generous acknowledgment to my friend and colleague, Professor John M. Nelson. The work herein set forth was begun with him and grew under his constant sympathetic support and kindly guidance. His sound advice and valuable suggestions call for my most cordial thanks.

I am also indebted to Professor Thos. B. Freas and his associates of the stock room for many favors and to Mr. S. J. Ballard, who made many of the drawings and prepared all for the publishers. My sincere thanks are also given to Dr. George Scatchard and Mr. William E. Morgan, and to many students whose friendly advice and helpful co-operation has been of the greatest assistance.

A special foreword concerning organic combustions which constitutes the subject of the second part of this work will be found just preceding that part.

HARRY L. FISHER

COLUMBIA UNIVERSITY,
June, 1919.

# CONTENTS

---

## *PART I*

## LABORATORY EXPERIMENTS

EXPT. NO. PAGE

* These experiments constitute the short course, see p. v.

## *PART II*

## ORGANIC COMBUSTIONS

### Division A

### The Determination of Carbon and Hydrogen

The apparatus is arranged in the following order and is discussed in this same order:

DIVISION B

## The Determination of Nitrogen

# PART I

# LABORATORY EXPERIMENTS

# LABORATORY MANUAL OF ORGANIC CHEMISTRY

## GENERAL NOTES AND SUGGESTIONS

Each **preparation,** if a liquid, is placed in a square 15 cc. glass-stoppered bottle,[1] and, if a solid, in a 20 cc. round wide-mouthed bottle,[1] and neatly labeled with the name of the substance, the corrected boiling-point or melting-point, **as found** by you, the yield of pure substance (always in **grams,** to the first decimal place, as originally obtained even though some material may have been used for special experiments), and the name of the student, for example:

Ethylene dibromide  
B. P. 131° cor.  
Yield, 20.2 grams  
JOHN SMITH

The **yield** is the amount of pure product actually obtained. The "theoretical yield" is the amount which would be obtained if the reaction went entirely to the right according to the ordinary equation, in other words, if the starting material was entirely converted into the product desired.

The yield given in the experiments is the amount usually obtained by following out the directions carefully. It is not the theoretical yield.

---

[1] Practically all the preparations will give amounts that will be contained by bottles of these sizes. Acetaldehyde ammonia and acet-o-toluidide will be found too bulky, but it is expected that only a sample of these will be handed in for inspection, the remainder being used for preparing another substance.

Only through the intimate acquaintance made in the laboratory in the actual handling and the preparation and purification of compounds can the student hope to gain a thorough, comprehensive knowledge of the properties and reactions of organic substances. Study the experiments first with the aid of the text-book and afterwards carry them out in the laboratory. *Always read through the entire experiment before beginning any work in the laboratory.* It is most important THAT YOU KNOW WHAT YOU ARE DOING WHEN YOU ARE DOING IT.

Wherever possible save time by looking ahead and working on more than one experiment at a time.

**Neatness** will be insisted upon in all laboratory work. Set up your apparatus neatly and in good shape, and do not allow unnecessary and unused apparatus to collect around it. Keep the desk top free from dirt and oil spots. The apparatus in the cupboards of the desks should be clean and neatly arranged. The desks will be inspected by the instructor periodically.

All apparatus and chemicals must be placed within the desk at the end of each laboratory period. Whenever it is necessary to leave apparatus on the desk a "red tag" permit will be issued by the instructor. In such cases do not leave out burners, or any other disconnected pieces of apparatus.

**Grades.**—The laboratory grade will be based upon (1) the quality and yield of preparations, and (2) the general manner in which the student performs his laboratory work, including his manipulation, neatness, knowledge of the experiment while the work is being done as evidenced by replies to oral questions, etc. *This second part is given several times the weight of the first.*

**Note-books.**—It is recommended that each student keep a note-book. Two pages should ordinarily be allowed for each experiment: the left-hand page for the Type of Reaction, the Object of the Experiment (for example, the Preparation of Ethylene dibromide from Ethylene and Bromine), the Equation for the Reaction, Materials to be used, any special notes, and references; and the right-hand page for the Method of Preparation, B.P. or M.P. of Substance as found, Yield, Theoretical Yield and Percentage Yield, which is the actual yield multiplied by 100 and divided by the theoretical yield, Chemical and Physical Properties, Notes, and any other data. The topics for the left-hand page given above refer particularly to the "preparations." For other experiments use special topics as needed. Make the Method of Preparation or Procedure *concise*: do not rewrite the directions as given in the laboratory directions. Use constitutional formulas throughout. The left-hand page should be written up before the apparatus is assembled and the experiment started. The right-hand page should be written up immediately after the experiment is completed. *Be brief.*

**Amounts of Chemicals.**—In every case carefully weigh or measure out *all* chemicals, regardless of what amount may be stated on the label. If a horn-pan balance is used for weighing, place papers in the scoops. Sometimes the exact amount is not necessary, as in the methane experiment. Although the laboratory work in organic chemistry is not carried out with the same degree of accuracy, as for example in quantitative analysis, the best results are obtained only when molecular quantities are used, and these are usually given in the directions. Chemicals should generally be weighed to the first decimal place.

For a liquid, the *specific gravity* equals the weight divided by the volume. This simple expression should always be borne in mind when making calculations where liquids are involved.

**Cutting Sticks of Solid Sodium or Potassium Hydroxide.**—Caustic alkali should not be handled with the fingers. Put the stick on a piece of filter paper, and turn up one side as a buffer. A common knife and a sharp blow upon it will quickly cut off the desired amount. Protect the eyes with goggles. For alkali in the eye, use castor oil. (See p. 6.)

**Rubber Stoppers** should not be left in any piece of apparatus which has been heated. They should be removed, if possible, as soon as the heating is discontinued. Otherwise the stopper will be molded to the shape of the opening by the contraction of the glass in cooling.

**Loosening Ground Glass Stoppers and Stop-cocks.**—The following is very often efficient in loosening glass stoppers and stop-cocks. Give a stout piece of twine one or two turns around the neck of the bottle and heat the glass by drawing the string rapidly back and forth.

In case this method does not work, compare opening of bromine bottles, Note 3, p. 33.

An excellent method of removing "frozen" stop-cocks is given by V. C. Allison (*Journ. Ind. and Eng. Chem.*, **11** (1919), 468). The handle of the key is slipped into a socket in a block of hard wood while the opening of the block rests as a collar on the shoulder of the barrel of the stop-cock. A plug of wood is placed against the other end of the key, and easy regular pressure brought to bear by means of a *vise.* Different sizes are given for the ordinary stop-cocks in use. The scheme is rapid and it works!

Following are the names of three concise and valuable **handy books** which contain a large amount of chemical data in compact ready-reference form:

Van Nostrand's "Chemical Annual," 8vo; "Chemiker-Kalender" (German), 2 vols., 12mo; "Handbook of Chemistry and Physics," 7th Ed., 1919, published by The Chemical Rubber Co., Cleveland, O., 12mo.

**Collection of Liquid Specimens in the "Preparations."**—In the Boiling-point Experiment (Experiment No. 1) you will observe the influence of radiation, superheating, etc., and this will give you an idea as to how even pure liquids behave during distillation in the ordinary apparatus. When you are making pure specimens the behavior of these pure liquids should be kept in mind. There will be a small portion passing over within 2–3° before the temperature has reached the proper boiling-point, and another small portion near the end as the temperature rises 2° or 3°. Usually in ordinary laboratory "preparation" work these first and last runnings are collected along with the major portion distilling at a constant temperature and the entire amount weighed as a specimen. Material boiling below or above these limits should be discarded. On the label state the range of temperature in which the material was collected and also give the corrected boiling-point where the temperature remained constant for a long interval.

**Sodium Residues.**—Great care should be exercised in handling residues of sodium. It should not be put into the sink or the waste jar, but should always be destroyed by adding it in *small* pieces to some alcohol or acetone in a beaker, waiting until practically all action has ceased with each piece before adding another. Then very carefully pour the solution into the sink. Also rinse the flask with alcohol or acetone before adding any water.

In the **laboratory directions** which follow, very detailed directions are given at first. Later, when the general manipulation should be well understood all the details are not given. Then the experience gained in the earlier part of the course should be properly used when necessary.

The **organic laboratory** is open during definite hours on the regular days and it is expected that students will do all their work during these specified times.

**Plan your work and work your plan!**

You can more readily show your interest in organic laboratory work by carrying it out according to well-studied plans than by dilly-dallying along at all hours and wasting your time and the time of others also!

**Don't** leave the gas, water, blast or steam turned on for *any* reason whatsoever when you leave the laboratory.

**Don't** make any unnecessary noise in the laboratory. (Please note especially in the use of the air blast.)

**Don't** forget that you will not get any more out of your work than you put into it!

## In Case of ACCIDENT or FIRE

**FIRE.—Fire extinguishers** are hung up all around the room.

In case of burning oil use the powdered **sodium bicarbonate** in the bottles on the racks.

The **blankets** are for wrapping round a person whose clothing is on fire. If necessary, use the **needle showers.**

**ACCIDENT.**—On the special shelf in the laboratory are:

**Boric acid solution, saturated,** for the **eyes.**

(Eye-cups hang below shelf.)

**Acetic acid, 1 per cent solution,** for washing alkali from the skin.

**Carron oil** (half linseed oil and half lime water), for all kinds of **burns,** including alkali and acid burns on skin. Shake well before using.

**Castor oil** for **eye burns,** especially **alkali** in the **eye.**

There is a first aid kit in the instructor's laboratory.

**ACIDS.**—On **skin:** wash with **much water** immediately, then with dilute sodium bicarbonate. Use carron oil (on shelf); on **clothing:** wash with dilute ammonium hydroxide solution.

**ALKALIES.**—In the **eye:** use saturated boric acid on shelf if injury is slight. Drop castor oil into the eye; on **skin:** wash with much water, then with dilute acetic acid, 1 per cent solution, or saturated boric acid solution. Use carron oil; on **clothing:** use some weak acid like acetic or boric, wash, and then neutralize any remaining acid with ammonium hydroxide or ammonium carbonate.

**BROMINE.**—On **skin:** wash with any solvent, like alcohol, benzene, gasolene, benzine, carbon tetrachloride, or dilute sodium bicarbonate. Then treat with carron oil or carbolated vaseline.

NOTE.—Post a copy of this sheet on the bulletin board and also give the name and telephone number of the nearest physician and the nearest hospital.

## Experiment No. 1[1]

## Determination of the Boiling-point and Standardization of the Thermometer in the Ordinary Distilling Apparatus

One of the characteristic physical constants of a liquid is its boiling-point, and a compound is generally considered pure when it distills at a constant boiling-point, under constant pressure. It may also aid in the identification of a compound. In regular laboratory work it is determined by means of a thermometer in a distilling flask and the temperature of the vapor entering the outlet tube is recorded as the boiling-point of the liquid. Obviously in this method, when the ordinary long-scale 360° thermometer is used, there are several errors, of which the following are most important: the true boiling-point is not usually found because the entire *column* of mercury is not surrounded by the vapor, the vapor is easily superheated, and the thermometer may be inaccurate. Since the boiling-point of each liquid compound prepared in the course must be determined with a fair amount of accuracy, the thermometer must be standardized at the beginning, and in order that any correction found may apply in the regular work the same general form of apparatus will be used in the standardization as in the regular work.

The error due to the cooling of the column of mercury which extends above the stopper of the flask, and therefore out of the vapor of the boiling liquid, often amounts to 6° or 7° for high-boiling liquids. It can be corrected as described in the notes at the end of the experiment, but the method of correction is open to grave errors, since it is seldom possible and not always convenient to obtain the required average temperature of the

---

[1] Have you read over the section entitled "General Notes and Suggestions"? p. 1.

exposed mercury column. Furthermore this correction varies and must be made every time a distillation is carried out. This so-called "stem correction" can be obviated by using a thermometer with a short scale and of such a size that the entire column of mercury will be surrounded by the vapors of the boiling liquid. In order that the ordinary range of boiling-points of common liquids may be covered you will use a set of three thermometers[1] each one of which has a short scale with a total range of 120°, No. 1, 15° to 135°; No. 2, 95° to 215°; No. 3, 175° to 295°. (See Fig. 1.) These thermometers "over-lap" each other by 40°, and this makes it possible to choose the one which can be employed to the best advantage. Pure liquids will be used in the tests and a comparison experiment will be made in at least one instance to show the extent of the stem correction by using both a short-scale and a long-scale thermometer[2] with the same liquid (aniline).

The error due to superheating can be made a minimum by proper heating of the liquid in the flask.

The temperature which is obtained under conditions where the errors mentioned above have been eliminated or reduced to a fraction less than the error of observation is generally considered as the *corrected boiling-point.* Such a temperature when written is followed by the abbreviation "cor." This distinguishes it from the multitude of unqualified (meaning generally uncorrected) boiling-points which unfortunately fill the literature and text-books. More corrected boiling-points are now being reported than ever before, and this is a good omen for future work. It is hoped that henceforth an unqualified boiling-point will mean a corrected boiling-point.[3] If the cor-

---

[1] The markings on solid stem thermometers often become very dim and difficult to read on account of the loss of the blackening from the fine lines. This can be remedied by rubbing a little graphite over the lines and wiping off the excess.

[2] A method of standardizing a long-scale thermometer is described in the notes, p. 20.

[3] Even this book contains some boiling-points which are unqualified, since it has not always been possible to find the data in the literature or to obtain the pure materials, etc., necessary.

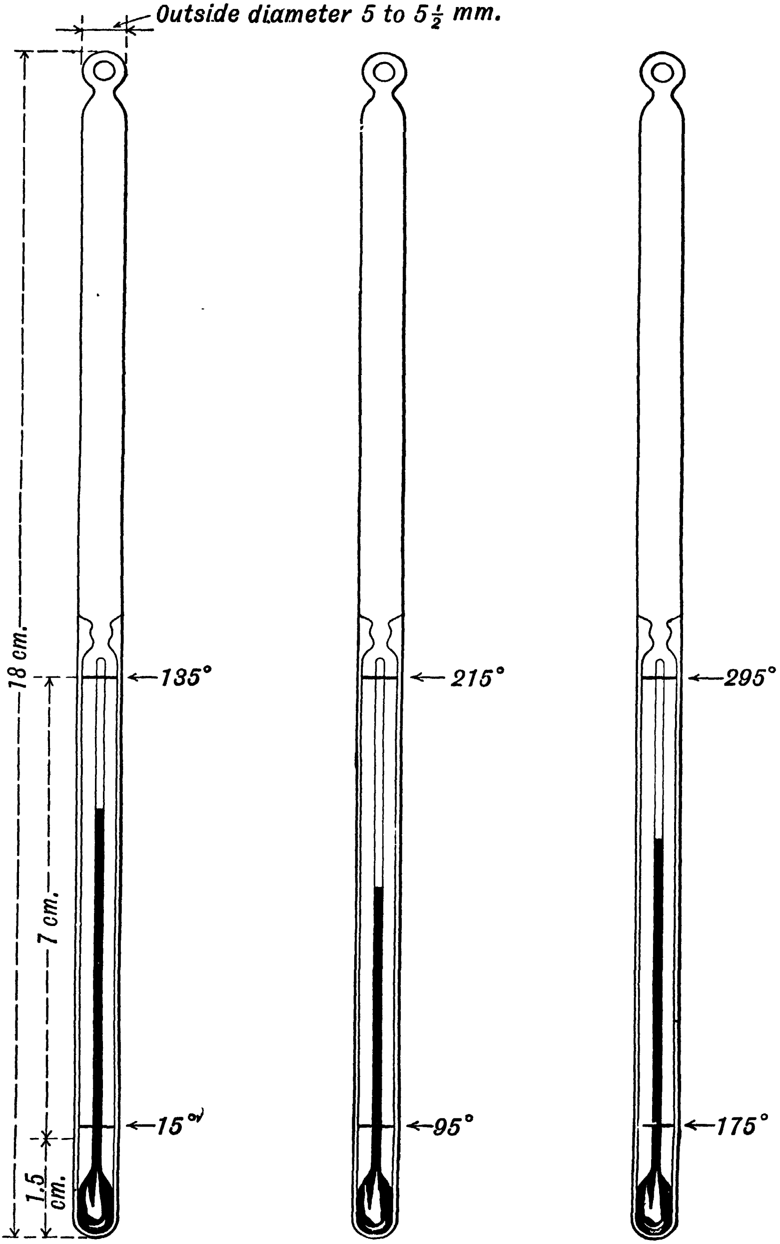


FIG. 1.—Short Scale Thermometers.
Manufactured by Eimer & Amend, N. Y., and sold under the name of Fisher Organic Thermometers.

rected boiling-point is for a pressure other than 760 mm., the pressure is placed as a subscript before the temperature, for example, "b.p. $_{735}$ 99° cor."

Set up a distilling apparatus, using a 60 cc. distilling-flask, style B (Fig. 2), and a condenser[1] with straight inner tube. Clamp the flask securely, but not too tightly, *above* the outlet tube (why?) and if possible just under the lip. (Why?) Select the thermometer which has the right temperature on the scale where it will be surrounded by the vapor of the liquid (water, in the first distillation) and fasten it in the neck of the flask with a sound well-bored cork. Fasten the outlet tube in the larger end of the condenser. The outlet tube should pass far enough into the condenser that the vapors will be delivered directly into the part of the condenser that is surrounded by the water. (Why?). Compare upper sketch in Fig. 3.

The bulb of the thermometer should be placed just *below* the outlet tube, but not in the bulb of the flask, and never in the liquid. (Why?) It must not touch the walls of the tube. (Why?) Be sure that the cork does not cover up the thermometer where the degrees must be seen. In this event raise or lower the thermometer, or cut off a *complete* portion of the cork or exchange the flask. When the short-scale thermometers are used this difficulty will seldom be encountered.

Soften the selected cork by means of a cork press. (There are cork presses on the side walls of the laboratory.) Or wrap it in a filter paper and roll it under foot. Make a hole with a *sharp* cork-borer which has a slightly smaller diameter than the desired opening. Hold the cork in the hand and turn the borer gently by means of the rod, which should be inserted through the holes in one end of the borer. In order to bore the hole straight it is often found convenient to keep turning the cork in the left hand after each slight twist of the borer, and not take the right hand from the handle of the borer at all. If the cork is placed on the desk, the borer under excessive pressure gouges out the inside of the cork and in addition plunges through to

---

[1] When the word "condenser" is used it ordinarily means a condenser with water jacket (Liebig condenser).

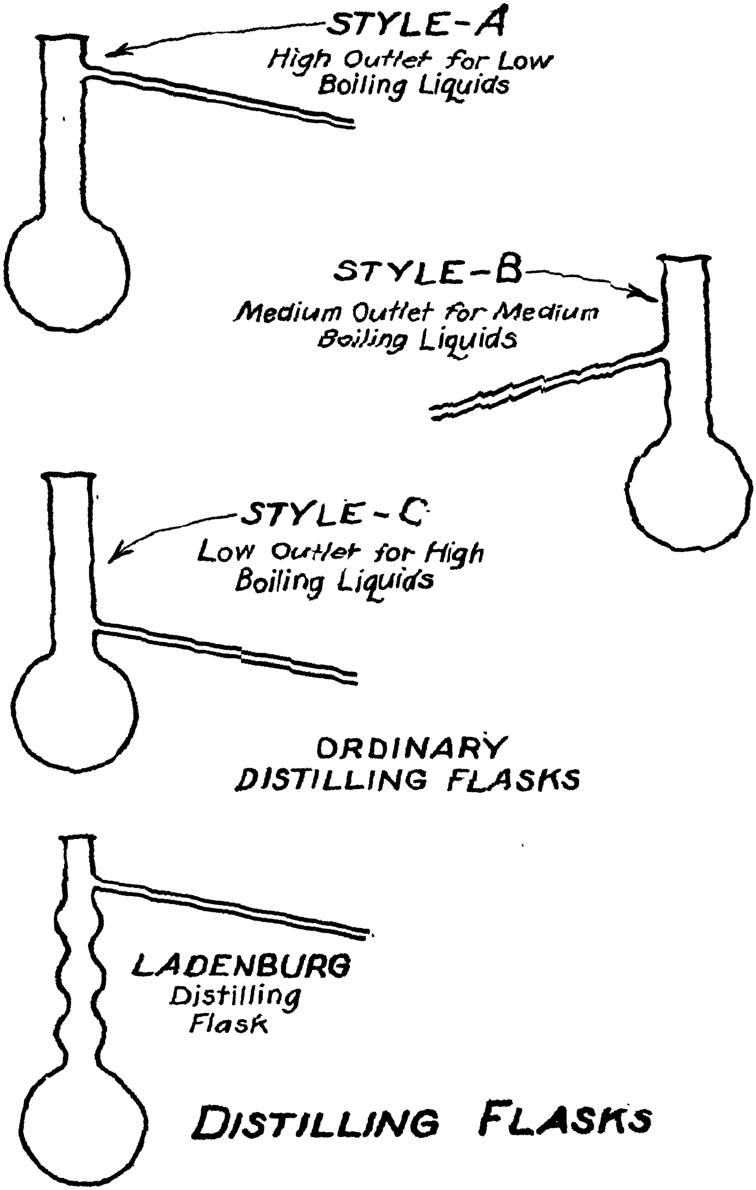

STYLE-A
High Outlet for Low Boiling Liquids
STYLE-B
Medium Outlet for Medium Boiling Liquids
STYLE-C
Low Outlet for High Boiling Liquids
ORDINARY DISTILLING FLASKS
LADENBURG Distilling Flask
DISTILLING FLASKS

FIG. 2.

the hard surface of the stone covering, and its cutting edge is ruined. As a rule it is well to pull out the borer when it is half through the cork, and push out the cork plug inside before continuing the boring. In this way a clean, even cut is made throughout. Use a rat-tail file to enlarge the opening and make it fit tightly. Place the cork on the desk and run the file back and forth, always pressing downwards and meanwhile rolling the cork. The cork should slide over the tube *with only moderate pressure.* **Never try to thrust a tube through a cork of too small aperture;** an injured finger or hand is very inconvenient, if not useless, for laboratory work. Take hold of the tube *near the cork* and twist it slowly as it is carefully forced in. It is advisable to use new corks as much as possible in organic work, and therefore a good supply of the different sizes should always be kept on hand.

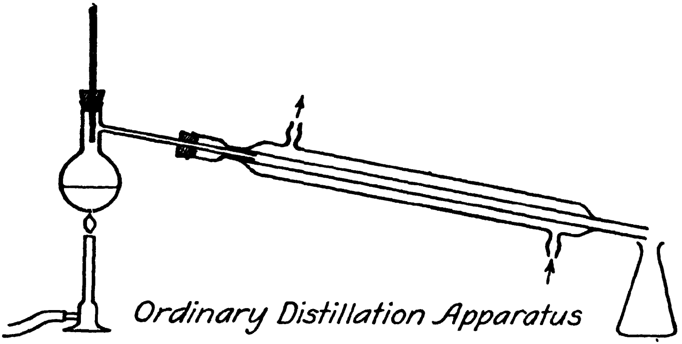
*Always remove the stopper from a flask or condenser before changing the position of any glass tube or thermometer in the hole of the stopper.*

Set the condenser at a convenient angle so that the condensed liquid will drop directly into the receiver, which should, as a rule, *rest upon the desk.* Use a large condenser clamp,[1] with the two prongs underneath, and turn the heavy base of the stand toward you where it will be underneath the condenser. The base of the stand to which the distilling-flask is attached should also be underneath the flask and turned toward you. It is not always necessary that the distilling-flask be absolutely vertical. The positions of the flask and the condenser can conveniently be arranged before connecting any parts of the apparatus by putting them in place with the upper part of the condenser in line with, but just behind, the outlet tube of the flask. Then when the apparatus has been adjusted for the proper angles, the condenser can be slid down through the large clamp and then brought up around the outlet tube of the distilling-flask and fastened.

In case it is desired to disconnect the distilling-flask with-

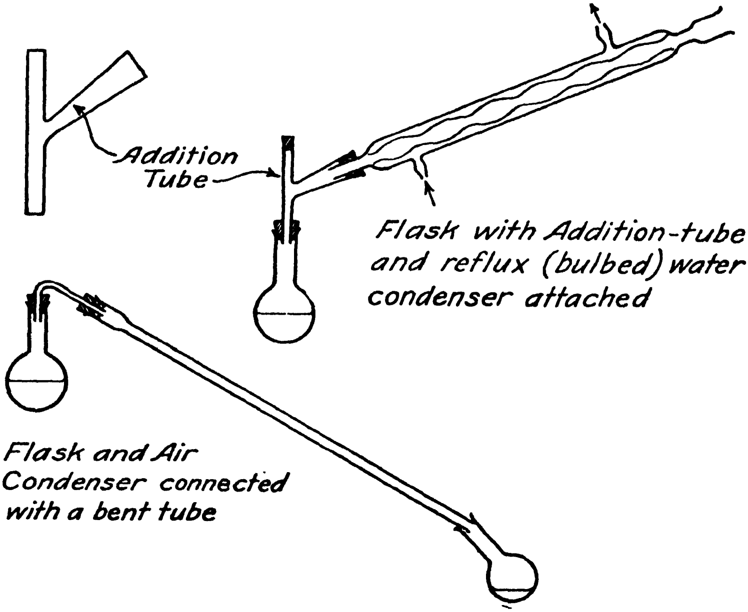
---

[1] The prongs of all clamps should be protected with white rubber tubing or strips of cork or felt.



Ordinary Distillation Apparatus

With Liebig straight water condenser and Erlenmeyer flask as receiver



Flask with Addition-tube and reflux (bulbed) water condenser attached

Flask and Air Condenser connected with a bent tube

Calcium Chloride Tube

FIG. 3.

out changing the clamps and adjustments, it is easier to do this by loosening the stopper in the upper part of the condenser and allowing the condenser to slide down through the large clamp *before* removing the distilling-flask, rather than to disarrange the setting of the clamps and stands by taking away the distilling-flask first. After the distilling-flask is ready, with fittings made, etc., and clamped in the original position, the condenser can then readily be replaced and connected without changing the angle and main position of any clamp.

The upper outlet for water from the condenser should be *above* the jacket so as to give the maximum condensing surface since the condenser will then be full of water. It should be somewhat slanted so that the rubber tube which carries the waste water will not kink. The rubber tubes slip on easily if a drop of water is used as a lubricant or if moistened by means of the breath.

Use a small Erlenmeyer flask as the receiver.[1]

Add 15 cc. of distilled water to the distilling-flask, using a funnel whose stem reaches *below* the opening of the outlet tube, and drop in several small pieces, not dust particles, of porous tile to prevent bumping. Heat the flask directly[2] with a small blue flame[3] not over 1 cm. in height, giving it a rotary motion at first, and hold the burner obliquely so that in case the flask breaks the hand will not be in danger. When the liquid distills regularly the burner should be set directly underneath and *with the flame touching the flask.* Do not heat the surface above the liquid as this will superheat the vapors. Avoid drafts; use a conical metal shield chimney for the burner or a large wind shield for the apparatus.

The temperature will rise rapidly at first until near the

---

[1] Such a receiver should never be fastened to the condenser by means of a stopper. (Why?)

[2] When a larger flask is used, as in some of the later experiments, it is protected with a wire gauze when being heated. This method, however, generally tends to superheat the vapor and therefore gives high results in distillations.

[3] Such a small flame can easily be obtained by cutting down the supply of air at the same time that the gas supply is lowered. Always regulate the gas supply (of the Tirrill burner) by means of the set screw at the base.

boiling-point of the substance, and then slowly until finally it will remain practically constant. Distill over at least one-half of the liquid.[1] The constant temperature within one-half of one degree at which most, if not all, of it distills is noted as the *observed* boiling-point. Toward the end of the distillation the temperature may rise slightly on account of superheating. Record the corrected barometer[2] reading also.

NOTE: *The salient points in connection with carrying out a distillation are a stable and well set-up apparatus, with receiver resting upon the desk, the thermometer properly placed, corks well bored, and a small-sized flame used in the right way to prevent superheating.*

Next, carry out another distillation, using the same amount of pure aniline, 184.4° cor., under the same general conditions, except that the water condenser is replaced with an "air" condenser[3] and a style C distilling-flask (Fig. 2) is used instead of style B. A water condenser with no water in it should not be used in place of the "air" condenser because of the danger of cracking at the joints. A flask with a low outlet tube is used for high-boiling liquids in order to avoid too much condensation and on this account excessive heating which causes a partial decomposition of the substance. The distilling-flask and condenser must be clean and *dry*, and fresh porous tiling should be used as before.

In order to dry a piece of apparatus rapidly, rinse it with alcohol and then with ether (keep all flames away). To remove the ether vapors connect a glass tube leading almost to the bottom of the flask with the suction or the blast. Since the air from the blast is likely to be contaminated with iron dust,

---

[1] The effect of superheating upon the temperature of the boiling-point can be seen if all the liquid is distilled over. There is practically no danger of cracking the flask if it is made of Pyrex glass.

[2] For correcting the barometer reading see p. 300.

[3] An air condenser is a long, straight, thin glass tube of 1.0–1.5 cm. diameter. The inner tube of a Liebig water condenser makes a very convenient air condenser (see Fig. 3). It is used when the substance boils above about 150–160°. If a substance solidifies readily it would clog the condenser, and is therefore collected directly from the end of the outlet tube. Compare Expt. No. 51, phenol.

oil, moisture, etc., it is better to use the suction. The wash alcohol and ether can be used again, and should be placed in bottles properly labeled and kept for this purpose. Acetone may be used instead of the alcohol-ether combination.

The substance distilled may have absorbed a little moisture in the handling, etc. This will be evidenced by a turbidity in the first runnings.[1]

Repeat the distillation with pure aniline, but this time use an ordinary long-scale 360° thermometer instead of the short-scale thermometer. Compare the temperature obtained in each case.

Since the boiling-point varies with the air pressure a correction must be applied unless the barometer shows 760 mm. For non-associated liquids, the correction[2] for a difference of *every* 10 mm. in pressure, in the *vicinity* of 760 mm., may be found by dividing the absolute temperature of the boiling-point by 850, that is,

$$\text{Corrected observed b.-p.} = \text{temp. of obs. b.-p.} + \left(\frac{273 + \text{temp. of obs. b.-p.}}{850} \times \frac{760 - \text{cor. barometric reading}}{10}\right).$$

For associated liquids, such as alcohols, acids, and hydroxyl compounds generally, divide by 1020, instead of 850. Water is an associated liquid, and aniline is a non-associated liquid.

For a more complete standardization, two temperatures, one near the bottom and one somewhat near the top of the scale of each of the three thermometers, should be checked up. The following combinations of liquids, all of which are found in the list given below, can be used: For thermometer No. 1, chloroform and water; for No. 2, water and aniline; and for No. 3, aniline and quinoline.

The following is a list[3] of liquids which when pure are suitable for testing the accuracy of thermometers at the *corrected* temperatures for 760 mm. given:

---

[1] Regarding the absorption of moisture by pure liquids when handled in ordinary operations, compare Young and Fortey, *Trans. Chem. Soc.*, **83** (1903), 65.

[2] Alex. Smith and Menzies, *Journ. Amer. Chem. Soc.*, **32** (1910), 907.

[3] Compare Young, "Fractional Distillation," 10.

| | |
|---|---|
| Carbon bisulfide[1] | 46.0° |
| Chloroform | 61.3° |
| Benzene | 80.2° |
| Water[2] | 100.0° |
| Ethylene dibromide | 131.2° |
| Chlorbenzene | 131.95° |
| Brombenzene[3] | 155.5° |
| Aniline | 184.4° |
| Nitrobenzene | 210.9° |
| Naphthalene | 218.0° |
| Quinoline | 237.5° |
| α-Bromaphthalene | 280.4° |
| Benzophenone | 305.9° |
| Mercury | 356.8° |

### NOTES ON BOILING-POINT AND DISTILLATION

1. The boiling-point of a liquid is that temperature at which the saturated vapor pressure of the liquid becomes equal to the external pressure, and usually this external pressure is the atmospheric pressure.

"The true boiling-point of a liquid is identical with the condensing-point of its vapor under the same pressure, provided that some liquid is present and that the vapor is not mixed with an indifferent gas or vapor, and it is generally more convenient to measure the condensing-point of the vapor than the boiling-point of the liquid. To do this an ordinary distillation bulb is generally employed." Young: "Fractional Distillation," p. 26.

"The correct boiling-point of a liquid at atmospheric pressure is best determined by wrapping cotton-wool, or, if the liquid attacks that substance, asbestos, round the bulb of the thermometer. By

---

[1] Carbon bisulfide is very inflammable and great care must be exercised in handling and distilling it. A bath of warm water can be used for heating it, but the vapor should not be superheated.

[2] Water is the only associated liquid in this list.

[3] Considerable difficulty has been encountered recently in obtaining brombenzene of the desired purity. That on the market is probably all prepared by direct bromination of benzene which was not properly purified. Preparation on a small scale from pure aniline by Sandmeyer's reaction is recommended.

this plan, even though the vapor may be superheated, yet the liquid in contact with the thermometer bulb must be at the true boiling-point, since it has a free surface of evaporation." Ramsay and Young, *Trans. Chem. Soc.*, **47**, (1885), 42. Compare Cottrell, "On the Determination of Boiling-points of Solutions," *Journ. Amer. Chem. Soc.*, **41** (1919), 721–9; and Washburn and Read, "The Laws of 'Concentrated' Solutions, VI, The General Boiling-point Law," *ibid.*, **41** (1919), 729–41. Figures of a special apparatus are given in both articles.

For the determination of correct boiling-points a special form of apparatus is used in which all possible errors from superheating, radiation, etc., are provided against. Short-scale thermometers which are made of normal glass and which have been properly standardized are employed. Normal glass is a special glass that has been aged by suitable treatment of heating, etc., until its behavior on further heating and cooling has become uniform. Such thermometers can be obtained with certificates showing the results of standardization by certain bureaus of different governments, like the U. S. Bureau of Standards.

2. A liquid ought to boil as soon as its vapor pressure becomes slightly greater than atmospheric, but it is a well-known fact that boiling does not necessarily take place under these conditions. Most liquids can readily be superheated.[1] The transformation of a liquid into the vapor phase will, however, take place *immediately* if the vapor phase—any inert gas—be introduced, but *not* otherwise.[2] For comparison we have the supercooling of a liquid which will solidify as soon as a particle of the solid phase is added, for example, ice in supercooled water.

Superheating cannot take place at the surface of a liquid since there the liquid is always in contact with the vapor phase. It always takes place in the interior and especially at the bottom where the heat is applied. It is of course not possible to go an unlimited distance into the metastable "area," since the further away we get

---

[1] It is of interest to note that chloroform, which ordinarily boils at 61°, has been heated to a temperature of 100° by suspending the drops in a zinc chloride solution of the same specific gravity, and that water has similarly been heated to 170° by suspending it in a mixture of oils. (Dufour, *Arch. de la Bibl. univ.* (1861) T. XII, 210; and *Poggendorf's Annalen*, **124** (1865), 295.)

[2] Aitken, "On boiling, condensing, freezing, and melting," *Trans. Royal Scottish Society of Arts*, **9** (1875), 240–87; Duhem, "Thermodynamics and Chemistry," trans. by Burgess, (1913), 365–8.

from equilibrium the greater is the tendency for the system to come to equilibrium. Finally this tendency will become so great that the system will be able to overcome its reluctance to a change of phase, vaporization will then take place suddenly and sometimes with great violence—in other words, **bumping** occurs. Stirring[1] helps to prevent bumping, since the liquid is thus evenly heated and vaporization will take place readily at the surface, as mentioned above. The best means to prevent bumping is to introduce the vapor phase directly, and this is done in several ways. (1) By passing a stream of air bubbles through a capillary tube into the liquid (see Expt. No. 15, Vacuum Distillation). (2) Another method which is very convenient for a short period is to place in the liquid a small glass tube, about 1 mm. in diameter and sealed at one end. It should be long enough to stand upright, and when in position the open end should be at the bottom. On warming the liquid the air in the tube expands and bubbles through the liquid. If the distillation is interrupted, a new tube must be introduced. (3) By using pieces of porous tiling which contains a large amount of air. Pumice cannot be used so well, since it floats in most liquids and therefore does not introduce the air bubbles at the seat of the trouble. Glass beads, and many substances with "points" are often used to prevent bumping, but their efficiency does not depend upon their "points," but upon the air which is adsorbed on their surfaces. As soon as this air has been driven off they are no longer of any use, unless they are removed, dried and heated before being used again.[2] Even platinum "triangles" after a time must be removed, heated, and allowed to cool in the air before being introduced again.[3] Fine particles of any sub-

---

[1] Morgan, "The Elements of Physical Chemistry," 5th Ed., (1914), 178.

[2] Ostwald-Luther, "Physiko-chemische Messungen," 3. Auflage, (1910) 219; Lehmann, "Molekularphysik," (1889), II, 151.

[3] E. C. Kendall, in a recent note, *Journ. Amer. Chem. Soc.*, **41** (1919), 1189, states that carbon in certain forms is an excellent aid to produce rapid boiling. "It was found, however, that the various forms of carbon differ greatly in their power to cause rapid boiling of a solution. While powdered charcoal or coke has slight power in this respec , anthracite coal is without exception the very best substance to bring about the rapid boiling of a solution. The formation of bubbles does not take place on the sharp edges and corners alone, but over the hard, smooth surfaces of the coal minute bubbles form with great rapidity, and under some conditions a piece of coal 2 cm. cube can be raised from the bottom of the flask by the rapid formation of bubbles on its surface. It acts in a similar manner in the acidification of a carbonate or sulfite solution. . . . . If the coal is kept under water indefinitely it becomes less active, but heating in an oven will

stance rapidly lose their adsorbed air and then they increase the tendency to bumping instead of decreasing it.[1]

3. The "stem correction," in degrees $= +N(t-t')0.000154$,

where $N$ = that portion of the mercury column which is not heated by the vapors, read in degrees;

$t$ = observed boiling temperature;

$t'$ = average temperature of the exposed column of mercury as found by a second thermometer hung beside the first one;

0.000154 = coefficient of apparent expansion of mercury in glass.

4. Standardization of a long-scale thermometer.

A long-scale thermometer is standardized by locating certain points found by means of the boiling-points of pure liquids such as those on p. 17, and also the freezing-point of water, and then by plotting these results on co-ordinate paper the correction for any one degree may be read off at any time. The correction is of course larger as the boiling-point increases, and often amounts to several degrees for higher-boiling liquids. The results are applicable only for the particular distilling flasks used in obtaining the data.

On a piece of cross-section millimeter paper, 100×300 mm., mark on the lowest heavy horizontal line as the abscissa the degrees of the thermometer every 50°, counting each millimeter as a degree. The corrections are generally to be added, and are therefore plotted above the main line. If any minus corrections are found, the heavy horizontal line chosen must, of course, be far enough above the bottom of the sheet to allow space for the proper corrections. The amount of the correction, that is, the difference between the "corrected observed reading" and the true boiling-point at 760 mm., is plotted on a perpendicular line as an ordinate, opposite the number on the abscissa corresponding to the "corrected observed reading," and counting each centimeter as a degree. Connect the four points thus found with a smooth curved line. From this curve it is now possible to tell at a glance the correction for any degree as follows: add to the corrected observed reading the difference in degrees between the main abscissa at the point of the corrected observed reading and the point where its ordinate cuts the curve.

---

restore its activity. . . . One or two pieces of about 1 cm. cube are better than many smaller pieces."

[1] I am indebted to a "seminar" paper on "Bumping" by Mr. Harold L. Simons for most of the material presented in Note 2.

Put all the data used in the plotting in a convenient corner of the same paper for reference.

The curve between 155° and 180° is not very accurate if the style of flask was changed. Explain. Mark the standardized thermometer for future identification with a piece of cord or wire in the loop.

## QUESTIONS

1. Define the boiling-point.
2. Give some of the errors in the ordinary method for determining the boiling-point.
3. What is a standardized thermometer? a normal thermometer?
4. How is the true boiling-point determined?
5. How may this be done for ordinary laboratory conditions?
6. What is meant by the "stem correction"? How is the "stem correction" determined practically? How can it be obviated?
7. Why should a cork be softened before using?
8. When are the different styles (A, B and C) of distilling-flasks used?
9. Why not place the bulb of the thermometer in the liquid?
10. Why is the flame given a rotary motion at first?
11. Explain how the porous tiling aids the boiling.
12. Why should porous tiling not be added to a hot liquid?
13. What is meant by an "associated" liquid? A "non-associated" liquid?
14. Why is water used in the condenser? Could mercury be used?
15. When the same quantities of water and aniline are each separately distilled from the same flask under identical conditions using the same size flame, etc., why does the aniline distill faster than the water even though it has a higher boiling-point? (This behavior is particularly noticeable in the case of brombenzene.)
16. After the plot for the corrections has been made could it be used for finding the correction if a distilling-flask of different style and size were used instead of one of the style and size used when the plot was made?

## Experiment No. 2

### FRACTIONAL DISTILLATION

### Fractionation of a Mixture of Ethyl Alcohol and Water

Measure separately in a graduated cylinder 50 cc. of ethyl[1] alcohol (95 per cent) and 50 cc. of distilled water and mix the two liquids in a beaker. Note the temperature of the mixture, cool to the temperature of the room by setting the beaker in water and then measure its volume again. Is it exactly 100 cc.? Place 1 cc. of the cooled liquid into an evaporating dish and apply a flame *momentarily*. Do not heat it. Does it catch fire? Transfer the dilute alcohol to a clean dry 125-cc. Ladenburg distilling flask,[2] add several small pieces of porous tile, insert a thermometer, and connect the outlet-tube with a condenser having a straight inner tube. Make two fractionations.

**First Fractionation.**—This will consist of four fractions. For receivers use clean dry Erlenmeyer flasks, two 125-cc. and two 60-cc., and label them from 1 to 4, using the larger ones for the first and last fractions. Have corks ready to fit. The temperature intervals at which the fractions are collected, as usually taken, are approximately equal. The number of fractions depends on the substances and the degree of separation desired. In this experiment allow all that comes over up to 83° to flow into the receiver labeled No. 1. When the temperature begins to exceed 83° exchange the receiver for No. 2, and collect the fraction up to 89°, similarly for No. 3, 89+° to 96°, and No. 4, 96+° to 100+°.

---

[1] Ordinary alcohol is ethyl alcohol.

[2] A sketch of the Ladenburg distilling flask is given in Fig. 2. It consists of a distilling flask and a simple still head (or fractionating column) combined. For supporting such a round-bottomed flask when unattached, use a suberite (pressed cork) ring.

Heat the flask first with a rotary motion of the burner. Use a small non-luminous flame not more than 2 cm. long. When the liquid is distilling regularly, set the burner directly under the center of the flask with the flame *touching* and do not remove it during the entire distillation. The drops of the distillate should form regularly and at such a rate that they can easily be counted, 90-100 a minute. Keep up this rate by very gradually increasing the flame. The distillation takes about thirty minutes. The slower the distillation the better is the separation. On account of superheating, the temperature may go slightly above 100° toward the end. It is not necessary to distill over all the remaining portion. Add it to receiver No. 4, cool under running water, and then measure the amount at the ordinary temperature.

Measure the volume of each fraction, and tabulate the results according to the following scheme:

| Fraction | I | II | III | IV |
|---|---|---|---|---|
| Temperature | Up to 83° | 83+° to 89° | 89+° to 96° | 96+° to 100+° |
| Volume | 20 cc. | 31 cc. | 8 cc. | 40 cc. |

**Second Fractionation.**—To make a further separation distill the fractions one after another according to the following procedure: Clean out the distilling-flask and pour into it the first fraction. After adding some new porous tile distill as above, collecting the distillate up to 83° in receiver No. 1. As the temperature begins to rise above 83°, although there will still be some liquid in the flask, interrupt the distillation by removing the burner. When the flask is cool add to it fraction No. 2, and again distill until the temperature just exceeds 83°, collecting this distillate in the same receiver, No. 1. Now add similarly No. 3, and finally No. 4, collecting in each case all that distills up to 83° in receiver No. 1. After No. 4 has been added do not stop the distillation at 83° but continue as in the first fractionation, and collect the distillates in receivers 2, 3 and 4, at the same temperature intervals as before.

The new results will appear somewhat as follows:

| Fraction | I | II | III | IV |
|---|---|---|---|---|
| Temperature | Up to 83° | 83+° to 89° | 89+° to 96° | 96+° to 100° |
| Volume | 47 cc. | 0.5 cc. | 7.5 cc. | 43.5 cc. |

Apply a flame to fraction No. 1. Does it kindle now?

A third fractionation made as described under the second fractionation would lead to a more thorough separation because of the altered composition of the fractions. Furthermore, any single fraction may be subjected to a similar process of fractionation by means of which its separation into alcohol and water could be made more nearly complete.

A mixture of ethyl alcohol and water containing 95.57 per cent of alcohol by weight has a minimum boiling-point, 78.15° (760 mm.), so that it is not possible by distillation alone to make a separation beyond this point. Pure alcohol boils at 78.30°. Alcohol of 90.7 per cent has the same boiling-point as pure alcohol.

## NOTE

The results given in the tables were obtained under the conditions described above, that is, the distillate came over at the rate of about 90–100 drops a minute. Under similar conditions, but using an ordinary distilling flask instead of the Ladenburg distilling flask, the results are somewhat as follows: First fractionation, 12, 31, 8, 40 cc., and second fractionation: 40, 2, 10 and 41 cc., respectively.

References for collateral reading on the fractionation of liquids which mix in all proportions: Morgan, "The Elements of Physical Chemistry," 5th Ed. (1918), 177; Walker, "Introduction to Physical Chemistry," 7th Ed. (1913), 84–6; Washburn, "Principles of Physical Chemistry," (1915), 180–1.

Alex. Smith, "Introduction to Inorganic Chemistry," New Ed. (1917), fractionation, 587–8; alcohol and water, 609; other constant boiling mixtures, 211–2, 273, 279.

For the boiling-point curve of mixtures of ethyl alcohol and water, see W. A. Noyes and Warfel, *Journ. Amer. Chem. Soc.*, **23** (1901) 468.

A still-head described by S. F. Dufton in an article on "The limits of separation by fractional distillation," *Journ. Soc. Chem. Ind.*, **38** (1919), 45, is said to be unusually efficient.

## QUESTIONS

1. Outline the theory of fractional distillation.
2. Discuss the fractional distillation of the three different cases of liquids which mix in all proportions.
3. Explain why pure alcohol is not obtained (See No. 2).
4. Of about what percentage alcohol does the first fraction of the second fractionation consist?
5. Why is the burner not removed after the distillation has begun?
6. Would the first fraction be increased or diminished if the flask was protected with a wire gauze during the heating?
7. What is a "still-head" or fractionation apparatus? See Fig. 4. Why used?

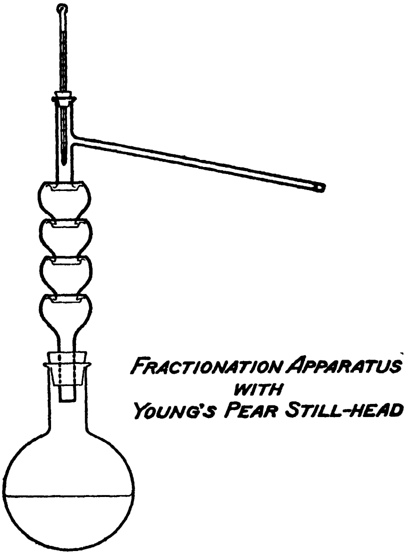


FIG. 4.

## Experiment No. 3

## Absolute Alcohol

The presence of water in alcohol may be shown by shaking 3 cc. with a very little white anhydrous copper sulfate in a dry well-stoppered No. 1 test-tube. After half an hour note any change in the copper sulfate. Explain.

In the following experiment, ordinary 95 per cent ethyl alcohol is dehydrated over quicklime (CaO). It is then distilled from the semi-solid residue and collected under anhydrous conditions.

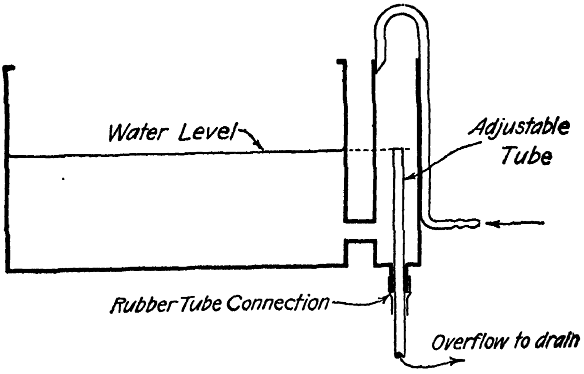
To a 1000-cc. flask attach the narrow end of a slanting condenser with bulbed inner tube ("reflux" condenser). (Compare Fig. 3.) The end of the tube should pass entirely through the cork so that the condensed liquid will drop free without touching the cork. This is a general rule always to be followed under similar conditions. If there is a small hole near the end of your condenser see that it is below the stopper. (What is the object of this small hole?) Arrange the apparatus so that the flask can be heated on the steam-bath.[1] Pour 300 cc. of ordinary alcohol into the flask, slant it and add about 150 grams of good quicklime, well crushed. (It should not be powdered.) Connect, and heat for an hour. During this time the alcohol will boil gently. If it condenses rapidly and the liquid rises in the condenser, lower the temperature of the bath slightly, and if necessary pour water over the flask. During the heating it is well to attach the filled calcium chloride tube mentioned below. (Why?)

---

[1] If a steam-bath is not handy or in working order, use a constant-level water-bath (Fig. 5). When working with inflammable liquids the flame under the water-bath should be enclosed in a chamber surrounded by a wire screen, in other words, a "safety water-bath" should be used.

If the alcohol is allowed to remain in contact with the lime for two or three days, heating for one-half hour will be sufficient before the absolute alcohol is distilled.

Prepare a calcium chloride tube[1] by first inserting a loose plug of glass wool or cotton into the bulb (not the narrow tube) and then almost filling the tube with small lumps of granular calcium chloride, free from dust particles, and covering this with another plug of glass wool or cotton. To keep the contents in place, and also to prevent an undue circulation of air, insert a cork containing a short piece of glass tubing open at both ends. If the apparatus is allowed to stand overnight, place the calcium chloride tube in the top of the condenser, fastening the narrow end in a cork.



CONSTANT LEVEL WATER BATH
CROSS SECTION

FIG. 5.

Also make ready a condenser with straight inner tube, dry inside, and a bent glass tube for connecting the flask with the larger end of the condenser in the position for distillation. The bend of the tube should be *just above* the cork stopper, and the tube should be cut off just below the stopper. (Why?) For the receiver attach a clean dry Erlenmeyer filter-flask by means

---

[1] See Fig. 3.

of a cork to the lower end of the condenser and connect its side tube with the narrow end of the calcium chloride tube by means of rubber tubing. Do not close this tube with a stopper during the distillation. (Why?) The receiver should rest upon the desk when the apparatus is ready for use.

**Bending Glass Tubing.**—Hold the dry tube lengthwise in the spreading even flame of a wing-top burner. If the wing-top does not give an even flame it should be exchanged or repaired. Keep turning the tube until it is soft, then *remove* it from the flame and bend to the desired angle. The bend should be round and strong, never angular. If the tube is thick or large it must be heated in the smoky flame. Always "round" the rough edges of *all* glass tubes by holding them in the flame until the edges have melted. This also applies to stirring-rods.

At the end of the hour cool the contents of the flask by allowing a stream of cold water to play upon the flask, which should be raised slightly in order that the waste water will run into the bath. When the alcohol ceases to boil, connect the flask as outlined above for distillation, and distill until no more drops come over, heating the flask on the steam-bath. Collect the first 10 cc. in an open, unattached test-tube, and the remainder in the filter-flask. Test the 10-cc. portion and a portion of the main distillate for moisture. (?) The distillation may be hastened by covering the flask and bent tube with a towel to prevent radiation. Sometimes the liquid bumps furiously, since all the air has been driven out of the lime. (Compare the Boiling-point Experiment, Note 2.) In this case, cool thoroughly, add a few pieces of porous tile, then heat again.

Keep the absolute alcohol in a dry, labeled bottle. It will be needed for later experiments.

Do not empty the waste lime into the sink!

## QUESTIONS

1. What is formed in the test for water in alcohol?
2. Why is a bulbed condenser preferable to a straight condenser for reflux work?

3. Why is the bulbed condenser not used for the distillation? Could it be used at all?
4. Why should the quicklime not be powdered? (Compare Note 2, p. 18.)
5. Why is a calcium chloride tube necessary?
6. Why must the calcium chloride tube not be stoppered with a cork?
7. Why is the first 10 cc. of the distillate discarded?
8. Does every part of the distillate as it drips from the condenser contain the same percentage of alcohol? Explain fully. (Compare with the curves showing the boiling-point and composition of the different mixtures of alcohol and water: see Walker's "Introduction to Physical Chemistry," 7th Ed. (1913), 85.)
9. Is the "absolute alcohol" prepared in this way absolutely free from water?
10. How can the driest ethyl alcohol be prepared?
11. Why cannot the following drying agents be used: calcium chloride; conc. sulfuric acid; phosphoric anhydride; solid potassium hydroxide?

## Experiment No. 4

## Tests for Carbon and Hydrogen in Organic Compounds

1. Effect of heat alone on an organic substance: *a.* Place a little cane sugar in a porcelain evaporating dish and heat gently with a small blue flame.

*b.* Repeat the above experiment, using benzoic acid instead of cane sugar. By using a small flame all the substance will sublime without charring, or leaving a residue. (The fumes produce coughing when breathed.)

2. Carbon and Hydrogen can be detected in organic compounds by oxidation:

In a porcelain evaporating dish dry about 2 grams of cupric oxide powder by heating to dull redness for several minutes. While it is cooling, heat a piece of glass tubing (6 mm.) about 15 cm. long in the Bunsen flame at a point 10 cm. from the end, and as it softens slowly draw it out and seal it. Intimately mix a *very small* amount of benzoic acid (from the end of a knife blade) with half the warm cupric oxide, transfer this to the 10 cm. sealed tube and add the remaining cupric oxide. Tap the tube horizontally on the desk so as to make a channel above the mixture and clamp it near the open end in a horizontal position. Connect it with a *short* piece of rubber tubing to another length of glass tubing bent at right angles and leading just below the surface of 3 cc. of clear lime water contained in a No. 1 test-tube. Now gently heat the layer of pure cupric oxide and then the mixture. What evidence is there of the formation of water and of carbon dioxide?

### QUESTIONS

1. What is sublimation?
2. Why is the glass tube not sealed by simply melting the edges together?
3. What causes the reddish-brown color in the tube after the heating?
4. How are carbon and hydrogen determined quantitatively?

## Experiment No. 5

### FORMATION OF A PARAFFIN HYDROCARBON BY REDUCTION OF A HALOGEN DERIVATIVE

### Methane from Chloroform and Chemical Properties of the Paraffin Hydrocarbons

Fasten a 125 cc. Erlenmeyer flask upright with a clamp, and place into it 10 grams of zinc dust[1] and 15 cc. of alcohol and 10 cc. of water. Insert a bent glass tube through a well-bored tight-fitting cork and connect with a short tube leading to a beaker or small pail of water arranged so that the gas that is formed may be collected by displacement. Now add to the flask 5 cc. of chloroform and 2 cc. of a $\frac{1}{80}$ molar solution of copper sulfate. The reaction will soon begin spontaneously. It may even be necessary to moderate it by cooling the flask with some water. Collect two test-tubes of the gas, discarding the first one, and then in addition fill two[2] glass-stoppered bottles of the capacity of the test-tubes.

*a.* Ignite the gas in the test-tube (Wrap the test-tube in a towel before doing so, because if the methane contains air an explosion might result of sufficient violence to shatter the tube.) Immediately after the gas is burned add 2 cc. of lime water, stopper and shake. What causes the turbidity of the solution? Why does the gas made by this method burn with a green flame? Is this characteristic of pure methane?

*b.* To a bottle of the gas add 2 cc. of bromine water and shake. Is there any change in color? Explain.

*c.* To 5 cc. of benzine ("benzolene," not benzene, see Note 1) add 1 cc. of a solution of 5 grams of bromine in 100 grams of

---

[1] See Note regarding weighing out chemicals, p. 3.

[2] One extra, in case a second trial of one of the tests is required.

carbon tetrachloride. Divide into two portions, set one in the dark and the other in direct sunlight. After several minutes compare them. What has happened in the one exposed to sunlight? Breathe across the top of the tubes. What does the formation of a cloud of vapor indicate?

*d.* Stability of paraffins toward reagents:

1. Add several drops of benzine to 1 cc. of conc. sulfuric acid. Shake. Is there any evidence of chemical action apparent by the formation of heat or by darkening? Does the mixture become homogeneous? Pour it slowly into cold water, cool further if necessary, stir, and then pour it into a *small* (No. 1) test-tube. Is a homogeneous solution obtained?

2. Repeat, using fuming sulfuric acid. Be careful when pouring the solution into water. Do so drop by drop. Pour upon ice if possible. (?)

3. Repeat, using conc. nitric acid. (?)

4. To 1 cc. of a *very* dilute solution of potassium permanganate (just rose color) add several drops of benzine. Shake. (Do not use a cork stopper.) Do you notice any change?

The above general reactions with bromine, sulfuric acid, nitric acid, and permanganate are given not only for showing the inertness of the paraffins, but also for laying the foundation of a general comparison of the properties of other types of hydrocarbons as shown by their reactions toward these same reagents. See under ethylene, acetylene, and benzene.

## NOTES

1. The benzine used in the above tests is a fraction of petroleum usually taken between 70° and 80°. It must not be confounded with benzene, $C_6H_6$, which boils at 82°. The compounds in pure benzine will react only *very slowly* with fuming sulfuric acid and the sulfonic acids formed are, like most sulfonic acids, soluble in water. The *ordinary* benzine sometimes contains impurities, probably "unsaturated" hydrocarbons formed in the large-scale distillation, and these substances are *rapidly* attacked by even conc. sulfuric acid and charred. These things must be borne in mind when interpreting the results in this particular case.

Since benzine and benzene are both pronounced the same, confusion as to which is meant often arises. Therefore it has been well suggested that the term "benzolene," which corresponds to the neighboring fraction, gasolene, be used instead of "benzine."

2. Opening sealed bottles: Wrap a towel around the bottle, leaving the neck exposed, and make a file mark on the neck. Then melt the end of a stirring rod in the flame and immediately touch the file mark with the melted glass. Generally this causes the glass tube to crack. If this fails the end of the neck may be knocked off with a sharp blow of the file. In any case, the bottle should be held over a casserole or beaker so that if the bottle is cracked the contents will do no damage. The fuming acid may be kept for a short time for laboratory use in a small glass-stoppered bottle.

3. Opening bromine bottles: The glass stoppers in bromine bottles are often "frozen" and are difficult to remove. If the method given in the general notes, p. 4, does not prove effective, the neck of the bottle must be broken off. Have ready a funnel large enough to hold the entire bottle, supported in a stand, and another bottle underneath ready to receive the bromine, all set near the draft pipe. Make a file mark around the neck, wrap the bottle all over with a towel, and while it is securely held in an upright position strike the top a sharp blow with the file or a small hammer. Carefully remove the towel, protect the hand with a towel or glove, and pour the contents into the funnel. Be sure that you hold the bottle in such a way that the bromine will not run down on your fingers, and hold the entire bottle over the funnel in order that none will run outside See p. 6 for treatment of bromine burns.

## QUESTIONS

1. What is the purpose of the copper sulfate solution?
2. Why is alcohol added to the mixture of zinc dust, etc.?
3. Why is the first test-tube of the gas discarded?
4. Why is carbon tetrachloride used as a solvent for bromine in these tests instead of water? (Noyes and Mulliken, "Class Reactions and Identification of Organic Substances," 3d Ed. (1915), 8.)
5. What is the object of pouring the mixture of benzolene and conc. $H_2SO_4$ into water? (Compare properties of sulfonic acids.) Why is a "*small*, No. 1, test-tube" used?
6. Are the paraffins ever acted upon by $H_2SO_4$ or $HNO_3$?

7. Give two other general methods (applicable to the entire paraffin series) of forming ethane.
8. Why must a cork stopper not be used when making the permanganate test?
9. What is the main constituent of the benzolene used? Could it be obtained pure by fractional distillation?
10. Why does the gas as prepared in this experiment burn with a green flame?

## Experiment No. 6

### FORMATION OF AN ALKYL HALIDE BY THE REPLACEMENT OF AN ALCOHOLIC HYDROXYL GROUP WITH HALOGEN

### Preparation of Ethyl Iodide from Ethyl Alcohol

To 2 grams of red phosphorus and 10 cc. of absolute ethyl alcohol in a glass-stoppered bottle add in small quantities 17 grams of powdered iodine. Shake and cool if necessary after each addition by immersion in water. Stopper the bottle and set it aside for twenty-four hours or longer. Then transfer the reaction-mixture to a small round-bottomed flask, rinse out the bottle with 2–3 cc. of absolute alcohol and add the rinsings to the main solution. Heat under a reflux condenser on the steam-bath for fifteen minutes. Then cool and dry the outside of the flask, connect with a straight water condenser by means of a bent glass tube, and distill[1] with care (without using a thermometer) until no more liquid passes over. The mixture will bump somewhat and this can more or less be avoided by keeping the flame in motion. Put the distillate into a Squibb's separatory funnel,[2] add some water and test with litmus. (?) Add a dilute solution of sodium hydroxide,[3] stopper securely and agitate gently in the following manner: Invert the funnel, holding the stopper in with one hand and placing the thumb

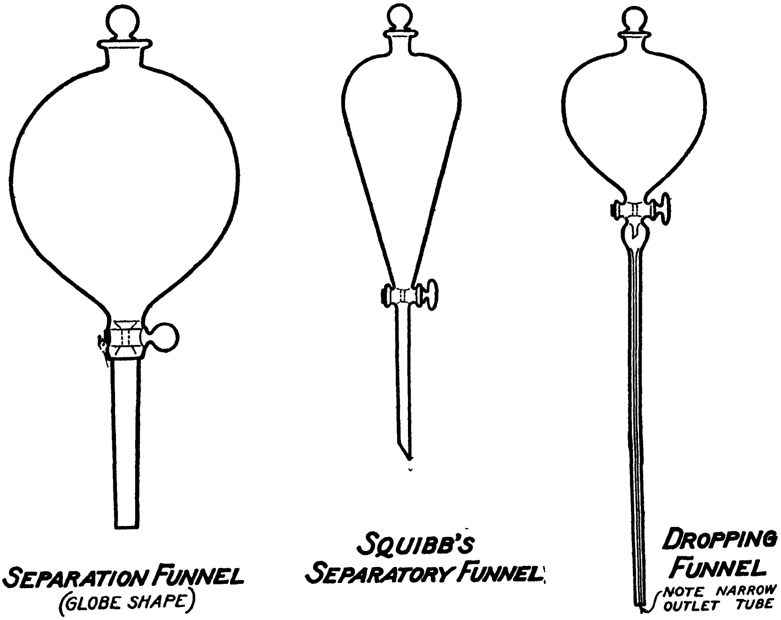
---

[1] Use a small flame Excessive heat may decompose the phosphorous acid formed in the reaction, giving phosphine.

[2] Fig. 6. When in use the stop-cock should be greased with a good stop-cock lubricant. Vaseline may be used, but it is not recommended, since it is too "thin" and has no "body." Be sure to clean the separatory funnel before leaving the laboratory, so that the stopper and the stop-cock will not stick. It is well to keep the ground parts separated but tied with a piece of twine. The separatory funnel is conveniently supported in a ring which is clamped to a stand.

[3] Cold dilute sodium hydroxide solution causes no appreciable hydrolysis under these conditions.

of the other hand on the handle of the stop-cock and the first two fingers on the other side of the stem, and shake. While it is still inverted open the stop-cock to release the pressure. (?) Repeat both these operations several times. Turn the funnel right side up, support it in a ring and as soon as the mixture has separated[1] into layers, remove the upper stopper, (Why?) and then allow the heavy lower layer of ethyl iodide to flow into a clean beaker, cutting off the stream when the upper layer flows through the stop-cock. The ethyl iodide is usually turbid on account of the presence of water. If the brown color (?) has not been removed and if the aqueous layer is not alkaline, treat it with a second portion of sodium hydroxide solution.


SEPARATION FUNNEL (GLOBE SHAPE)

SQUIBB'S SEPARATORY FUNNEL

DROPPING FUNNEL (NOTE NARROW OUTLET TUBE)

FIG. 6.

---

[1] Alkaline solutions sometimes form difficultly separable emulsions. If the separation is not complete within an hour and if it is inconvenient to let it stand overnight, add dilute acid until the mixture just reacts acid. This procedure will usually break up an ordinary emulsion.

Separate as above. Remove any water from the stop-cock and the stem, and again return the lower layer for one more washing with water. This time make a very careful separation,[1] allowing the lower layer to run into a small dry Erlenmeyer flask. The liquid still contains a small amount of water, although there may not be enough to make it turbid. This last trace of water is removed by allowing the liquid to remain in contact with a good drying agent such as calcium chloride for several hours, or better overnight. Add several pieces of granular anhydrous calcium chloride, stopper the flask, (Why?) and set aside until the next laboratory period. The Erlenmeyer flask is used in order that practically all the liquid may be in close proximity to the drying agent. Such flask should never be more than half full. For a discussion of drying agents, etc., see Gattermann, " Practical Methods of Organic Chemistry, 3d Amer. Ed., pp. 53–6; and Weyl, "Die Methoden der Organischen Chemie," II (2) (1911), 1357–64.

When the liquid is clear and dry filter it through a funnel, containing a *small* plug of glass wool pushed well down in the stem, into a small dry distilling flask (the stem of the funnel should reach below the opening of the delivery tube), but do not allow any of the droplets of the solution of calcium chloride that may be present to flow into the flask with the dry ethyl iodide. Distill through a water condenser with a straight dry inner tube, using a dry, weighed specimen bottle[2] as the receiver.[3] Ethyl iodide boils at 72° cor., and its specific gravity is 1.994 (14°). Compounds containing a halogen, and particularly those containing iodine, have a tendency to decompose on strong heating. Therefore a very small flame should be used in this instance, and the heating should not be continued until the last traces are decomposed because some of the products, which are colored, will pass over and contaminate the pure distillate. Yield, 16 grams.

---

[1] If drops of ethyl iodide float on the water, they can be made to drop to the bottom by sudden jars to break the surface tension, or by filling the funnel with water, thereby lessening the area of the upper surface.

[2] See p. 1.

[3] A turbid distillate shows the presence of moisture. It must be dried again over night with fresh calcium chloride.

What is the corrected boiling-point? Calculate the theoretical yield on the basis of the alcohol used, also of the iodine, and compare with the actual results. What is the percentage yield on each basis? The product becomes dark on standing, especially in the presence of light. A globule of mercury placed in the bottle will keep the specimen colorless. (Why?)

Bottle the product, label as directed in the "Notes," p. 1, and place in the proper tray for inspection by the instructor.

Before handing in the preparation perform the following experiments:

*a.* Test the action of silver nitrate solution on a drop of ethyl iodide. Is there an immediate precipitate? Repeat with chloroform. (?)

*b.* Dissolve 1 gram of potassium hydroxide in 10 cc. of alcohol. Use the KOH marked "purified by alcohol."[1] To 1 cc. of this solution, which is commonly known as "alcoholic potash," add nitric acid until the solution reacts acid, and then add distilled water to dissolve any precipitate. (?) To this solution add a drop of silver nitrate solution. Is there any precipitate or is the solution turbid? (Why?)

*c.* Boil 1 cc. of "alcoholic potash" containing one drop (no more) of ethyl iodide for one minute. Cool and acidify with nitric acid, dissolving any precipitate (?) with distilled water. If an emulsion is formed add alcohol, or repeat, using a smaller amount of the halide. Then add a drop of silver nitrate solution. Is there an immediate precipitate? How do you account for it?

Reference for the preparation of alkyl iodides in large quantities, Adams and Voorhees, *Journ. Amer. Chem. Soc.*, **41** (1919), 789–98.

## QUESTIONS

1. Could yellow phosphorus be used in preparing ethyl iodide? (See reference to Adams and Voorhees, p. 31.)
2. Why is a glass-stoppered bottle used?

---

[1] If this is not available, dissolve some ordinary stick potassium or sodium hydroxide in absolute alcohol and filter from any chloride or carbonate. Or use a solution of metallic sodium in alcohol. In the latter case only clean bright sodium should be used, the parings being returned to the bottle.

3. Why is *absolute* alcohol used?
4. Why is the reaction mixture set aside overnight?
5. Why is the bottle rinsed with a *small* amount of alcohol?
6. Account for the formation of the hydrogen iodide which is evidenced by the cloud of vapor when the reaction-mixture is transferred.
7. Why is a thermometer not used in the first distillation?
8. When is *fused* calcium chloride used for drying liquids?
9. What causes the " brown color "? How is it removed? Write the reactions.
10. How does the mercury keep the specimen colorless?
11. Give two other methods for forming ethyl iodide.
12. Why cannot ethyl iodide be prepared by the direct action of iodine on ethane?
13. Compare the preparation of ethyl iodide and of hydrogen iodide.
14. Why is the halogen in alkyl halides not generally precipitated with silver nitrate solution?
15. What is the qualitative test for halide-ion in aqueous solution?
16. What is the brown precipitate formed when not enough nitric acid has been added to make the solution react acid?
17. What would happen in (*c*) if aqueous potash were used? Try it.
18. What is a general method of detecting the halogens in organic compounds? Can the sodium-decomposition be used if nitrogen is also present? Compare Expt. No. 28.
19. What impurities does the ordinary potassium hydroxide contain? Acidify a dilute solution of potassium hydroxide with nitric acid and add silver nitrate solution. (?)
20. How are the halogens determined quantitatively?
21. What is alkylation?

## Experiment No. 7

### FORMATION OF AN OLEFINE HYDROCARBON

### AND

### ADDITION OF A HALOGEN TO AN OLEFINE HYDROCARBON

### Preparation of Ethylene (Ethene) and Ethylene Dibromide (1.2-Dibrom-ethane)

In this experiment ethylene is prepared by heating ethyl alcohol and phosphoric acid, and the ethylene thus made is purified by passage through conc. sulfuric acid and then run into bromine, which absorbs it with the formation of ethylene dibromide. After the ethylene dibromide is made, the gas itself is collected and studied.

Set up the apparatus shown in Fig. 7. Use rubber stoppers.

Care must be exercised in putting the glass tubes through the rubber stoppers. Be sure to round the edges of all tubes in the flame. (See p. 28.) Use a drop of water or of glycerine as a lubricant. Always take hold of the tube *near* the stopper and twist it slowly as it is carefully being forced in. Never, for example, grasp a long thermometer at one end to push the other end through the stopper. With these precautions accidents resulting in more or less serious cuts would be avoided.

As a rule it is not necessary to enlarge the hole in a rubber stopper. In case a larger hole is required a cork borer can be used. It must be moistened frequently, and only very slight pressure is needed, otherwise a tapering hole will be made.

The connections with rubber tubing are easily made if you breathe through the rubber tubing before pushing it over the glass. Here again the sharp edges of the glass tube should be well rounded in the flame.

Fit a 250 cc., round-bottomed, short-necked flask with a three-holed stopper through which pass a thermometer, a bent outlet tube, with the bend near the stopper,[1] and an inlet tube drawn into a narrow tube, 1.5–2 mm. in diameter, with the lower end bent upwards about 5 mm. The size of this tube is important. If it is larger or smaller than designated it will not deliver the alcohol properly. The tapering should begin *just below* the stopper and the tube should extend almost to the bottom of the flask, so that the alcohol can be delivered well below the surface of the liquid. Turn the bend away from the thermometer.

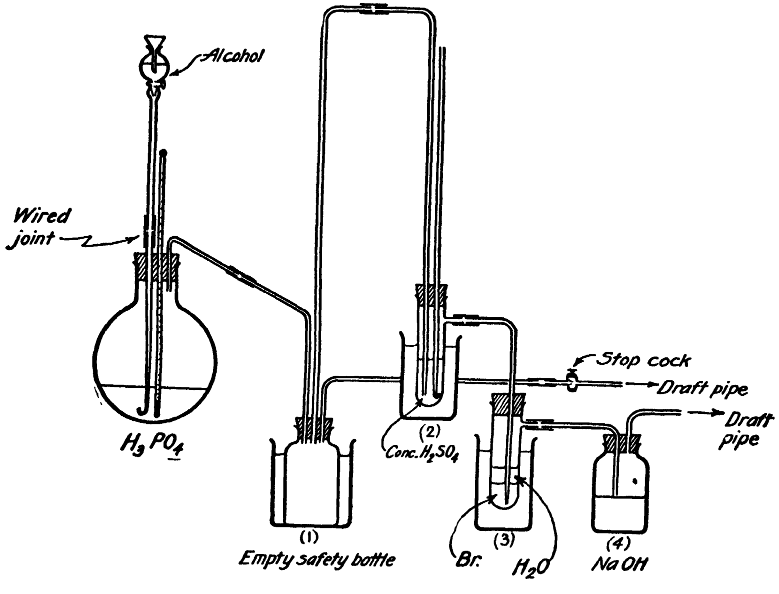


*Diagram of Apparatus for Ethylene Dibromide*

FIG. 7.

---

[1] The apparatus should be so arranged that the alcohol which condenses below the first bend in the outlet tube will not drip upon the lower part of the thermometer and cause it to crack. In order to avoid back flow of any condensation liquid slant the outlet tube as shown.

To make the inlet tube, heat evenly a piece of glass tubing held lengthwise in the flame of a burner provided with a wing-top, rotating it and moving it from left to right until it becomes very soft, then *remove* it from the flame and slowly at first and then much more rapidly draw it out as desired. Very rapid drawing makes the tube too narrow. It must be made in one heating. A smoky flame need not be used as long as the tube is slowly warmed in the blue flame. The narrow tube is easily broken where a file mark is made. It is bent by softening the tube near the end in the flame and quickly touching the end to a hard surface when it will bend very readily. Do not fuse the capillary or change its bore.

Connect a dropping-funnel (Fig. 6) with rubber tubing to the upper part of the inlet tube above the stopper, and wire the connections.[1] Lead the gas (1) through an empty 250 cc. wide-mouthed bottle as a safety bottle, using a three-holed stopper. The three tubes in this stopper should be cut off just below the stopper. Insert a glass stop-cock and attach a piece of rubber tubing to lead away the gases to the draft pipe. From this bottle lead the gas through a long high glass tube into (2) a 2 cm. test-tube with side neck, where it is washed by passing through 10 cc. of conc. sulfuric acid. This test-tube should be provided with an open safety tube 30 cm. long which should be drawn out and bent slightly upwards at the bottom, opening under the surface of the liquid. The long high connection is used in order that the operator may be able to see the conc. sulfuric acid rising in case of back pressure in the apparatus and have time to prevent its being drawn into the first bottle by equalizing the pressure by opening the stop-cock momentarily. Then (3) through another test-tube with side neck containing 7 cc. of bromine[2]

---

[1] This rubber connection must be wired since the rubber absorbs alcohol and swells so much that the joint becomes loose

[2] Not bromine water. Do not add the bromine until just before the experiment is begun. If the bromine is allowed to stand in the tube for several days before the experiment is begun it attacks the rubber stopper. Colored compounds are formed which run down the walls into the bromine. Since their color is red or reddish-brown they make it very difficult to tell when all the bromine is decolorized with the ethylene. Always handle bromine near the draft pipe or under

covered with 10 cc. of water. The two tubes leading the gas into the sulfuric acid and into the bromine should be drawn out to a small opening so that the issuing bubbles will be small. Both tubes should open *near the bottom* of the test-tubes. The two test-tubes can conveniently be arranged and supported on one ring-stand. Set the first bottle and the two test-tubes in beakers full of cold water. Finally (4) through a tube opening *just above* the surface of a normal sodium hydroxide solution contained in a bottle provided with a vent. Or the bromine vapors may be adsorbed by passing the gas through a calcium chloride tube filled with adsorbent charcoal. In either case lead the gases finally into the draft pipe.

Into the generating flask put a mixture of 40 cc. of syrupy phosphoric acid (sp. gr. 1.7) and 20 cc. of alcohol. Almost fill the main bulb of the dropping-funnel with alcohol, and in order to displace the air in the tube allow some of the alcohol to flow into the flask. Heat the flask over a wire gauze until the thermometer in the mixture indicates 230°. Only a small flame is necessary after the flask is heated through. During the preliminary heating have the stop-cock open. When the evolution of ethylene has well begun close the stop-cock, and let the alcohol run in slowly at such a rate (about one drop a second) as will give a good constant stream of gas. Keep the temperature between 230°–250°. Drafts cool the flask and cause such a back pressure that the sulfuric acid and bromine may be drawn into the preceding bottles. This back flow may readily be avoided by opening the stop-cock, as mentioned above. The liquid in the flask should appear as if filled with bubbles and will foam as the ethylene is regularly generated. The temperature may rise even above 250° but should not be allowed to reach 300°. Continue the passage of the gas until the bromine has changed completely to a straw-colored liquid. This will

---

the hood. If you get any on your hands wash it off immediately with alcohol, and then rub in some carron oil (half linseed oil and half lime water) or carbolated vaseline. Benzene and gasoline are good solvents and may also be used for removing bromine. See p. 6.

*For opening bromine bottles,* compare Note 3, under Methane, p. 33.

take about thirty minutes. Much more time will be necessary if the gas is not delivered near the bottom where it will stir up the bromine and be more readily absorbed. Purify it according to the directions given below.

### NOTES ON THE GENERATION OF ETHYLENE

1. *Be sure* to open the stop-cock before turning out the flame.
2. The generation of the gas may be stopped and resumed at any time.
3. When carrying out this experiment it is well to protect the eyes with goggles.
4. Do not try to burn the gas leaving the apparatus unless the end of the delivery tube is drawn into a capillary opening. (Why?)
5. The method can be used for preparing fairly large quantities of ethylene. However, the phosphoric acid attacks the glass and after about 16–20 hours running the inlet tube is generally "eaten off" and finally the flask itself will leak.

After the color of the bromine has disappeared disconnect the second test-tube, connect the outlet tube of the sulfuric acid tube with a tube leading to a beaker or small pail of water, and when a test-tube of the gas collected over water burns quietly fill two 250 cc. narrow-necked, glass-stoppered bottles and a 250 cc. ordinary wide-mouthed bottle with the gas by displacement.

*a.* Into one narrow-necked bottle pour 1 cc. of bromine water. Insert the glass stopper immediately and shake. (?)

*b.* To the second narrow-necked bottle add 1 cc. of a very dilute solution of potassium permanganate.[1] Close with the glass stopper and shake vigorously. (?)

*c.* Ignite the gas in the wide-mouthed bottle (near the draft pipe) and immediately add water to displace the gas. Is the flame distinctly luminous?

Repeat the above experiments using city gas. Conclusions. (?)

---

[1] For the oxidation of ethylene, see Stoddard, "Introduction to Organic Chemistry," p. 156; of other olefines, see Moore, "Outlines of Organic Chemistry," 2nd Ed., p. 129.

Test amylene or pinene for the "double bond" as follows: Use 1 cc. in each case.

*a.* Add 1 drop of conc. sulfuric acid. (Care!) Result?
*b.* Add 1 drop of conc. nitric acid. (Care!) Result?
*c.* Add a solution of bromine in carbon tetrachloride. (?)
*d.* Add 1 cc. of potassium permanganate solution as above and shake. (Do not use a cork stopper.)

Compare the results with those obtained with benzine. (Expt. No. 5, p. 31.)

Transfer the crude ethylene dibromide to a Squibb's separatory funnel: add some dilute sodium hydroxide solution; agitate gently, and separate.[1] Return the heavy liquid to the separatory funnel, and treat again with a dilute solution of sodium hydroxide unless the aqueous layer remained alkaline in reaction. Finally wash once with water, and draw off into a dry Erlenmeyer flask. The product may be slightly colored. This is due to the fact that some decomposition took place on account of the heat of the reaction between the ethylene and bromine with the formation of a small amount of colored by-products. This color cannot be removed with alkali. Add several pieces of calcium chloride to the cloudy ethylene dibromide, cork the flask (?), and set aside for several hours (overnight) to dry the liquid. Filter through a funnel containing a plug of glass wool in the stem into a dry distilling flask, just as in the ethyl iodide experiment, but do not allow any of the droplets of the calcium chloride solution[2] that may be present to flow into the flask with the dry ethylene dibromide. (Why?) Distill through a water condenser with dry inner tube, using a dry-weighed specimen bottle as the receiver, observing the precautions mentioned under ethyl iodide. The substance boils at 131.2° cor., melts at 9.5°, and its specific gravity is 2.1774 (21°/4°). Yield, 20 grams. Cal-

---

[1] For separating an emulsion, see foot-note, p. 36.

[2] If there is a layer of calcium chloride solution, even though some of the solid is still present, it is quite probable that the product is not very dry. It should be separated, treated with fresh calcium chloride, and allowed to stand for several hours longer.

culate the theoretical yield from the amount of bromine used. What is your corrected observed boiling-point?

Repeat tests *a* and *c* as given under ethyl iodide (p. 38), with pure ethylene dibromide, and compare the results with those obtained with ethyl iodide. Write the equations.

### NOTE ON TAKING APART THE APPARATUS

The glass tubes often stick in the rubber stoppers. In such cases do not try to pull out the tube directly. Work the rubber away from the tube with the fingers and allow water to flow in and moisten it as fast as it is separated. In this manner the tube soon becomes free and can be withdrawn easily.

## QUESTIONS

1. What objection is there to an inlet tube with a diameter less than 2 mm.? Greater than 2 mm.?
2. Why must the alcohol be delivered below the surface of the liquid? Why is the inlet tube turned up at the bottom?
3. What substances are caught in the empty safety bottle? Account for them. Is this the only purpose of this bottle?
4. Why must the gas be passed through conc. $H_2SO_4$? Could fuming $H_2SO_4$ be used? dilute $H_2SO_4$?
5. Why should the alcohol vapors not be allowed to go over into the bromine?
6. Why are the bottles surrounded with cold water?
7. Why is the bromine covered with a layer of water?
8. What substances are caught in the sodium hydroxide solution? Account for them.
9. Why is the apparatus disconnected before extinguishing the flame?
10. What is the brown precipitate formed in the permanganate test?
11. What unsaturated hydrocarbons are in the city gas? What are illuminants? Name some.
12. How are the unsaturated hydrocarbons in illuminating gas estimated?
13. Is an addition or substitution product formed with amylene and sulfuric acid?

14. In the purification of ethylene dibromide why must the sodium hydroxide solution be used?
15. Why avoid the emulsion which would be formed by vigorous shaking?
16. Why is a 250 cc. Squibb's separatory funnel used instead of a dropping-funnel although the volume of liquid is small? (Fig. 6, p. 36.)
17. Why not dry the product in a small distilling flask and distill directly without removing the calcium chloride?
18. Why is glass wool used instead of a filter paper in the funnel?
19. What compounds are in the " amylene "?
20. Look up the formula for pinene.
21. Why not use the weight of the alcohol instead of the bromine in calculating the theoretical yield?
22. Is ethylene dibromide a saturated or unsaturated compound? Of what hydrocarbon is it a derivative?
23. What happens when ethylene dibromide is heated with alcoholic sodium hydroxide? With aqueous sodium hydroxide?
24. What other methods can be used for preparing ethylene?
25. How did the United States Government prepare ethylene in large quantities for the manufacture of " mustard gas " (dichlor-diethyl-sulfide) during the war? (Ref., Dorsey, *Journ. Ind. and Eng. Chem.*, **11** (1919), 288.

## Experiment No. 8

### FORMATION OF AN OLEFINE HYDROCARBON

### Ethylene from Ethyl Alcohol (for Short Course)

Weigh directly into a large test-tube (No. 3), 4 grams of phosphorus pentoxide. Connect the test-tube by means of a closely fitting cork with a reflux air condenser; immerse the tube in cold water, and pour 5 cc. of ethyl alcohol slowly through the condenser. The alcohol should be added cautiously in small portions and the test-tube shaken under water, since much heat is evolved when alcohol comes in contact with phosphorus pentoxide. Remove the condenser, support the test-tube at an angle of about 45° with the desk top by means of a clamp, and connect it with a delivery tube arranged to collect gas over water. Heat the tube carefully until the mixture becomes homogeneous; then more strongly until a steady stream of gas is evolved. Fill two 250 cc. narrow-necked glass-stoppered bottles and a 250 cc. wide-mouthed bottle with the gas over water by displacement.

*a.* Into one narrow-necked bottle pour 1 cc. of bromine water. Insert the glass stopper immediately and shake. (?)

*b.* To the second narrow-necked bottle add 1 cc. of a very dilute solution of potassium permanganate. Close with the glass stopper and shake vigorously. (?)

*c.* Ignite the gas in the wide-mouthed bottle (near the draft pipe) and immediately add water to displace the gas. Is the flame distinctly luminous?

Repeat the above experiments, using city gas. Conclusions. (?)

Test amylene or pinene for the "double bond" as follows: Use 1 cc. in each case.

*a.* Add 1 drop of conc. sulfuric acid. (Care!) Result?

*b.* Add 1 drop of conc. nitric acid. (Care!) Result?

*c.* Add a solution of bromine in carbon tetrachloride. (?)

*d.* Add 1 cc. of potassium permanganate solution as above and shake. (Do not use a cork stopper.)

Compare the results with those obtained with benzine, Expt. No. 5., p. 31.

## QUESTIONS

1. Compare the action of ethyl alcohol with that of water on phosphorus pentoxide. Write structural formulas of the compounds in each case and name them.
2. What is the action of heat on the compounds formed by the action of ethyl alcohol and of water, respectively, on phosphorus pentoxide?
3. Write the equation for the reaction of bromine and ethylene.
4. What happens when ethylene is treated with dilute potassium permanganate?
5. What is the brownish precipitate formed in the permanganate test?
6. Define an addition product; a substitution product. Illustrate.
7. Is ethylene dibromide a saturated or an unsaturated compound? Of what hydrocarbon is it a derivative?
8. Is an addition or substitution product formed with amylene and sulfuric acid?
9. What unsaturated hydrocarbons are in the city gas?
10. What are “ illuminants ”? Name some.
11. How are the unsaturated hydrocarbons in illuminating gas estimated?

## Experiment No. 9

### FORMATION OF AN ACETYLENE: 1. BY HYDROLYSIS OF AN ACETYLIDE

### Acetylene from Calcium Carbide

Set up a gas generator consisting of a filtering-flask and dropping-funnel. Into the dry flask place several lumps[1] of calcium carbide and allow water to drop very slowly upon it. (Care!) Pass the gas through an empty safety-bottle and then fill with the gas by displacement over water a test-tube, two narrow-necked glass-stoppered bottles, and a wide-mouthed bottle in the order named.

*a.* Ignite the gas in the wide-mouthed bottle, holding it near the draft pipe. Notice the luminosity of the flame and the amount of carbon deposited.

*b.* To one narrow-necked bottle add 2 cc. of bromine water and shake. (?) Compare with methane, p. 31, and ethylene, p. 44 or p. 48.

c. To the other narrow-necked bottle add 1 cc. of a very dilute solution of potassium permanganate. Shake. Are there any signs to denote unsaturation?

*d.* Dilute 0.5 cc. of silver nitrate solution to about 3 cc. From a test-tube add this silver nitrate solution to a test-tube of the gas. What is the white precipitate? Filter with suction and let it dry on filter paper. Explode it by heating small pieces in the flame.[2] Note the presence of carbon on the knife blade after the explosion.

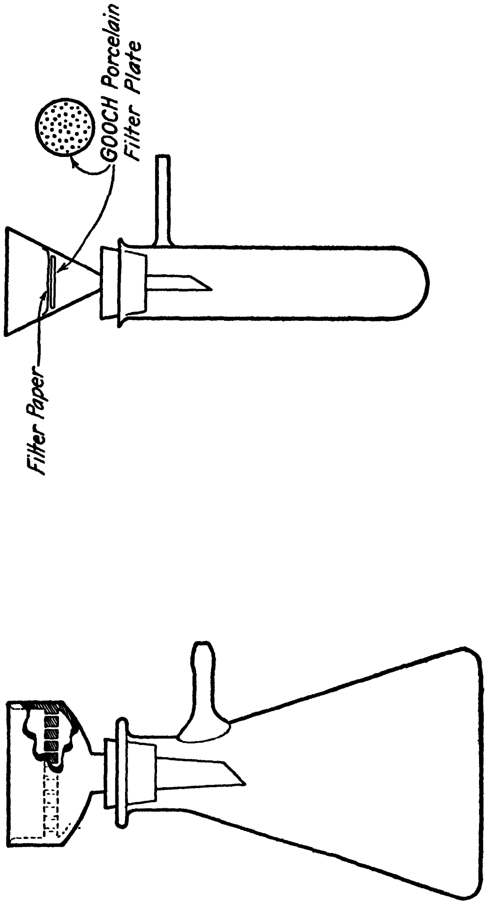
*e.* Prepare a solution of cuprous chloride as follows: Dissolve 0.5 gram of copper sulfate crystals in a little water, add

---

[1] The powder is generally useless since it is mostly decomposed.

[2] Destroy all the remaining silver precipitates before leaving the laboratory, either by explosion or by warming with dilute hydrochloric acid.

2 cc. of conc. ammonium hydroxide and 1.5 gram of hydroxylamine hydrochloride. Dilute with water to about 25 cc. It may be kept colorless by placing it in a tightly corked bottle containing some copper turnings. The bottle should be full in order to avoid oxidation by any air present. This will be used in both parts of this experiment.



BUCHNER FUNNEL & ERLENMEYER FILTERING (OR SUCTION) FLASK

APPARATUS FOR FILTRATION OF SMALL QUANTITIES

FIG. 8.

Pass acetylene into 5 cc. of the cuprous chloride solution. What is the reddish-brown precipitate? Filter the solution with suction and wash the precipitate. Let it dry on the filter paper, and then explode small portions of it in the flame Try its solubility in dilute hydrochloric acid solution.

**Filtration with Suction.**—In order to filter with suction fit the porcelain Buchner funnel, Fig. 8, p. 51, tightly into the neck of a filtering-flask with a good cork or rubber stopper, and connect the outlet tube to the filter pump with heavy rubber tubing. In the bottom of the funnel place a filter paper cut so that it covers all the holes and lies flat *without being folded on the sides.* Moisten the paper with some of the liquid used, start the suction, and then pour in the mixture. Oftentimes with bulky material it is convenient to press it down with a flat-topped glass stopper. At the end of the filtration carefully disconnect the tube from the flask *before* stopping the suction.

For the filtration of small quantities, see p. 56.

## 2. By the Action of Alcoholic Potassium Hydroxide on an Alkylene Dihalide

### Acetylene from Ethylene Dibromide

To a 100 cc. flask set on the steam-bath attach an addition tube with reflux condenser connected with its side opening.[1] From the top of the condenser run a tube leading into 5 cc. of the ammoniacal cuprous chloride solution. *Have all connections tight.* Good corks, well bored, must be used. Collodion sometimes may be used to aid in making a cork gas-tight, but it is not a substitute for an evenly bored cork. Rubber stoppers may also be used if desired. Heat 2 grams of potassium hydroxide, "purified by alcohol,"[2] in 12 cc. of alcohol in the flask for about ten minutes. Cool and add through the addition tube 2 cc. of ethylene dibromide. Heat again. What is the precipitate formed in the cuprous chloride solution? At the end of the reaction dissolve the precipitate (?) in the flask by adding some distilled water, add nitric acid to a small portion of this

---

[1] See Fig. 3, p. 13.

[2] Or use an equivalent amount of metallic sodium in alcohol. Connect the condenser to the flask after the sodium is added, since the alcohol becomes hot and hydrogen is given off.

until it reacts acid, and then add a drop of silver nitrate solution. What is the precipitate? Account for it.

### NOTE

Only a small amount of the ethylene dibromide is converted into acetylene. The major portion is converted into vinyl bromide (mono-brom-ethylene) which is a gas at room temperature and passes out of the reaction mixture before it can be reacted upon further and completely transformed into acetylene. If no acetylene is detected in your experiment it is because there were leaks in your apparatus. Some is always formed.

## QUESTIONS

1. What two compounds may be formed when acetylene and bromine react?
2. What happens when an acetylide is boiled with dil. hydrochloric acid?
3. What kind of a reaction is the decomposition of calcium carbide?
4. What causes the bad odor of the gas? Source?
5. What style of acetylene hydrocarbons form metallic derivatives?
6. When the copper sulfate is reduced to the cuprous form, what becomes of the hydroxylamine?
7. Why is an *ammoniacal* solution of cuprous chloride used?
8. Why is ammonium hydroxide not used also with the silver nitrate?
9. Are all acetylides explosive?
10. What is meant by an exothermic compound? an endothermic compound?
11. Write the reactions for the formation of acetylene from ethylene dibromide, giving the different products formed.
12. Explain why the acetylene burns with a smoky flame in the experiment, while in certain lamps, such as automobile lamps, it burns with an exceedingly bright flame.
13. Discuss the reactions, in the treatment of the residual "alcoholic potash" solution.
14. What advantages has a Buchner funnel over the ordinary funnel?
15. In the suction filtration why is the tube disconnected from the flask before the water is turned off?
16. Why should the filter paper not be allowed to "run up" the sides of the Buchner funnel?

## Experiment No. 10

### Alcohols, Reactions of

*a.* Add a small piece of bright sodium to 2 cc. of ethyl alcohol. What gas is evolved? What is the white solid that separates as the solution cools? Add more sodium if nothing separates the first time. Is this reaction characteristic of all alcohols? How do you name the compounds formed?

*b.* Add a few drops of conc. sulfuric acid to 0.5 cc. of glacial acetic acid and 1 cc. of ethyl alcohol. Warm, with shaking. Pour it on a large cover glass and neutralize with sodium carbonate. To what is the pleasant odor due? To what class of organic compounds does it belong?

Repeat, using iso-amyl alcohol. (This alcohol usually produces coughing when breathed.)

*c.* Make a dilute solution of sodium dichromate, add a drop or two of conc. sulfuric acid and then several drops of ethyl alcohol. Heat. Notice the odor of the vapors. What is formed? What causes the green coloration?

## Experiment No. 11

### THE IDENTIFICATION OF AN ALCOHOL

### The Methyl Ester of 3.5-Dinitrobenzoic Acid

It is seldom possible to identify organic substances in the same general manner as inorganic substances. Class reactions[1] are relied upon to tell the nature of the substance, that is, its class, such as a hydrocarbon, an alcohol, etc., and physical constants will often show what member of the class the substance is. Then, in order to make certain, the substance is transformed into a derivative which can readily be prepared on a small scale, and a physical constant taken upon this. On account of the difficulties in purifying liquids in small amounts,[2] a solid derivative is chosen whenever possible. The following experiment illustrates this point in the case of the lower alcohols.

In a small dry test-tube heat together 0.3 gram of 3.5-dinitrobenzoic acid and 0.4 gram of phosphorus pentachloride over a low flame. Keep the tube in motion and finally allow the mixture to boil gently for a minute. Then while it is still liquid pour the product upon a small dry watch glass. When the acid chloride (?) has solidified remove the liquid by-product, phosphorus oxychloride, adhering to it, by pressing out the

---

[1] Noyes and Mulliken, "Class Reactions and Identification of Organic Substances," and Clarke, "A Handbook of Organic Analysis." For a more extended work, see the three monumental volumes by Mulliken, "Identification of Pure Organic Compounds."

[2] For a method of determining the boiling-point of a very small amount of liquid, see Mulliken, Vol. I, p. 222; also Alex. Smith and Menzies, *Journ. Amer. Chem. Soc.*, **32** (1910), 897.

mixture with a porcelain spatula[1] on the smooth side of a piece of clean porous tile.[2]

Put the dry material into another small test-tube, add eight drops of methyl alcohol, stopper the tube and shake now and then. The reaction is soon complete and after a few minutes the ester can be recrystallized. To do this, place the product into a 60 cc. flask under a reflux condenser, add 20 cc. of dilute alcohol (3 volumes of alcohol and 1 of water), and heat to boiling by heating on the steam-bath or by immersing the flask in hot water. If the substance does not completely dissolve after a short time add a little more dilute alcohol and boil again. There may be some foreign particles which will not go into solution. Filter the hot solution through a small filter paper into a beaker and allow the filtrate to cool. The ester crystallizes in shining leaflets. Separate these by filtering with suction.

**Filtration of Small Quantities with Suction.** Use a Gooch perforated porcelain plate in a No. 1 funnel, and place upon the plate a piece of filter paper just large enough to cover it and extend to the walls of the funnel. Fasten the funnel in a stopper in the neck of a test tube with side opening. Moisten the filter paper with dilute alcohol, start the suction, and proceed as usual. (See Fig. 8, p. 52, and compare p. 52.)

Allow the crystals to dry between filter papers or under a watch glass on a porous tile, and then determine the melting-point according to the directions given in Expt. No. 12, p. 58. The pure substance melts at 107° (uncor.).

Other esters[3] of this acid may be employed to identify the corresponding alcohols. They may be prepared according to the directions given above for the methyl ester. The ethyl ester melts at 92°–93°, 1°-propyl ester, 73°; 1°-normal-butyl ester, 64°; 1°-iso-butyl ester, 83°–84°.

---

[1] In ordinary cases where no corrosive substance is present a steel spatula can be used. It should be cleaned previously with soap to remove traces of rust and dirt.

[2] A porous unglazed tile is good for one drying, unless only a portion of the surface has been used. Obviously it cannot be washed.

[3] Mulliken, "Identification of Pure Organic Compounds," Vol. I (1904),

## QUESTIONS

1. Why is the solid ester of 3.5-dinitrobenzoic acid made for the identification of an alcohol instead of the liquid ester, for example, of acetic acid?
2. Write the equations for the reactions for preparing the methyl ester. (Compare Stoddard, " Introduction to Organic Chemistry, 2d Ed. (1918), p. 354, last paragraph, and p. 99, No. 3, near bottom of the page, p. 114, No. 2 and p. 116, No 3.)
3. What is the object of the porous tile? Why not use filter paper?

## Experiment No. 12

### Determination of the Melting-point[1]

The melting-point is the physical property most generally used as a criterion of the purity of a solid organic compound. It also serves for the characterization and recognition of a compound. On account of its significance the melting-point should be very carefully and accurately determined. The method employed is to heat a small amount of the substance in a capillary tube attached to a thermometer in a suitable bath until the substance becomes a clear liquid[2] and the temperature at this point is recorded as the melting-point. A substance is regarded as pure when it melts within 0.2–0.4 of a degree,[3] provided that the temperature is kept as nearly constant as possible, and if after repeated crystallization it does not change. Slow melting over several degrees usually indicates an impure compound, provided the rate of heating is all right. Some pure substances, however, especially those of high molecular weight, do not show a sharp melting-point in the ordinary method (compare phenylglucosazone, Expt. 34, p. 129).

Set up a melting-point apparatus like the one illustrated in Fig. 9. It consists of two tubes, one inside the other. The outer one is 32 mm. in diameter and about 14.5 cm. long;[4] the inner one is 17 mm. in diameter and 14 cm. long, and has a series of

---

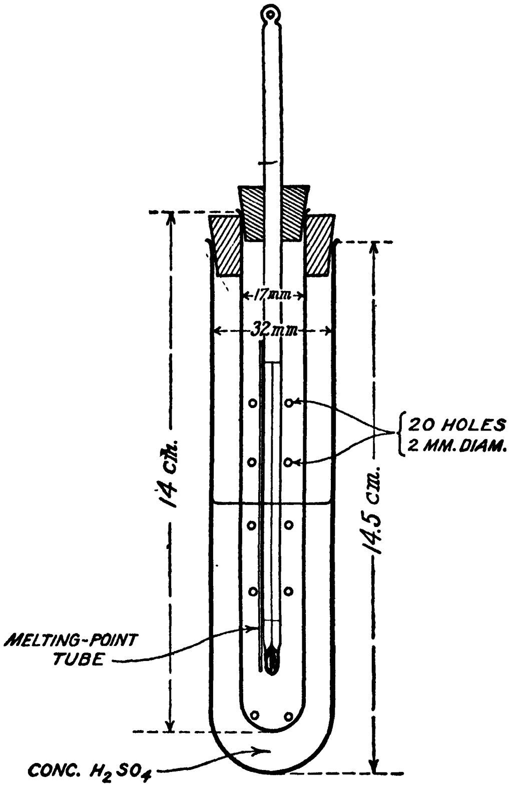
[1] See G. A. Menge, "A Study of Melting-point Determinations," *U. S. Hygienic Laboratory Bulletin*, **70** (1910), for an excellent description and discussion of the methods of determining melting-points, common errors, etc. NOTE: This bulletin is out of print, but may be consulted in the general library.

[2] Frequently the temperature of decomposition (often coincident with the melting-point) is taken, but in this case there is the possibility of a greater amount of divergence due to manipulation.

[3] This error is about equal to the error of observation.

[4] The outer tube of a Beckmann freezing-point apparatus is suitable.

small holes[1] not over 2 mm. in diameter—four at each height—as indicated in the figure. In order that the behavior of the substance can be watched there are no holes opposite the bulb of the thermometer. The inner tube can be supported in the outer tube by means of a cork as shown, with a narrow channel cut



MELTING-POINT APPARATUS

FIG. 9.

---

[1] In case an inner tube all perforated is not at hand, the holes can be blown in as follows: Select a test-tube of the proper dimensions, stopper it with a good cork which carries a glass tube to which is connected a piece of rubber tubing for blowing. Heat a tiny area of the glass at the desired point with a fine blast

along the edge to allow the heated vapors to escape, or, when the thermometer is in position and securely held in alignment by a cork,[1] it can be supported by holding the top of the thermometer in a clamp.

The outer tube should be supported by clamping it firmly but not too tightly under the lip. Add enough conc. sulfuric acid to come up to a height of 6 cm. from the bottom of the *inner* tube when it is in place.[2] The apparatus is heated with a *small* flame which should be protected with a metal chimney. The liquid in the inner tube is regularly heated and stirred mainly by means of convection currents made possible by the series of small holes. The liquid near the thermometer always shows an even downward flow all around the stem.[3] Moreover, the inner liquid can be heated uniformly and steadily since it is not affected by ordinary drafts.

Make several capillary tubes, the so-called melting-point tubes, as follows: Heat *evenly* a piece of glass tubing held lengthwise in the blue[4] flame of a burner provided with a wing top, rotating it and moving it from left to right until it softens, then *remove* it from the flame and draw it out very slowly at first and then, as the glass begins to cool and harden, much more rapidly, into a long, straight, thin-walled, narrow tube of about

---

flame, and when it melts remove it from the flame and blow a bubble, not a hole. Repeat this at every point. Then complete the making of the holes by melting each little bubble or by breaking the glass with a file and "rounding" the edges of each hole with the flame. Remember that the holes should be not more than about 2 mm. in diameter.

An apparatus like the one described above but without the holes in the inner tube has been in use for many years in different laboratories. It is believed, however, that the *perforated* inner tube is new and is an advantage since it permits good stirring and more rapid heating and cooling.

[1] If a long-scale 360° thermometer is used, this cork should have a longitudinal section cut out to form a canal through which the degrees of the thermometer can easily be read at this interval.

[2] If more acid is used the melting-point tube is likely to drop off in the liquid, since too small a length of it is held by capillary attraction.

[3] The currents in the liquid can be seen very nicely if a little finely divided carbon is put in the acid.

[4] A smoky flame need not be used provided the tube is slowly warmed in the blue flame.

1 mm., (± 0.2 mm.), inside diameter.[1] Rapid drawing in the very beginning makes the tube too narrow. It must be made in one heating. The wing-top should give an even flame. If the flame is irregular the glass will not be heated evenly and the narrow tube will consequently be uneven. Test-tubes give excellent melting-point tubes. They are heated in the ordinary Bunsen flame. It is sometimes difficult to make a tube of circular cross-section, but the walls are sure to be thin and this is an advantage since there will be less glass through which the heat must be conducted to the substance. Cut the long narrow tube into lengths of 9 cm. by means of file marks (do not try to break it otherwise) and seal one end of each tube by carefully heating the edges in the outer mantle of a small flame. Do not fuse too much of the glass, since this thickens the walls, thus diminishing the diameter of the tube, and causes the formation of a glass bead at the sealed end. Smaller lengths should not be used because they will not remain attached to the thermometer as described below. If possible, it is advisable to cut the original capillary into lengths of 18 cm. and seal both ends. When needed the double-length tube is broken at the center and serves for two determinations.

Make a little mound of *dry*, *powdered*[2] substance and force some of this into a melting-point tube by gently thrusting the open end directly into the material, and giving it a rotary motion at the same time. This operation cuts out a little cylindrical cake of the substance. Shake this down by letting the sealed

---

[1] Lengths of 30 to 60 cm. are readily made in this way. Larger tubing of soft glass, such as "bomb" tubes, can be drawn out rapidly, with the aid of an assistant, into a length of several meters, and a good stock of melting-point tubes cut therefrom.

The advantages of the long *straight* melting-point tube over the tapering tube with a cup at the top which has often been described are threefold: (1) many tubes can be made at the same time; (2) they can be attached more easily to the thermometer; and (3) most organic compounds are light and fluffy, and on this account they cannot be made to drop readily to the bottom of the melting-point tube, but since the straight tube has an even bore, the little cylinder of material which is cut out, as described in the next paragraph above, will usually slide down to the bottom without difficulty.

[2] Large crystals do not form a compact mass and therefore the material is not heated as evenly and quickly as when powder is used.

end of the tube drop gently upon the desk.[1] Repeat until a layer 3 mm. deep is formed. Rub off the substance adhering to the outside of the tube so that it will not be charred by the acid and discolor the bath. Remove the thermometer from the apparatus, allow most of the acid to drain off, and touch the bulb to the upper part of the melting-point tube, thus leaving behind a droplet of the liquid. Place the tube with the sealed end down against the thermometer stem and it will adhere by capillary attraction. The substance should be *opposite the bulb* of the thermometer. Return the thermometer, with the tube attached, to the apparatus. The melting-point tube should extend about as far along the thermometer above the liquid as it does in the liquid in order that the capillary force will be great enough to hold it to the thermometer. Now begin to heat the liquid with a small flame.[2] The heating may be fairly rapid until within about 15° of the melting-point (already known or approximately determined in a preliminary trial) and then **slowly, 3° a minute**, until the substance melts. *Do not guess at the rate, time it*, and then you will obtain consistent results. Substances generally soften and contract, and often become discolored before melting.

It is absolutely essential to use a *small flame,* and heat *regularly*, especially when within 10°–15° of the melting-point. Alternate heating with a large flame never gives consistent results. The small flame can easily be obtained if the air supply of the burner is properly cut down. Drafts should of course be avoided as much as possible.

The temperature of the bath can be carried up to about 280° if pure conc. sulfuric acid is used. If water has been absorbed the diluted acid will begin to boil at a lower tempera-

---

[1] If the substance does not drop readily to the bottom of the tube try either of the following methods: Hold a piece of ordinary glass tubing, about 60 cm. long, open at both ends, in an upright position on the desk and touching the desk top, then let the melting-point tube, with sealed end down, drop through it. Repeat this several times if necessary. Or, draw the flat side of a triangular file horizontally across the tube a little below the substance. The powder, loosened by the vibration set up in the glass, will quickly slide down to the bottom.

[2] If the burner is held in the hand, hold it in an oblique position in order o avoid accident in case the apparatus cracks.

ture and cannot be used for the higher temperatures. If it begins to boil the heating should be discontinued. The boiling-point of the acid may be increased by boiling it in a flask or beaker under the hood.

The errors in this determination are generally due to the variation of the thermometer, rate of heating,[1] physical condition of the compound,[2] and individual manipulation. For an extended discussion of these errors the student is referred to the bulletin mentioned in the foot-note above. The true melting-point is obtained by the use of short-stem, normal, standardized thermometers whose mercury thread is entirely immersed in the bath. Since these are expensive and are not always available, the set of three short-scale thermometers mentioned in connection with the Boiling-point experiment, p. 8 and Fig. 1, should be used.

Experience in determining the melting-point and checks on the accuracy of the thermometer can be obtained by using substances whose melting-points are near the bottom and somewhat near the top of the scale in each case, as mentioned in the first experiment. The following substances are suitable. The temperatures given are *corrected:*

| | |
|---|---|
| Naphthalene. . . . . . . . . . . . . . . . . . . . . . . . . | 80.8° |
| Benzoic acid. . . . . . . . . . . . . . . . . . . . . . . . . | 122.5° |
| Salicylic acid. . . . . . . . . . . . . . . . . . . . . . . . | 159.8° |
| Anisic acid. . . . . . . . . . . . . . . . . . . . . . . . . . | 184.2° |
| Anthracene . . . . . . . . . . . . . . . . . . . . . . . . . | 216.0° |
| Carbazol. . . . . . . . . . . . . . . . . . . . . . . . . . . . | 246.0° |
| Anthraquinone. . . . . . . . . . . . . . . . . . . . . . . | 285.0° |

All these substances in addition to giving good melting-points have a special advantage in that they are easily obtained

---

[1] Probably more errors are made in manipulation by improper heating than in any other way. The rate of heating must not be so rapid that an appreciable rise of temperature occurs during the time necessary for the attainment of the same temperature throughout the entire mass. Otherwise the temperature may rise several degrees during the interval between incipient and complete melting.

[2] Compare preceding foot-note, and foot-note [2], p. 61.

and are readily purified by sublimation.[1] It is seldom necessary to use a substance melting below naphthalene. If necessary one of the following can be used: *p*-toluidine, 45°; hydrocinnamic acid, 48.7°; α-naphthylamine, 50°; or diphenylamine, 54°. Compare the results with those obtained with the same thermometers in the boiling-point experiment.

If the set of three thermometers mentioned above is not at hand, an ordinary long-scale thermometer may be standardized for the conditions obtaining in the laboratory work by determining the melting-points of some of the pure substances given in the list, for example, naphthalene, salicylic acid, anthracene and carbazol. Then by plotting the results on co-ordinate paper, as described in note 4, Boiling-point experiment, p. 20, the correction for any one degree may quickly be read off at any time.

The influence of changes in atmospheric pressure on the melting-point is negligible.

The abbreviation " cor." is placed after a corrected melting-point. It is to be noted that almost all the melting-points given in the literature and the text-books are unfortunately uncorrected.[2] Melting-points determined under uncorrected conditions cannot always be duplicated by other workers. This is especially true of melting-points above about 125°.

## NOTES

1. The Thiele melting-point apparatus is shown in Fig. 10. It uses a small amount of acid and can be heated and cooled quickly. The flame is placed under the bend of the side loop, and the liquid is stirred by means of convection currents. The hot current, however, usually goes down the side near the loop, and the remainder of the liquid is heated mainly by conductance. The temperature of the sulfuric acid bath can be carried up to about 250°. Then the liquid begins to boil, and bubbles sometimes form rapidly and exert such pressure in the narrow side loop that the tube may be cracked. Very good results can be obtained with this apparatus

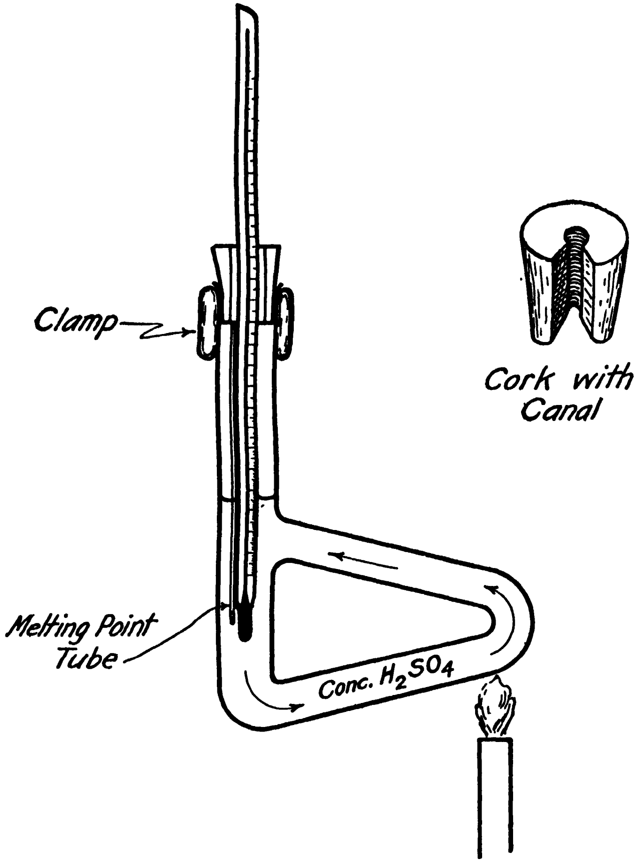
---

[1] For a simple method of sublimation, see Anthraquinone, Expt. 65, p. 210.

[2] The data given in this book are not all "corrected," since they cannot always be found in the literature and very pure material has not been available.

when the heating is properly carried out. It is quickly affected by drafts.

2. Discoloration of the sulfuric acid on account of charring of



Thiele Melting-point Apparatus

FIG. 10.

organic matter may be prevented to a limited extent by the addition of very small amounts of potassium nitrate, sodium persulfate, etc., or the discolored acid may be treated with conc. nitric acid and boiled in a flask or beaker under the hood until the fumes of nitric oxides are no longer evolved.

3. A micro-burner is convenient to use for determinations under 100°.

4. Water can advantageously be used for determining low melting-points.

5. A skillful operator can attach several different melting-point tubes to the same thermometer and make all determinations by one continuous heating of the bath.

6. For temperatures between 220° and 320°, Mulliken[1] recommends a bath prepared by cautiously boiling together for 5 to 10 minutes, under a hood, a mixture of 70 parts by weight of conc. sulfuric acid and 30 parts of neutral potassium sulfate, and stirring until the sulfate is completely dissolved; or by similar treatment of a mixture of 55 parts by weight of the acid with 45 parts of acid potassium sulfate. The mixture has the consistency of glycerol, does not fume badly, and is less corrosive and less easily discolored by traces of organic matter than sulfuric acid. By increasing the proportion of neutral sulfate from 30 to 40 per cent this bath may be used for temperatures up to 370°. This mixture, however, is solid at the ordinary temperature.

For temperatures between 370° and 500°, fused zinc chloride, free from dust, may be employed.

The student is referred to the reference cited for the method of handling these mixtures.

7. Certain substances which decompose at high temperatures giving off water vapor, carbon dioxide, or ammonia, give better melting-points when heated in melting-point tubes sealed at both ends. Complete data as to size of tube, quantity used, etc., are necessary for comparison, because they will vary many degrees with a change in conditions on account of the differences in the gas pressures of the decomposition products.

Similarly substances which readily sublime are sometimes heated in melting-point tubes sealed at both ends.

8. It is not always possible to determine the melting-point a second time on the same sample previously melted in the tube, since in many cases the substance decomposes. It should also be mentioned that in some cases the substance undergoes a change in its crystalline condition, being converted from an unstable form into the stable

---

[1] "Identification of Pure Organic Compounds," Vol. I, 218–9.

form,[1] like iodine monochloride, and phosphorus. For example, the labile or metastabile form of benzophenone melts at 26°, but after having been melted and allowed to solidify, if heated again, it is found to melt at 48°. Sometimes the difference is much greater than in this example, sometimes it is very much less. The changes from one form to the other may be very rapid or very slow. If the melting-point is taken very slowly the metastabile form may be transformed into the stable form and only the melting-point of the stable form actually noticed. .

In other cases the stable form *may* have the lower melting-point. The stable form of benzaldoxime melts at 34–5° and the unstable at 130°. These two forms, however, are isomeric,[2] not polymorphic like benzophenone, and the change is supposed to be stereoisomeric.

Furthermore there are a few known cases where the substance melts sharply at a definite temperature to a *milky liquid,* which on being further heated suddenly becomes clear also at a definite temperature. On cooling the reverse series of changes occurs. Since these milky or turbid liquids show properties of both liquids and solids they have been called *liquid crystals.*[3] The crystalline structure of the turbid liquid cannot be detected by the microscope, but is indicated by the double refraction exhibited by the liquid, and by the formation of the figures characteristic of double-refracting crystals between crossed Nicol prisms in converging light.

---

[1] Such a substance is called monotropic. For a discussion of this phenomenon, see Findlay, "The Phase Rule," 4th Ed. (1914), 46–9; and Holleman, "Organic Chemistry," 4th Ed. (1914), 430; and Lehmann, "Molecularphysik" (1888), Vol. I, 193–213, 291–309, 687–695. The following common substances exist in these two modifications: benzophenone, *p*-tolyl-phenyl-ketone, $\beta\beta$-dibrom-propionic acid, mono-chloracetic acid, acetanilide, $\alpha$-triphenyl-guanidine, *m*-chlor-nitrobenzene, *p*-nitrophenol, diphenyl-naphthyl-methane, triphenylmethane, pentamethyl-leucaniline, styphnic acid, *m*-dinitro-benzene, resorcinol, hydroquinone, trinitro-*m*-cresol, phthalic acid, stilbene-dichloride, benzoin, mandelic acid, cinnamic acid, carbostyril, mercury-diphenyl, limonene-tetrabromide, etc.

[2] See Findlay, "The Phase Rule," 4th Ed. (1914), 208–11; Holleman, "Organic Chemistry," 4th Ed. (1914), 431–3; and Sidgwick, "The Organic Chemistry of Nitrogen," (1910), 118.

[3] For discussion see Findlay, 'The Phase Rule," 4th Ed. (1914), 55–8; and Holleman, "Organic Chemistry," 4th Ed. (1914), 408. Cholesteryl benzoate melts to a milky liquid at 145.5° and to a clear liquid at 178.5°. Azoxyanisole, azoxyphenetole, and *p*-methoxy-cinnamic acid also show a similar behavior.

## QUESTIONS

1. Discuss some of the errors in the ordinary method of determining the melting-point.
2. Why is it necessary to heat slowly when the temperature is near the melting-point?
3. Why should the substance be powdered?
4. What objection is there to the use of a rubber band for holding the melting-point tube to the thermometer?
5. What advantage does conc. sulfuric acid have over glycerine and cottonseed oil as used in the melting-point apparatus? (Compare behavior on heating.)
6. What bath is used for taking melting-points above 300°?
7. What is the object of adding sometimes a crystal of potassium nitrate or sodium persulfate to the conc. sulfuric acid bath?
8. Given two substances having the same melting-point, if one is known, how can you tell whether the other compound is identical with the first by means of the melting-point determination? Explain.
9. What advantage has water over conc. sulfuric acid for determining low melting-points? (Compare specific heats.)

## Experiment No. 13

### FORMATION OF A TERTIARY ALCOHOL BY MEANS OF GRIGNARD'S REACTION

### Preparation of Dimethyl-ethyl-carbinol (2-methyl-butanol-2)[1]

The success of this experiment depends on the absence of water until after the ketone is all added. Therefore the apparatus and substances used must be perfectly dry. Dry the acetone with anhydrous potassium carbonate or anhydrous sodium sulfate, the ethyl bromide with calcium chloride, and the " absolute " ether with very thin slices of clean sodium in a flask provided with a calcium chloride tube.[2] Let them all stand at least overnight. Use larger amounts than called for below since some is absorbed by the drying agents. The " ether over sodium " or " absolute " ether as obtained from the stockroom must be dried again because it cannot be kept free from water in the ordinary containers. The ordinary ether can be used for this experiment if it is treated as follows: Shake it two or three times with different portions of a saturated solution of salt in order to remove the alcohol and dry first with calcium chloride and then with sodium.[3] If it is turbid at the end of the drying, it should be distilled under anhydrous conditions (see Absolute Alcohol, p. 26), and then dried again with sodium before use in the experiment.

---

[1] The Geneva or official nomenclature is outlined in *Amer. Chem. Journ.*, **15** (1893), 50.

[2] During warm weather a small reflux condenser in addition should be used to prevent excessive evaporation of the ether.

[3] **Sodium residues:** Great care should be exercised in handling the residue of sodium. It should not be put into the sink or the waste jar, but should always be destroyed by adding it in small pieces to some alcohol or acetone in a beaker, waiting until practically all action has ceased with each piece before adding another. Then (Care!) pour the solution into the sink, a little at a time. Also rinse the flask with alcohol or acetone before adding any water.

**Ether Distillation.**—Ether must be kept away from flames. Its vapor is heavier than air and very inflammable, and therefore the heating for the distillation must be done with steam or warm water. In ether distillation use an Erlenmeyer suction flask as a receiver connected as in the Absolute Alcohol experiment, p. 27, but with a long rubber tube attached to its outlet tube and leading below the level of the desk to carry away the fumes. When small quantities are distilled an ordinary flask may be used as a receiver and the space between the condenser tube and mouth of the flask loosely plugged with cotton to prevent the circulation of the vapors.

Have all necessary connections ready before the experiment is started.

To a 250 cc. flask containing 5 grams of dry magnesium turnings attach an addition tube and reflux condenser with inner tube dry.[1] Insert a dropping-funnel[2] in the addition tube and connect a calcium chloride tube filled half with calcium chloride and half with soda lime (to remove carbon dioxide). The soda lime should be next to the large open end of the tube. Add 25 cc. of dry ether to the flask. Place a solution of 30 cc. (44 grams) of dry ethyl bromide (twice the theoretical amount required according to the equation) in 15 cc. of dry ether into the bulb of the funnel, stopper loosely and let this slowly drop into the flask. A vigorous reaction begins after the first small portion has been added. Moderate by surrounding the flask with cold water. If it does not start spontaneously, warm the flask with the hand or add a crystal of iodine. Shake frequently. After the reaction is well started add 50 cc. of the dry ether direct to the mixture by pouring it through the condenser. When practically all the magnesium has disappeared cautiously add, with shaking and *good cooling*, a solution of 15 cc. (12 grams) of dry acetone and 10 cc. of dry ether from the dropping-funnel. Each drop reacts with a hiss and causes a white precipitate which at first redissolves but later settles down as a bluish-gray, viscous mass.

---

[1] See Fig. 3, p. 13.

[2] The connection can sometimes be made with a piece of rubber tubing instead of a cork.

After the reaction is complete cautiously decompose the addition product by adding, from the funnel during about thirty minutes, the calculated amount of sulfuric acid[1] in 140 cc. of water. During this treatment place the flask in ice and shake frequently. A flocculent white precipitate is formed at first but is later dissolved. (?) Separate the ethereal solution which contains the product, and dry with fused potassium carbonate. Remove the ether by distillation, observing the precautions mentioned above, and fractionate the residue in a small distilling flask. Since the carbinol is volatile with ether collect the distillate in the following fractions: 70°–95°, 95°–105°, 105°–110°, then redistill each, collecting the portion distilling 100°–104° as the sample. Pure dimethyl-ethyl-carbinol boils at 102° and has a specific gravity of 0.8069 at 25°. Yield, 40 per cent of the theory.

Test the first runnings of the distillate for unsaturated compounds with bromine in carbon tetrachloride, and with dilute potassium permanganate. (?)

### Note

Magnesium turnings for use in the Grignard reaction must be prepared fresh or kept in a bottle whose cork has been covered with melted paraffin to prevent the entrance of moisture. Otherwise the magnesium becomes coated with the hydroxide, etc., and does not react well.

### References

Gattermann, "Practical Methods of Organic Chemistry," 3d Amer. Ed., 350–4; Wren, "The Organometallic Compounds of Zinc and Magnesium" (Van Nostrand, 1913), 1–26, 72–9; Nelson ana Evans, "Electromotive force developed in cells containing nonqueous liquids," *Journ. Amer. Chem. Soc.*, **39** (1917), 82.

## QUESTIONS

1. How does moisture cause trouble in this experiment?
2. Why is absence of water unimportant after the ketone has been added?

---

[1] Conc. sulphuric acid of sp. gr. 1.84 contains approximately 96% $H_2SO_4$ by weight. Make sure of your equation before making this calculation.

3. Why isn't ordinary ether used and dried directly with calcium chloride as in the case of the acetone?
4. Why cannot the acetone be dried with metallic sodium?
5. What other solvent besides ether can be used for this experiment? Why?
6. What reactions take place when ether, magnesium, and ethyl bromide are brought together?
7. Why is the flask containing this reaction mixture kept in cold water?
8. Why is the acetone added cautiously?
9. Can the acetone be added directly with the ethyl bromide to the ether and magnesium mixture? (Compare Davies and Kipping, *Jour. Chem. Soc.*, **99** (1911), 296–301.)
10. What would happen if carbon dioxide came in contact with the Grignard reagent?
11. Is the magnesium oxidized or reduced in the experiment?
12. What would be formed if only water was added at the end of the reaction?
13. What is the purpose of adding acid? Is it absolutely necessary?
14. Could conc. $H_2SO_4$ be used in place of dilute acid?
15. What causes the bubbling that often occurs after all the dilute acid has been added?
16. What might be some of the impurities in the crude tertiary alcohol? (Compare the properties of the "first runnings" of the distillate.)
17. Explain what is meant by the term "volatile with ether." (Compare fractionation of liquids which mix in all proportions.)
18. Why use a small distilling flask in the redistillation of dimethyl-ethyl-carbinol?
19. How does this pentyl (amyl) alcohol differ from the isomyl alcohol of commerce?
20. The amount of ethyl bromide (30 cc.) is twice the amount required by the theoretical equation. Why is it necessary to use an excess?

## Experiment No. 14

### REDUCTION OF A KETONE TO A SECONDARY ALCOHOL (SODIUM ALCOHOL REDUCTION)

### Preparation of Methyl-phenyl-carbinol from Acetophenone (Methyl-phenyl-ketone)

Dissolve 10 grams (10 cc.) of acetophenone in 125 cc. of alcohol in a 500-cc. flask, with an addition tube attached and a reflux condenser connected with the side tube. Prepare 10 grams of clean metallic sodium [1] cut in strips narrow enough to slip through the vertical tube easily. Add these strips to the alcoholic solution through the vertical tube a few at a time and let the reaction abate somewhat before the addition of others. The reduction should be strong and the alcoholic solution should boil vigorously, but at the same time the reaction must be kept in hand.

When all the sodium has dissolved, distill off as much as possible of the alcohol, *in vacuo*. Since it is difficult to transfer the reaction-mixture, which is very viscous, and since there is a great deal of foaming during the distillation, the original flask is used for this first distillation instead of the Claisen flask described in the accompanying directions for vacuum distillation, Expt. 15, p. 76. Slant the flask in order to allow the foam to " break " against the walls and not pass out into the distillate. Connect it with a bent tube leading into a distilling-flask which acts as a receiver (Compare Fig. 11). The receiver need not be cooled in this case; let the alcohol vapors pass through uncondensed. The receiver is used to catch any of the product which sometimes distills or goes over with some foam. Heat the main flask

---

[1] Use a common knife or pen-knife to cut the sodium and dip the blade frequently into the kerosene with which the sodium is covered Return all residues to the original bottle or destroy them with alcohol, as mentioned under Dimethyl-ethyl-carbinol, p. 69.

with water kept at 50°–60°, and frequently shake the flask somewhat to change the surface of the mixture and thus permit rapid vaporization. The distillation requires from one to two hours. As it progresses the mixture becomes a darker brown, and pasty.

When practically all the alcohol is distilled over add 50 cc. of water and then exactly neutralize the solution with acetic acid. Distill off the remaining alcohol *in vacuo* from the same flask and in the same manner as before.

**Ether Extraction.** Transfer the residue to a separatory funnel with the aid of water and a little ether, and extract it with ether as follows: Add about 30 cc. of ether (and if necessary enough water to dissolve any precipitate), stopper securely, invert the funnel, holding the stopper in with one hand and placing the thumb of the other hand on the handle of the stop-cock and the first two fingers on the other side of the stem and shake. While it is still inverted open the stop-cock to release the pressure[1] within the funnel. Close the stop-cock and shake again, frequently releasing the pressure. Turn the funnel right side up, support it in a ring, allow to settle, draw off the aqueous layer into a beaker, and pour the ethereal solution from the *top* of the funnel into a dry Erlenmeyer flask. Return the aqueous layer to the funnel, repeat the extraction with about the same amount of ether, and add the ethereal solution to the first portion in the Erlenmeyer flask.

If some of the product was distilled over into the receiving flask, the material thus collected should be extracted with ether, provided it contains practically no alcohol, and added to the main ethereal solution. If it contains much alcohol it cannot very well be extracted with ether (?), and the alcohol must be evaporated off before extraction.

If the main ether extract is acid to litmus, neutralize it by shaking with a solution of sodium carbonate.

Dry the ethereal solution with fused potassium carbonate, transfer it to a Claisen distilling-flask, remove the ether by

---

[1] In this laboratory there are two cases on record where the separatory funnel exploded on account of carelessness in disregarding this procedure.

distillation under the usual conditions and then distill the residue *in vacuo*, in accordance with the directions given in Expt. 15, following this. Some ether will pass over first, the temperature then rises and the carbinol distills. It boils at 118° at 40 mm., 106° at 21 mm., and 98° at 15 mm. At atmospheric pressure, it boils with partial decomposition at about 202°. The yield is about 40 per cent of the theoretical amount.

### REFERENCES FOR ETHER EXTRACTION

Walker, "Introduction to Physical Chemistry," 7th Ed. (1913), 59-61; Alex. Smith, "Introduction to Inorganic Chemistry," 3d Ed. (1917), 189.

## QUESTIONS

1. Why is alcohol used in this experiment?
2. Is all the alcohol used up during the reaction?
3. What becomes of the sodium ethoxide?
4. Point out what is reduced and what is oxidized.
5. Is the methyl-phenyl-carbinol formed acted upon by sodium?
6. What other organic compound is likely to be formed?
7. Is this a " higher " or " lower " reduction product of the ketone?
8. Why is sodium used instead of some other metal like zinc?
9. Why does sodium react with alcohol while zinc does not?
10. Where does the " remaining alcohol " come from?
11. How could you calculate how much of this " remaining alcohol " there would be?
12. Why is it necessary to distill off this alcohol before extracting with ether?
13. Why is the ethereal solution poured from the *top* of the separatory funnel?
14. Discuss the extraction of aqueous solutions and mixtures of organic substances with immiscible liquids, such as ether, chloroform, benzene, etc.
15. What is meant by the Coefficient of Partition or Distribution? (See references above.)
16. Why is it necessary to distill in a vacuum?
17. What is the boiling-point of acetophenone?
18. How could the presence of any unchanged acetophenone be shown in the product?
19. Is the methyl-phenyl-carbinol as prepared in the laboratory optically active? Explain.

## Experiment No. 15

### Distillation *in vacuo* or under Diminished Pressure

Distillation *in vacuo* or under diminished pressure is always resorted to if the compound decomposes when heated at atmospheric pressure, but is volatile without decomposition at lower pressures. The apparatus employed is indicated diagrammatically in Fig. 11. A Claisen distilling-flask is used since it has a side arm which helps to prevent any liquid from being sprayed up into the outlet tube if the liquid should bump violently, and since tighter joints can be obtained by connecting the thermometer and the capillary extension tube with heavy rubber tubing outside than when rubber stoppers are used. Attach an ordinary distilling-flask as the receiver with a rubber stopper, making certain that the outlet tube of the Claisen flask projects into the bulb of the receiver in order that the vapors of the distillate may not be carried off by the suction. During the distillation cool it with running water.[1] Support both flasks with clamps. If the temperature of the distillate under the diminished pressure exceeds 160° the rubber stopper in the receiver should be changed for a good cork stopper. Rubber stoppers soften and gradually melt above this temperature. A good cork stopper can sometimes be made air-tight by coating it with collodion after the apparatus has been fitted up. Connect the delivery tube of the receiver by means of rubber " pressure " tubing to a manometer and a water pump. By using glass tubing and short rubber connections only a small amount of the expensive " pressure " tubing is necessary. All glass connecting tubing should have smooth, rounded ends.

---

[1] The cooling is made more efficient if a piece of cloth is wrapped around the bulb of the receiving flask.

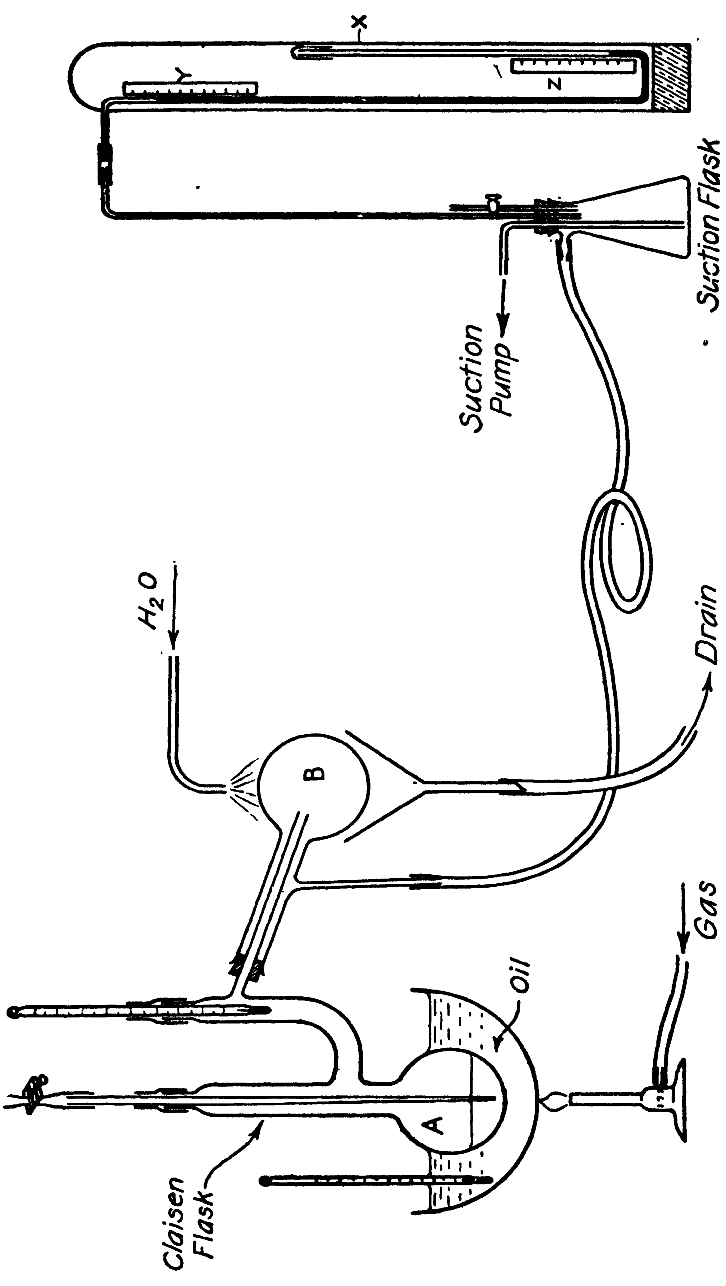


FIG. 11.—DISTILLATION IN VACUO

A good water pump will give a pressure in the apparatus as low as the vapor tension of the water at its particular temperature. In winter when the temperature of the water may be 8°, at which the vapor tension of the water is 7.99 mm., the pressure within the apparatus may approach 8 mm., but in summer when the temperature of the water may be as high as 23° a pressure cannot be obtained lower than 21 mm., which is the vapor tension of the water at that temperature.[1]

The general connections for vacuum distillation are made as follows: Outlet tube of the receiver to an Erlenmeyer suction flask and the latter to the water pump and the manometer. The tube connecting the suction flask with the pump should extend to the bottom of the flask in order that any water which may come over on account of unequal pressure in the water main will be sucked right out as soon as the greater water pressure returns. A three-holed rubber stopper is used in the mouth of the suction flask. This provides for the tube to the pump, just mentioned, for the tube connecting the manometer, and for a glass stop-cock which is used for equalizing the pressure when necessary (or this glass stop-cock may be placed between the receiver and the suction flask). A " vacuum " valve[2] may be placed just before the pump. Instead of using a distilling-flask as the receiver it is often convenient for small amounts of high-boiling liquids or solids to use a " suction " test-tube— a test-tube with a side outlet tube. In some cases, a sample tube can be placed inside, and then it will not be necessary to transfer the distillate.

In order to prevent bumping the vapor phase is introduced

---

[1] For pressures lower than these, a good oil pump must be used. Then it is possible to go down to 0.1 mm.

A table of the vapor pressure (tension) of water at different temperatures is given on p. 301.

[2] Not shown in the figure. A "vacuum" valve consists of a glass tube bent in the form of a narrow inverted U with elongations at the ends for connecting purposes. One arm contains a free-moving hollow glass plunger which is ground at one end to fit into a corresponding ground glass seat formed by a constriction. When the pressure suddenly changes the plunger moves up into the ground seat and closes the tube automatically, and moves out again when the pressure is reversed. It serves to keep water from being drawn into the apparatus.

by using pieces of porous tiling[1] in the liquid, or better by passing a rapid continuous stream of tiny air bubbles through the liquid (see discussion in note 2, p. 18, of the Boiling-point experiment). An ordinary glass tube is drawn out into a fine capillary, and cut off at the proper length. To the wide end is attached a short piece of rubber tubing with a screw clamp at its upper end to regulate the bubbling.[2] Sometimes the capillary can be made so fine that no other regulation will be necessary. A slight drawback to this method is that it introduces an error in the boiling-point, as the pressure registered when air is present will be the sum of the partial pressures of the vapor and of the air.

The distilling-flask should not be more than *one-third* full. It is heated by means of a water or an oil-bath,[3] according to the temperature required. Good results are obtained by immersing the bulb of the flask at least *two-thirds* into the bath. The vapor is not superheated so much as under ordinary conditions on account of the rarefaction of the vapor and less heat conductance. A thermometer is kept in the oil and the temperature of the oil should not ordinarily be more than 20°–30° higher than the temperature at which the liquid in the flask distills. The heating is not begun until the apparatus is exhausted. Sometimes it is necessary to prevent radiation by wrapping filter or asbestos paper around the neck of the flask below the outlet tube.

---

[1] The porous tiling loses its efficiency within a short time, probably because the air is given up more rapidly under the reduced pressure.

[2] If an ordinary distilling-flask is used instead of the Claisen distilling-flask, and if there is not space enough for both thermometer and the glass bubbling tube in the neck, the thermometer may be placed within the tube and a one-holed stopper used.

[3] Rape-seed oil is good to use. Paraffin or paraffin oil smokes a great deal. The rape-seed oil also smokes somewhat at first and gives off a pungent odor, but after two or three heatings it does not smoke so much. It can be carried up to about 300°. A metal bath has the advantage that it does not smoke and is not liable to catch fire, but it is solid at ordinary temperatures. Following are alloys which can be used for low-melting baths: Wood's metal, 1–2 parts of cadmium, 2 of tin, and 7–8 of bismuth, melts at 71°; Rose's metal, 2 parts of bismuth, 1 of lead, and 1 of tin, melts at 95°; an alloy of 1 part of lead and 2 of bismuth, melts at 120°. If the flask which is heated in such metal baths is coated with graphite the metal will not stick to the glass.

It is best to test the apparatus before putting in the substance in order to determine whether the glass is perfect and the joints are tight. In this way a loss of material may often be avoided.

When carrying out a vacuum distillation it is advisable to protect the eyes with goggles, or use a glass screen.

At the end of the distillation the stop-cock should be *gradually* opened before the water is turned off. If the stop-cock is used between the receiver and the suction flask, the stopper itself is gradually and carefully removed. This allows the mercury column to settle slowly and also prevents water vapor from being sucked into the apparatus.

**The Manometer.** The manometer consists of a glass tube bent in such a way as to hold a column of mercury, a scale, and a stand for a support, as shown in the figure. The short length of the glass tube should be about 50 cm. long and the longer length 85 cm. The lower bend can be made by one heating in a smoky flame. After the mercury has been poured in,[1] insert a plug of cotton to keep out foreign matter and place a small test-tube over it. By slanting the manometer when the mercury is added any air bubbles will come out readily, especially if the tube is tapped. The glass tube should be dry and free from dust, grease, etc. If the mercury does not run free from bubbles wash the tube with alcohol and ether and remove the adhering ether with a current of air. The column of mercury is of such a height that when the apparatus is exhausted the lower and upper limits of the mercury will be opposite some point on the scales described below. The glass tube is connected with the suction flask.

**To Make the Scale.** Select *any* point, *X*, *not less than* 38 cm. above the lowest bend in the glass tubing, and attach narrow strips of paper (*Y* and *Z*) near the top and the bottom of the stand in the positions shown. Measuring from the point *X* mark on the papers numbers showing 28 to 38 cm. up and down respectively. Ruled centimeter paper is very convenient, and when this is used it should not be attached until a definite point opposite a centimeter line has been located.

---

[1] Use a small funnel connected by means of rubber tubing to the manometer tube.

Instead of these scales a meter stick can be fastened to the stand and the different heights read directly.

**To Calculate the Pressure within the Apparatus.** Add the figures on the lower and upper scales opposite the top of the mercury meniscus [1] in each case and subtract the sum of these numbers from the barometric reading. Record both the boiling-point and the pressure, for example b. p.$_{22}$ 145°. The temperature of the bath should also be recorded for reference.

It is not always possible to obtain exactly the same pressure at which the boiling-point is given in the text. However, the difference in boiling-points at the given pressure and the pressure actually used can be estimated. The distillate is, of course, always collected while the temperature (and pressure) remains constant.

There is no set rule or exact method of calculation for finding the boiling-point under diminished pressure when only the boiling-point at 760 mm. is known. A few general hints may be given. A substance that boils around 100° at 760 mm. will boil about 60° lower at 25 mm., and one that boils around 200° at 760 mm. will boil about 80°–100° lower at 25 mm. The variation in the boiling-point becomes greater for each degree at the lower pressure, and is very marked as the pressure drops below 3 or 4 mm.

## NOTES

1. *Purification of mercury:* If the mercury is wet or dirty it can be purified by running it through a dry filter paper which has a pin hole in the bottom. The impurities stick to the paper, which also absorbs the moisture. Several treatments may be necessary with clean filters each time.

2. If the water pump does not "catch," and the water runs out straight without causing proper suction, hold the hand close to the bottom of the pump while the water is turned on and cause a slight back pressure until the suction is all right.

3. Never use an ordinary flat-bottomed flask in the apparatus for vacuum distillation. Explain.

---

[1] Tap the glass tubing before taking the reading in order to bring the mercury to rest and overcome the "lag."

4. Sometimes for more complete cooling a water condenser must be placed between the distilling-flask and the receiver.

5. An apparatus for collecting fractions without interrupting the distillation is described by M. T. Bogert, *Journ. Ind. and Eng. Chem.*, **7** (1915), 785-6.

6. If water should splash into the oil, the distillation must be stopped and the wet oil replaced with fresh oil. If this happens while the oil is hot it will foam very much and great care must be used to prevent any of the hot oil from getting on your hands, etc. Oil with even a very small amount of water in it is useless.

## QUESTIONS

1. In " vacuum distillation " how is bumping avoided?
2. Why should the outlet tube of the distilling-flask extend into the bulb of the receiver?
3. Why should the distilling-flask be not more than one-third full?
4. Why is the stop-cock opened before the water is turned off?
5. Why is the tube from the suction flask to the pump run down to the bottom of the suction flask?
6. What advantages has a Claisen flask in distillation *in vacuo*?
7. Why should an ordinary flat-bottomed flask never be used in the apparatus for vacuum distillation?
8. How low a pressure can be obtained with a water pump?
9. Why is it not necessary to have an absolutely definite volume of mercury in the tube?
10. Do air bubbles along the walls make any difference?
11. Does the mercury drop exactly as far as it rises?
12. Which reading on the barometer should you use for calculating the pressure within the apparatus, the " corrected " or " uncorrected "?

## Experiment No. 16

### OXIDATION OF A PRIMARY ALCOHOL TO AN ALDEHYDE

### Preparation of a Solution of Acetaldehyde

In this experiment ethyl alcohol is oxidized to acetaldehyde by means of sodium dichromate in dilute sulfuric acid solution. Since it is difficult to separate the acetaldehyde, which boils at 21°, from the impurities by fractionation, the crude acetaldehyde is usually absorbed in ether and converted into the crystalline aldehyde ammonia, which is easily purified, and then used for making pure acetaldehyde. This is a long process, however, and requires elaborate apparatus, as described in Expt. 17.

For making a crude product which can be used in the aldehyde tests, proceed as follows:

Attach a dropping-funnel to a 250-cc. distilling-flask connected with a long water condenser, and arrange a receiver set in ice. On account of its low boiling-point care must be exercised in catching the distillate. A small Erlenmeyer flask makes a good receiver. The end of the condenser should extend into it as far as possible and the flask should be entirely surrounded by ice. Add a mixture of 20 cc. of conc. sulfuric acid and 50 cc. of water. Fill the dropping-funnel with a solution of 20 grams of sodium dichromate in 30 cc. of water and 25 cc. of alcohol, and during the course of about fifteen to twenty minutes allow this to drop slowly into the flask. Heat the mixture to gentle boiling with a very small flame. After all the solution has been added continue the gentle heating for several minutes. *Redistill very slowly*, collecting the portion boiling between 20° and 45° in an ice-cooled receiver. Acetaldehyde boils at 21°. The product (which need not be handed in) contains some water, but can be used in the experiments entitled "Tests for Aldehydes," Expt.

19, p. 91. For study, use the questions given under the preparation of acetaldehyde from aldehyde ammonia, Expt. No. 18, p. 90.

### NOTE

This experiment and the tests which follow should if possible be carried out during one laboratory period. Otherwise extra precautions must be taken to keep the solution of the aldehyde properly stoppered and cooled.

## Experiment No. 17

### OXIDATION OF A PRIMARY ALCOHOL TO AN ALDEHYDE

### The Preparation of Acetaldehyde Ammonia

In this experiment ethyl alcohol is oxidized to acetaldehyde by means of sodium dichromate in dilute sulfuric acid solution. Since it is difficult to separate the acetaldehyde, which boils at 21°, from the impurities by fractionation, the crude acetaldehyde is absorbed in ether and converted into the crystalline aldehyde ammonia, which is easily purified, and then used for preparing pure acetaldehyde.

Set up the following apparatus and have it ready to start the experiment at the beginning of the laboratory period. If the experiment cannot be completed in one period, it must at least be continued until the aldehyde has all been absorbed in ether (one hour) which solution can then be set aside in the icebox in a well-stoppered bottle.

To a 500 cc. flask attach an addition tube (Fig. 3, p. 13), insert a dropping-funnel (Fig. 6, p. 36), and connect the side arm with a long slanting reflux condenser (60 cm.). Through a cork in the upper end of the condenser attach a bent tube and connect this with a 100 cc. pipette leading into a 250 cc. wide-mouthed bottle (with a vent) set in an ice mixture. Place a thermometer inside the inner tube of the condenser and support it with a thread held fast by the cork stopper at the upper end. The bulb of the thermometer should be as near the center of the condenser as possible. Insert another thermometer through the stopper at the upper end in order that the temperature of the issuing vapors may be noted.[1] Use good corks and make

---

[1] A second addition tube can be used here also if desired.

*tight* connections throughout. Rubber stoppers may be used with advantage.

Into the bottle surrounded by ice pour 100 cc. of anhydrous ether. The pipette should open about 1 cm. below the surface of the ether. Add a mixture of 17 cc. of conc. sulfuric acid and 75 cc. of water to the flask, and during the course of thirty minutes allow a solution of 35 grams of sodium dichromate in 60 cc. of water and 50 cc. of alcohol to drop in slowly. During this time heat the solution to **gentle** boiling, and allow the water to run *very slowly* through the condenser. Regulate the heat and water flow so that the temperature indicated by the thermometer in the condenser does not register higher than 45°. (What is the *lowest* temperature limit?[1] Why must a large flame *not* be used?) After all the mixture has been added continue the heating with the same precautions for an additional thirty minutes. If the ether solution at any time should rise high in the pipette, add a little more of the solution, or if this has all been added simply open the stop-cock of the dropping-funnel momentarily. All the aldehyde has been driven over when its pungent odor is not very strong in the funnel opened for the test.

When the apparatus is disconnected note the most pronounced odor from the mixture in the flask. To what is this due? How can you account for it?

Through a *wide* tube, such as the large part of a calcium chloride tube or an adapter, or a funnel, pass a stream of anhydrous ammonia from a cylinder into the ether solution contained in the wide-mouthed bottle packed in ice and salt near the draft pipe. The solution will be saturated in about five minutes. Filter off the white crystals of aldehyde ammonia with suction and dry them until all the ether has completely evaporated. This can be done conveniently in a vacuum desiccator. The aldehyde ammonia is somewhat soluble in ether and a second crop of crystals can be obtained by concentrating the mother

---

[1] In wintertime warm water should be added to the condenser to bring the temperature within the proper limits.

liquor. Determine the melting-point. Yield, 13 grams.[1] The aldehyde ammonia often becomes yellow and brown on standing and loses its crystalline character, probably due to slow "resinification." For this reason the product should not be allowed to remain in the desiccator more than a day. This chemical change can be noted by the lowering of the melting-point.

### NOTES

1. In case an addition tube is not at hand, use a two-holed stopper through which pass the stem of the dropping-funnel and the small end of an adapter. The condenser is then connected with the adapter.

2. If an ammonia cylinder is not available, the dry ammonia gas can be obtained by boiling the ordinary conc. ammonium hydroxide solution, sp. gr. 0.90, and passing the vapors through a drying tower containing calcium oxide, care being taken that a *wide* tower is used.

3. Vacuum desiccator. A vacuum desiccator is like an ordinary desiccator, but has as top-cock on a ground-in stopper in the cover. Put some calcium chloride or conc. sulfuric acid in the bottom and place the watch glass containing the substance on a support, such as a perforated porcelain disk or a wire gauze, across the constricted part of the desiccator. Grease the stop-cock, and the other ground surfaces. Attach the outlet to the suction with a *heavy* rubber tube, open the stop-cock and evacuate. 15–30 minutes usually suffices. Close the stop-cock and then remove the rubber tube before shutting off the suction (?). When ready to open the desiccator turn the stop-cock just enough to let in the air slowly, otherwise the rush of air may blow the dry particles about.

It is well to insert a stout empty bottle in the connection between the desiccator and the pump. Then if there is any back pressure and the water begins to flow back it will be caught in the bottle and you will have time to disconnect before it reaches the desiccator.

Never go away and allow the stop-cock to remain open with the suction on, especially when a water-pump is used. The change in water pressure may cause the water to be drawn in and flood the desiccator.

---

[1] This amount is too bulky for the usual preparation bottle. Hand in a sample, stating the total yield on the label, and use the major portion for the preparation of acetaldehyde itself in the next experiment.

Liquids will evaporate about six to seven times faster in a vacuum desiccator than in an ordinary desiccator, as shown recently by Mr. W. E. Morgan.

The efficiency of the conventional vacuum desiccator can be increased if it is provided with a second inlet tube, with stop-cock attached, in the lower part of the desiccator. While the suction is on, allow air, which is thoroughly dried by passage through some of the same kind of drying agent used within the desiccator, to enter very slowly through this inlet tube.

## QUESTIONS

1. Write equations for all the chemical changes involved in the formation of acetic aldehyde from ethyl alcohol by this method.
2. Point out in the above reactions what is oxidized and what is reduced.
3. Why cannot a simple water solution of sodium dichromate be used instead of one that has been acidified with sulfuric acid?
4. What causes the green coloration? (Compare Mellor, "Modern Inorganic Chemistry" (1912), 652.)
5. Could hydrochloric or acetic acid be used in place of sulfuric acid?
6. Why is a dropping-funnel necessary? Why not add the mixture of dichromate and alcohol all at one time?
7. Why not omit heating the mixture in the reaction flask until after the alcohol and the dichromate has all been added?
8. Why is the condenser attached to the reaction flask held in a slanting position?
9. Why is it important to keep the temperature of the condenser at about 45°?
10. Why is it necessary to absorb the acetic aldehyde in anhydrous ether? Why is water not used in place of ether? Alcohol?
11. Why is it necessary to keep the ethereal solution of the aldehyde cold?
12. How does anhydrous ammonia react with acetic aldehyde? Write equation.
13. Do all aldehydes react in a similar way when treated with anhydrous ammonia? Compare formaldehyde and benzaldehyde.
14. How does water react with formaldehyde?

15. Could aqueous ammonia be used in place of tne anhydrous ammonia?
16. Why is a *wide* tube used to pass the ammonia gas into the ethereal solution?
17. Explain how a mixture of ice and salt is colder than ice alone.
18. What advantage does a vacuum desiccator have over an ordinary desiccator for drying these crystals?
19. What impurities are liable to contaminate the crystals of aldehyde ammonia? Name four and account for them.
20. Since the object of making the aldehyde ammonia is not only to show the formation of the addition product but also to obtain pure acetaldehyde, why not make the pure acetaldehyde directly by simply catching the main distillate in a flask in a freezing-mixture and then fractionating this?

## Experiment No. 18

### The Preparation of Acetaldehyde from Aldehyde Ammonia

From the aldehyde ammonia (which should be entirely free from ether) prepared in the preceding experiment prepare acetaldehyde as follows: Provide a distilling-flask with a dropping-funnel, connect with a condenser and attach to the latter a tube leading to the bottom of a second distilling-flask which is set in a mixture of ice and salt. Dissolve 10 grams of aldehyde ammonia in 25 cc. of water and allow this to drop into a solution of 8 cc. of conc. sulfuric acid in 20 cc. of water in the distilling-flask heated with *boiling* water. Dry the distillate with calcium chloride in the flask in which it was collected by shaking for a few minutes, and then distill from this same flask *without* removing the calcium chloride, using the precautions noted above. Pure acetaldehyde boils at 20.8° cor. Use the product in the following experiments. (Keep the product in a well-stoppered bottle in the ice-box if it is not used on the same day it is made.)

### QUESTIONS

1. Write all equations for reactions involved in the formation of the aldehyde from its aldehyde ammonia.
2. Why should the aldehyde ammonia used be *entirely* free from ether?
3. Why is the aldehyde ammonia dissolved in water before being added to the dilute sulfuric acid?
4. Why should the end of the condenser be extended to the bottom of a small distilling flask?
5. Why is this distilling flask surrounded by a freezing mixture?
6. Why is it necessary to redistill the aldehyde?
7. Could any other drying agent besides calcium chloride be used for drying the acetic aldehyde?
8. What advantage has the porous calcium chloride over fused stick calcium chloride in this case?
9. Why is the drying agent not removed before the distillation in this case while in practically all other experiments the drying agent is removed before the distillation?

## Experiment No. 19

### Tests for Aldehydes

1. *Silver-mirror test.* Make an ammoniacal solution of silver nitrate by treating 4 cc. of N/10 silver nitrate with 3N ammonium hydroxide drop by drop until the precipitate (?) which is first formed just redissolves. Add a single drop of the aldehyde, quickly mix by shaking, and set the tube in the rack. A deposit of metallic silver will begin to form at once and soon makes a beautiful mirror. If the test-tube is not perfectly clean only a black precipitate of silver will be obtained. If necessary, clean the tube with boiling sodium hydroxide solution.

Sometimes a very small amount of dilute sodium hydroxide solution must be added in order to get the reduction. Compare Benzaldehyde experiment, p. 182. A mixture of sodium hydroxide and silver nitrate constitutes Tollens' reagent for aldehydes.

Do not heat the silver solution or let it stand for a long time, since explosive compounds are formed. See Smith, "Inorg. Chem.," p. 753; Alfred Tingle, "Ammoniacal Silver oxide Solution," *Journ. Ind. and Eng. Chem.*, **11** (1919), 379; and E. J. Witzemann, *ibid.*, **11** (1919), 893; also, note, 884.

2. *Reduction of Fehling's Solution.* Mix 3 cc. of each of the two portions of Fehling's Solution ("copper half" and "alkaline tartrate half"), and bring the clear, deep blue solution to a boil. Note whether a precipitate is formed. If not, add a drop of the aldehyde and boil for a minute. A yellow precipitate of cuprous hydroxide is generally formed at first and this is rapidly converted into bright red cuprous oxide. If the amount of reduction is small the cuprous oxide sometimes cannot be seen until after the solution has been allowed to stand long enough for it to settle out. Or the solution can be filtered. Note the odor during the boiling, and compare test 4.

Fehling's solution is kept in two parts because it gradually deteriorates on standing after being mixed.

3. *Polymerization.* To a little of the aldehyde add a single drop of conc. sulfuric acid on a stirring rod. (Care!) What is formed?

4. *Resin Formation.* Gently heat a little aldehyde and a few drops of a conc. solution of sodium hydroxide. (?)

5. *Schiff's Aldehyde Test.* Schiff's aldehyde reagent consists of a very dilute solution of fuchsine decolorized with sulfurous acid. It is also known as "Fuchsine-sulfurous acid reagent," and is furnished ready for use by the stockroom.

Add a drop of the aldehyde to 5 cc. of water and then add a drop of the reagent. The development of the original reddish-violet color of the fuchsine indicates the presence of an aldehyde.

Schiff's reagent can be prepared by dissolving 0.2 gram of pure fuchsine or rosaniline (in the form of the hydrochloride or acetate) in 15 cc. of water and passing in sulfur dioxide until the solution is saturated. This requires but a few minutes and the solution will be colorless, provided *pure* rosaniline or its salt were used. Then dilute to 200 cc. It should be kept in a dark-colored glass-stoppered bottle. If the bottle is not properly stoppered the liquid will gradually lose sulfur dioxide and then of course the color will return even before any aldehyde is added.

Do not boil the reagent! Why? What would happen if a weakly alkaline substance was added to the reagent?

The reactions in the Schiff's Aldehyde Test are not completely understood. The manner in which the aldehyde removes the sulfurous acid is probably similar to the reaction of an aldehyde and sodium bisulfite. See Acetone,. p. 98.

## QUESTIONS

1. Discuss the reactions involved when the acetic aldehyde is mixed with ammoniacal silver nitrate.
2. What is the purpose of the alkali in this test for aldehydes? (Stieglitz, "Qualitative Chemical Analysis," I, 290–2.)
3. Is it necessary to employ the nitric acid salts for this oxida-

tion of the aldehyde, or could silver acetate be used just as well?

4. What advantage does Fehling's solution have over an ordinary aqueous solution of copper sulfate in testing for aldehydes?
5. How is heating advantageous in the Fehling's solution test for aldehydes?
6. In the polymerization of acetic aldehyde by means of sulfuric acid, why is it necessary to add only a trace of acid instead of a drop?
7. Why is it best to cool the aldehyde with a freezing mixture before adding the acid?
8. Write equation and structures in the reactions involved in the polymerization of the aldehyde by acid.
9. Is the above reaction reversible?
10. Write equations and structures for reactions which take place when acetic and formic aldehydes are each treated with conc. and with dil. solutions of sodium hydroxide.

## Experiment No. 20

### HYDROLYSIS OF METHYLENE DIETHERS (ACETALS)

### Methylal[1]

1. Does its odor resemble that of the ethers? To what alcohols are these ethers related?

2. To 3 drops of methylal in a test-tube add 2 drops of conc. sulfuric acid. Heat *gently* over a small flame until the liquid begins to boil, and then allow to cool. What is the white solid that is deposited on the walls of the tube? Note the odor of the gas evolved. (Care!) Outline the "steps" in the reactions of this experiment.

3. Repeat the above experiment, using dilute sulfuric acid. Any white solid formed? Odor?

4. Try the action of dilute sodium hydroxide solution on methylal. (?)

5. What is an ortho-ester?[2] What is formed when an ortho-ester is warmed with an alcoholic solution of potassium hydroxide?

6. Does methylal reduce Fehling's solution, or ammoniacal silver nitrate? (See under Acetaldehyde, p. 91.)

### QUESTIONS

1. Write equations for reactions involved in the chemical change produced by the action of conc. sulfuric acid on methylal.
2. What is polymerization? Show by structure how this polymerization of formaldehyde to paraldehyde differs from a polymerization like formaldehyde to formose.

---

[1] Methylal boils at 42°.

[2] Richter's "Organische Chemie," 11. Auflage (1909), Vol. I, 273, 316.

3. What is the structure of the formaldehyde in the water solution obtained when dil. sulfuric acid reacts with the methylal?
4. How is methylal formed? Two methods.
5. Show how it is related to ethers by its behavior when hydrolyzed.
6. Can diethyl ether be hydrolyzed by sulphuric acid?
7. Can aqueous alkali cause hydrolysis of methylal or ethyl ether?
8. Of what alcohol is methylal an ether? Does it exist? Compare chloral hydrate.

## Experiment No. 21

### Formaldehyde

1. Dissolve 2 drops of methyl alcohol in 3 cc. of water in a small test-tube (No. 1). Make a compact spiral of fine copper wire by winding it around a glass rod. The spiral should be about 2 cm. long and should have a straight piece about 20 cm. long. Oxidize the spiral by moving it rapidly through a Bunsen flame, and plunge the red-hot wire into the alcohol solution. Repeat this operation several times.

Pour the solution from the solid particles into another small test-tube, and add 1 drop of a fresh 0.5 per cent solution of resorcinol.[1] Carefully pour this solution down the sides of a second test-tube containing about 5 cc. of conc. sulfuric acid. If the second tube is properly inclined the mixture will form a distinct layer upon the surface of the acid.

A red zone, slightly violet in color, will appear, and above the zone there will be a light flocculent precipitate. This reaction is characteristic of formaldehyde; other aldehydes do not show this behavior. The composition of the colored substance and of the precipitate is not well understood.

*(Reprinted with permission from Jones, "A Laboratory Outline of Organic Chemistry," p. 25.)*

2. Evaporate 5 cc. of "formalin" (commercial 40 per cent solution of formaldehyde) to dryness on the water-bath, under the hood. What is the residue?

3. **Preparation of Hexamethylenetetramine.** In a round-bottomed flask mix 25 cc. of "formalin" and 15 cc. of conc.

---

[1] If the resorcinol solution is allowed to stand for some time it gradually develops a brownish flocculent precipitate, and then it is worthless for this test.

ammonium hydroxide. Insert an inlet tube drawn out to a capillary at the lower end and opening near the bottom of the flask, and an outlet tube connected with a suction flask, stop-cock, and water pump, and evaporate approximately to dryness *in vacuo* (compare, Expt. 15, p. 76), over the steam-bath. By attaching a piece of rubber tubing with a screw clamp to the inlet tube the stream of bubbles can be regulated. Then add a second portion of ammonium hydroxide and evaporate again.

Dissolve out the residue with hot absolute alcohol and filter while hot. The hexamethylenetetramine crystallizes out of the filtrate in colorless, well-formed rhombohedra. The crystals should of course be filtered off before the solution is allowed to evaporate to a small bulk since the mother liquor contains a considerable amount of by-products as impurities. The substance sublimes when heated, and is very soluble in water.

It is used in medicine, usually under the name of " urotropine," also for preparing condensation products of phenols (Bakelite), for absorbing poisonous gases, in gas-masks, as an " accelerator " (catalyst) in the vulcanization of rubber, etc.

## QUESTIONS

1. Explain the formation of formaldehyde from methyl alcohol.
2. What is " formalin "? How prepared commercially?
3. What is obtained when the " formalin " evaporates to dryness?
4. What is trioxymethylene? For what is it used in commerce?
5. Write the formula proposed for hexamethylenetetramine. (Richter's " Organic Chemistry," trans. by Spielmann, Vol. I, p. 211.)
6. Compare the action of ammonia on formaldehyde, acetaldehyde and benzaldehyde.

## Experiment No. 22

### Acetone

1. Mix 5 cc. of acetone with 7 cc. of a saturated solution of sodium bisulfite.[1] Shake vigorously. Note the heat developed. What is the product that separates? How may acetone be regenerated from it? How is this reaction used in analysis? Do *all* ketones respond to this test? How does KCN react with the bisulfite addition product?

2. Try the action of the fuchsine-sulfurous acid reagent on acetone. (?)

3. Does acetone reduce Fehling's solution, or an ammoniacal solution of silver nitrate?

*4. Write the structure of dibenzalacetone (dibenzylidene acetône). (Compare Perkin and Kipping, "Organic Chemistry," p. 456.) How can it be formed? Explain the reaction for its preparation. What is its significance in organic analytical chemistry?

5. How can you prepare iodoform from acetone? Is this reaction characteristic of most ketones which contain the $CH_3CO$ group?

---

[1] The saturated solution of sodium bisulfite is prepared by means of sodium hydroxide solution and sulfur dioxide, or by passing sulfur dioxide into a mixture of sodium bicarbonate in three parts of water until the solution smells strongly of the gas. On long standing unless properly stoppered it is slowly converted into the sulfate. This can generally be noticed by loss of the yellowish color of the saturated solution and by the presence of a white sediment. It will then no longer give the crystalline addition-product with acetone, etc.

* Need not be studied by students in the "short" course.

## Experiment No. 23

### FORMATION OF A KETONE BY THE OXIDATION OF A SECONDARY ALCOHOL AND THE FORMATION OF A KETOXIME

### Preparation of *l*-Menthone from *l*-Menthol

Pour 3 cc. (no more) of conc. sulfuric acid into 40 cc. of water and dissolve 5 grams of sodium dichromate in this solution. Transfer to a *small* glass-stoppered bottle, and add 5 grams of powdered *l*-menthol. Shake frequently during the next half hour and let stand overnight or longer. When the mixture is allowed to stand the solid lumps should be in contact with the liquid and not sticking to the walls of the bottle above the liquid. These dark-colored, insoluble masses probably consist of the ester of menthol and chromic acid which is first formed, and they gradually disappear, leaving a dark but clear solution with the menthone floating as an oil on the surface. Extract the mixture in a separatory funnel with about 25 cc. of ether. Filter the ether solution into a small weighed beaker and evaporate the ether by means of *warm* water. Support an inverted funnel over the beaker and connect with the suction to carry away the ether vapors. As soon as the fumes of ether are no longer evident as shown by the odor, cool and then determine the yield of crude menthone (about 4.5 grams). It is somewhat volatile at the ordinary temperature and pressure, and therefore it should not be heated too long.

An excess of sulfuric acid must be avoided since it gradually changes the levo-compound into the dextro-variety. Menthone is one of the chief constituents of the oil of peppermint. It is a colorless liquid boiling at 109° at 36 mm.

It need not be further purified for the following experiment.

## Preparation of *l*-Menthone Oxime from *l*-Menthone

Dissolve 2 grams of the crude menthone in three times its weight of about 90 per cent alcohol (sp. gr., approximately 0.83) in a small beaker (No. 00). Add an amount of powdered hydroxylamine hydrochloride equal to 1.3 times the theoretical amount required by the equation. It will not all dissolve. Then, during ten minutes, add in portions with stirring slightly more than the theoretical quantity of sodium hydrogen carbonate required to neutralize the hydrochloric acid of the first salt and free the hydroxylamine. Let stand for thirty minutes with occasional stirring. Pour the mixture into 75 cc. of cold water and stir vigorously. The oxime separates immediately as an oil or a white semi-solid mass which soon solidifies. Cool further if necessary to help solidification. Filter with suction. Dissolve the product in hot, approximately 50 per cent alcohol, 50 cc. for each gram, filter while hot if necessary to remove any insoluble particles, and set aside for crystallization. Before setting aside cover the beaker with a watch glass. After the first crop of crystals has been filtered off a second may often be obtained by longer standing. White needles of a characteristic persisting odor are obtained which melt at 60°. The product may be dried by letting it stand overnight on a clean porous tile covered with a watch glass. In this way their crystalline shape is preserved. Yield, 80 per cent of the theory.

Try the action of a dilute solution of sodium hydroxide on a small amount of the oxime. (?)

### NOTES

1. When the oxime is hydrolyzed with dilute sulfuric acid, the angle of rotation of the resulting menthone is changed.

2. Like most terpene compounds menthone oxime is somewhat volatile and therefore should not be left in the open or in a vacuum desiccator under diminished pressure for any length of time.

## QUESTIONS

1. What becomes of the sodium dichromate?
2. Write the general structure of the esters of chromic acid.
3. Why must an excess of sulphuric acid be avoided?
4. Write the structures of menthone oxime and of hydroxylamine hydrochloride.
5. In hydroxylamine hydrochloride why does not the hydrochloric acid neutralize the OH-group?
6. What is the purpose of the 90 per cent alcohol? Why not use 95 per cent alcohol?
7. Why is sodium hydrogen carbonate used?
8. What other substances could be used in place of the sodium hydrogen carbonate?
9. Is it necessary to use the hydrochloride of hydroxylamine or could the free hydroxylamine be added directly? Which one reacts?
10. How can an aldehyde or a ketone be regenerated from the oxime?
11. How do oximes behave towards alkalies? towards boiling alcohol and sodium?
12. Show how oximes can be used in organic analytical chemistry.
13. Give an experiment which will show that menthone is a ketone and not an aldehyde.
14. How can you prepare menthol from menthone?
15. What compound is formed when menthone is treated with ethyl magnesium iodide and the product hydrolyzed?
16. Give structure and name of acid formed by treatment of menthone with HCN and hydrolysis of the cyanhydrin compound:
17. How does menthone behave toward chlorine?
18. Give the structures of the stero-isomeric forms of menthone oxime.

## Experiment No. 24

### FORMATION OF AN ACID CHLORIDE FROM THE ACID

### Preparation of Acetyl Chloride from Acetic Acid

The apparatus in this experiment consists of a 60 cc. distilling-flask, provided with a dropping-funnel (Fig. 6, p. 36), and attached to a condenser. A second distilling-flask of the same capacity tightly connected with the condenser (if a good cork connection cannot be made, use a piece of rubber tubing as you would a bored cork) serves as the receiver, the outlet tube being connected to a calcium chloride tube.[1] The calcium chloride in the tube is protected at each end with a plug of glass wool or cotton. Since the receiving flask is used later as the distilling-flask without transferring the distillate, a thermometer and well-fitting cork should be ready before the operation is started. All the apparatus must be perfectly dry and the connection should be so made that the product does not come in contact with any cork or rubber. Use cork stoppers throughout, except as noted above. The experiment must be carried out *under a hood*, or the calcium chloride tube connected with a tube opening just *above* the surface of a dilute sodium hydroxide solution contained in a bottle and the fumes then led into the draft pipe. The acetyl chloride fumes in the air, being decomposed by moisture into acetic acid and hydrochloric acid. *Care must be exercised in handling both reagents and product to keep them from the skin and to avoid inhaling the vapors.* Acetyl chloride attacks both rubber and cork; therefore the apparatus should be disconnected as soon as the experiment is completed, and the product should be

---

[1] Be careful that the calcium chloride tube does not become stopped up during the distillation.

kept in a sealed bottle[1] instead of the ordinary specimen bottle, although it can be kept for a few days in a glass-stoppered bottle.

Acetyl chloride has a high vapor pressure and therefore good corks must be used and the joints made **tight**, otherwise serious losses will occur. It is best to plan to perform the experiment during one laboratory period.

Add 12 cc. of glacial acetic acid to the distilling-flask, which is immersed in cold water in a beaker. Then add slowly from the dropping-funnel 7.5 cc. of phosphorus trichloride. When all this has been added, mix the liquids by gently shaking the flask and allow to stand for about one hour. Then warm the water to 40°–50° and continue the heating at this temperature for a short time. The liquid, which was homogeneous before heating, finally separates into two layers; the upper layer consists mainly of the acetyl chloride, and the lower of phosphorous acid. Slowly heat the water to boiling until nothing further distills. The distillate contained in the same distilling-flask, now provided with the thermometer, is carefully redistilled. Collect the portion that distills between 52° and 55° in a receiver protected with a calcium chloride tube, or with absorbent cotton to prevent circulation of air.

Acetyl chloride is a colorless liquid with a pungent odor, it fumes in contact with moist air; b.p. 53°, sp.gr. 1.105 at 20°.

After the yield has been determined perform the following test-tube experiments:

### NOTE

The reactions with acetyl chloride are usually very vigorous. Therefore, when carrying out experiments with it care should be taken that the test-tube is held in such a position that its contents cannot be shot out into the face of the experimenter or of anyone else.

1. Add a few drops of acetyl chloride to about 3 cc. of water in a test-tube. The acetyl chloride sinks to the bottom of the

---

[1] A thin-walled bottle of soft glass with an extended neck which can be sealed off as described at the end of this experiment.

tube, but on shaking rapidly dissolves, and heat is evolved. What are the products?

2. To about 1 cc. of ethyl alcohol add 1 cc. of acetyl chloride drop by drop, cooling the test-tube under the tap. Then add an equal volume of water, the tube being cooled as before. Make weakly alkaline with sodium carbonate solution and add common salt until no more dissolves. What is the pleasant-smelling substance that separates out as a mobile layer on the surface of the water solution?

3. To 1 cc. of aniline add 1 cc. of acetyl chloride, drop by drop. A vigorous reaction occurs, and a solid separates. Cool the mixture with water and add about five times its volume of water. What substance is formed? What is its trade name? Recrystallize by dissolving it in hot water and allowing the solution to cool. It is obtained in leaflets which melt at 114° cor. Determine the melting-point; see Expt. 12, p. 58.

Write equations for all the above reactions.

Place the remainder of the product in a sealing tube or bottle and seal off the neck by means of a *small*, blast-lamp flame. On account of the volatility of the acetyl chloride the lower part of the sealing tube must be kept cool by means of a cloth saturated with ice water. Total yield, 12–14 grams.

## NOTE

For an excellent discussion of the reaction between acetic acid and phosphorus trichloride, see Brooks, *Journ. Amer. Chem. Soc.*, **34** (1912), 492–9.

## QUESTIONS

1. Write the equation for this reaction.
2. When is $PCl_5$ used to replace OH groups with Cl?
3. What is the product remaining in the first flask?
   Is the second equation on p. 142 in Gattermann correct?
4. Account for the HCl gas.
5. What two objections are there to the use of $PCl_5$ in certain cases?
6. Why does acetyl chloride fume in the air?

7. Compare acetyl chloride and benzoyl chloride with regard to their stability toward water, alkalies, etc.
8. Compare the physical characteristics of the acyl chlorides with the acid from which they are derived.
9. How can the following classes of compounds be prepared from acyl chlorides: esters, amides, acid anhydrides, * ketones and * 3°-alcohols?
10. How is acetyl chloride used for detecting and estimating OH groups, and * for distinguishing between 1° or 2° and 3° amines?
*11. What is the Schotten-Baumann reaction?
12. What is meant by acylation? Acetylation?
13. What other reagents are used for acetylation?
14. How can acid chlorides be distinguished chemically from alkyl chlorides?
*15. How are the sulfone chlorides formed?
*16. What is Hinsberg's method of distinguishing between 1°, 2° and 3° amines? (Bernthsen, "Organische Chemie," 11th Ed., 2d par., p. 440; Noyes, "Org. Chem. for the Lab.," 2d Ed., p. 160; Clarke, "Org. Anal.," p. 36.)
17. What is sulfuryl chloride and how formed? Thionyl chloride?
18. Compare the boiling-point of acetyl chloride with that of phosphorus trichloride.

* These questions are not required for study in the "short" course.

## Experiment No. 25

### FORMATION OF AN ESTER FROM THE ALCOHOL AND THE ACID

### Preparation of Ethyl Acetate

To a small distilling-flask connected with a condenser add a mixture of 10 cc. of absolute ethyl alcohol and 12 cc. of conc. sulfuric acid. Insert the stem of a dropping-funnel into the neck of the flask and let the end reach *below* the surface of the liquid. Heat the flask in an oil-bath.[1] When the temperature of the oil reaches 145° allow a mixture of 15 cc. of absolute alcohol and 15 cc. of glacial acetic acid to drop slowly into the liquid, and as soon as the reaction proceeds regularly add the mixture at about the same rate at which the products distill. Keep the temperature at about 145°–150° until all the mixture has been added. When no more distills over treat the distillate in a beaker with a concentrated solution of sodium carbonate until there is no further effervescence (?), separate the layers in a separatory funnel, and wash the upper layer with about its own volume of saturated salt solution. (?) Separate again, dry with anhydrous sodium sulfate or fused potassium carbonate, and distill. Ethyl acetate boils at 77°, its specific gravity is 0.9239 at 0°, and it is soluble 1 part in 17 parts of water at 17.5°. Yield, 11 grams or more.

### NOTE

The slower the distillation in the first reaction the better the yield will be. It will be noticed that practically nothing distills over until the temperature has almost reached 145°.

### Hydrolysis of an Ester

In a small flask with reflux condenser attached heat for ten minutes 5 cc. of ethyl acetate, 50 cc. of water, and 2 grams of

---

[1] A shallow iron dish and rape-seed oil are convenient for this purpose. For discussion of heating-baths, see foot-note, p. 79.

sodium hydroxide. Then distill over about half the liquid. Test the distillate for alcohol with potassium dichromate (see Expt. 10, "Reactions of Alcohols," p. 54). Empty the remainder of the original solution into a porcelain dish and evaporate to dryness. Dissolve the residue in water and acidify with sulfuric acid. Note the odor. (?)

How could you test for the acid by a chemical method?

Outline a procedure for preparing a derivative of the alcohol to confirm your qualitative findings (compare methyl ester of 3.5-dinitrobenzoic acid, p. 55).

## QUESTIONS

1. Is it necessary to use absolute alcohol in the preparation of ethyl acetate?
2. Could hydrochloric acid be used in place of conc. sulfuric acid? dilute sulfuric acid? Explain.
3. What would be the effect if some water was added to this reaction mixture? or methyl alcohol? or ethylene?
4. Would any ethyl acetate be formed without the presence of sulfuric acid? If any, how much compared to the yield when sulfuric acid is present?
5. What is the object of keeping the temperature between 145° and 150°? What happens when the temperature is raised?
6. Would it make any difference if a mixture of 25 cc. of acetic acid and 50 cc. of alcohol was run into the reaction flask instead of a mixture of 25 cc. of each?
7. Why is this mixture introduced through a dropping-funnel, and led *underneath* the surface of the solution?
8. Is the yield of ethyl acetate affected in any way by distilling off the ethyl acetate as it is being formed?
9. Why is the distillate treated with sodium carbonate? Could sodium hydroxide solution be used instead?
10. Why is the ester washed with salt solution instead of water?
11. Why cannot other drying agents, such as calcium chloride and solid potassium hydroxide, be used for the drying of the ethyl acetate?
12. Solve the problems on p. 161, in Gattermann.
13. Point out *all* the conditions that are used to give a maximum yield of the ester.
14. What would you expect to happen when methyl acetate is heated with dry hydrogen chloride? with an alcoholic solution of hydrogen chloride?

## Experiment No. 26

## Hydrolysis (Saponification) of Butter

Dissolve 2 grams of sodium hydroxide in 2 cc. of water. In a porcelain dish, such as a casserole (not a glass beaker. Why?) heat 10 grams of butter until it melts, add the concentrated solution of sodium hydroxide, and continue the heating *cautiously* with good stirring until the mixture becomes of a creamy consistency. Pour it into 15 cc. of water and transfer this solution to a distilling-flask. Acidify with 20 cc. of dilute sulfuric acid (1 part of acid to 4 of water), and distill over about 15 cc.

*a.* Test the reaction of the distillate with neutral litmus. (?)

*b.* To what is the odor of the distillate chiefly due?

*c.* Of what does the oily residue in the flask consist? How could you prove it?

*d.* Remove the oily layer, wash it several times with water (?) and see if it dissolves in dilute sodium hydroxide solution. Add a drop of dilute acetic acid to the solution thus made. (?)

*e.* Test a small portion of butter for unsaturated radicals with a solution of bromine in carbon tetrachloride.

### QUESTIONS

1. What is a fat? a fatty oil? a mineral oil?
2. What are soaps and how are they prepared?
3. In your experiment what solution contained the soaps?
4. What is the by-product when fats are saponified? How is it purified?
5. What is rancid butter? Explain.

*6. What is meant by the " saponification number "?

7. What advantage has an alcoholic solution of potassium hydroxide over an aqueous solution in saponifying fats?

*8. How is the number of hydroxyl groups in a compound determined?

---

* Not required for study by students in the "short" course.

9. What would happen if "nitroglycerine" was boiled with an alcoholic solution of potassium hydroxide?
10. What is the difference in the behavior of the two esters, triolein and ethyl bromide, when boiled with alcoholic potassium hydroxide?
11. Can acids be used for hydrolyzing esters? Compare the rate of hydrolysis with alkali and with acid of corresponding "strengths."
12. What is the irritating gas formed when a fat is heated alone? Explain.
13. What are the products formed when lecithin is saponified with alkali? (Compare Expt. 27, p. 110.)
14. What is a wax? What difference from a fat is noted on saponification?
15. How could you distinguish in the laboratory between a fatty oil and a mineral oil? between a fat and a wax?

## Experiment No. 27

### ISOLATION AND STUDY OF A NATURAL PRODUCT

### Lecithin from Egg-yolk

Grind the yolk of one hard-boiled egg with 50 cc. of ether. Filter and wash the solid material twice with 10 cc. of ether. Discard the solid material. Evaporate the combined ether extracts and washings on the steam-bath. Extract this residue twice with hot alcohol, using 10 cc. each time. Pour off the alcohol from the heavy oil through a small filter. Evaporate off the alcohol from the alcoholic filtrate, dissolve the residue in 10 cc. of cold ether, and add 20 cc. of acetone. Stir until the particles of precipitated lecithin adhere together and form a ball. Describe its properties.

Boil about one-fourth of the lecithin with about 10 cc. of a 2N solution of sodium hydroxide. Note the odor of the gas evolved. What is it? Cool the solution. Is there any evidence of the formation of a soap? Filter, dissolve the precipitate in warm water and add dilute hydrochloric or acetic acid to the solution. What is precipitated?

Test a part of the lecithin for nitrogen and for phosphorus (See Expt. 28, p. 112). Results?

### REFERENCES

MacLean, "Lecithin and Allied Substances," (1918) (Longmans); Levene and West, "Lecithin, I.—Hydrolecithin and its bearing on the constitution of cephalin," *Journ. Biol. Chem.*, **33** (1918), 111–7. Levene and West, "Lecithin, II.—Preparation of pure lecithin; composition and stability of lecithin cadmium chloride." *Journ. Biol. Chem.*, **34** (1918), 175–86.

## QUESTIONS

1. Write the structural formula of lecithin.
2. Is lecithin a name for a single substance or is it a generic term? Explain.
3. Why is the first extraction residue treated with hot alcohol?
4. What are the physical properties of lecithin?
5. What elements did you find present?
6. What other methods could be used for decomposing the organic matter before testing for phosphate?
7. What is choline? How is neurine related to it? Muscarine? Betaine?

## Experiment No. 28

## Detection of Nitrogen, Sulfur, the Halogens and Phosphorus in an Organic Compound

Support a clean, dry, hard-glass (Pyrex) tube (9 mm. by 100 mm.) in a clamp, using two pieces of cork about 5 mm. thick for protection, or pass the tube through a hole in an asbestos disc in such a way that the tube is supported by the flare at the top. Prepare a small piece of bright metallic sodium,[1] not more than 2 cmm. and drop it into the tube. Apply a very low blue flame (1.5 cm. long) now and then until the sodium melts and there is a layer of sodium vapor 1 cm. deep. Drop a small amount of the substance to be tested (diphenylthiourea, $C_{13}H_{12}N_2S$, or lecithin) into the tube from the point of a knife blade, and continue the gentle heating while the decomposition is progressing, being careful not to drive the vapors of the substance out of the tube by too strong heating. Finally bring the mass to red heat for a minute and then allow to cool to room temperature.

In the meantime (for the sulfur test) prepare about 2 cc. of a dilute solution of ferrous sulfate, and also a very dilute solution of sodium nitroprusside, $Na_2(NO)Fe(CN)_5$, by adding a small crystal to 2 cc. of water.

To the cool reaction-tube add two or three drops of alcohol to destroy any unused sodium. Use a stirring-rod to break up the charred mass. When the evolution of hydrogen has ceased cautiously add a drop or two of water. When it is certain that all the sodium is destroyed add more water. Filter through a small wet filter paper and rinse out the tube with three or four portions of water, making the total volume used about 3 cc. The filtrate should be water-white. If it is colored, the decomposition was not complete and should be repeated.

---

[1] Return all sodium residues to the bottle.

Make alkaline with sodium hydroxide solution, if not already so. Divide the filtrate into three portions.

To one portion in a test-tube add two or three drops of the freshly prepared ferrous sulfate solution, and a very small amount of potassium fluoride.[1] Stopper the tube and rotate the contents only enough to mix the substance. Allow to stand five to ten minutes. Then acidify with dilute sulfuric acid (approx. normal). If nitrogen was present in the sample, a precipitate of Prussian blue will be formed.

### NOTE

Hydrochloric acid is not used because the yellow color of the ferric chloride and the blue color of the fine precipitate will give a green color at the end, and sometimes no blue precipitate is formed.

Dilute two or three drops of the second portion of the filtrate to 2 cc. and add a drop of the sodium nitroprusside solution. The presence of sulfur is shown by the appearance of a violet or purplish-violet color. This is a very delicate test for alkaline sulfides. An idea of the amount of sulfur present may be gained by acidifying the remainder of the second portion of the original filtrate with acetic acid and adding a solution of lead acetate. (?)

To the third portion add just enough dilute hydrochloric acid to make the solution react acid, and then add two or three drops of ferric chloride solution. If a blood-red color is formed it indicates the presence of a thiocyanate. However, although nitrogen and sulfur may originally be present in the sample, this test may not be positive because the sodium thiocyanate first formed is sometimes decomposed by the metallic sodium into sodium sulfide and sodium cyanide.

### REFERENCE

Viehover and Johns, "On the Determination of Small Quantities of Hydrogen Cyanide," *Journ. Amer. Chem. Soc.*, **37** (1915), 601–7.

This same general procedure can be used also for the detection of other elements such as the halogens and phosphorus.

---

[1] It is not definitely known why the potassium fluoride is more efficient in aiding the precipitation of the Prussian blue than any other salt. Compare Viehover and Johns' reference above.

For the halogens the fusion is carried out in the usual manner and the water-white filtrate is acidified with nitric acid, boiled (?) and treated with a few drops of silver nitrate solution. If it has already been shown that nitrogen and sulfur are absent it is not necessary to boil the solution (?).

For phosphorus, use about 1 cc. of the filtrate from the sodium decomposition in the nitrogen test and boil this for one minute with 3 cc. of conc. nitric acid (?). Cool the solution and add twice its volume of ammonium molybdate reagent. Heat the tube to such a temperature that it can just be held in the hand, then set aside. If phosphorus was present in the original sample a yellow crystalline precipitate of ammonium phospho-molybdate will form.

## QUESTIONS

1. At the end of the sodium decomposition, in what chemical combinations are the nitrogen and the sulfur found?
2. How does the alcohol destroy the unattacked sodium? Why not use water at first?
3. Write equations for the reactions involved in the test for nitrogen.
4. Why is the mixture acidified with sulfuric acid rather than with hydrochloric acid?
5. How else may sulfur be detected?
6. Explain the ferric chloride test.
7. Can the sodium method be used for detecting a halogen? Suppose a halogen and nitrogen are both present. (?)
8. How is nitrogen detected, and also estimated, by the soda-lime method?
9. In what combination is the nitrogen when it can ordinarily be detected by the soda-lime method?
10. What is the Kjeldahl method for the estimation of nitrogen?
11. What is the Dumas or absolute method for the estimation of nitrogen?

## Experiment No. 29

### FORMATION OF AN ACID AMIDE FROM THE AMMONIUM SALT OF THE ACID

### Preparation of Acetamide from Ammonium Acetate

The ammonium acetate used in this experiment should be as free from water as possible. Press out the material on a porous tile [1] if necessary.

*First Method*

Under a reflux condenser heat to *gentle* boiling a mixture of 15 grams of dry ammonium acetate and a little more than the same amount of glacial acetic acid for three to four hours. Cool, transfer the liquid to a 60-cc. distilling-flask connected with a water condenser, and distill until the temperature reaches 160°. Discard this portion. (Of what does it chiefly consist?) Replace the water condenser by a small distilling-flask, allowing the outlet tube of the first one to pass through the neck of the second one so that the distillate will be collected in the bulb of the second one.[2] Continue the distillation and collect the portion distilling above 160°. Redistill this slowly as previously, but for a receiver attach to the outlet tube of the distilling-flask a small ordinary flask or large test-tube, which has been weighed, and with a cork containing a channel cut in the side. This time collect the portion distilling 210°–215°. The product solidifies to a white crystalline mass. A third distillation may be necessary if it does not solidify on cooling. Pure acetamide boils at 222° cor. Yield, 10 grams.

---

[1] For use of porous tile, compare, foot-note, p. 56.

[2] It is not usually necessary to cool the receiving flask. If this is done, however, care must be taken not to allow the condensate to solidify in the outlet tube of the main distilling-flask, since it may clog it and cause trouble.

The peculiar odor characteristic of mice excrement in the crude substance is due to an impurity which can generally be removed by re-crystallization. Acetamide is deliquescent and volatile at the ordinary temperature and pressure. It is easily soluble in chloroform and in alcohol, and difficultly soluble in ether.

**Recrystallization of Acetamide.** Determine the weight of the crude product by weighing the receiver again. Add some chloroform, 1 cc. for each gram, to the flask or tube, attach a reflux condenser and heat to boiling by means of warm water. Chloroform boils at 61°, and all the acetamide will be dissolved within a few minutes. Disconnect, and pour the clear hot solution into a small beaker and cover with a watch glass. Within a very short time the crystals will commence to form and the entire mass will quickly set to an apparent solid. Note the supercooling, and evolution of heat when crystallization begins. (Explain.) Cool further by placing the beaker in cold water or ice. Break up the crystalline mass with a stirring-rod and filter *rapidly* with suction, using a 5 cm. Buchner funnel (Fig. 8, p. 51), or the method for suction filtration of small quantities, p. 56. In the latter case use a 6–7 cm. funnel and moisten the little filter paper with chloroform before turning on the pump. Press the material down slightly with a spatula or glass stopper. On account of the very hygroscopic nature of acetamide the filtration must not be prolonged, otherwise the substance will liquefy. Yield, 80 per cent of crude product.

1. Heat some acetamide with dilute sodium hydroxide solution. What gas is evolved? Acidify with dilute sulfuric acid, and note the odor. (?)

2. Heat a second portion of acetamide with dilute sulfuric acid. Odor of vapors? Neutralize the resulting mixture with dilute sodium hydroxide. (?)

## NOTE

Save a one-gram sample of the acetamide for the methylamine experiment, p. 120.

### *Second Method* (*Sealed Tube Method*)

Put 15 grams of ammonium acetate into an ordinary soft glass "bomb" tube, packing it in with a glass rod flattened at one end. The tube should not be more than half full when sealed. Two tubes may be used if desired.

**Sealing the Bomb Tubes.** The open end of the tube is now sealed in the blow-pipe flame. This operation requires some care and a little skill. It is advisable to practice with an empty tube first. Grasp the tube about the middle with the left hand and while it is inclined at an angle of 45° heat about 5 cm. of the tube at the open end very gradually by revolving it for several minutes in a small smoky flame. Increase the size of the flame *slowly* until it is large enough to make the desired blue flame later by simply turning on the air only. *Slowly* turn on the air until a good blast flame, about 10 cm. in length, is obtained, and heat the end of the tube until it softens. At the same time heat the end of a glass rod, about 12 cm. long, held in the right hand, and seal it into the inside of the tube. Care must be taken to make a good seal—not just to stick it on—otherwise it will crack off when the tube is drawn out. Remember that the hottest part of the flame is at the end of the inner blue cone. The glass is allowed to cool down slowly in the heat above the flame with the rod perfectly in line with the tube, and then smoked. Now warm the tube further down with the smoky flame, low at first. Gradually make the flame as hot as possible and about 7–10 cm. long, and heat the tube very hot around a point about 4 cm. below the open end to which the glass rod is attached, the glass rod now serving as a support while the tube is slowly rotated. The glass, evenly heated, begins to thicken where the flame plays upon it, and the inside diameter of the tube contracts. Rotate it carefully, do not draw it out, and keep the tube in line. This can be done easily if the glass rod is held as you would hold a pencil. When the inside diameter of the tube is reduced to about 5 mm. the tube is removed from the flame, and while held in a *vertical* position a capillary is formed by *very slowly* drawing out the thickened part of the tube, and holding it there until it becomes rigid. It is then sealed off so as to leave a capillary about 4 cm. long. The capillary is necessary as will be seen later in opening the tube. Smoke the sealed end and allow the tube to stand with the warm end up until cold. Then remove the soot with filter paper or a cloth. *The instructor must pass on all sealed tubes before they are heated in the furnace.*

**Heating the Tube.** Protect the eyes with goggles. The sealed tube is gently put into an iron jacket with the capillary at the open end. (See instructor.) Place it in the bomb furnace so that the open end of the jacket is towards the wall. Slide in the guard, see that the end of the furnace near the wall is raised and properly fastened, and then place a thermometer in the top of the furnace. *Gradually,* thirty to forty minutes, raise the temperature up to 200°–210°, at which temperature the bomb is heated for three hours. Do not allow the temperature to go higher because an explosion will result. The temperature should be noted about every thirty minutes. The heating can be interrupted at any time.

**Opening the Sealed Tubes.** The tubes are always allowed to cool overnight. *No one should enter the cannon room without wearing goggles to protect the eyes. In no case whatsoever should a sealed tube be taken out of the iron casing for examination or for any other purpose. When being opened the tube is held in such a position that neither the operator nor anyone else can be injured in case of bursting. The tube should be opened in the cannon room. It should never be taken out into the laboratory unopened.*

The contents of the tube are now *liquid.* The protecting case of iron, containing the tube, is removed from the furnace and held in a slightly inclined position, the end of the capillary being higher than the rear end. By means of a slight jerk the capillary of the glass tube is caused to project from the jacket. The extreme end of the capillary is now held in the flame of a Bunsen burner. If there is any internal pressure in the tube, the glass on becoming soft will be blown out and the gases will escape from the opening thus made. Should no gas be released even at red heat (which sometimes is the case in this experiment) the end may be broken off by a sharp blow with a file. The glass tube is *now* taken out of the iron jacket. A deep file mark is made in the wide part of the tube about an inch below the "shoulder," and this is touched lightly with the hot end of a glass rod previously heated to fusion in the blast flame. If the crack caused by this does not extend entirely around the tube, the extreme end of it is extended by applying the hot end of the glass rod again so that the conical end may be lifted off.

Purify the product as in the first method above.

### QUESTIONS

1. Why must the ammonium acetate be dry?
2. Explain why the acetic acid is used in the first method.
3. By means of structural formulas indicate the "steps" in the hydrolysis of a cyanide.
4. How can acetamide be prepared from methyl cyanide?
5. What is the action of phosphorus pentoxide on acetamide?
6. What other methods are used for forming amides?
7. How are the substituted amides prepared? E.g., acetanilide.
8. What are the chemical properties of the amides as shown by their behavior toward (1) dry HCl in ether, (2) bromine, (3) bromine and potassium hydroxide, *(4) mercuric oxide, (5) nitrous acid, *(6) $PCl_5$, (7) aq. HCl? (8) aq. KOH?

*9. What is an imide? How formed? Ex. succinimide.

*10. What is the action of alc. KOH on an imide? What use is made of this reaction?

11. Look up the structure of urea and show how it is related to the amides. What is its chemical name?

* These questions are not required for study in the "short" course.

## Experiment No. 30

### FORMATION AND STUDY OF A PRIMARY AMINE

### Methyl-amine from Acetamide

In a 60 cc. distilling-flask dissolve 2.5 grams of sodium hydroxide in 6 cc. of distilled water (ammonia free). Cool, and then (under the hood) cautiously add through a funnel 1 cc. of bromine (not bromine water). Shake and cool. Now add 1 gram of acetamide, stopper with a cork, slant the flask a little and allow the end of the outlet tube to dip just below the surface of 6 cc. of distilled water (ammonia free) contained in an open test-tube. Heat carefully with a small, moving flame[1] until the mixture becomes clear and vapors are vigorously evolved; then remove the flame, but resume the heating and continue for several minutes after the main reaction has subsided. If the water in the receiver begins to run back remove the stopper temporarily.

1. Note the odor. Is it exactly like that of ammonia?

2. Test the reaction of the solution with neutral litmus. (?)

3. Add a drop of the solution to 1 cc. of a very dilute solution of ferric chloride. (?) Repeat with dilute ammonium hydroxide instead of the amine solution. (?) Compare.

4. Add a drop of the solution to 1 cc. of a very dilute solution of cupric sulfate. If the precipitate first formed does not dissolve add another drop of the solution. (?) Repeat, using dilute ammonium hydroxide. (?) To what is the color in each instance due?

5. To the remainder of the solution in an evaporating dish add conc. hydrochloric acid drop by drop with stirring until

---

[1] Strongly alkaline solutions bump considerably.

the solution reacts acid to litmus. What are the fumes? Evaporate to dryness on the water-bath. What is the white residue? Transfer the residue,[1] which is hygroscopic, to a test-tube and add a small amount of sodium hydroxide solution. Boil gently. Again note the odor of the vapors. Hold a stopper moistened with conc. hydrochloric acid near the mouth of the tube. (?) Test the inflammability of the gas.

6. Add a drop of silver nitrate solution to a very dilute solution of ethyl ammonium chloride (ethylamine hydrochloride). Explain your result.

## QUESTIONS

1. Explain the formation of methyl amine from acetamide.
2. Why should you expect methyl amine to give an alkaline reaction in aqueous solution?
3. Is methyl ammonium hydroxide a "stronger" base than ammonium hydroxide? Explain.
4. Write the equations for the reaction with ferric chloride and with cupric sulfate.
5. How does methyl amine react with hydrochloric acid? the product with sodium hydroxide?
6. Compare the reaction of ethyl ammonium chloride and ethyl chloride with silver nitrate. How can you account for the difference?
7. What is the carbyl amine (isonitrile) test for 1° amines?
8. How can you distinguish between 1°, 2°, and 3° amines?
9. What compounds are formed by the treatment of amines with chlorplatinic acid? How can these salts be used for determining the molecular weights of the bases?
10. Compare the action of bromine and sodium hydroxide on urea with the action of this same reagent on acetamide.
11. What practical use is made of the reaction in No. 10?

---

[1] Save a few crystals of the hydrochloride for making methyl mustard oil, p. 123.

## Experiment No. 31

### Ethyl Isocyanate

Grind together equal parts (about 0.5 gram) of dry potassium or sodium cyanate [1] and dry potassium ethyl sulfate. Place the mixture in a dry test-tube and heat carefully. A liquid soon begins to distill and partially condenses on the walls of the test-tube. Note its odor. (Care!)

1. What is its structural formula?
2. Why must the reacting substances be dry? Explain fully.
3. What happens when the liquid obtained above is boiled with water?
4. How do the isocyanates react with alcohol? Show how this reaction can be used in the identification of alcohols; also amines.
5. Give the reasons for assigning the accepted structural formula for the isocyanates.
6. Do esters of cyanic acid itself exist? Can you give any reason?

---

[1] Not cyanide.

## Experiment No. 32

### Methyl Mustard Oil (Methyl Isothiocyanate)

In a test-tube mix a few crystals of methyl amine hydrochloride (Expt. 30, test 5, p. 120), one drop of carbon bisulfide, and one or two drops of a strong solution of sodium hydroxide. After a few seconds add a little water and slightly more than enough silver nitrate solution (N/10) to react with the potassium hydroxide. (?) Bring to a boil. The odor of the mustard oil will at once become pronounced.

1. Outline all the " steps " in this reaction.
2. Do all amines (1°, 2°, 3°) give this reaction? Therefore, what use can be made of the reaction?
3. How can you distinguish chemically between an isocyanate and a thiocyanate?
4. Which compound of this series is found in true mustard oil? Does the name of its hydrocarbon radical have any significance in organic nomenclature?

## Experiment No. 33

## HYDROLYTIC PREPARATION, SEPARATION AND PURIFICATION OF AN AMINO ACID

### Preparation of Glycocoll (Glycine) from Hippuric Acid

Heat to slow boiling 1 gram of hippuric acid and 15 cc. of conc. hydrochloric acid in a 250 cc. flask under reflux condenser for thirty minutes. During this time have a tube connected with the top of the condenser to lead the fumes into a flask containing dilute sodium hydroxide solution. The opening should be *above* the surface of the alkaline liquid and the flask should be loosely stoppered with cotton. Toward the end of the hydrolysis crystals (?) are deposited on the inside walls of the condenser.

After the thirty minutes' heating disconnect the apparatus, add 10 cc. of water to the main reaction mixture and cool with running water. Filter off the crystals with suction and save both the precipitate and the filtrate. Dry the white crystalline product and determine its melting-point. Test its solubility in ether. Dissolve out the deposit in the condenser with ether, evaporate the ether, and determine the melting-point of the residue. Compare with that obtained from the hydrochloric acid solution.

Evaporate the filtrate to dryness on the water-bath. Add 15 cc. of water and filter off any insoluble matter. Neutralize *exactly* with dilute sodium hydroxide solution, using litmus paper for the tests. Filter again, if necessary. Add about 0.5 gram of basic copper carbonate and warm with stirring. A deep blue color is obtained which is characteristic of the solutions of the copper salt complexes of many of the monamino acids. Filter the solution while still hot and allow the filtrate to cool. Separate the blue needles of the copper salt complex which have been formed, and concentrate the filtrate to obtain a second portion. Dissolve the combined product in 20 cc. of warm water, saturate the warm solution with hydrogen sulfide gas (which has been washed with water), filter and carefully evaporate to dryness at a low temperature, 40°–50°, or allow to evaporate at room temperature. Complete the drying on the steam-bath. Extract the residue with a little water and filter off any copper sulfide with suction. Sometimes gravity filtration and the use of a very small wet filter paper is better, especially for a second filtration. The filtrate should be water white.[1] Concentrate the clear colorless solution to a small volume and allow to crystallize in a small round-bottomed crystallizing dish. Beautiful crystals can be obtained in this way. Otherwise, when the volume of the solution is about 1 cc. or less, pour it into 3–4 cc. of alcohol with stirring. White needles will be precipitated. Set aside for complete precipitation, and filter before all the mother liquor has evaporated. (Why?) Dry and determine the melting-point of the pure white amino acid thus obtained. (?) What is the *chemical* name of this compound? Hand in the product and put the melting-point which you have found upon the label.

### NOTE

The above experiment is a sort of "index" of your experimental skill. Only by very careful manipulation can the small amount of *pure* product be obtained.

---

[1] Sometimes considerable difficulty is experienced in removing all the copper sulfide and in getting the solution colorless. Apparently the copper sulfide forms a soluble complex with the amino-acid, or is peptized by the excess of hydrogen sulfide and becomes colloidal. Similar difficulties are found in removing mercuric sulfide from organic solutions. Warming with a good decolorizing carbon helps to remove both the copper sulfide and any color. If it is due to colloidal cupric sulfide then an excess of hydrogen sulfide should be avoided. An electrolyte cannot be added to precipitate the colloidal material since it will contaminate the product, although a *trace* of an aluminium salt (which contains a trivalent ion) would be helpful if properly used. If the solution is heated too much the color is deepened and it is not easy to get rid of it. It is known, however, that you can evaporate a solution of *pure* glycocoll almost to dryness *over a free flame* without producing any color; in fact, no color is developed even if a little sulfuric acid is present.

## QUESTIONS

1. What is the structure of hippuric acid? Point out its chemical groupings.
2. In the hydrolysis of hippuric acid what compounds are formed? Write their structures.
3. Of what does the deposit in the condenser consist?
4. Why is the reaction mixture diluted?
5. Why is the filtrate evaporated to dryness?
6. What is left after the evaporation to dryness?
7. Write the reaction for the neutralization. (See also question No. 11.)
8. Why not use copper sulfate for preparing the copper salt? Could it be used at all?
9. What advantage has a round-bottomed crystallizing dish over a flat-bottomed one.
10. Discuss the structure of amino-acetic acid (glycocoll, glycine). Account for its high melting-point.
11. How are amino acids estimated?
12. Give three methods of forming glycocoll, including its preparation, for example, from gelatine.
13. How can you prepare hippuric acid?
14. What is glycyl-glycine? Its preparation by two different methods?
15. Compare the structure of hippuric acid with that of a dipeptide.
16. How are polypeptides prepared?
17. How are the amino acids separated and identified in the mixture obtained by the hydrolysis of a protein?
18. Give names and structures of the important amino acids.

## Experiment No. 34

## Hydrolysis of Cane Sugar and Preparation of Phenylglucosazone

Dissolve 2 grams of cane sugar in 20 cc. of water. Test a few drops of this solution with Fehling's solution (mix 5 cc. of each part, boil, and then add the solution to be tested), and also test with ammoniacal silver nitrate. Result? Add 0.5 cc. of conc. hydrochloric acid to the main solution, and place the tube in water kept at 70° for five minutes. Cool under running water. Exactly neutralize 2–3 cc. with dilute ammonium hydroxide solution, and then test again with Fehling's solution and also with the ammoniacal silver nitrate. (?) If a light colored precipitate is obtained with the silver solution add more ammonium hydroxide until it dissolves. (?) Explain all results.

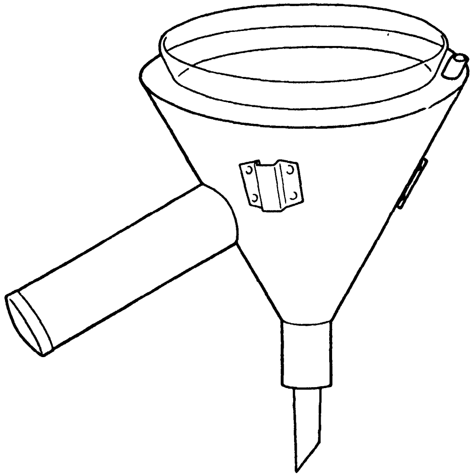
Neutralize with ammonium hydroxide 10 cc. of the hydrolyzed sugar solution, make up to 20 cc. with water, place the solution in a large test-tube (No. 3), and add 2 cc. of phenylhydrazine[1] and 3 cc. of glacial acetic acid. Mix well. Stopper loosely with a cork to prevent evaporation, and set the tube into water which has been brought to boiling[2] and let stand for one-half hour. Masses of fine yellow crystals of the osazone soon settle out. Cool, filter off the osazone in a Buchner funnel, and wash with cold water. Recrystallize as follows: Place the yellow product in a 250 cc. Erlenmeyer flask and add a mixture of 120 cc. of alcohol and 60 cc. of water, attach an upright condenser or cover with a small watch glass, set the flask on the steam-bath and heat until all or practically all the substance is dissolved.

---

[1] Phenylhydrazine is poisonous. Its vapors should not be breathed, and it should not be allowed to come into contact with the skin since it produces an intolerable itching. Dilute acetic acid will remove phenylhydrazine.

[2] Do not heat after placing the tube into the bath, otherwise a dark product will be obtained.

In order to prevent crystallization in the filter, the solution should be filtered[1] at once through a fluted filter in a glass funnel set in a hot-water funnel, using a stirring rod to direct the flow of the hot solution into the filter. The hot-water funnel consists of a double-walled copper jacket for an ordinary funnel, with a side tube for heating the water within (Fig. 12). Steam may be passed into it instead of using water. If a burner is used, it must be removed when you are filtering inflammable liquids, as in this case. The stem of the glass funnel should not project more than 2–3 cm. below the neck of the hot-water funnel.



*HOT WATER FUNNEL*

FIG. 12.

---

[1] A fluted filter is made by first folding a large circular filter paper in the ordinary way. Then half open it, and bring one corner *in* to the center of the hemicircle and crease the paper. Bring back this same corner to the edge of the fold just made, and crease again. Now fold this back to the middle line of the original hemicircle. Repeat with the other quadrant. This gives an alternating series of folds. When completely opened, it will be noticed that there are two places where the paper would lie flat against the walls of the funnel. Fold each one of these in a half fold to make them similar to the others. A fluted filter gives very rapid filtration. (Why?)

(Why?) The osazone almost immediately begins to crystallize out of the filtrate. Filter, when cold, with suction, and set aside the product to dry on a porous plate covered with a watch glass. Determine the melting-point. Pure phenylglucosazone is a bright yellow finely crystalline substance which melts at 205°–206° uncor.; or 208° cor., when the rate of heating is 1° in two to three seconds.[1]

The osazone should be prepared and recrystallized during one laboratory period. Yield, about 1.2 grams.

## NOTES

1. Solubility of phenylglucosazone:

0.01 part dissolves in 100 parts of boiling water.
0.0042 part dissolves in 100 parts of water at 20°.
0.031 part dissolves in 100 parts of 5% acetic acid at 20°.

2. If the phenylhydrazine is not available, use instead of it and the acetic acid, 2 grams of phenylhydrazine hydrochloride and 3 grams of crystalline sodium acetate. Explain.

Phenylhydrazine hydrochloride when pure is a white crystalline substance, but when moist or impure it rapidly decomposes and darkens on keeping. Unless the pure white substance is used dark tarry spots will be found in the reaction mixture. These will be removed in the recrystallization unless there is a large amount.

In connection with the identification of sugars by means of the rate at which the osazone begins to precipitate, Mulliken describes the method of obtaining pure phenylhydrazine hydrochloride from phenylhydrazine, "Identification of Pure Organic Compounds," Vol. I, foot-note, p. 32.

In order to prevent the decomposition Böeseken advises using the sulfite salt instead of the hydrochloride, *Chem. Weekblad,* **7**, 934; *Chem. Abs.*, **5** (1911), 2078.

3. Phenylglucosazone is also known as phenylfructosazone, and also as phenylmannosazone. (Why?)

---

[1] Garard and Sherman: *Journ. Amer. Chem. Soc.*, **40** (1918), 957, and compare, p. 58 of melting-point experiment.

## QUESTIONS

1. Why would you expect cane sugar to be soluble in water?
2. What are the two mono-saccharides in invert sugar?
3. Write the structural formulas for cane sugar and the substances in invert sugar.
4. Show by means of its structure that cane sugar is an acetale.
5. What does the behavior of cane sugar toward Fehling's solution and ammoniacal silver nitrate solution indicate in its structure?
6. Why is the invert sugar solution neutralized with ammonium hydroxide solution before it is tested with Fehling's solution?
7. What is the white precipitate formed when insufficient ammonium hydroxide is used in the silver mirror test?
8. Explain why the same concentration of acetic acid as of hydrochloric acid in water would not hydrolyze cane sugar as rapidly.
9. How can you show that cane sugar is an alcohol?
10. Explain why it is that invert sugar can be oxidized by Fehling's solution although the larger portion of the mono-saccharides in it are known to be in the lactone form.
11. Explain how the reaction between Fehling's solution and invert sugar can be used as a quantitative method for the estimation of cane sugar in the presence of known amounts of glucose.
12. Explain why invert sugar yields only one osazone.
13. For what purpose is acetic acid added in the formation of the glucosazone from the hydrolyzed cane sugar?
14. Could strong hydrochloric acid be used in place of the glacial acetic acid in the formation of the osazone?
15. Can invert sugar form hydrazones and if so what would be their chemical structure?
16. Explain how the hydrazones and osazones are of value to the analyst in identifying sugars?

*17. Could any other hydrazines besides phenyl hydrazine be used for the purpose? Are they ever used, and why?

*18. Can you give any reason why the hydrazones of glucose and mannose should be different in physical properties since the two mono-saccharides differ only in a sterochemical way?

*19. What is formed when the osazone is heated with conc. hydrochloric acid?

*20. How can *d*-glucose be transformed into *d*-fructose? into *d*-mannose?

*21. How can *d*-fructose be transformed into *d*-glucose?

22. What is $\alpha$-methyl glucoside? How prepared?

23. Of what does the Benedict-Fehling solution consist? What advantage has it over the Fehling solution in the test for glucose in a physiological solution like urine? (Hawk, "Practical Physiological Chemistry," 5th Ed. (1916), 27, 417–8; Plimmer, "Practical Organic and Bio-chemistry (1915), 191.)

---

* These questions are not required for study in the "short" course.

## Experiment No. 35

## Pentoses (Furfural Test)

A solution of a pentose is first made by the acid hydrolysis of a pentosan such as gum arabic or an ordinary corn cob, and then the presence of the pentose is shown by the colored compound formed by the action of the decomposition product of the pentose with hydrochloric acid and aniline acetate.

Make up 30 cc. of a solution of dilute hydrochloric acid (sp.gr. 1.06) by mixing 9 cc. of conc. hydrochloric acid and 21 cc. of water. Pour 10 cc. of this dilute acid into a 100 cc. flask and add about 0.2 gram of gum arabic. Slowly bring to a boil over a low flame and boil *gently* for five to ten minutes. Withdraw the flame, and while the vapors are coming out place in the mouth of the flask a roll of filter paper which has been soaked in a solution of aniline acetate, and from which the excess of the solution has been removed by pressing between filter papers, The test should be made while the paper is still moist. The aniline acetate solution is prepared by mixing 2 cc. each of aniline, glacial acetic acid and water. A bright crimson color on the aniline acetate paper indicates the presence of furfural from the action of the hydrochloric acid on the pentose.

Repeat the above experiment, using 0.2 gram of ground corn cob.

Some of the hexoses also give a pink color in this same test, but the color generally is not so pronounced. Repeat the experiment, using the same amount of cane sugar, and compare the color produced with that from the pentoses.

### REFERENCES

For a discussion of this test see Sherman's "Organic Analysis," and for the probable composition of the colored compound formed on the test paper, see Richter's "Organische Chemie," 11. Auflage, Vol. II, 713.

## QUESTIONS

1. Write the stereo structures of the different possible pentoses, and name them.
2. What substance is formed by the action of hydrochloric acid on a pentose?
3. What are the pentoses obtained from gum arabic, cherry gum, corn cobs, bran, etc.?
4. To what class of cyclic compounds does furfural belong?
5. What is a pentosan?
6. How can pentoses be obtained from the pentosans?
7. Name some substances which are or contain pentosans.
8. Compare the pentosans with starch and cellulose.
9. What is a galactan?
10. What is the phloroglucinol test for furfural?
11. How can the phloroglucinol test be used for the quantitative estimation of pentoses? (See Sherman's "Organic Analysis.")
12. Show how arabinose can be converted into glucose.
13. Show how glucose can be converted into arabinose.
14. What is a pentonic acid? How prepared?

## Experiment No. 36

### OXIDATION OF A SUGAR

### Mucic Acid from Lactose

In a porcelain dish, 13–14 cm. in diameter, evaporate over a free flame a solution of 12 grams of lactose in 150 grams of nitric acid [1] of sp.gr. 1.15 to a volume of about 25 cc. with stirring towards the end. In order to remove the fumes support a large funnel over the dish and connect it with the suction pump. Do not heat so strongly that the material is charred on the sides of the evaporating dish. Brown fumes (?) are evolved, and the mass finally becomes thick and pasty owing to the separation of mucic acid. When cold, dilute with water, filter with suction, and wash with small amounts of cold water. In order to determine the yield of crude product, dry it on a watch glass on the steam-bath or in an oven.

To purify, dissolve the crude dry material in a cold solution of sodium hydroxide and re-precipitate with hydrochloric acid. Only the neutral salt is easily soluble in water, and its solubility is decreased by excess of alkali. (?) It is best therefore to calculate approximately the amount of N/2 sodium hydroxide solution necessary. Do not add dry solid sodium hydroxide to the water containing the mucic acid—use a cold solution. Filter if necessary. If the solution is dark brown, decolorize by gently warming with animal charcoal, or filter through a funnel containing animal charcoal. Cool and add the equivalent of 5N hydrochloric acid [2] to set free the mucic acid. The hydro-

---

[1] The calculations can be made from the following data: The specific gravity of ordinary conc. nitric acid is 1.42.

Nitric acid, 1.15, contains 24.84% $HNO_3$ by weight (15°)

Nitric acid, 1.42, contains 69.80% $HNO_3$ by weight (15°)

[2] Conc. hydrochloric acid, sp. gr. 1.19, contains 37% HCl by weight (15°).

chloric acid must not be added while the liquid is warm because part of the mucic acid may be converted into the easily soluble lactone. To complete the crystallization, allow the liquid to stand, then filter with suction, wash with cold water, and dry. Yield, 4 grams. Determine the melting-point. (?) Mucic acid is soluble one part in 100 of water at 14°.

Try the action of Fehling's solution on lactose. What does this indicate?

### NOTE

The term "mucic" comes from the Latin word "mucus," meaning mucus or slime. Mucic acid has been known for many years, having early been prepared by the action of nitric acid on some plant mucilaginous material which contained galactans. The German name for mucic acid is "Schleimsäure."

### QUESTIONS

1. Write the equations for all reactions involved in the production of mucic acid from lactose, indicating the various reactions by means of stereochemical structures.
2. Explain why it is necessary to use nitric acid of about this particular strength, and give reasons.
3. What is the action of conc. nitric acid on lactose?
4. What significance is there in the fact that lactose reduces Fehling's solution?
5. Which of the two mono-saccharides combined in the lactose molecule contains the " free " carbonyl group? How can this be shown? (The structural formula of lactose in Stoddard, " Introduction to Organic Chemistry," 2d Ed., p. 215, should be reversed.) Compare Holleman's " Organic Chemistry."
6. What becomes of the saccharic acid and how does it differ from mucic acid structurally? Is it optically active?
7. Can you give any reason why you would expect mucic acid not to have the same solubility as saccharic acid?
8. Is this acid named *d*, *l*, racemic or meso mucic acid? Give reasons.
9. What is the salt formed when sodium hydroxide reacts with mucic acid? Name?
10. Why is it necessary to neutralize so carefully with sodium hydroxide?

11. Write the structure of the lactone of mucic acid.
12. To what class of organic compounds do the lactones belong?
13. Are compounds like the lactones often formed by boiling water?
14. Indicate the difference between an " acid lactone " and a " sugar lactone."
15. What is the chief organic impurity removed by the recrystallization and washing? Is this obtained from other sugars likewise?

## Experiment No. 37

## Cellulose Acetate

In a small Erlenmeyer flask place 20 cc. of glacial acetic acid, 6 cc. of acetic anhydride, 2 drops of conc. sulfuric acid, and 0.5 gram of absorbent cotton. Press the cotton into the solution with a glass stirring-rod, and after a few minutes stir it so that most of the air bubbles are removed. Stopper and let it stand overnight or longer. Pour the clear solution which is obtained in a thin stream, and with stirring, into 500 cc. of water. Filter with suction, using a large funnel. Press out between filter paper or on a porous tile until dry. Put about one-half the dry product in a small beaker or test-tube and add 20 cc. of chloroform. After standing some time the acetate should pass into solution. Pour the solution upon a watch glass and let it evaporate slowly. When the chloroform has evaporated, put some water into the watch glass and allow it to stand for a minute or two. Lift the edge of the film and remove it slowly from the glass. Dry the film and try its burning qualities. Test the solubility of the remainder of the acetate in glacial acetic acid, in alcohol, and in ether.

### QUESTIONS

1. How is cellulose related to the simple sugars?
2. Outline, in general, the reaction with acetic anhydride.
3. What conclusion as to the groups in cellulose can you draw from this reaction?
4. How does conc. sulfuric acid affect cellulose?
5. How does a mixture of conc. nitric and sulfuric acids react with cellulose?
6. What is a " tetra-nitrate," a " hexa-nitrate " of cellulose?
7. What is smokeless powder? Celluloid? Collodion?
8. How is artificial silk made?
9. What is viscose? Explain its formation and use.
10. What is mercerized cotton?
11. Compare the action of the reagents mentioned in questions 2, 4, and 5 on starch.

## Experiment No. 38

### BENZENE: CHEMICAL PROPERTIES

*a.* To 2 cc. of benzene, labeled " thiophene free," add 0.5 cc. of a dilute solution of bromine in carbontetrachloride. Does the color of the bromine disappear immediately? At all?

*b.* (Hood.) Add several drops of bromine (not bromine water) to 5 cc. of benzene. Divide the solution into equal portions, and to one add some iron powder. Note the difference in the velocity of the reaction in the two tubes. Breathe across the top of them. (?)

*c.* Add several drops of benzene to 1 cc. of conc. sulfuric acid. Shake. Is there any evidence of chemical action apparent by the formation of heat or by darkening? Does the mixture become homogeneous? Pour it into 6 cc. of cold water, cool, stir, and then transfer to a No. 1 test-tube. Is a homogeneous solution obtained? Does benzene dissolve in hot conc. sulfuric acid?

*d.* Repeat *c.*, using fuming sulfuric acid. Pour the mixture drop by drop into cold water or better, upon ice. Result? (A solid substance, diphenylsulfone, may separate in the water solution. Explain.)

*e.* Add several drops of benzene to 1 cc. of conc. nitric acid. Shake well for two minutes. Any heat formed? Then add slowly with cooling 1 cc. of conc. sulfuric acid. Shake. Any change? Pour into cold water and stir well. What is the heavy yellow oil that settles out in droplets? Note the odor.

Is benzene reacted upon by fuming nitric acid? Try it.

*f.* To 1 cc. of a very dilute solution of potassium permanganate in a small glass-stoppered bottle, add 1 cc. of benzene (" thiophene free "). Is there any change noticeable?

Compare all the above reactions with benzine (in the Methane experiment, p. 31) and pinene (in the Ethylene experiment, p. 45).

*g.* Determine the freezing-point of benzene by freezing some in a test-tube placed in ice and water. Stir the benzene with a thermometer until it solidifies. Note any super-cooling also.

The true freezing-point of benzene is 5.483.° See Richards and Shipley, "The Freezing-point of Benzene as a Fixed Point in Thermometry," *Journ. Amer. Chem. Soc.*, **36** (1914), 1825.

*h.* Small quantities of aromatic hydrocarbons are conveniently identified by converting them into solid nitro derivatives, usually the di-nitro-compound, and determining the melting-point.

Mix 1 cc. of conc. sulfuric acid and 1 cc. of conc. nitric acid in a dry test-tube and add three drops of benzene. Heat to boiling and boil for thirty seconds. Cool and pour slowly into 10 cc. of water in another test-tube. Shake. Filter off the bulky precipitate with suction, collecting it upon a small filter[1] and wash until the washings are no longer colored. Dissolve the substance with shaking in a boiling mixture of 4 cc. of alcohol and 4 cc. of water and set aside to crystallize. It crystallizes in long fine needles which are nearly white. Filter with suction and allow to dry upon a porous tile. Determine the melting-point of the *m*-dinitrobenzene formed, which should be 89.72 cor.[2]

Write the structure of the compound formed in this reaction. Can a similar compound of toluene be prepared with the *same* kind of acid mixture?

### HISTORICAL NOTE

Faraday, in 1825, discovered a liquid hydrocarbon in compressed coal-gas which he called "bicarburet of hydrogen," since it had the empirical formula $C_2H$ (on the basis of the atomic weight of carbon being 6 which was used at that time). Mitscherlich, 1834, obtained the same hydrocarbon by the distillation of benzoic acid with slaked lime and termed it "benzin." He assumed that it was formed from the benzoic acid by the removal of $CO_2$. Liebig denied this, adding the following editorial note to Mitscherlich's memoir in the "Annalen": "We have changed the name of the body obtained by Prof. Mitscherlich by the dry distillation of benzoic acid and lime and termed by him *benzin*, into *benzol*, because

---

[1] For filtration of small quantities with suction, see p. 56.

[2] For this method of preparation, see Mulliken, "Identification of Pure Organic Compounds," Vol. I, 200.

the termination 'in' appears to denote an analogy between strychnine (German, strychnin) and quinine, etc., bodies to which it does not bear the slightest resemblance, whilst the ending in 'ol' corresponds better to its properties and mode of production. It would have been better perhaps if the name which the discoverer, Faraday, had given to this body had been retained, as its relation to benzoic acid and benzoyl compounds is not any closer than it is to that of the tar or coal from which it is obtained." A. W. Hofmann, in 1845, isolated the hydrocarbon from coal-tar. Later the name benzene came into use in accordance with the ending of unsaturated hydrocarbons.

For many years, however, the ending "ol" has been used to denote an alcohol or a phenol. The term *benzol* is, therefore, considered a hybrid and a misnomer. Unfortunately the pronunciation of benzene is the same as that of benzine—one of the petroleum fractions, but this can be remedied by using *benzolene* instead of *benzine* (see Note 1, p. 33).

### REFERENCES

Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. III, Pt. III (1897), 64; and "Resolution Concerning Organic Nomenclature," *Journ. Ind. and Eng. Chem.*, **10** (1918), 944.

## Experiment No. 39

### FITTIG'S SYNTHESIS OF AN AROMATIC HYDROCARBON

### Preparation of Ethylbenzene from Benzene and Ethyl Bromide

Weigh out 12 grams of metallic sodium in lumps from which all the crust has been removed. Use a common knife or a penknife and dip the blade frequently into the kerosene with which the sodium is covered. Return all residues to the original bottle. Put the sodium into a dry 200 cc. round-bottomed flask and cover with 30 cc. of commercial xylene. Attach an addition tube and bulbed condenser with sealed joints[1] as a reflux condenser. Stopper the tube and heat the flask *gently* over a wire gauze until the sodium melts (m.p. 95.6°, the xylene boils at 136°–141°). Do not heat the xylene to boiling. On account of the crust which forms about the sodium while exposed to the air, it often appears that the sodium does not melt because the melted globules are held by this covering. Disconnect while hot, stopper the flask with a good cork, place a folded towel at the bottom of the flask and another at the top to protect the hands, hold the flask in an upright position and shake *vigorously* in a *vertical line* for a *moment* until the sodium is broken into small globules—" bird-shot " sodium. Let the flask rest upon a suberite ring[2] until cold. Do not shake too long, since the melted sodium may form one large lump. Now decant[3] the xylene into a dry beaker and quickly wash the sodium twice by decantation with 20 cc. portions of dry ether (" absolute ether "

---

[1] If a condenser with rubber connections is used, the joints must be wired to make them perfectly tight.

[2] A suberite ring is a ring of pressed cork for supporting round-bottomed flasks.

[3] Do not decant the xylene or the ether into a wet beaker or into the sink. Particles of sodium may thus come in contact with water. Destroy the sodium by adding alcohol.

or "ether over sodium"). Add 50 cc. of dry ether and reassemble the apparatus, setting the flask in a beaker. In twenty to thirty minutes the ether, which is very hygroscopic and cannot ordinarily be kept dry, will be dry enough and practically no more bubbles will be given off. Now pour through the addition tube a mixture of 30 grams (20 cc.) of brombenzene and 30 grams (20 cc.) of ethyl bromide (an excess of the theoretical amount), and let stand overnight. If the liquid begins to boil vigorously cool by pouring cold water into the beaker. It should be watched for about an hour before leaving the laboratory. Do not allow the water to run through the condenser outside of laboratory hours!

During the reaction the sodium is changed to a blue powder and an ethereal solution of ethylbenzene is formed. The next day remove the ether by distillation observing the ordinary precautions. The ether is practically all distilled when no more drops come over. Dry the outside of the flask, connect it in an inclined position, with the extreme end of the neck clamped loosely, to an air condenser with adapter attached leading into a receiver and loosely plug the annular space in the mouth of the receiver with cotton. Distill the crude ethylbenzene from the apparently dry residue by heating with a luminous flame which is kept in constant motion. Toward the end of the distillation the heat may be increased. Since the ether is not entirely removed in the first distillation care must be taken in this operation and the eyes should be protected with goggles.

Then subject the crude product to at least two fractionations. Use a small distilling flask and place into it a piece of pumice or tiling to aid ebullition. Carefully heat the flask directly with a very small flame. Collect separately the portions boiling below 115°, between 115°–140° and above 140°. Redistill each portion, collecting as the sample the part boiling between 133°–136°. The boiling-point of pure ethylbenzene is 135.98° (760 mm.)[1] cor. It is of great advantage in this fractionation to use a small round-bottomed flask surmounted by a Young four-pear still head, see Fig. 4, p. 25. Yield, 8 grams.

---

[1] T. W. Richards and F. Barry. *Journ. Amer. Chem. Soc.*, **37** (1915), 998.

The residue in the original flask contains some sodium and must be handled with care. Remove the material and add it in small pieces to ethyl alcohol or acetone in a beaker, waiting until all the sodium in each piece has been destroyed before adding another. Dilute with water (Care!) before pouring the solution into the sink. Rinse out the flask with alcohol before adding any water.

Sometimes crude amyl alcohol is used for destroying sodium residues. Its action is much slower, and, furthermore, globules of sodium are often found at the end of the main reaction coated with sodium amyl oxide, and their presence is sometimes not noticed until after water has been added!

## QUESTIONS

1. Of what does the crust on the sodium consist?
2. Name some other liquids that might be used to cover the sodium in the bottle.
3. Why must the xylene be removed after making the " birdshot " sodium?
4. Compare the molecular and structural formulas of ethyl benzene and the xylenes.
5. How could you distinguish chemically between the isomers, ethyl benzene and *m*-xylene?
6. Why not add the brombenzene and the ethyl bromide separately?
7. Why must you wait until the ether is dry before proceeding?
8. What two other organic compounds are formed in this reaction? What becomes of them?
9. Is the reaction applicable to the aliphatic series?
10. What is the object of the ether? Why is the " ether over sodium " used? What other substances could be used?
11. Why must the condenser be perfectly tight?
12. Why does not all the ether come over in the first distillation, since it boils at 35°?
13. Why is the flask dried after the distillation of the ether?
14. Why is the flask inclined?
15. What is the cause of the blue color?
16. Why is the luminous flame kept in constant motion?
17. Write the structure of the compounds formed when ethyl alcohol and sodium, and amyl alcohol and sodium react.
18. Outline an apparatus for heating a reaction mixture above its boiling-point in a flask. (Gattermann, p. 280.)

## Experiment No. 40

### SYNTHESIS OF AN AROMATIC HYDROCARBON BY MEANS OF FRIEDEL-CRAFTS' REACTION

### Preparation of Diphenylmethane from Benzene and Benzyl Chloride

Attach an addition tube and dry reflux condenser to a dry 300 cc. flask. Connect the top of the condenser with a tube leading into the draft pipe. Put 60 cc. of benzene, and 17 cc. of benzyl chloride [1] into the flask. Weigh out 5 grams of finely-pulverized anhydrous aluminium chloride [2] in a dry test-tube closed by a cork and add this in two portions (the second after the first reaction has subsided) to the mixture in the flask. Let stand until the evolution of hydrogen chloride has nearly stopped (thirty minutes). Then disconnect the apparatus and add 40 grams of finely ground ice. (?) Shake, and after the ice has melted, separate the layers in a separatory funnel. The upper layer of benzene contains the diphenylmethane, and after the lower layer has been drawn off pour the upper layer from the top of the funnel.

In order to remove the benzene most quickly and also leave the crude diphenylmethane in a small flask ready for the final fractionation, the solution is fractionated in portions under diminished pressure or *in vacuo* as follows: Connect a 125 cc. Claisen and an ordinary distilling-flask for distillation *in vacuo*

---

[1] The vapors of benzyl chloride are very irritating to the eyes and the mucous membranes of the nose and mouth.

[2] The sealed bottles in which the anhydrous aluminium chloride comes often contain considerable pressure. Great care is therefore necessary in opening them. Use the method described on p. 33, and completely wrap the bottle in a towel before striking the neck above the file mark a blow with the file. The aluminium chloride must be in good condition or the experiment will be a failure.

(Expt. 15, p. 76), fill the upright one not more than one-third full of the solution, and, keeping the bath 40°–50°, distill until practically all the benzene and water have gone over. Equalize the pressure by slowly opening the stop-cock, take away the bath, cool, then add more of the solution. Continue these operations until all the benzene and water have been removed. The last time raise the temperature and stop the distillation when the diphenylmethane begins to distill. Attach a clean receiving-flask and then distill the residue. By keeping the temperature of the oil-bath constant where the diphenylmethane distills regularly no trouble with excessive foaming will be experienced. If the product is colored or does not completely solidify, redistill *in vacuo* after adding two or three small pieces of sodium. (Why?) Destroy the sodium in the residue with alcohol. At 22 mm. pressure diphenylmethane boils at 145° (at 760 mm., 263°). It is a clear heavy liquid which crystallizes to a solid white mass of needles on standing in the refrigerator or after adding a crystal of the substance ("seeding"). M. p., 25°–26°. It is partially decomposed when distilled under ordinary atmospheric pressure, and has an odor resembling that of orange-peel. Yield, 15 grams.

## QUESTIONS

1. Why is the aluminium chloride weighed out in a closed test-tube?
2. What causes the initial brown color when the $AlCl_3$ is added?
3. What is the purpose of the ice?
4. What becomes of the aluminium chloride?
5. Why is the product distilled *in vacuo*?
6. Is there any advantage in removing the benzene *in vacuo?*
7. Why is the benzene distilled off in portions in a small flask?
8. What other possible compounds are formed in the reaction and remain in the "tar" in the fractionating flask? (Compare Gattermann, p. 323.)
9. At the end of the distillation of the diphenylmethane the temperature often drops considerably although the bath is still at a high temperature. Explain.

10. What other class of compounds can be made by the Friedel-Crafts reaction?
11. Diphenylmethane on oxidation with chromic acid mixture yields benzophenone. Is this reaction general with aromatic hydrocarbons? Compare triphenylmethane and diphenyl.
12. What kind of halogen derivatives are used in the Friedel-Crafts reaction, aliphatic or aromatic, or both?
13. Would there be any reaction between brombenzene and benzene in the presence of aluminium chloride?
14. How could you prepare triphenyl-methane?
15. From its structure would you expect diphenylmethane to be soluble in benzene?
16. Discuss the use of the aluminium-mercury couple in place of the aluminium chloride for preparing diphenylmethane, etc. (J. B. Cohen, " Organic Chemistry for Advanced Students," Pt. I, 2d Ed. (1918), 198; and Norris, " Experimental Organic Chemistry " (1915), p. 132.)

## Experiment No. 41

### FORMATION OF A FREE RADICAL

### Triphenylmethyl

Place 0.5 gram of triphenylchlormethane[1] and 1 gram of powdered zinc into a clean, dry, No. 1 test-tube. Seal a glass rod in the open end, soften the glass near this end in the blast flame and draw it out to a narrow tube about 2 mm. in diameter (compare sealing of a bomb tube, p. 117). When cold, pour in 4 cc. of dry benzene[2] and after letting it drain well seal off the end of the tube. (Care!) Shake and allow it to remain in a horizontal position for two days. The heavy brown oil which separates on the bottom is a double compound of triphenylmethyl and zinc chloride. At the end of the time specified open the tube and quickly divide its contents into two test-tubes. Have ready a solution of iodine in benzene and immediately test the unsaturated nature of the compound by slowly adding the iodine solution. (?) The other portion rapidly absorbs oxygen from the air and the insoluble triphenyl-methyl-peroxide is precipitated.

### REFERENCE

Gomberg, "The Existence of Free Radicals," *Journ. Amer. Chem. Soc.*, **36** (1914), 1144–70.

---

[1] Triphenylchlormethane must be kept in sealed bottles, since it will slowly be hydrolyzed by moisture in an ordinary cork-stoppered bottle.

[2] If the tube is so narrow that the benzene does not flow down readily, alternately warm the lower part of the tube with the hand, and cool, when the liquid will be drawn into the tube in small portions. Sometimes it will run down easily if the tube is inclined and the liquid poured in very slowly.

## QUESTIONS

1. Is there any objection to the use of a larger test-tube in this experiment?
2. Why must *dry* benzene be used?
3. Explain the ready absorption of iodine by the solution.
4. Write the formula for the compound formed when the solution is exposed to the air.
5. Compare some of the higher homologues of triphenylmethyl with triphenylmethyl itself, in regard to physical and chemical properties. (See *Journ. Amer. Chem. Soc.*, **36** (1914), 1165–6.)
6. Discuss the question of the existence of free radicals.

## Experiment No. 42

## HALOGENATION OF AN AROMATIC HYDROCARBON

### Preparation of Brombenzene

NOTE.—This experiment must be allowed to stand overnight, but not longer than two or three days, since the monobrombenzene first formed is gradually converted into higher bromination products.

Into a 200 cc. flask containing two small iron nails place 20 cc. of benzene and 13 cc. (42 grams) of bromine (draft pipe). Immediately attach a reflux condenser with top connected with the draft pipe by means of a tube. In a short time an energetic action will begin, generally spontaneously, with the evolution of hydrogen bromide.[1] If necessary, warm slightly to start the reaction. Let stand overnight. Add water to the flask and wash twice by decantation, then in a separatory funnel wash with dilute sodium hydroxide solution[2] until the liquid is no longer acid, and again with water. Separate the liquids (sp. gr. of brombenzene is 1.489 at 21°), dry with calcium chloride,[3] and distill, using an air condenser (p. 15). Collect the portion boiling between 140°–170° and fractionate this two or three times narrowing the limits each time, collecting finally the portion between 154–6°. The boiling-point of pure mono-brombenzene is 155.5° cor. Yield, 18 grams.

The crystals which are sometimes present in the original flask and the residue boiling above 170° in the distilling-flask

---

[1] This is a good method for preparing hydrobromic acid by absorption of the gas in water.

[2] If an emulsion is formed, it can be "broken" by making the mixture slightly acid with hydrochloric or sulfuric acid.

[3] If sufficient water has been extracted by the calcium chloride to form a solution of the salt sometimes floating on the surface of the liquid, separate this aqueous layer and add fresh calcium chloride. (Why is this necessary?)

consist mainly of *p*-dibrombenzene. Dissolve this material in 10–20 cc. of hot alcohol and filter the hot solution. If the filtrate is not water-white decolorize by adding animal charcoal, in small amounts to avoid excessive foaming of the hot liquid, cover with a watch glass, heat on the steam-bath for several minutes, and filter again while hot. Set the beaker aside for crystallization. Finally filter off the crystals of *p*-dibrombenzene with suction, dry and determine the melting-point. (?)

*a.* Repeat experiment *c* under ethyl iodide (p. 38) using only a portion of a drop of brombenzene. Result?

*b.* Repeat the same experiment using benzyl chloride.

*c.* Repeat the above experiments, but use distilled water in place of the alcohol. Do not mistake an emulsion for a precipitate. Compare results with those with the alcoholic solution.

## QUESTIONS

1. What is the object of the iron nails? Why not use iron filings? Under what condition could the latter be used?
2. What dibrom product is obtained in the experiment? Are any of the other two possible dibrom products formed at all?
3. Why should the reaction mixture not be allowed to stand more than one or two days after the bromine has been added?
4. What is the reddish-brown precipitate sometimes formed when the sodium hydroxide solution is added?
5. How is benzyl bromide prepared?
6. What are alpha- and beta-benzene hexabromides? (J. B. Cohen, "Organic Chemistry for Advanced Students," Pt. II, 2d Ed. (1918), 260–3.) How prepared?
7. What advantages has a separatory funnel over decantation, and decantation over a separatory funnel, for washing purposes?
8. Compare the stability toward hydrolyzing reagents of the aryl halides with the alkyl halides.
9. What compounds, if any, are formed by the action of alcoholic KOH on benzyl chloride; on 1-phenyl-2-chlorpropane; picryl chloride; brombenzene?
10. How can brombenzene be converted into benzene? Into diphenyl?

11. Give some of the modifications in the methods of using bromine for brominations.
12. Give methods for preparing chlorbenzene from aniline; from chlorbenzoic acid; and for benzyl iodide from benzyl chloride.
13. How are the iodo-derivatives prepared?
14. Explain the action of the boneblack in decolorizing the solution of dibrombenzene.

## Experiment No. 43

### SULFONATION OF AN AROMATIC HYDROCARBON

### Preparation of Benzene Sulfonic Acid, Sodium Salt

To 5 cc. of fuming sulfuric acid in a test-tube, add in small portions 3 cc. of benzene, shaking vigorously and cooling after each addition. When the benzene has all dissolved and the liquid is clear, slowly pour it into 20 cc. of water in a flask, cooling it under running water. Filter off with suction any diphenylsulfone which separates. Partly neutralize by adding 4 grams of crystalline sodium carbonate, then add 5 grams of common salt. Warm and stir till it dissolves, filter while hot through a fluted[1] filter paper, and cool. Stir well when the solution is almost cold. The sodium benzene-sulfonate separates out in a mass of white lustrous plates. It may be necessary to set the beaker in ice in order to promote and complete the crystallization. Filter with suction. Press as dry as possible while it is in the funnel. Allow to dry on filter paper or press out on a porous plate. Recrystallize from hot alcohol. The pure sodium salt melts at about 450°. Such a melting-point cannot be taken with the ordinary apparatus. Yield, 4 grams.

### NOTES

1. A greenish color often develops during the sulfonation. This usually disappears in the recrystallization from alcohol.

2. Sometimes the material does not crystallize out of the alcoholic solution very well. Possibly a soluble "alcoholate" similar to a "hydrate" is formed. Evaporation, thorough cooling, and stirring generally overcome the difficulty.

---

[1] See foot-note, p. 128.

## QUESTIONS

1. What is fuming sulfuric acid?
2. Could conc. sulfuric acid be used? How?
3. Account for the formation of the diphenyl-sulfone. Would a lesser amount of sulfuric acid tend to increase or diminish the amount formed?
4. Why is the mixture partly neutralized with sodium carbonate?
5. Is it necessary to use the sodium carbonate for the formation of the sodium benzene-sulfonate which crystallizes out, or would the sodium salt be formed and precipitated by adding sodium chloride alone?
6. How could you filter a fuming sulfuric acid solution?
7. What impurities does the sodium benzene-sulfonate contain before recrystallization?
8. How may the product be freed from these impurities (No. 7)?
9. Explain the formation of the sodium salt of benzene sulfonic acid by the theory of " salting out."

*10. How are the corresponding calcium and barium salts prepared?

*11. How is the free sulfonic acid obtained from these salts (No. 10)?

12. How is the free sulfonic acid obtained from the lead salt?

*13. What mono-sulfo derivatives of naphthalene are prepared by direct sulfonation?

14. Compare the structures of the sulfonic acids and of the nitro-compounds with relation to the acids from which they are derived.
15. How can the sulfo-acids be converted into the parent hydrocarbon?
16. How can the sulfo group be replaced by OH, by CN?

---

* These questions are not required for study in the "short" course.

## Experiment No. 44

### NITRATION OF AN AROMATIC HYDROCARBON

### Preparation of Nitrobenzene

In a flask carefully mix 18 cc. of conc. nitric acid and 18 cc. of conc. sulfuric acid, cooling under running water after each addition of one acid to the other. When the solution has come to the room temperature add it slowly from a dropping-funnel to 13 cc. of benzene contained in an open 300 cc. flask, under the hood. (Do not use any cork or rubber connection.) Shake well and cool frequently under running water, keeping the temperature of the liquid below 50°. When all the mixture has been added, half immerse the flask in water maintained at 50° by means of steam or a burner kept burning low and let it remain at this temperature for thirty minutes connected with a tube leading to the draft pipe. Since the mixture separates into layers on standing, it must be shaken occasionally during the heating. The nitration is complete when a drop which is added to water sinks to the bottom. The presence of any unchanged benzene will cause it to float. In performing this test stir well to make certain that any drops on the surface are not held up by surface tension alone.

Pour the contents of the flask into about 500 cc. of water in another flask, shake thoroughly, cool it, and separate the lower turbid yellow layer of nitrobenzene by means of a separatory funnel. Return it to the funnel and wash the oil with sodium hydroxide solution until free from acid, and finally wash with water. Separate as completely as possible and return the oil to a dry separatory funnel. Add calcium chloride and shake. If an aqueous solution of the salt separates, remove it and add fresh calcium chloride. Repeat, and then transfer the liquid to a small

Erlenmeyer flask, add several pieces of fresh calcium chloride, stopper, and allow to stand overnight to complete the drying. Be sure to clean the separatory funnel so that the stopper and stop-cock will not stick. It is well to keep the parts separated, but tied with a piece of twine. When dry the nitrobenzene will be clear. Filter through a funnel as usual containing a plug of glass wool into a dry distilling-flask with low outlet tube (style C). The stem of the funnel should reach below the opening of the delivery tube. Distill. Catch the first runnings, which consist chiefly of benzene and traces of water, direct from the outlet tube. When the clear yellowish nitrobenzene begins to distill attach a dry air condenser and distill, using a dry weighed specimen bottle as the receiver. Do not in any case allow the temperature to go more than 5° above the boiling-point: the residue sometimes decomposes explosively.[1] B.p. 210.9° cor. Yield, 17 grams.

## NOTE

Nitrobenzene is a poison. Its vapor should not be breathed excessively and it should not be allowed to remain in contact with the skin.

## QUESTIONS

1. Can nitrobenzene be prepared by adding benzene to the acid mixture, instead of the acid mixture to the benzene? Why is the method used in the laboratory preferred?
2. What compound is formed if the temperature is allowed to rise much above 50°?
3. What is the object of the sulfuric acid?
4. What compounds are formed by the "nitronation"[2] of toluene? Under what conditions does toluene yield benzoic acid when treated with nitric acid?

---

[1] This is most likely to happen when the product contains polynitro derivatives and also nitro derivatives of homologues of benzene if a good quality of benzene was not used.

[2] The word "nitration" at present stands for the formation of both a true nitro derivative like nitrobenzene and of a nitrate like the cellulose nitrates. The term "nitronation" is suggested for the formation of a nitro derivative just as "sulfonation" stands for the formation of a sulfo derivative in a similar manner.

5. Name some important classes of nitro-compounds and indicate their uses.
6. Why must nitrobenzene not be heated above its boiling-point?
7. How are most nitro-compounds purified?
8. Are different products obtained when nitrobenzene is chlorinated and when chlorbenzene is nitrated?
9. How are the conditions of nitration varied? Compare the preparation of nitrobenzene and of nitrophenol.
10. What is the general chemical influence of the nitro-group?
11. How are the aliphatic nitro-compounds prepared? Two methods.
12. How is phenyl-nitro-methane prepared? Why is this soluble in alkali?
13. Compare the structure of nitro-compounds and the isomeric nitrites.
14. What are the products of the reduction of nitro-compounds and of nitrites?
15. What is a pseudo-acid?
16. How are the alpha- and beta-mono-nitronaphthalenes prepared?
17. How can the three different classes of aliphatic mono-nitro compounds be distinguished?

## Experiment No. 45

### REDUCTION OF A NITRO-COMPOUND TO AN AMINE

### Preparation of Aniline from Nitrobenzene

To 15 grams of nitrobenzene and 35 grams of granulated tin, contained in a 500 cc. flask with a vertical air condenser attached, add in *small portions* 100 cc. of conc. hydrochloric acid. Shake the flask frequently. The mixture will become so warm that the reaction must be controlled by occasionally cooling the flask, but not enough to prevent the liquid from boiling quietly. After the first 50 cc. of acid have been added the second may be added in larger amounts of about 15 cc. with the same precautions. In order to effect the complete reduction of the nitrobenzene the mixture is finally heated for one-half hour on the steam-bath. The reaction mixture must be watched when first heated on the steam-bath, since if it were kept so cold in the beginning that the reaction was cut down too much, it will now suddenly become so violent that the unreduced nitrobenzene and the hydrochloric acid will be driven out of the tube of the condenser. During the reaction (and especially when cooled) the double salt of aniline hydrochloride and stannic[1] chloride $(C_6H_5NH_2HCl)_2$, $SnCl_4$, separates out as a white crystalline solid. At the end of the operation when the odor of nitrobenzene has entirely disappeared, and a drop of the reaction mixture gives a clear solution in water (Why?), add enough water to dissolve the salt, cool thoroughly, then pour off this solution from any unused tin into a separatory funnel. If any of the salt separates on cooling add more water to dissolve it. Extract the liquid twice with 60 cc. portions of ether, following the directions on p. 74. Remember when

---

[1] Stannous chloride forms a similar double salt, and a mixture is obtained here.

working with ether to keep away from free flames! Ether boils at 35°, has a very high vapor pressure, and is very inflammable. Finally draw off the aqueous layer into a flask. The ethereal extracts should be discarded.

(If the entire experiment cannot be completed at one time it should be interrupted at this point in order that the neutralization with sodium hydroxide may be directly followed by the steam distillation, and the heat of neutralization thereby utilized.)

The free amine (aniline) is obtained from the double salt in the extracted acid solution by adding gradually a solution of about 50 grams of sodium hydroxide in 90 cc. of water. Stannic and stannous hydroxides form at first and partially dissolve. The precipitate may be entirely dissolved by adding more sodium hydroxide, but this is not necessary. The mixture should have a strongly alkaline reaction. (Why?) If boiling occurs during the addition of the alkali, cool the solution under running water before adding more. (Why?) Most of the aniline rises to the top as an oil.

The aniline could now be extracted with ether, but this is not advisable, since the alkaline solution forms a difficultly separable emulsion with the ether.

**Distillation with Steam.**[1] The free aniline is separated by steam distillation, using the apparatus shown in Fig. 13.

Steam is passed into the flask through a tube which is bent in such a way that it reaches almost to the bottom (Why?) when the flask is inclined. (Why is the flask inclined?) The outlet tube should be cut off just beneath the stopper (?) and the bend should be just above the stopper. (Why?) The outlet tube also should be of a larger diameter than the inlet tube. (?) The flask should *not be more than half full* when the distillation is begun. Use a long water condenser. Make the rubber connections as short as possible and attach the rubber tube to the

---

[1] References for the principles involved in distillation with steam: Morgan, "The Elements of Physical Chemistry," 5th Ed. (1918), 177–8; Smith, "Introduction to Inorganic Chemistry," 3d Ed. (1917), 563; Walker, "Introduction to Physical Chemistry," 7th Ed. (1913), 87.

inlet tube of the flask in such a way that it can easily and quickly be removed if occasion demands. Set the flask into a Babo-funnel[1] or upon a wire gauze, and heat gently during the operation. (?) It is well to wrap a towel around the upper part of the flask (?). If the steam is passed into the solution when cold a " cracking " sound is often heard. This disappears as soon as the liquid becomes hot.

The steam on the desk can be used as the supply. Since there is always considerable condensation water, a 500 cc. flask should be placed as a trap between the steam nozzle and the apparatus. Use a three-holed stopper in this flask. The inlet and outlet tubes should be cut off just below the stopper. Into the third hole pass a glass tube leading to the bottom of the flask, bent downwards above the stopper and connected with a piece of rubber tubing to act as a siphon. Use a screw clamp to shut off the siphon. When the flask is nearly filled with water open the clamp and the water will go out and it is not necessary to stop the distillation during this time. If the screw clamp

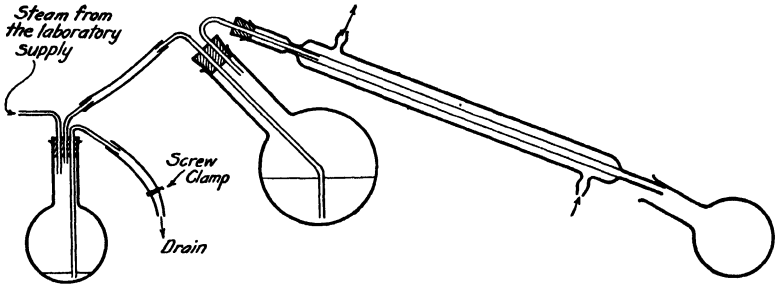


Diagram of Apparatus for Steam Distillation

FIG. 13.

---

[1] A Babo-funnel is an iron funnel partially lined with strips of asbestos, and is often used in place of an iron gauze.

is partly opened and properly adjusted the water will pass out regularly without requiring further attention.

Or steam can be generated in an ordinary tin oil-can, provided with a safety tube 50 cm. long; the spout is used for the outlet. Or a flask may be used with a safety tube and outlet tube. The safety tube should extend almost to the bottom, and if a wide one is used, such as a condenser tube, it will also serve for pouring in the water, especially when the " boiler " is hot (although in such a case the " boiler " must not be connected with any apparatus when the water is being added unless boiling water is used).

The distillation is considered complete when no more oily drops come over in the distillate (1 to 1½ hours). Remove the rubber connection from the main flask before turning off the steam or extinguishing the flame. Collect about 300 cc. of the cloudy distillate. Some of the aniline separates as an oil at the bottom of the receiver. Toward the end of the distillation, just after the oily drops have ceased to come over, collect separately 2 cc. of the clear distillate and make the following two tests for dissolved aniline.

To one portion add some bromine water. What is the white precipitate?

To another portion add a small amount of a filtered water solution of *good* bleaching powder. (?)

**Ether Extraction.** Saturate the steam distillate contained in a liter separatory funnel with powdered sodium chloride, 25 grams for every 100 cc. of liquid. Then extract the aniline with ether, using three successive portions of ether, 50 cc. at first, then 30 cc. and 30 cc. Test a portion of the aqueous solution after the ether extractions to see if any aniline remains, in same manner that you tested the steam distillate above. Dry the combined ethereal solutions in an Erlenmeyer flask by adding two or three small sticks of solid sodium hydroxide. Stopper the flask with a cork and let stand overnight. If an aqueous solution of sodium hydroxide forms at the bottom, the layers should be separated, fresh sodium hydroxide added, and the mixture allowed to stand overnight again. (?) (Calcium chloride cannot be used for drying in this case because it forms a double compound with aniline.)

**Distillation.**—In order that the small amount of aniline remaining after the removal of the ether may be left in a small flask for the final distillation, the ether is distilled over in the following manner: Attach a dropping funnel to a 50 cc distilling flask. The stem of the funnel should reach into the bulb of the flask. Put in one or two pieces of porous tile. Do not add these after the solution has become warm since it may cause violent ebullition with loss of solution by overflow and imminent danger of fire. Connect the outlet tube with a straight water condenser and attach an adapter to the lower end of the condenser by means of a cork. In order to avoid circulation of ether vapors loosely plug the remaining space in the mouth of the receiver with cotton. Add the ethereal solution to the flask until it is one-third full. Heat the flask gently over the steam-bath and continue the addition at about the same rate at which the ether distills.

When all the ether is distilled over, disconnect the apparatus and remove the ether distillate. Dry the outside of the distilling-flask. (Why?) Insert a thermometer, connect with a dry air condenser, and distill the aniline, using a small free flame. Since there may be some ether remaining in the flask the initial heating should be carefully done. Collect the pure aniline in a dry weighed specimen bottle. It boils at 184.4° cor.; its specific gravity is $1.02_{16^{\circ}}^{4^{\circ}}$; and 100 cc. of water dissolves 3.48 cc. of aniline at 22°, and 100 cc. of aniline dissolves 5.22 cc. of water at 22°. When pure it is a colorless, oily, strongly refracting liquid, which becomes yellow and red on standing, especially when in the presence of air, and light, and possesses a peculiar odor common to many amines. Yield, 10 grams.

*a.* Shake a drop of pure aniline with a few cubic centimeters of pure distilled water (ammonia free), and test the clear solution with a piece of neutral litmus paper. What is the reaction?

*b.* Add some of this solution to a solution of ferric chloride, and of zinc chloride. In view of the reaction shown in *a*, how do you account for the observation which you have made with these salt solutions?

*c.* Dissolve two or three drops of aniline in the least possible amount of dilute hydrochloric acid. Why does aniline dissolve easily in acids while it is soluble with difficulty in water? Neutralize with sodium hydroxide solution. (?)

*d.* To four or five drops of conc. sulfuric acid in a small porcelain evaporating dish add a drop of aniline on a stirring-rod. What is the white solid formed? Now add two or three drops of a water solution of sodium dichromate and stir. (?) Compare Holleman, "Organic Chemistry," 4th Ed. (1914), 457, 463.

*e.* Add two or three drops of nitrobenzene to 0.5 cc. of aniline. Note the deep red color that is formed. (Compare Biron and Morguleva, "Color of Mixtures of Anilines with Aromatic Nitro Compounds." *Journ. Russ. Phys. Chem. Soc.*, **46** (1914), 1598; *Chem. Abstracts*, **9** (1915), 2069.

## QUESTIONS

1. Write the equation for the reduction of nitrobenzene.
2. Explain why only a little acid is necessary in the production of aniline commercially from nitrobenzene by means of iron as the reducing agent.
3. Why is not all the hydrochloric acid added at one time when the nitrobenzene is reduced by tin and hydrochloric acid?
4. Calculate the amount of hydrochloric acid necessary for this experiment.
5. What is the nature of the salt formed from stannic chloride and aniline hydrochloride? How would this salt behave in a water solution?
6. Is there any difference between a double salt and a complex salt?
7. Why is it necessary to cool before extracting the nitrobenzene with ether? What is the principle underlying ether extraction?
8. What does the ether extract contain and why is it desirable to perform this extraction?
9. Could any other method be used in place of the ether extraction?

10. How does sodium hydroxide react with the double salt? Write all equations for this chemical change.
11. Show how aniline hydrochloride can be converted into aniline, writing the equation from the ionic standpoint.
12. Why is it necessary to be careful in adding the sodium hydroxide solution to the solution of the double salt? Explain why the liquid becomes hot.
13. What is the gray precipitate that forms when a large excess of sodium hydroxide has been used? Account for it. (References, Mellor, "Modern Inorganic Chemistry," 790–1, and Ditte, *Ann. Chem. Phys.* [5], **27** (1882), 145.)
14. Discuss fully the principles involved in steam distillation.
15. How can you tell by chemical means when all the aniline has been distilled over with steam?
16. Why not continue the steam distillation until the distillate gives no test for aniline?
17. Does aniline react alkaline toward litmus? Is it a true base?
18. In a short time after the steam distillation has begun a considerable amount of aniline collects in the receiver, and by the time the distillation is completed practically all this aniline has disappeared. Explain.
19. During the steam distillation some of the aniline collects at the bottom of the receiver, some floats on the water. Explain.
20. Explain why aniline hydrochloride is not volatile with steam while aniline is.
21. Would you expect phenyl ammonium hydroxide to be volatile with steam?
22. What is the object of adding sodium chloride to the steam distillate before the ether extraction?
23. Explain why the ether solution is dried with solid sodium hydroxide instead of calcium chloride or anhydrous sodium sulfate. Could the latter be used?
24. Why is no jacket necessary for the condenser; would it do any harm if a condenser jacket were used?
25. Point out the relationship between the double salt of stannic chloride and aniline hydrochloride, and ammonium chlorplatinate.

## Experiment No. 46

### ACETYLATION OF AN AROMATIC AMINE

### Preparation of Acet-*o*-toluidide from *o*-Toluidine

To 5 cc. of acetic anhydride[1] in a 125 cc. Erlenmeyer flask, add 2 drops of conc. sulfuric acid. Then add slowly in small portions, with shaking and cooling under running water after each addition, 4 cc. of *o*-toluidine. Allow the mixture to stand at room temperature for one-half hour or longer. The entire product then appears like a solid mass. If it does not solidify, scratch the inside wall of the vessel with a glass rod to promote crystallization. Now add 30 cc. of water and warm on the steam-bath. This loosens the product and with the aid (careful!) of a stirring-rod disintegrate and transfer it to a 250 cc. flask. Make the volume up to 160 cc., using some of this water to rinse out the flask. Neutralize with ammonium hydroxide solution. (Why not NaOH?) Heat the flask on the steam-bath until solution takes place. Generally a pink solution is obtained. Sometimes the substance melts and collects at the bottom of the flask. Shake to dissolve it. Decolorize by adding, in small amounts, two spoonfuls of animal charcoal. Continue the heating for about twenty minutes, with occasional shaking, then filter while hot through a large fluted filter in a hot-water funnel (see p. 128), and set the solution aside to crystallize. If the crystals obtained are colored they should be re-dissolved as before in hot water and heated again with animal charcoal. Filter off the needle-like crystals with suction by means of a Buchner funnel and let them dry between filter papers, or in a desiccator, or press them out on a porous tile. Concentrate the filtrate *on*

---

[1] Acetic anhydride attacks the skin and the mucous membranes. *Be careful in handling it.*

*the steam-bath* to about 30 cc. volume, decolorize, if necessary, filter as before, and allow to cool. M. p., 110°. Yield, 5 grams.[1]

*a.* Heat some of the crystals of acet-*o*-toluidide with a strong solution of sodium hydroxide. What is formed? Boil a few crystals with dilute sulfuric acid (1 : 1). Notice the odor of the vapor. (?)

*b.* To 2 cc. of acetyl chloride add 1 cc. of *o*-toluidine carefully. Warm and treat the product with water. Separate the crystals and recrystallize the substance from a little boiling water. Compare the melting-point of these crystals with the melting-point of a sample of the acet-*o*-toluidide prepared above.

*c.* Grind together small dry portions of the pure acet-*o*-toluidide obtained in the main experiment and of the substance prepared in *b*, and determine the melting-point of the mixture. If the substances were not of the same chemical composition would the melting-point of the mixture be the same even though each substance originally had the same melting-point?

*d.* Warm 1 cc. of acetyl chloride with 1 cc. of mono-methylaniline; then heat 1 cc. of acetyl chloride with 1 cc. of dimethylaniline. Pour each product into water. Is there evidence of chemical change in each case? Are the reactions illustrated in *b* and *d* typical of primary, secondary, and tertiary amines in general?

## REFERENCES

W. M. Dehn, "Acetylations in Ether Solutions," *Jour. Amer. Chem. Soc.*, **34** (1912) 1399; Dehn and Ball, "Benzoylations in Ether Solutions," *ibid.*, **36** (1914) 2091.

## NOTE

Solutions of organic compounds should seldom be evaporated over a free flame. If any evaporation is necessary in the above experiment use a steam-bath. At low temperatures there is the least decomposition, and for this reason it is often best to evaporate under diminished pressure.

---

[1] This amount is too much for the usual preparation bottle to contain. Hand in a sample, stating the total yield on the label, and use the major portion for the preparation of acetanthranilic acid (p. 189).

## QUESTIONS

1. Compare the structures of acetic anhydride, acetyl chloride, and acetyl sulfuric acid. How is the anhydride prepared?
2. Explain the use of the " two drops of conc. sulfuric acid."
3. Why is it necessary to neutralize the solution?
4. What product is neutralized with ammonium hydroxide?
5. What objection would there be to the use of sodium hydroxide? Could it be used at all?
6. Why is a hot-water funnel used? Why must the stem of the funnel not project much below the metal collar?
7. By means of structural formulas show how acet-*o*-toluidide differs from *o*-toluidine acetate.
8. What would be obtained by heating dry ammonium acetate? dry *o*-toluidine acetate? Compare No. 9.
9. To what class of organic compounds does acet-*o*-toluidide belong?

*10. What advantage has acetic anhydride over acetyl chloride for acetylation?

11. How is aniline acetylated commercially? Use of product?

12. Do 3°-amines react at all with acetyl chloride? (See special references above.)

*13. What is the structure of diacetanilide? How prepared?

*14. Of what use in the laboratory is the acetylation of amines?

* These questions are not required for study in the "short" course.

## Experiment No. 47

### SULFONATION OF AN AROMATIC AMINE

### Preparation of Sulfanilic Acid from Aniline

Pour 50 grams of conc. sulfuric acid into a 100 cc. round-bottomed flask, *then* attach an air condenser, and through it add cautiously with moderate shaking 15 grams of aniline. Do not shake so vigorously that the sulfuric acid comes in contact with the upper portion of the flask or the lower part of the air condenser. The first reaction product (?) deposited at these places is not easily got down into the main portion. Half immerse the flask in an oil-bath, which consists of a shallow iron dish partly filled with rapeseed oil,[1] and heat the mixture of aniline sulfate and sulfuric acid at a temperature of 175°–180°,[2] thermometer in the oil, for three hours. Pour the partially cooled product with stirring into about 250 cc. of cold water, when the sulfanilic acid will separate out in crystals. Allow to stand for about twenty-four hours, then filter off the product with suction in a Buchner funnel. Wash once with a little cold water.

Suspend the crystals thus obtained in 100 cc. of water and dissolve them by adding a 2N solution of sodium hydroxide until *neutral* to litmus. If the solution is water-white filter from any impurities, otherwise heat to boiling, decolorize by heating for about half an hour on the water-bath with the addition of animal charcoal (added in small quantities to prevent foaming) and filter. Precipitate the sulfanilic acid in the filtrate by adding the calculated amount of hydrochloric acid (based

---

[1] Do not allow any water to come in contact with the hot oil. It causes violent foaming. Compare note 6, p. 82.

[2] A higher temperature causes considerable decomposition. The heating may be interrupted at any time.

on the theoretical yield) to liberate the acid from its sodium salt. Allow to stand overnight, filter with suction, wash with a little water, and dry the crystals between filter paper. Large rhombic plate crystals may be obtained by dissolving the sulfanilic acid in just the sufficient amount of hot water for complete solution and allowing to cool slowly. The crystals contain 2 molecules of water of hydration, which is slowly lost in the air and the crystals fall to a powder. They are soluble in hot water but not very soluble in cold water. Yield, 15 grams. It has no definite melting-point, but decomposes 280°–300°.

## QUESTIONS

1. What is the white solid first formed?
2. If necessary, how could you filter the hot acid solution?
3. Name sulfanilic acid to show its chemical groups and their position.
4. Trace the changes from the compound first formed through the amide-form and the rearrangement to sulfanilic acid. (See J. B. Cohen, "Organic Chemistry for Advanced Students," Pt. II, 2d Ed. (1918), 371.)
5. Why must the mixture not be heated above 180°?
6. How could a test be made to show that all the aniline has been converted into the sulfanilic acid?
7. Why must an excess of sodium hydroxide be avoided?
8. If you have added an excess of sodium hydroxide in trying to make the solution neutral how could you treat the solution in order to obtain all the sulfanilic acid?
9. Although sulfanilic acid is soluble in hot water the material is bone-blacked in an alkaline solution. Why?
10. Explain the action of bone black (animal charcoal).
11. Why must the calculated amount of HCl be used? Why not simply add HCl to acid reaction?
12. What is naphthionic acid?
13. Compare the chemical properties of the amino sulfonic acids and the amino carboxylic acids.
14. What use is made of sulfanilic and similar acids?
15. How can the meta-compound corresponding to sulfanilic acid be prepared?

## Experiment No. 48

### Benzidine Rearrangement

Dissolve 2 grams of powdered sodium hydroxide in 20 cc. of alcohol in a large (No. 3) test-tube. Add 2 cc. of nitrobenzene and warm gently. During the course of several minutes add, in small quantities, about 5 grams of zinc dust. At first the solution becomes deep red in color. This is due to the formation of azo-benzene. Later this color is discharged on account of the formation of hydrazo-benzene. Sometimes instead of a colorless solution a light brown solution is obtained. Then pour the mixture into about 50 cc. of water containing more than enough sulfuric acid to neutralize the sodium hydroxide used. (Why?) A colorless or slightly yellow precipitate of benzidine sulfate separates. There should be no oil (?) floating upon the surface.

### QUESTIONS

1. Write the structures of the compounds formed in this reaction.
2. Are all sulfates of mono- and di-amines insoluble in water?
3. How could you prepare pure benzidine from this salt?
4. Tabulate some important reactions in which it is believed the "benzidine rearrangement" takes place. (Ex., *p*-aminophenol from phenyl hydroxylamine, *p*-phenylenediamine from phenyl hydrazine, sulfanilic acid from the amide of aniline sulfate, salicylic acid from sodium phenolate and carbon dioxide, amino-azobenzene from azo-amino-benzene, etc. J. B. Cohen, "Organic Chemistry for Advanced Students," Pt. II, 2d Ed. (1918), 369–75.)
5. For what is benzidine used commercially? Example.
6. Of what hydrocarbon is hydrazobenzene a derivative? benzidine?

## Experiment No. 49

## DYES

### FORMATION OF AN AZO DYE

### Preparation of Methyl Orange

NOTE

Use amounts as nearly correct as possible.

Make ready a solution of 1.0 gram of sodium hydroxide in 10 cc. of water. In a small beaker, No. 0, dissolve 1.0 gram of sulfanilic acid in 5 cc. of water and 2.4 cc. (1 mol.) of the sodium hydroxide solution. Set the beaker in ice and diazotize by adding first a solution of 0.42 gram (1 mol.) of sodium nitrite (which should be powdered to make it dissolve readily) in 2 cc. of water, and then slowly, with stirring, a solution of 0.5 cc. (1 mol.) of conc. hydrochloric acid in 2 cc. of water. A reddish solution is often obtained.

In a separate small beaker or test-tube mix 0.74 gram (about 20 drops [1]) (1 mol.) of dimethylaniline and 0.37 gram (about 13 drops [1]) (1 mol.) of glacial acetic acid. Add this solution drop by drop, with constant stirring, to the diazotized solution. The dye begins to separate at once and forms a thick, dark red mass. Treat this with the remaining 7.6 cc. (3 mol.) of the sodium hydroxide solution and stir well. Filter off the reddish-yellow product with suction, using a hardened filter paper [2] or two ordinary filter papers in the bottom of the funnel. Recrystallize the crude methyl orange from 20 cc. of hot water.

---

[1] From the lip of a 10 cc. graduated cylinder.

[2] A hardened filter paper is one which has been treated with conc. sulfuric acid. It is tough and smooth and has no loose fibres.

Leaflets with a golden luster are thus obtained. Allow to dry on filter papers. Yield, 1.2 grams.

### NOTES

Methyl orange is the sodium salt of the sulfonic acid, and its aqueous solution has a yellow color. On the addition of an acid the free sulfonic acid (Helianthine) is obtained, which has a red color in aqueous solution. The use of the dye as an indicator in acidimetry and alkalimetry depends upon this change in color. (For further discussion of this color change see Cohen, "Organic Chemistry," Vol. II (1913), p. 380.)

## STUDIES OF TRIPHENYLMETHANE DYES

### Phenolphthalein

Mix 0.1 gram of phthalic anhydride and 0.1 gram of phenol in a test-tube, and add 2 drops of conc. sulfuric acid. Heat *gently* over a small flame with constant agitation for about two minutes. The melt will become dark red and the heating should not be so strong that the material blackens on account of extensive decomposition. When cold treat with 5 cc. of water, and add *very gradually* with shaking a dilute solution of sodium hydroxide until a permanent pink color is obtained (no more). Dilute a portion of this solution and test the suitability of the dissolved phenolphthalein as an indicator by adding first a trace of acid and then a trace of alkali. (?)

### Fluorescein

Mix 0.1 gram each of phthalic anhydride and resorcinol in a test-tube and add 3-4 drops of conc. sulfuric acid. Heat gently for two minutes. Allow to cool, add 5 cc. of water, and make alkaline with sodium hydroxide. Transfer a drop of this solution to a test-tube full of water. (?) View by both reflected and transmitted light.

### Crystal Violet

Place 0.1 gram of Michler's ketone (*pp'*-tetramethyl-diaminobenzophenone), 5 drops of dimethylaniline, and 2 drops of phosphorus oxychloride in a test-tube, and heat the tube in boiling water for one-half hour. Add 10 cc. of water and stir.

1. Add a drop of liquid to about 20 cc. of water and note the color.

2. Add several drops to 20 cc. of water and treat with a little ammonium hydroxide solution. Let stand until the color has disappeared and white flocks are found in the liquid (several minutes). Explain.

To a portion of this decolorized solution, add very dilute hydrochloric acid until the color returns. Explain.

3. To a second dilute portion of the original solution add dilute hydrochloric acid. What makes the green color which changes to yellowish? (See E. Q. Adams and L. Rosenstein, "The Color and Ionization of Crystal Violet," *Journ. Amer. Chem. Soc.*, **36** (1914), 1452–73.)

4. To a third dilute portion of the original solution add a small amount of zinc dust and warm for a few minutes. Why does the color disappear?

5. Allow the remainder of the original solution to stand overnight when crystals of crystal violet, which have a greenish luster, will separate out on the walls of the test-tube.

### References

Holleman, "Organic Chemistry," 4th Ed. (1914), 528.

For a general discussion of color and structure, see Curtiss, "Relation between Color and Constitution," *Journ. Amer. Chem. Soc.*, **32** (1910), 795.

## QUESTIONS

### Methyl Orange

1. What is diazotization?
2. What is the diazo structure? the diazonium structure?
3. Write the structure of benzene diazoic acid; of benzene diazonium hydroxide. Why are these formulas assigned to the two isomers?
4. Using structural formulas and equilibria equations, trace the course of the reaction in the formation of an amino-azo dye with the simplest preparation in the series, *p*-amino-

azo-benzene from aniline as follows: (1) phenylammonium hydroxide formed when aniline is dissolved in water, (2) the salt formed with hydrochloric acid (this is partially hydrolyzed), (3) the salt (nitrite) formed when nitrous acid is present, (4) the amide formed from this, (5) the tautomeric change to the diazoic acid, (6) the formation of the phenylammonium salt between the diazoic acid and a second molecule of phenylammonium hydroxide (added after the diazotization is complete), (7) the compound formed through the amide formation (azo-amino stage), (8) and the final rearrangement to the *p*-amino-azo-benzene.

5. Follow out the same scheme with sulfanilic acid and dimethyl aniline, using the proper modifications due to the presence of the sulfo group.
6. Why is acetic acid used in the second part of the experiment instead of hydrochloric? Could hydrochloric be used?
7. Why is sodium hydroxide added at the end of the reaction?
8. What is a chromophore, an auxochrome group? Point out any such groups in methyl orange.

*9. Write the structure of methyl orange to show the presence of a quinoid nucleus, and also the changes involved in its use as an indicator. (Cohen, " Organic Chemistry," II (1913), 380.)

10. What is the leuco base of an azo dye? How obtained?
11. How can it be proved that in the making of methyl orange the coupling has taken place at the para position to the dimethylamino group?
12. How is the coupling carried out (in acid, neutral, or alkaline solution)? Why? (Möhlau and Bucherer, " Farbenchemisches Praktikum," 118.)
13. What are the congo dyes? How used in dyeing?

*14. What is a syn-diazo compound, and an anti-diazo com-compound?

*15. Which one enters into a reaction? (Holleman, 413, 417–9; Möhlau and Bucherer, 70.)

*16. Why should the diazotized solution not stand overnight before coupling?

*17. How are the salts of the anti-diazo acid obtained? (Möhlau and Bucherer, 71.) Salts of the diazonium hydroxide in solid form? Give structures.

18. How can you prepare phenylhydrazine?
19. What is benzidine? How prepared? For what used?
20. What are poly-azo dyes? How prepared?

*21. What is Bismarck brown? How is *m*-phenylenediamine hydrochloride used in the test for nitrites?

## PHENOLPHTHALEIN AND FLUORESCEIN

22. What are the structural formulas of phenolphthalein and fluorescein?
23. What are some of the derivatives of fluorescein?
24. What is the theory for the color change in the use of phenolphthalein as an indicator?

## CRYSTAL VIOLET

25. What is the structural formula (quinoid) for crystal violet?
26. Trace the course of the reaction beginning with the addition product formed from Michler's ketone and dimethylaniline, through the tautomeric change to the true base, and then the formation of the dye by neutralization with hydrochloric acid.
27. Point out any chromophore and auxochrome groups in crystal violet.
28. What is the parent substance of the fuchsine series?
29. What is a color base? Illustrate in the case of crystal violet. How formed?
30. Explain the changes that take place in the presence of the alkali.
31. What is the structure of the leuco-base of crystal violet? How formed?
*32. What happens when crystal violet is treated with conc. hydrochloric acid?
*33. How is Michler's ketone manufactured?
34. Are all colored substances *dyes*?
35. What is a mordant? How used?
36. What is a lake?
37. What is a vat dye? How used? Ex. Indigo.
38. What is rosaniline, fuchsine, or magenta? Para-rosaniline? How used in Schiff's aldehyde reagent?
*39. What is malachite green? How prepared?
*40. What is aurin? rosolic acid? How prepared?
41. What is indigo? Summarize the steps in its manufacture.
*42. What is alizarin?
*43. What is the structure of indanthrene? (Möhlau and Bucherer, 225–6.)

---

* These questions are not required for study in the "short" course.

## Experiment No. 50

### FORMATION OF A TRIPHENYLMETHANE DYE

### Preparation of Crystal Violet from Michler's Ketone and Dimethyl Aniline

Heat a mixture of 6 cc. of dimethyl aniline, 2.5 grams of Michler's ketone (*pp'*-tetramethyl-diamino-benzophenone), and 2 cc. of phosphorus oxychloride, in a porcelain evaporating dish for 2½ hours on the steam-bath. Then transfer the blue-colored mass to a flask with water, make alkaline with a solution of sodium hydroxide (calculated on the basis of the amounts of the hydrolytic products of the phosphorus oxychloride), and distill with steam (see p. 158) until no drops of the unattacked dimethylaniline pass over (about three hours). After the addition of the sodium hydroxide the blue color should disappear either on standing or soon after the distillation is begun, and a reddish precipitate formed. If it does not, add more sodium hydroxide. (Explain the color change.) After cooling, filter the reddish, solidified color-base remaining in the distillation flask from the alkaline solution, wash with water, and boil with a mixture of 250 cc. of water and 2 cc. of conc. hydrochloric acid. Filter the blue solution while hot from the undissolved color-base; and boil the latter again with a fresh quantity of the dilute hydrochloric acid. This operation should be repeated until the substance is almost entirely dissolved. On cooling and standing, the crystal violet separates out in beautiful needle crystals of a greenish color. Filter and dry in the air on filter paper. A further quantity may be obtained by adding finely pulverized salt to the filtrate (" salting out "). Yield, about 4 grams.

Make a dilute solution of the crystal violet and perform experiments 2–4 given under crystal violet on p. 172.

## QUESTIONS

1. What is a " condensing " agent?
2. Why must the mixture be alkaline before distilling with steam?
3. Why must *dilute* hydrochloric acid be used for preparing the dye? What happens when stronger acid is used?

Answer also questions 25-43, p. 174.

## Experiment No. 51

## FORMATION OF A PHENOL FROM A PRIMARY AROMATIC AMINE BY MEANS OF THE DIAZO REACTION

### Preparation of Phenol from Aniline

Pour 10 cc. of conc. sulfuric acid rapidly, with stirring, into 50 cc. of water, and to the hot solution slowly add 10 cc. of aniline, with constant stirring to make complete solution.[1] (What is the white solid first formed?) Transfer to a liter flask, then add 200 cc. of water. Diazotize by treating the cold solution with the **calculated** amount of sodium nitrite (powdered to make it dissolve readily) contained in about 40 cc. of water. Heat on the steam-bath for thirty minutes at a temperature between 40°–50°, with the thermometer in the liquid. (What gas is evolved?) The phenol is then distilled over with steam. (See Aniline Experiment, p. 158.)

Collect about 600 cc. of distillate (about 1.5–2 hours are required). When near the end of the distillation test the clear distillate with bromine water and ferric chloride, according to the directions given below in *c* and *d*. (?) Compare with aniline, p. 160. Saturate this distillate, contained in a liter separatory funnel, with finely powdered sodium chloride, 25 grams for every 100 cc. of liquid, and extract the solution three times with ether (p. 74), using 50 cc. of ether for the first extraction and 30 cc. each for the other two.

Filter the combined ethereal extracts through a fluted filter[2] to remove any brownish impurities from the salt, and then dry with anhydrous sodium sulfate. In order that the small amount of phenol remaining after the removal of the

---

[1] Any precipitate which separates on cooling will dissolve when the solution is diluted.

[2] See foot-note, p. 128.

ether may be left in a small flask for the final distillation, the ether is distilled over in the manner described in the Aniline Experiment, p. 161. Distill the residue, using a short wide tube or an adapter as an air condenser. B.p. 183°, m.p. 42.5°. The specimen should be white and should solidify, especially when the tube is placed in cold water. If it is colored re-distill carefully. Yield, 8 grams.

### *Reactions of Phenol and Derivatives*

*a.* Test the reaction of an aqueous solution of phenol with neutral litmus paper.

*b.* Add a little sodium hydroxide solution to 1 gram of phenol. Now acidify with hydrochloric acid. Do not use too much water. Any change?

*c.* Dissolve a drop of phenol in water and add bromine water until it is no longer absorbed. Filter off the precipitate and wash it with a dilute solution of sulfur dioxide or of sodium hydrogen sulfite until there is a strong odor of sulfur dioxide. Wash with water. Dissolve in about 5 cc. of hot alcohol, filter, add 10 cc. of hot water, and set aside to crystallize. Dry it on a porous tile and determine its melting-point. For what is this reaction used? Compare with the action of bromine and of bromine water on benzene (p. 138), and on amylene (p. 45).

#### NOTE

The sulphur dioxide converts any $Br_3C_6H_2OBr$ into tribromphenol, $Br_3C_6H_2OH$.

*d.* To a dilute solution of phenol add a drop of $\frac{1}{5}$ molar ferric chloride solution. (?)

*e.* Add a drop of ferric chloride solution to dilute solutions of catechol, resorcinol, salicylic acid and gallic acid. (?) Compare the structures of these compounds.

*f.* Try the action of ferric chloride on a solution containing a drop of acetacetic ester and on another containing a drop of acetylacetone. Use alcohol in each case to make the solution homogeneous. What is meant by the enol and the keto form?

To which one is this color reaction supposed to be due? Do all hydroxyl compounds give color reactions with ferric chloride?

Also compare the action of ferric chloride on aromatic amines (aniline), and on alpha-hydroxy acids, like tartaric acid.

## QUESTIONS

1. How does aniline differ from ammonia? Compare the action of nitrous acid in each case.
2. Why is aniline first treated with sulfuric acid?
3. What compound is formed when aniline and sulfuric acid react?
4. Would there be any objection to using too little sodium nitrite? too much?
5. What reason is there for heating the diazotized solution?
6. Calculate the amount of sulphuric acid theoretically necessary for converting 10 grams of aniline into phenol, and compare with the amount used.
7. Explain the principle of steam distillation.
8. Why is steam distillation used in this experiment?
9. How can you tell by chemical means when all the phenol has been distilled over with steam?
10. Why not continue the steam distillation until the distillate gives no test for phenol?
11. Why is the distillate saturated with salt before extraction?
12. What advantage is there in extracting the solution *three* times with small amounts of ether, instead of once with a larger amount of ether?
13. How can anhydrous sodium sulfate be used as a drying agent?
14. Where does the moisture taken up by the sodium sulfate come from?
15. Is this method for the formation of phenols practical?
16. Can this method of replacing an amino group with hydroxyl be used in the case of aliphatic amines?
17. What advantage is there in distilling the ether from a small flask?
18. How can phenol be prepared from benzene sulphonic acid?
19. Compare the behavior of ethyl alcohol and phenol when treated with bromine.
20. Compare the action of the halogens and of nitric acid on phenol and on benzene.
21. What is the action of acetyl chloride; and of zinc dust, on phenol?

## Experiment No. 52

### ALKYLATION OF AN HYDROXYL GROUP

### Preparation of Anisole (Methyl-phenyl Ether) from Phenol and Dimethylsulfate

Perform this experiment with apparatus connected with the draft pipe. Dimethylsulfate has no odor, but it is very poisonous to some people. Be careful not to breathe its vapors and since it is readily absorbed do not allow any to come in contact with the skin. If any be spilt upon the clothes these should be changed immediately.

Dissolve 12 grams of phenol[1] in a solution of 10 grams of sodium hydroxide and 100 cc. of water. Pour this into a 250 cc. flask and add slowly and with continuous shaking 25 grams of dimethylsulfate.[2] Place a thermometer in the mixture. There is a slight rise in temperature, which should not be allowed to exceed 40° (cooling is usually not necessary). The clear liquid becomes turbid and in a few minutes a layer of oil will float on the surface. The reaction may be considered complete when the temperature no longer rises and the products cool.

To destroy the excess of dimethylsulfate (dry the flask if it has been placed in water), attach an upright air condenser, and heat the mixture to the boiling-point with frequent shaking. (How does this destroy the dimethylsulfate?) Finally, cool the liquid, add a solution of 6 grams of sodium hydroxide in 60

---

[1] Melt it by placing the bottle in warm water. If phenol should come in contact with the skin use dilute alcohol immediately.

[2] Opening sealed bottles: Wrap the bottle in a towel, leaving the narrow sealed end protruding, and make a file mark around the tube near the end. Hold it over a beaker in a slanting position and knock off the end with a sharp blow of the file, or touch the mark with the hot fused end of a glass rod.

cc. of water, and extract once with ether. The liquid must be alkaline when the extraction is made. It cannot be tested directly since the oil would prevent the litmus paper from absorbing water and indicating. Test a drop drawn off from the liquid in the separatory funnel. Dry the ethereal solution with calcium chloride. Remove the ether by distillation, observing the ordinary precautions (see p. 70), and then distill the anisole. The boiling-point of anisole is 153.9° cor. The yield amounts to about 95 per cent of the theory.

## QUESTIONS

1. Write all the reactions involved in the formation of anisole from phenol, upon the assumption that an " oxonium " compound is formed as an intermediate product.
2. How is dimethylsulfate prepared?
3. What advantages has it over methyl iodide as a methylating agent? over diazomethane?
4. Why is the sodium hydroxide used?
5. Why must the temperature of the mixture be kept under 40°?
6. Would an excess of dimethylsulfate be likely to affect the yield of anisole?
7. To what class of organic compounds does anisole belong? dimethylsulfate?
8. Could dimethylsulfate be used for alkylating the hydroxyl group in water, ethyl alcohol, and acetic acid? Equations.
9. Does it make any difference as to the order in which the dimethylsulfate, phenol, and sodium hydroxide are mixed?
10. Why is the anisole mixture made slightly alkaline before extracting with ether?
11. Could anhydrous sodium sulfate be used in place of calcium chloride for drying the ethereal solution of anisole?
12. How can anisole be changed into phenol?
13. What is the Zeisel method of estimating methoxy groups in alkaloids, etc.?
14. Could dimethylsulfate be used for methylating amino- and imino-groups? Examples.
15. How can pure *mono*-methyl aniline be prepared?
16. What is the action, if any, of bromine, conc. nitric acid, conc. sulfuric acid, conc. sodium hydroxide, potassium permanganate, and alcoholic potassium hydroxide at a high temperature, on anisole?

## Experiment No. 53

### BENZALDEHYDE

Perform the following reactions:

1. *Silver-mirror test.* Make an ammoniacal solution of silver nitrate, as given under Acetaldehyde, p. 91, and add a drop of sodium hydroxide solution. If a precipitate forms dissolve it with a little more ammonium hydroxide. Add a single drop (or a lesser amount) of benzaldehyde, shake, and let stand. The mirror forms very slowly.

2. Try the action of the fuchsine-sulfurous acid reagent (Schiff's aldehyde reagent) p. 92, on benzaldehyde. If the drop of benzaldehyde is run down the side of the test-tube it will float on the surface of the solution and will assume the color of the fuchsine without coloring the entire solution.

3. Does benzaldehyde reduce Fehling's solution? Try it.

4. Add several drops of benzaldehyde to 2 or 3 cc. of a saturated solution of sodium bisulfite, and shake vigorously. Of what do the white crystals consist? Filter with suction and then warm with a solution of sodium carbonate. (?)

5. Add a drop of benzaldehyde to a solution of a drop of phenylhydrazine in 3 cc. of dilute acetic acid (1 : 1). What is the yellow precipitate?

6. Rub a drop of benzaldehyde on a watch glass. What are the crystals that form after a short time?

7. Make a very dilute solution of soluble starch and add to it a few drops of dilute potassium iodide solution. Spread a drop of benzaldehyde on a watch glass with the aid of a stirring-rod. Allow it to remain for a minute or two, and then add a few drops of the starch-potassium iodide solution. Set the watch glass over a filter paper, and stir with the rod. Explain the formation of the blue color (see Question 9 below).

Which of the above reactions are also characteristic of ketones?

8. In a test-tube thoroughly mix about 0.1 gram of cinnamic acid and about 5 cc. of a cold strong solution of potassium permanganate. Note the odor. Explain.

What type of unsaturated aromatic compounds, with relation to the position of the double bond, undergo this reaction?

Outline the commercial preparation of vanillin from eugenol and of piperonal from safrol. (Holleman, " Organic Chemistry," 4th Ed. (1914), 482–5; Stoddard, " Introduction to Organic Chemistry," 2d Ed. (1918), 347, 342.)

## QUESTIONS

1. Does benzaldehyde react with Fehling's solution?
2. Write equations and complete structures involved in the reactions between benzaldehyde and sodium hydrogen sulfite, and between the product and sodium carbonate.
3. Could a dilute solution of acid sodium sulfite be used instead of the concentrated?
4. Could any other reagent be used in place of the sodium carbonate?
5. Write equations and structures for the reaction with phenylhydrazine.
6. Could 50 per cent hydrochloric acid be used in place of the 50 per cent acetic acid?
7. Could phenylhydrazine hydrochloride be used? What modification is generally necessary?
8. Could hydrazine itself be used? *Semicarbazide? (Perkin and Kipping, " Organic Chemistry," New Ed., (1911), 456.
9. What happens when benzaldehyde is exposed to the air? (For discussion of autoxidation, see Holleman, " Organic Chemistry," 4th Ed. (1914), 428; and Bayliss, " Principles of General Physiology " (1915), 580.)
10. Explain what takes place in the experiment with starch and potassium iodide.
11. Write equations for the reactions occurring when benzaldehyde is treated with the following reagents: (*a*) phosphorus pentachloride, (*b*) mixture of nitric and sulfuric acids at 0°, (*c*) hydroxylamine hydrochloride and sodium carbonate, *(*d*) acetone and sodium hydroxide solution (compare Perkin and Kipping, 456), *(*e*) alcoholic solution of potassium cyanide, *(*f*) ammonia, (*g*) aniline.

*** These questions are not required for study in the " short " course.**

## Experiment No. 54

### ADDITION OF HYDROGEN TO AN ETHYLENE DERIVATIVE

### Preparation of Hydrocinnamic Acid (Phenylpropionic Acid) from Cinnamic Acid

The 3 per cent sodium amalgam used in this experiment is prepared as follows: Weigh out in a dry evaporating dish or casserole 145 grams of pure dry mercury. Warm on the steam-bath to 75°. Prepare 4.5 grams of sodium, free from crust and from the liquid which can be removed with filter paper. Cut off slices and immediately press them to the bottom of the warm mercury in rather rapid succession by means of a short moderately thick glass rod, drawn out to a point and bent at a short right angle. Use a pestle if necessary in the above operation. After each piece is added a somewhat violent reaction takes place. If the operation is conducted quickly all the sodium can be added before the mass solidifies. *This operation must be carried out under the hood, using the glass door as a shield; protect the eyes with goggles and the hands with gloves. These precautions are absolutely necessary because pieces of burning sodium are often projected in different directions from the dish.* Break up the semi-solid amalgam at once and transfer it to a tightly stoppered dry bottle.

Into a 250 cc. flask put 5 grams of cinnamic acid, 80 cc. of water containing 1.4 grams of sodium hydroxide, and 150 grams of sodium amalgam (3 per cent) in small portions. Shake the mixture well after each addition. At the beginning the amalgam liquefies rapidly, very little hydrogen is evolved and the solution becomes warm. Toward the end the amalgam does not liquefy at all readily and numerous bubbles of hydrogen are evolved. Add more water, if necessary, to dissolve any precipitate. (?)

Take out a few drops of the solution, dilute, acidify with dilute hydrochloric acid, neutralize with and add a slight excess of sodium carbonate and then a drop of a very dilute solution of potassium permanganate. If the permanganate is decolorized or turns brown at once, cinnamic acid is still present and the solution must be warmed on the steam-bath, shaken occasionally, and, if necessary, more amalgam added till the solution no longer decolorizes permanganate. This permanganate test is of great value for the detection of unsaturated compounds. (Compare test for "double bond," p. 44-5.) The test cannot be applied to the solution when there is fixed alkali *in excess* because it is sometimes masked by the formation of a green manganate.

When the reduction is complete, pour off from the mercury, filter and then precipitate the hydrocinnamic acid by adding 18 cc. of concentrated hydrochloric acid, or more, depending on the amount of amalgam used. The product usually separates as an oil which crystallizes when the solution is cooled and stirred. Filter off, test the filtrate for more of the product by adding dil. hydrochloric acid and allowing to stand, and recrystallize from about 200 cc. of hot water. Yield, 4.5 grams.

Hydrocinnamic acid crystallizes in long colorless needles which melt at 49°. It boils at 280°. It is easily soluble in boiling water, in alcohol, and in ether. It is volatile with water vapor, and solutions of it cannot be concentrated by boiling without loss. It is soluble 1 part in 168 parts of water at 20°.

The reduction of an unsaturated acid by sodium amalgam can only be carried out, apparently, when the double bond is adjacent to the carboxyl. When the double bond is further removed the reduction may often be carried out by first adding hydriodic acid and then reducing with zinc dust or the zinc-copper couple in an alcoholic solution and in presence of a little dilute acid. The reduction may also be effected electrolytically.

### NOTE

The German name for cinnamic acid is Zimmtsäure, and of hydrocinnamic acid, Hydrozimmtsäure.

## QUESTIONS

1. What is cinnamic acid?
2. How is cinnamic acid prepared? (Perkin's reaction.)
3. Explain why the amalgam is used instead of metallic sodium.
4. Point out what is oxidized and what is reduced.
5. What is the white precipitate that sometimes forms toward the end of the reduction? Explain its formation.
6. In the test for unattacked cinnamic acid, explain why the solution must first be acidified with hydrochloric acid and then made alkaline with sodium carbonate. How else could the same condition be obtained? What effect would the sodium hydroxide have on the test?
7. Could the following compound be reduced with sodium amalgam in water: $C_6H_5 \cdot CH : CH \cdot CH_2COOH$?
8. How does sodium amalgam react in an ethyl alcohol solution? Give an example. (Perkin and Kipping, "Organic Chemistry," New Ed. (1911), 385–6, 628.) When is amyl alcohol used? What advantage is there in using alcohol?
9. What other reducing agents are used for reducing the olefine bond?
10. How can benzene be reduced to cyclohexane? (Perkin and Kipping, 365, 623.)
11. Discuss the hydrogenation (reduction) of oils. See C. A. Ellis, *Journ. Industrial and Eng. Chem.*, 5 (1913), 95–106; and his book, "The Hydrogenation of Oils," published by Van Nostrand.

## Experiment No. 55

### REPLACEMENT OF A DIAZO-GROUP BY CYANOGEN (SANDMEYER REACTION)

### Preparation of *p*-Tolunitrile (*p*-Tolylcyanide) from *p*-Toluidine

Perform all the operations *under the hood.* Dissolve 12 grams of powdered copper sulfate crystals in 50 cc. of water in a 500 cc. flask by heating on the steam-bath; then add gradually, with continuous heating, a solution of 14 grams of powdered potassium cyanide in 25 cc. of water. *Since cyanogen is evolved the greatest care must be taken not to breathe the vapors.*

While the potassium cuprous cyanide solution is further gently heated on the steam-bath, prepare the toluene diazonium chloride solution as follows: Warm 5 grams of *p*-toluidine with a mixture of 10 cc. of concentrated hydrochloric acid and 25 cc. of water until solution takes place. Then set the beaker in ice and stir in order that the toluidine hydrochloride may separate out in as small crystals as possible. To this ice-cooled mixture add gradually with good stirring a solution of 4 grams of powdered sodium nitrite (more than 1 molecular equivalent) in 15 cc. of water until a drop of the reaction mixture gives a permanent blue color with starch-iodide [1] paper, or until you just notice the odor of the oxides of nitrogen from the excess of nitrous acid. The temperature of the mixture should not rise above 0° at any time. Pour this diazotized solution, in small portions during ten minutes, into the hot cuprous cyanide solution, with frequent shaking. A rapid effervescence occurs, nitrogen and some hydrocyanic acid being evolved. Heat for about a quarter of an hour on the steam-bath. Then distill over the tolunitrile with steam (see p. 158). If the solid separates in the condenser tube shut off the water, and after the material

---

[1] Prepared by soaking strips of filter paper in a very dilute solution of starch and potassium iodide. The papers are dried and kept in a closed bottle.

melts and flows through, *slowly* turn on the water again. This, operation must also be carried out under a hood with a good draft, as not only is hydrocyanic acid liberated, but a small quantity of the isonitrile which is formed in the reaction produces a disagreeable odor. Continue the distillation until no more of the oil passes over.[1] The nitrile solidifies in the receiver on cooling as a yellow crystalline mass. Cool thoroughly, decant off the water, and press out the substance on a porous tile. Distill the product from a small flask, using a short tube as an air condenser. Best results are obtained by distilling the nitrile *in vacuo* (p. 76). If the oil does not solidify, extract with ether, shake the ethereal solution with sodium hydroxide solution to remove the cresol (?), and then after separating and drying with anhydrous sodium sulfate and evaporating the ether in a small flask as in the Aniline Experiment (p. 161), distill the residue directly. Boiling-point, 218° at 760 mm. and about 103° at 21 mm., melting-point, 29°. Yield, 3.7 grams.

## QUESTIONS

1. Give equations to show the formation of the cuprous cyanide, and of the nitrile.
2. Why is it advantageous to have the toluidine hydrochloride separate in small crystals?
3. Why is the solution kept cold during the diazotization?
4. Explain the starch-iodide test for free nitrous acid.
5. What is the formula for the isonitrile?
6. How can you account for the presence of any cresol?
7. How is the cresol removed?
8. What is the Gattermann modification of the Sandmeyer reaction?
9. What other derivatives can be prepared by means of the Sandmeyer reaction?
10. Is it necessary to use cuprous iodide in order to prepare phenyl iodide from aniline?
11. How is the *p*-tolunitrile converted into *p*-toluic acid? Give the " steps " in this reaction.
12. How can you prepare aceto-nitrile (methyl cyanide) from acetamide? from methyl iodide?
13. What is the action of sodium and alcohol on a nitrile?

---

[1] The residue in the flask should not be emptied where acid might be added and thus cause evolution of HCN.

## Experiment No. 56

### OXIDATION WITH POTASSIUM PERMANGANATE IN A NEUTRAL SOLUTION

### Preparation of Acetanthranilic Acid (*o*-Acetamino-benzoic Acid) from Acet-*o*-toluidide

In a 500 cc. flask dissolve 8 grams of potassium permanganate and 6 grams of magnesium sulfate crystals in 250 cc. of water. Add 3 grams of acet-*o*-toluidide (Expt. 46, p. 164); connect the flask to an upright condenser and heat slowly to boiling. Continue the boiling with a *low* flame and shake frequently until all the permanganate has been used up (1–1.5 hours[1]). Test by filtering a few cc. (?) Filter the hot solution (it filters more rapidly when hot) of potassium acetanthranilate from the brown precipitate (?) with suction in a 10-cm. Buchner funnel, using two filter papers. If the filtrate begins to boil under the diminished pressure, allow air to enter by squeezing the rubber tube over the outlet of the suction flask until a small opening is made momentarily. The filtrate will probably be colored at first with the fine brown particles. As soon as it comes through water-white and clear remove the tube and transfer the brown liquid in the filtering flask to the flask containing the main bulk of the solution, then continue the filtration. If necessary, filter again, by gravity. What is the reaction of the filtrate with neutral litmus? Then carefully add to the clear colorless filtrate with stirring the calculated amount of sulfuric acid (as approximately normal solution) based upon the theoretical yield, to set free the acetanthranilic acid. Let stand until cold.

---

[1] If the permanganate has not all disappeared in this time the little that remains can be destroyed by adding in very small amounts through the top of the condenser 1 or 2 cc. of alcohol, or a little sulfurous acid or a sulfite. (Explain the action.)

Filter off with suction the acetanthranilic acid, which is precipitated as fine white needle crystals, and wash with a little cold water. Test the filtrate for complete precipitation by adding more sulfuric acid. Melting-point, 185°. Yield, 75 per cent of the theory.

### NOTE

The brown stains can easily be removed from the hands and apparatus by means of a solution of sodium bisulfite.

## QUESTIONS

1. What is the specific object of the magnesium sulfate?
2. Why is it necessary that this object be attained?
3. What becomes of the potassium and of the manganese of the potassium permanganate during the oxidation?
4. How can anthranilic acid be prepared from acetanthranilic acid?
5. Why cannot anthranilic acid be formed by the direct oxidation of *o*-toluidine?
6. What is meant by " blocking " or " protecting " the amino group?
7. How can anthranilic acid be obtained from its potassium salt?
8. What is the best method for purifying anthranilic acid? (Same as used for any amino acid.)
9. How is anthranilic acid obtained from phthalic acid? Where is this reaction used commercially?
10. What is the effect of hydrochloric acid on anthranilic acid? Is the product soluble in water?

## Experiment No. 57

### FORMATION OF AN AROMATIC ESTER FROM THE ACID AND THE ALCOHOL[1]

### Preparation of Methyl Salicylate (Oil of Wintergreen) from Salicylic Acid and Methyl Alcohol

Place 17 grams of salicylic acid in a 125 cc. round-bottomed flask, add 30 cc. of methyl alcohol and then gradually and with shaking, add 4.5 cc. of conc. sulfuric acid. Add a few pieces of porous tiling, connect with an upright or reflux condenser, and heat on a steam-bath for about 2.5 hours. When the reaction has proceeded for some time the oil of wintergreen formed stays at the bottom of the flask and sometimes when stirred by the boiling and dripping from the condenser forms an emulsion which resembles a precipitate. Distill off the methyl alcohol over the steam-bath in the regular manner, transfer the residue to a separatory funnel, add about 40 cc. of water, shake, separate the lower layer which is the methyl salicylate, and wash it in the separatory funnel first with water, then with dilute sodium carbonate solution (Why?) and finally with distilled water. Separate from the water, dry over anhydrous sodium sulfate, and purify by distillation under diminished pressure (p. 76). If an emulsion is formed in the washing, allow to stand thirty minutes, and if it does not subside, separate the layers as well as possible, and then dry over anhydrous sodium sulfate. The turbid water layer contains only a very small amount of product.

All the ester distills at constant temperature provided the pressure remains constant. The boiling-point of methyl salicylate is 224° at 760 mm., and 115° (approx.) at 20 mm. Its specific gravity is 1.197 at 0°. Yield, 17 grams.

---

[1] Compare ethyl acetate, p. 106.

## QUESTIONS

1. Define an ester.
2. Why not use the term " ethereal salt "?
3. What is the structure of salicylic acid?
4. Explain why conc. sulfuric acid is used.
5. Could dilute sulfuric acid be used?
6. Could conc. hydrochloric acid be used?
7. Why is not methyl sulfate formed instead of methyl salicylate in the experiment?
8. What effect has an excess of methyl alcohol on the yield of methyl salicylate? an excess of salicylic acid?
9. Calculate the theoretical amounts and compare with the amounts used.
10. Would there be any methyl salicylate formed if the alcohol and acid were heated alone?
11. Why must the methyl alcohol be removed before the mixture is poured into water?
12. Why is sodium carbonate used in the washing? Could sodium hydroxide be used? Why?
13. Can you suggest any other drying agents that could be used instead of anhydrous sodium sulfate?
14. What is E. Fischer's method of esterification?
15. How is Fischer's method used in the analysis of proteins? (Perkin and Kipping, " Organic Chemistry," New Ed., (1911), 554).
16. Outline three other methods of preparing esters.
17. Compare the physical properties of acids and their esters (boiling-point, solubility, conductivity, etc.).
18. Show by means of structural formulas the difference between the methyl ether of salicylic acid (methyl salicylic acid) and the methyl ester of salicylic acid (methyl salicylate).
19. How could you differentiate chemically between the two compounds in No. 18?
20. How could you separate by chemical means salicylic acid and methyl salicylate?
21. How is salicylic acid prepared commercially?
22. Discuss the chemical combination of oil of wintergreen as found in nature.

## Experiment No. 58

## Tannin (Tannic Acid)

Make up 25 cc. of an approximately 1 per cent solution of tannin[1] for the first three experiments:

1. Add a few drops of $\frac{1}{3}$ molar ferric chloride solution to about 5 cc. of the solution of tannin. (?) Dilute 1 cc. of the original solution of tannin to 50 cc. and add a drop of the ferric chloride solution. (?) Repeat, using gallic acid. (?) Compare with section *e* under Phenol Experiment (p. 178).

2. Add to the dilute solution of tannin a normal solution of lead acetate. Repeat, using copper sulfate. Results?

3. Dissolve about 0.1 gram of gelatin in 10 cc. of warm water, cool, and add some of the dilute 1 per cent solution of tannin.

4. *Ink.* Dissolve 1 gram of tannin in 10 cc. of hot water, 0.5 gram ferrous sulfate in 5 cc. of hot water, and 0.05 gram of gum arabic in 5 cc. of hot water. Cool the solutions and mix them. Write on a piece of paper with some of the ink, using a new pen. Add a few drops of ferric chloride to a little of the ink and write with the mixture. Compare the results in the two cases and explain. Put the paper away and examine the writing with the two samples of ink at the next exercise. Explain.

### NOTE

The ferrous sulfate should contain no ferric sulfate. Use the pure greenish solid. If it is colored yellow or brown it has been oxidized in the air and is worthless.

### REFERENCE

Holleman, "Organic Chemistry," 4th Ed. (1914), 473.

---

[1] This solution must be freshly prepared, since it slowly decomposes on standing.

## QUESTIONS

1. Where is tannin obtained?
2. Is tannin a true organic (carboxylic) acid?
3. What is Fischer's proposed formula for tannin? (For an extended discussion of the subject, see Emil Fischer, " Synthesis of Depsides; Lichen-substances and Tannin," *Journ. Amer. Chem. Soc.*, **36** (1914), 1170. For formula, read pp. 1193–4.)
4. With lead acetate, does tannin precipitate lead tannate or a complex of lead acetate and tannin?
5. Compare the reaction with gelatine to the use of tannin in tanning hides. Also with the reaction of milk in tea.
6. Why is gum arabic used in the ink?
7. What changes take place in the ink on the paper after standing?
8. In commercial ink how is the ferrous salt kept from oxidation?
9. As far as you can, show how the " depsides " are synthesized. (See Fischer's article above.)
10. How is tannin used in dyeing?

## Experiment No. 59

### ADDITION OF A HALOGEN ACID TO AN OLEFINE

### Preparation of *Trans*-1,8-Dichlor-terpane (*d*-Limonene-dihydrochloride) from *d*-Limonene

To a 50 cc. distilling-flask with an air condenser attached add 20 cc. of crude *d*-limonene [1] and a small amount of bright sodium. Distill and collect separately the fraction between 170°–176°. Redistill this fraction, using another small piece of clean sodium, and collect the portion boiling close to the boiling-point of pure *d*-limonene, 175° (uncor.). It is necessary to use pure *d*-limonene in the experiment. Destroy the sodium in the residues by treatment with alcohol before the apparatus is cleaned with water.

Arrange an Erlenmeyer suction flask with a dropping-funnel as a generator for hydrochloric acid gas.[2] Place about 25 grams of sodium chloride in the flask and cover it with conc. hydrochloric acid. From the dropping-funnel allow conc. sulfuric acid to drip into the mixture. Pass a slow stream of the gas through an empty safety bottle and then into a 250 cc. wide-mouthed bottle through a tube opening *above* a solution of 10 cc. of the purified *d*-limonene in 5 cc. of glacial acetic acid. Keep this solution cold by placing the bottle in a freezing mixture consisting of ice and a small amount of salt. The unused gas is not allowed to come out into the room, but is absorbed by a sodium hydroxide solution in a third bottle, as the bromine vapors were absorbed in the experiment for preparing ethylene dibromide (p. 43).

---

[1] If only a very crude oil is available purify it first by distilling with steam, drying with calcium chloride, and subjecting to an ordinary distillation.

[2] A very convenient generator for preparing hydrogen chloride from conc. hydrochloric acid and conc. sulfuric acid, is described by Sweeney, *Journ. Amer. Chem. Soc.*, **39** (1917), 2186.

In a short time the liquid solidifies to a crystalline mass. About forty-five minutes is required. It should not become appreciably discolored. Transfer it to a beaker with cold water. Use a few cc. of alcohol to dissolve out the residual particles and add this to the main portion. Dilute to 200 cc., stir well, and filter off the solid product with suction in a Buchner funnel (p. 52).

Dissolve the product in about 45 cc. of alcohol, filter from any insoluble particles, and pour in a thin stream, with stirring, into 200 cc. of cold water. The dichlorterpane separates immediately in small white crystalline lumps. Filter again with suction and press out with a spatula[1] on the smooth side of a clean porous tile (p. 56) to remove the last traces of moisture. Since the substance evaporates very slowly when left in the open, it must be covered with a watch glass if allowed to stand any length of time before it is bottled. *Trans*-1,8-dichlorterpane is a white crystalline solid, melting at 50°. It can be recrystallized from warm alcohol. Yield, 30 per cent of the theory.

## NOTES

1. Since the product decomposes when standing in the presence of acid, the experiment should be completed in one laboratory period. If this is not possible, let the product remain in water.

2. The *cis*-form of 1,8-dichlorterpane melts at 25° and is usually liquid at ordinary temperatures. If this is obtained instead of the solid *trans*-form it is probably due to the use of *d*-limonene that has not been properly purified, or to allowing the temperature to go too high.

3. The specific gravity of *d*-limonene is 0.846 at 18°.

4. The substance is also named 1,8-dichlor-menthane, dipentene-dihydrochloride, and *trans*-terpin dichloride.

5. If the dichlorterpane does not crystallize out after being poured into water cool the entire material in ice and then remove the lumps and press them out on a porous tile. If there is any of the *trans*-form present it will generally remain on top after the liquid impurities have been absorbed. Then recrystallize from alcohol, etc.

---

[1] If a steel spatula is used it should always be previously cleaned with soap to remove traces of dust and rust.

## REFERENCES

Cohen, "Organic Chemistry for Advanced Students," Pt. III (1918), Chap. V; Semmler, "Die Aetherischen Oele," Vol. II (1906), 339; Stewart, "Recent Advances in Organic Chemistry," 3d Ed. (1918), 41–52.

## QUESTIONS

1. What is the source of *d*-limonene?
2. Name *d*-limonene according to the terpene system of nomenclature.
3. What does the "*d*" in *d*-limonene and the "*trans*" in *trans*-1, 8-dichlorterpane signify?
4. Show by means of the structural formula why limonene can exist in both *d*- and *l*- forms.
5. How many molecules of HCl combine with each molecule of *d*-limonene, and how can this be shown experimentally?
6. What is the purpose of the glacial acetic acid? What is the melting-point of glacial acetic acid?
7. What is the object of the porous tile? Why not use filter paper?
8. Why must the product not be left in the open?
9. What compound is formed by the addition of HCl to propene?
10. Can sodium be used for purifying hydrocarbons in general?
11. Is limonene an aromatic or hydroaromatic compound? Why?
12. Of what use in terpene chemistry is the formation of the "hydrochlorides"?

# SYNTHESIS OF CAMPHOR FROM PINENE

(In Five Steps)

## Experiment No. 60

### (1) Pinenehydrochloride from Pinene (Rectified Oil of Turpentine)

Perform this experiment under the hood, or connect the outlet tube with the suction pump and let the water run *very slowly*. In the latter case pass the gases through a tube opening just above the surface of a 2N sodium hydroxide solution contained in a bottle, and then to the pump.[1]

Provide a 250 cc. short-neck, round-bottom flask with a three-holed rubber stopper, through which pass (1) a gas inlet tube reaching almost to the bottom of the flask, (2) a calcium chloride tube, (3) and a thermometer. Saturate 200 grams of pinene contained in this flask with dry hydrogen chloride, which is generated in the following apparatus. Fit up an ordinary liter flask or bottle with a dropping-funnel and an outlet tube inserted through a two-holed stopper. Connect this (1) with an empty wash bottle, (2) with a Woulff bottle [2] or a 250-cc. wide-mouthed bottle containing conc. sulfuric acid, provided with a safety tube 2 feet long, (3) another wash bottle also containing conc. sulfuric acid, and (4) with an empty wash bottle, from which the gas is led into the pinene flask. The empty wash bottles act as guards and prevent any danger of serious explosions in case there is back pressure in the apparatus. Use rubber stoppers and glass tubing throughout, joining the glass

---

[1] Test the apparatus for leaks with the gas under pressure before turning on the water. Otherwise bubbles of air may be mistaken for hydrogen chloride.

[2] A wide bottle with three apertures.

tubing with as short rubber connections as possible. The two wash bottles with sulfuric acid are necessary for thoroughly drying the gas.

The pinene flask is imbedded in a mixture of cracked ice and a small amount of common salt. As the reaction proceeds more salt may be necessary. When the apparatus is all ready put 500 grams of common salt in the generating flask, add enough conc. hydrochloric acid to cover the salt, and then allow conc. sulfuric acid to drop upon this mixture from the dropping-funnel. The gas should be run into the pinene *continuously* at a fairly rapid rate (about two hours are necessary), *care being taken that the temperature does not exceed* 20°. The reaction does not take place readily below 0°. The best temperature is about 5°–15°. Sometimes it is necessary to take the ice away in order to allow the temperature to rise and the reaction to start. After the gas has been passing in for some time the temperature may rise to 60°. This will do no great harm, other than to color the mixture on account of slight decomposition, but the temperature should not be allowed to stay up. A higher temperature should be avoided. A slower stream of gas and further cooling will soon bring the temperature down. *The success of the experiment depends upon the dryness of the gas and the temperature of the reaction.*

After about two hours when no more gas is absorbed and the pinene has been transformed into a semi-solid mass disconnect the flask and close it with a good cork or rubber stopper. Cool it to − 10° to − 15° in a freezing mixture consisting of about two parts of cracked ice and one of salt and let it remain for thirty minutes or overnight (in the ice-box). In case it is left overnight, care should be taken that no water from the melting ice will get into the flask, by fastening the flask upright with a clamp. On the next day it must be packed again and cooled for an hour. Filter off the crystallized pinenehydrochloride with suction[1] and press out on a porous tile. Cool the filtrate and thus obtain more of the product. Now dissolve the entire

---

[1] It is convenient to use a flat-topped glass stopper to press down the cake in the Buchner funnel.

crude product in about 80 cc. of warm alcohol contained in a beaker and heated on the steam-bath. It will remain milky white. Then cool to – 5°, with stirring to avoid the formation of a solid mass. Filter and press out as above. Yield, 100–125 grams. The snow-white crystalline powder, which has an odor resembling camphor, melts at 118°–120°. This product is used for the next experiment. It is somewhat volatile at the ordinary temperature and pressure, and therefore should not be left uncovered for any length of time.

## NOTES

1. Arrange your time so that the experiment may be started at the *beginning* of a laboratory period. The pinenehydrochloride should be recrystallized from alcohol the same afternoon or on the following day, since it decomposes slowly on standing. If it does not crystallize after the gas has been run in for 2½ hours, the pinene used probably contained moisture or was otherwise impure, or the temperature was too low.

2. Perfectly pure and stable pinenehydrochloride which melts at 125° can be obtained by crystallization from petroleum ether, but a large amount of the substance is lost by this method.

3. At one time pinenehydrochloride was known as "artificial camphor," on account of its odor. Now, however, this is a misnomer, since camphor itself can be synthesized.

4. **Rectification of Oil of Turpentine.** Pinene (boiling-point, 155°) is the chief constituent of the oil of turpentine. It is obtained fairly pure by distilling the oil in a flask with metallic sodium and using a Young's pear fractionating column or still-head (Fig. 4, p. 25). The portion going over between 154° and 160° consists almost entirely of pinene. For this experiment use 300 cc. of crude pinene and about 4–5 grams of sodium.

5. The brown resinous mass remaining in the flask is treated with alcohol to destroy any unattacked sodium before water is added and then the flask is cleaned.

6. Save a specimen of at least 1 gram of each of the products in the synthesis of camphor from pinene, and hand them in.

### GENERAL REFERENCES FOR STUDY

Stewart, "Recent Advances in Organic Chemistry," 3d Ed. (1918), Chap. III; and Cohen, "Organic Chemistry for Advanced Students," 2d Ed., Pt. III (1918), Chap. V; and Semmler, "Die Aetherischen Oele," Vol. II (1906).

## QUESTIONS

1. Outline the terpene system of nomenclature and write all the reactions in the synthesis of camphor from pinene on this basis, using only the skeleton formula.
2. Discuss Baeyer's Strain Theory.
3. Review the properties of the olefines as shown by their reactions when treated with (1) halogens, (2) halogen acids, (3) hydrogen in presence of colloidal platinum or finely divided nickel (at high temperature), (4) hypochlorous acid, (5) nitrosyl chloride, (6) conc. and fuming sulfuric acid, (7) ozone, (8) potassium permanganate, (9) heat alone, or with strong acids and pressure.
4. What addition products are used for the identification of the terpenes?
5. What compounds are formed when pinene is treated with moist hydrochloric acid, and particularly with alcoholic sulfuric or nitric acids?
6. Is pinene regenerated when pinene hydrochloride is boiled with "alcoholic potash" or potassium phenolate? What does this indicate?
7. Can sodium be used in general for the purification of hydrocarbons?

## Experiment No. 61

### (2) Camphene from Pinenehydrochloride

In a 400 cc. round-bottomed flask melt 190 grams of phenol[1] and then add 75 grams of potassium hydroxide[2] (crushed). The mixture becomes heated spontaneously and the alkali dissolves. Shake. Warm, if necessary, to produce complete solution. Now connect the flask with a condenser for distillation, insert a thermometer with the bulb in the neck (not in the liquid), and carefully heat over a metal gauze to distill off the water formed in the reaction. A small amount of phenol also goes over. After the temperature reaches 150° exchange the water condenser for an air condenser. When all the water has been distilled off and the temperature has risen to 180°, allow the flask to cool somewhat, disconnect, and add 100 grams of pinenehydrochloride,[3] **in three portions**, the second and third after the preceding reaction has subsided. Attach an upright air condenser to the flask after each addition and heat carefully at first since there may be a violent reaction. Finally keep the mixture boiling for two or three hours, shaking the flask frequently. The vapors must not be allowed to rise more than one-half the length of the air condenser. *If the heating is very strong, fumes will come out of the top and these will settle down and become ignited.* If the heating is interrupted and the potassium phenolate is allowed to solidify the flask must be cautiously heated around the sides until the solid material melts before heat is applied at the bottom.

[1] If any phenol comes in contact with the skin apply alcohol at once.

[2] Sodium hydroxide cannot be used on account of the high melting-point of the sodium phenolate.

[3] Prepared in the previous experiment.

Then, in order to obtain the camphene, subject the mixture to distillation in the same manner as the water was distilled above, using an air condenser, until the temperature of the vapor reaches 180° (the boiling-point of phenol). At first pure camphene distills (150°–160°), later it is contaminated with increasing amounts of phenol. The distillation is stopped when a drop of the distillate entirely dissolves in dilute sodium hydroxide. (Why?) The distillate is then shaken in a flask with dilute sodium hydroxide (Why?), and cooled with ice, whereby the camphene solidifies in crystalline lumps. If the camphene does not crystallize out well from the alkaline solution, warm, separate and then cool. Filter with suction and wash with ice water, retaining the filtrate for recovering the phenol, if desired (see below). If a small amount of an oily constituent should pass through the filter paper, separate it from the remainder of the filtrate and add to the main portion. Heat the camphene in a small flask on the steam-bath until it melts. When it is liquid, and a good separation can be made, pour off from the drops of water into an Erlenmeyer flask and again melt in the same way with addition of a few pieces of calcium chloride, decant, and finally fractionate in a round-bottomed flask surmounted by a good fractionating column such as the apparatus of Young (Fig. 4, p. 25), to which is connected an air condenser. Protect the distilling apparatus from excessive radiation and consequent condensation by surrounding it with paper or a towel. Collect the fraction distilling between 155° and 160°.[1] This solidifies on cooling to a colorless, crystalline mass. Yield, 60 grams. Pure camphene melts at 51°–52° and boils at 160°.

The product should be chlorine-free. Test for chlorine according to the directions on p. 114. If the product is not chlorine-free, redistill until the distillate gives no test for halogen.

The residue in the flask contains a small amount of pinene-hydrochloride.

If it is desired, the student may recover the phenol used

---

[1] Use only this fraction for the next experiment. The lower boiling fraction (around 147°) contains other hydrocarbons which, if allowed to remain, apparently causes trouble in the crystallization of the isoborneol later on.

in this experiment, part of which is in the main residue and part in the sodium hydroxide washings, by making the combined residues acid with hydrochloric acid and then extracting with ether. Dry the ether solution for twenty-four hours over anhydrous sodium sulfate, decant and remove the ether in the ordinary way by distillation and then distill the phenol, using a short air condenser. Boiling-point, 181.5° Yield, 150–160 grams.

## QUESTIONS

1. Why is potassium phenolate used instead of potassium alcoholate?
2. Why not use sodium phenolate?
3. How is the camphene separated from the phenol?
4. Give two reactions which show that camphene is chemically different from bornylene.
5. What is formed when camphene is oxidized with chromic acid?

## Experiment No. 62

### (3) Isobornylacetate from Camphene

To a solution of 50 grams of camphene[1] in 125 cc. of glacial acetic acid contained in a flask, add a mixture of 2 cc. of conc. sulfuric acid and 3 cc. of water. Warm on the steam-bath to 50°–60° (thermometer in the flask) for 2½ hours, with frequent shaking. The reaction product separates in two layers at first which finally disappear after heating.

Transfer the reddish-colored solution of the ester to a large beaker, rinse the flask with 100 cc. of water and add this to the beaker. Neutralize with powdered sodium carbonate *crystals* (about 300 grams). Separate and dry the ester with calcium chloride, and then fractionate *in vacuo*. At 12 mm. pressure the first runnings up to 95° contain some camphene; the main portion then distills between 95° and 105° at 12 mm., chiefly 100°–102°. Yield, 60 grams. Isobornyl acetate is a colorless liquid which smells like valerian. Specific gravity, 0.9905 at 15°. Boiling-point, 102° at 12 mm.; 106°–107° at 15 mm.

### QUESTIONS

1. Explain the use of the sulfuric acid.
2. Why is the crystalline sodium carbonate preferred to the anhydrous sodium carbonate or to sodium hydrogen carbonate? (Compare heats of solution.)
3. Why is the isobornyl acetate so carefully purified?

---

[1] Experiment No. 61.

## Experiment No. 63

### (4) Isoborneol from Isobornylacetate

The isobornylacetate is hydrolyzed (saponified) with potassium hydroxide and converted into isoborneol as follows: In a 250 cc. flask dissolve 50 grams of isobornylacetate[1] in a solution of 100 cc. of alcohol and 20 grams of potassium hydroxide, and heat to boiling for three hours under reflux condenser on the steam-bath. Pour the solution into cold water. The isoborneol separates as a white or light yellow solid. If it remains as an oil or a semi-solid mass, place the beaker in ice and stir with a mechanical stirrer[2] for ½ to 2 hours. The isoborneol gradually becomes white and crystalline. If it does not crystallize, but remains as an oil or an oily lump, separate, add fresh water, and stir again. Break up any lumps. Or continue the hydrolysis with fresh "alcoholic potash" for ½ to 1 hour. Filter off the crystals with suction, and wash with cold water, press out and dry on a porous tile. Melting-point of this crude product, 203°–205°. Yield, 35 grams. The isoborneol thus obtained is pure enough for conversion into camphor, as described in the next experiment. Crystallized from petroleum ether, absolutely pure isoborneol is obtained, melting at 212° (in a closed tube, see foot-note 7, p. 66).

#### QUESTIONS

1. Compare the preparation of glycol from ethylene dibromide through the acetate.
2. How can ethyl alcohol be prepared from ethylene?

---

[1] Experiment No. 62.

[2] An electric mixer such as are used at soda water fountains is excellent for this purpose.

3. What chemical reaction of isoborneol shows that it is a tertiary alcohol?
4. Why cannot a good melting-point of isoborneol be taken in an open tube?
5. How does changing the water aid in the crystallization of the product?
6. Is alcoholic KOH generally used for hydrolysis? (Compare the analysis of fatty oils, etc.)
7. How can tertiary alcohols be prepared by the Grignard reaction?

## Experiment No. 64

### (5) Camphor from Isoborneol

*Perform this experiment under the hood or near the draft pipe.* Make a mixture of 60 grams of concentrated nitric acid (sp.gr. 1.42) and 12 grams of red fuming nitric acid (sp.gr. 1.60) in a 250 cc. flask, cool to 20°–25°, and keeping the temperature between 20°–25°, cautiously add in small amounts 30 grams of isoborneol.[1] Each portion of isoborneol dissolves in the acid with rise in temperature and evolution of nitric oxides. During the operation the mixture must be well stirred, shaken and cooled. At the end, a compound of camphor and $N_2O_5$ separates as a slightly colored oily layer. Continue the stirring and shaking as much as possible for about thirty to forty minutes, and then, while shaking, slowly pour out the contents into some cracked ice in a beaker. The camphor separates out in white lumps. If it does not, melt the ice, separate, and add cold water to the camphor layer. It will then crystallize out, especially on cooling. Filter with suction and wash with ice water. This crude product melts at about 168° and contains some oxides of nitrogen. In order to purify the camphor treat it in a 500 cc. flask with a dilute solution of 3 grams of sodium hydroxide and 5 grams of potassium permanganate, and then distill with steam through an air condenser[2] into a wide-mouthed bottle which is cooled in cold running water. Dry the purified product on a porous tile. It should be perfectly white, and melt at 172°–173°. Yield, 21 grams. Camphor is volatile and care must be used to carry on all operations under good cooling.

---

[1] Experiment 63.

[2] The camphor separates out in a water condenser, and therefore if one is used the distillation must be discontinued now and then, and the camphor pushed out with a long rod. Otherwise it will clog the condenser.

By neutralizing the nitric acid filtrate obtained above with sodium carbonate and distilling this with steam, about 2.5 grams more of camphor can be obtained.

## NOTES

1. Do not leave the product in the open air longer than is necessary to press out on the porous plate.

2. *d*-Camphor melts at 175°, boils at 209°, and sublimes at the ordinary temperature; sp.gr. 0.992 at 10°. Camphor obtained from isoborneol consists of a racemic mixture. Camphor from the camphor tree (*Laurus camphora*) is dextro-rotary.

## REFERENCE AND ACKNOWLEDGMENT

This series of experiments in the synthesis of camphor is based upon those given in Ullmann's "Organisch-Chemisches Praktikum" (1908), 230–6, and the author is glad to make acknowledgement here.

## QUESTIONS

1. How is camphor obtained from isoborneol?
2. Point out the asymmetric carbon atoms in camphor.
3. Is the product obtained optically active? Why?
4. Give several reactions which show that camphor is a ketone.
5. How can it be shown that there is a $CH_2$-group adjacent to the carbonyl group?
6. Discuss the oxidation products of camphor.
7. Outline Komppa's synthesis of camphoric acid.
8. How can camphor be synthesized from camphoric acid?

## Experiment No. 65

### DIRECT OXIDATION OF A HYDROCARBON

### Anthraquinone from Anthracene

Connect a flask containing 2.5 grams of anthracene with an addition tube and a reflux condenser. Pour in 20 cc. of glacial acetic acid and heat on the steam-bath. Prepare a solution of 4.5 grams of chromium trioxide in a little water and add 7 cc. of glacial acetic acid. Add this solution in small amounts to the flask and continue the heating for five minutes after the addition of the last portion. It will not all dissolve. Pour the green mixture into water, and stir well. Filter off the precipitate with suction, wash, and dry it. Recrystallize as follows: Pour over the dry product in a flask 110 cc. of toluene. Connect with an upright condenser and heat carefully over a wire gauze to boiling for several minutes. Do not use such a large flame that some of the vapors come uncondensed out of the top of the condenser. The vapors are heavy and will settle down and become ignited. The solubility of anthraquinone is 2.56 parts in 100 parts of toluene at 100°. Immediately after disconnecting, filter the solution through a fluted[1] filter paper in a glass funnel set in a hot-water funnel,[2] using a stirring-rod to direct the flow of the hot solution into the filter. When filtering inflammable liquids, the burner under the side tube must always be removed. The anthraquinone rapidly crystallizes out. It is separated with suction[3] and allowed to dry

---

[1] See p. 128.

[2] See p. 128.

[3] If it is desired to concentrate the toluene solution, distill off the toluene in the usual way from a distilling flask. This, however, generally gives dark-colored crystals.

between filter papers. Large well-formed crystals are obtained if the filtrate is allowed to cool very slowly. This can be done by placing the beaker in warm water and letting all cool together. However, the finer crystals formed by rapid cooling are more likely to be the purer product. Melting-point 285.5°, cor. Yield, 2.5 grams.

Sublime a sample of the anthraquinone as follows: Place a small amount of the material on an 8-cm. watch glass, cover with an 8-cm. filter paper which has been perforated with a number of tiny holes, and then put another watch glass of the same size, convex side up, over these. Set on a wire gauze and place a very small flame underneath. Light-yellow crystals soon begin to deposit on the cold surface of the upper watch glass and the paper will prevent them from falling back to the lower one. An inverted funnel can be used instead of the upper watch glass. Determine the melting-point of this sublimed sample as well as of the recrystallized product.

## QUESTIONS

1. Is anthraquinone a true chemical derivative of anthracene?
2. Compare anthracene and diphenylmethane in regard to oxidation with chromic acid.
3. Does anthraquinone have any aliphatic characteristics? Compare it with *p*-benzoquinone.
4. Explain why you should expect the 9 and 10 carbon atoms of anthracene to be more easily oxidized than the others.
5. What naturally occurring dye is related to anthraquinone?
6. To what is the green color of the reaction mixture due? (Compare question 4, Acetaldehyde Ammonia, Expt. 17, p. 88.)
7. Why cannot alcohol or water be used in place of the acetic acid in this experiment?
8. Why is a fluted filter paper used?
9. Why are the finer crystals more likely to be purer?
10. Explain sublimation.
11. Does anthraquinone contain auxochrome or chromophore groups?
12. How can anthraquinone be reconverted into anthracene?

13. What compound is formed when anthraquonine is shaken with zinc dust and sodium hydroxide solution? How can this be changed back into anthraquinone?
14. Discuss quinone monoxime relative to its structure and method of preparation from quinone, and from phenol.
15. What are the naphtho-quinones? How prepared?

## Experiment No. 66

### NITROGEN HETEROCYCLES

### Pyridine

1. Dissolve a few drops of pyridine in pure ammonia-free water and test its reaction with neutral litmus.

2. To an aqueous solution of pyridine add a drop or two of $\frac{1}{8}$ molar ferric chloride solution. (?)

3. Mix 1 cc. of pyridine and 0.9 cc. of methyl iodide[1] in an ordinary No. 2 test-tube supported in a rack. Stir with a thermometer. A vigorous reaction sets in and a yellowish solid is formed. Note the temperature as the reaction continues. It may become so hot that the product melts. Recrystallize the product by adding 5 cc. of absolute alcohol and heating the tube in warm water until solution takes place, and then allow to cool. Filter with suction and wash the crystals with a small amount of cold absolute alcohol. The crystals are usually in the form of flat pencils which are sometimes aggregated in rosettes. They very slowly deliquesce. Melting-point, 117°.

Test the solubility of a small portion of the recrystallized product in water. To this solution add a drop of silver nitrate solution. Is there an immediate precipitate? What is it? Account for it.

### Quinoline

1. Test the solubility of quinoline in water. Does the aqueous layer react alkaline toward litmus?

2. Add a little hydrochloric acid to a few drops of quinoline in water. (?)

---

[1] Methyl iodide is somewhat poisonous. Be careful not to breathe its vapors or get it on the skin.

3. To a hydrochloric acid solution of quinoline add **a solution** of potassium dichromate. (?)

## QUESTIONS

### PYRIDINE

1. Write the equation to show the substances formed in the condition of equilibrium when pyridine is dissolved in water.
2. Explain the action of the aqueous solution of pyridine on ferric chloride. What is the precipitate?
3. What type of substance is formed by the reaction between pyridine and methyl iodide? Write its structure.
4. Explain the action of silver nitrate on the aqueous solution of the pyridine iodmethylate (or methiodide). Compare with ethylammonium chloride used in a previous experiment (under Methyl Amine, p. 121).
5. What is formed when the pyridine iodmethylate is treated with potassium hydroxide?
6. What is formed when the pyridine iodmethylate is heated alone to 300°? Compare with the preparation of *o*- and *p*-toluidine from methyl aniline.
7. How could you tell experimentally when a substance contains a tertiary nitrogen atom as in pyridine and when it contains a secondary nitrogen atom as in pyrrole, coniine, etc.?
8. Look up the formulas for nicotine, coniine, tryptophane and indigo. What nitrogen heterocycles do they contain?

### QUINOLINE

9. Write the structures of the compounds formed when quinoline is treated with hydrochloric acid, and this solution with potassium dichromate.
10. Why does the quinoline dissolve in dilute hydrochloric acid?
11. How can quinoline be prepared synthetically?
12. How does isoquinoline differ from quinoline?
13. Look up some alkaloids which contain the quinoline nucleus; also the isoquinoline nucleus.

# PART II

# ORGANIC COMBUSTIONS

# FOREWORD

The determination of carbon and hydrogen and of nitrogen in organic substances is very important because it is fundamental, and yet, in spite of its importance, the operations are not always as successful as they should be, and are often regarded in organic laboratories as a somewhat " necessary nuisance," and as F. G. Benedict says,[1] " exasperatingly vexatious." It is practically impossible to find a commercial laboratory that will undertake the task, and usually one must set up his own apparatus and attend to it himself unless he is so fortunate as to be located in a large research laboratory where someone is employed for this sole purpose.

Organic combustions, as the operations are commonly called, will continue to be more or less difficult, since some variation must be added in the case of each individual substance. Combustions should be considered as a means to an end, not the end in itself, and therefore the methods should be so clearly and exactly defined that they can be carried out with the greatest possible accuracy in the minimum amount of time and with the smallest amount of energy. If all the mechanical details and the more useful forms of apparatus are adequately described and the pitfalls in manipulation pointed out, there is no good reason why anyone with a knowledge of and skill required in ordinary quantitative analysis should not be able to master the method and obtain good results from the very beginning. Accordingly, if the directions in the following pages come anywhere near accomplishing this end, the hopes of the author will be realized.

The methods selected for description are the outgrowth of our experience covering several years. Like most workers in the subject the author has taken the liberty of describing some of his own modifications, especially in apparatus, and he is willing to assume the responsibility for the direct statements made herein.

---

[1] " Elementary Organic Analysis," Preface.

Where he has not been very familiar with a certain procedure or with certain kinds of apparatus he has tried to show that lack in the wording of the text. The descriptions ordinarily refer to work on the common organic compounds usually met with in laboratory practice.

It is believed that many of the difficulties in carrying out an organic combustion arise from the fact that the operator, as is very natural, is not thoroughly familiar with the apparatus and its possibilities. For this reason, the apparatus has been very carefully described, and many of those little " kinks " which are very helpful but not always available in writing are also added. Lest the student lose track of his work on account of the length of some of the descriptions and notes, he is referred to the important " Topical Outline of General Method of Procedure," which is a concise summary of the necessary operations arranged to save both time and energy. It must be remembered that you cannot run a combustion just by keeping a set of directions beside your apparatus. *You must study the method in detail.* Then the topical outline will help bridge the gaps.

The author has tried to give due credit to the proper authorities in special cases by numerous references in appropriate places. Acknowledgments are hereby gladly made to such standard works as:
Gattermann's " Practical Methods of Organic Chemistry ";
W. A. Noyes' " Organic Chemistry for the Laboratory ";
Sudborough and James' " Practical Organic Chemistry ";
Cohen's " Practical Organic Chemistry ";
F. G. Benedict's " Elementary Organic Analysis ";
Dennstedt's " Anleitung zur vereinfachten Elementaranalyse."

The author also wishes to extend his grateful thanks for many helpful suggestions to his colleagues, especially Professors John M. Nelson, H. T. Beans, and Harold A. Fales, and to his former students and co-workers in the organic laboratory at Columbia University, who have borne with him in his efforts to standardize organic combustions and to make them more easy and fruitful.

HARRY L. FISHER

COLUMBIA UNIVERSITY, NEW YORK,
June, 1919.

# DIVISION A

## THE DETERMINATION OF CARBON AND HYDROGEN

### I. Historical[1] Introduction

In the year 1781 Lavoisier, working on the theory of combustion, established with a fair degree of accuracy the quantitative relation of carbon and oxygen to carbon dioxide, and of hydrogen and oxygen to water, and also showed that carbon dioxide and water were the sole products of the combustion of organic substances such as "spirit of wine," oil, wax, sugar, and resins. In 1784 he burned weighed portions of some of these organic substances in a known volume of oxygen, and collected the gaseous products in a bell-jar over mercury. These gaseous products he analyzed by volume, absorbing the carbon dioxide in a potash solution, and measuring the residual oxygen. He then calculated the weight of the water indirectly, and in this way he was able to determine the composition of the substance.[2] For the more difficultly combustible substances he used, instead of free oxygen gas, mercuric oxide and manganese dioxide, which give up oxygen when heated.[3] Thus he laid the very foundations of elementary organic analysis.

---

[1] Dennstedt has given us an excellent detailed account of the historical development of organic combustions in his article, "Die Entwickelung der organischen Elementaranalyse," in Ahrens' "Sammlung chemischer und chemisch-technischer Vorträge," IV (1899), 1–114. The article also contains a very complete bibliography.

[2] Ladenburg, "History of Chemistry," trans. by Dobbin (1899), 289.

[3] Ernst von Meyer, "A History of Chemistry," trans. by George McGowan, 3d English edition (1906), 410–2; Armitage, "A History of Chemistry," (1906), 54. Dennstedt, on pages 2 and 3, of his history mentioned above, gives a detailed

Gay-Lussac and Thénard,[1] in 1810, extended Lavoisier's work and modified the method of burning the substance by mixing it with a known weight of potassium chlorate. The mixture was worked into a paste with water and formed into pellets, which were dried in an air-bath and dropped into a hot vertical tube. The gases given off were collected over mercury and analyzed as in gas analysis. The results obtained were considered as accurate as the best mineral analyses known at that time. Violent explosions often occurred in this method, and Berzelius[2] in 1817 made a marked improvement, which reduced the possibility of an explosion to a minimum. He mixed the organic substance with potassium chlorate and a large amount of sodium chloride, and then gradually decomposed this mixture by heating in a *horizontal* tube. He was the first to pass the gases through a straight tube containing fused calcium chloride, and thus he obtained directly the amount of water absorbed by weighing the tube before and after the combustion. He also determined the carbon dioxide directly by weight. For this purpose he used solid potassium hydroxide which was contained in a small glass vessel. It was weighed before, and after standing in the bell-jar for twenty-four hours, it was weighed again. It was no longer necessary to take into account the residual oxygen.

Cupric oxide was introduced as the oxidizing agent by Gay-Lussac[3] in 1815, and its general use thenceforth was established.

---

account of the method with illustrations of the apparatus, used by Lavoisier. Compare H. Meyer, " Analyse und Konstitutionsermittelung organischer Verbindungen," 2. Auflage (1909), 146-53.

A short history of organic combustions is also given in Lassar-Cohn's " Arbeitsmethoden," Allgemeiner Teil, Vierte Auflage (1906), 274-5.

For early work and analyses, see the following books by Emil T. Wolff, which are replete with examples and references, although no description of the methods is given; "Quellen Literatur der theoretisch-organisher Chemie" (1845), 18-26; and "Vollständige Uebersicht der Elementar-analytischen Untersuchungen organischer Substanzen" (1846). The author is indebted to Prof. F. B. Dains for Wolff's work.

[1] Dennstedt, 9; Armitage, 129.

[2] Dennstedt, 10-11; von Meyer, 412.

[3] Dennstedt, 12; von Meyer, 413; Armitage, 139.

The U-form of tube for calcium chloride appeared in 1822, being first used by Bussy.[1]

The whole procedure of organic combustions was put upon a firm basis by the very careful and painstaking work of Justus von Liebig, who improved the details and simplified the determination of carbon dioxide by the introduction of a convenient bulb-shaped apparatus—the Liebig potash bulb.[2]

For many years Liebig's outline was the standard. Modifications were introduced, especially in the manner of heating the tube. He had used a charcoal furnace. This was replaced first by gas furnaces and now by electric combustion furnaces. Oxygen [3] was used instead of air in some instances. Soda lime was first used in 1858 by Mulder.[4] It absorbs carbon dioxide more rapidly than the potassium hydroxide solution and is more convenient to handle. The chief modification was brought out by Köpfer [5] in 1876, who used platinum black, and later platinized asbestos, as a catalytic oxidizing agent, burning the substance in a stream of oxygen, without any copper oxide, etc. In this method the tube is shortened and only a few gas burners are required; furthermore, the combustion itself can be carried out in a much shorter time, and many organic substances which could not be properly burned by the older method could be burned completely. Köpfer's method was improved by F. Blau,[6] but has been perfected and most successful in the

---

[1] *Journ. de Pharm.* (1822), 580; Dennstedt, 10.

[2] Dennstedt, 18–20; von Meyer, 413; Armitage, 149. Liebig, " Ueber einen neuen Apparat zur Analyse organischer Körper und über die Zusammensetzung einiger organischen Substanzen," Poggendorff's *Annalen*, **21** (1831), 1.

Liebig published the details of the method in a pamphlet entitled, " Anleitung zur Analyse organischer Körper," (1837); a second edition being published in 1853. It was translated into English by Wm. Gregory, and published in 1839 under the title, " Instructions for the Chemical Analysis of Organic Bodies."

[3] Dumas and Stass first used oxygen in combustions in redetermining the atomic weight of carbon. See Dennstedt, 77. Liebig had used air in his combustion method.

[4] *Jahresber.* (1858), 589; Dennstedt, 28.

[5] *Ber.*, **9** (1876), 1377; *Zeitschr. anal. Chem.*, **17** (1878), 1; Dennstedt's history, 81.

[6] *Monatshefte für Chemie*, **10** (1889), 357–71.

hands of Dennstedt.[1] It requires a double inlet for two carefully regulated streams of oxygen. One stream goes through a short inner tube which contains the boat and substance, and the other stream goes outside this tube, and furnishes an abundant supply of oxygen just as the products of combustion come out of the inner tube and meet the catalyst. Considerable practice is necessary to handle the operation, but it gives excellent results. The platinum is " poisoned " by some substances and requires frequent treatment with conc. hydrochloric acid to activate it.

Another method, which was being developed at about this time but which has not yet seen its full development, is the combustion of the substance in a bomb with oxygen under pressure.[2] There have been many limitations in experimenting with this method, but these are gradually disappearing with the perfecting of the bombs for calorimetric work, and the present author feels that the day will soon come when the variations in the burning of each individual substance will no longer cause any difficulty, since it will be possible to have a bomb in which any substance can be burned within a few seconds under the same general conditions, and connections arranged for the absorption of both water vapor and carbon dioxide in the usual manner.

The use of platinum as a catalyst heated by a burner outside a combustion tube naturally led to the electrical heating of the platinum. This method has been shown to be rapid and very efficient, but the apparatus is not generally available. It was first described by Morse and Taylor[3] in 1905, and is given in

---

[1] Dennstedt, " Anleitung zur vereinfachten Elementaranalyse," (1903); Dritte Auflage (1910).

Also, H. Meyer, " Analyse und Konstitutionsermittelung organischer Verbindungen," 2. Auflage (1909), 170–6; Gattermann, " Practical Methods of Organic Chemistry," 3d English ed. (1914), 113–29; and Sudborough and James, " Practical Organic Chemistry," (1915), 50–5.

[2] Berthelot, *Comp. rend.*, **114** (1892), 318; **129** (1899), 1002; *Ztschr. anal. Chem.*, **40** (1901), 124; Hempel, *Ber.*, **30** (1897), 202; Zuntz and Frentzel, *Ber.*, **30** (1897), 381; Langbein, *Ztschr. angew. Chem.*, Year 1900, 1227, 1259; and Year 1901, 516.

The method is also described in the catalogue of the Emerson Fuel Calorimeters (1915), 17–23.

[3] Morse and Taylor, *Amer. Chem. Journ.*, **33** (June 1, 1905), 591; and Morse and Gray, *Amer. Chem. Journ.*, **35** (1906), 451; and almost at the same time by

detail in Morse's "Exercises in Quantitative Analysis," (1905), 537-45.

All these combustion methods require from 0.2-0.5 gram of substance for each determination. Oftentimes such an amount is not available, and on this account, Pregl[1] devised a scheme by which it is possible to make a complete analysis for carbon and hydrogen on only 0.005 gram of the substance. Platinum as the catalyst or cupric oxide on asbestos are used in a tube about 20-40 cm. long. A special balance[2] is required. The method is spoken of as micro-combustion in contradistinction to the ordinary method, which is termed macro-combustion.

In 1913 Bekk[3] published a modification of Dennstedt's method using cerium dioxide as the catalyst instead of platinum, and by using a long train of the catalyst (30 cm. of the tube filled with cerium dioxide deposited on asbestos) and by placing the substance in a special small tube inside the larger combustion tube he was able to do away with Dennstedt's complicated double inlet. He claimed even greater rapidity for his method over Dennstedt's, and furthermore showed that the cerium dioxide was not only an excellent catalyst, but also that it was much cheaper and not "poisoned" by the common materials that destroy the catalytic action of the platinum.

---

Carrasco, *Atti R. Accad. dei Lincei Roma* [5] **14**, II, 608-18 (Dec. 3, 1905); *Chem. Central.*, 1906 (I), 699-701. See also Bretau and Leroux, *Comp. rend.*, **145** (1907), 524-6, *Chem. Central.*, 1907 (II), 1653.

[1] Pregl, "Die quantitative Mikroelementaranalyse organischer Substanzen," in Abderhalden's "Handbuch der Biochemischen Arbeitsmethoden," V (1912), 1307-32.

Other references on micro-combustions: Dubsky, *Chem. Ztg.*, **40** (1916), 201-3; Rinkes, *Chem. Weekblad*, **13** (1916), 800-3; Fisceman, *Rend. acad. sci.* (Napoli), **22** (1916), 31-8; and Noorduijn, "An electric furnace for micro-elementary analysis," *Chem. Weekblad*, **14** (1917), 1131-5.

[2] Pregl describes the Kuhlmann balance used by him in his article mentioned above. See also Emich, "Micro-balances and their application in chemical analysis," *Naturwissenschaften*, **3** (1915), 693-8.

That an ordinary sensitive balance can be used, provided the investigator can use as much as 0.012-0.022 gram of substance, has been shown by L. E. Wise, "A simplified micro-combustion method for the determination of carbon and hydrogen," *Journ. Amer. Chem. Soc.*, **39** (1917), 2055.

[3] *Ber.*, **46** (1913), 2574.

Professor Marie Reimer,[1] in an article entitled, "On Rapid Organic Combustions," in 1915, combined the good points of the old Liebig method and of Bekk's method and showed that copper oxide and cerium dioxide could be used together advantageously for the rapid determination of carbon and hydrogen.[2] The technique of the method was improved by Levene and Bieber.[3] The copper oxide is added to oxidize any products of incomplete combustion, like carbon monoxide, if they happen to get beyond the catalyst or in case the supply of oxygen is momentarily used up. This is the method outlined in the following pages.

The use of alumina [4] as the absorbent for water in place of the time-honored calcium chloride has only recently been described. It is believed that it has several advantages over calcium chloride, for example: (1) it is a better absorbent for water,[5] (2) when it has absorbed water it does not crystallize and "freeze" to the walls of the absorption bottle, (3) it does not require "soaking" with $CO_2$ before using, and (4) the same bulk of material has less weight. Its chief advantage over phosphorus pentoxide is that it does not liquefy when it absorbs water; and over conc. sulfuric acid, that it is a solid and therefore readily handled and produces no appreciable back pressure.

In the general description which follows, it is assumed that the substance to be analyzed is a solid and contains no other elements than carbon, hydrogen and oxygen. Further on, the manner of dealing with substances containing in addition nitrogen, the halogens, sulfur, phosphorus, etc., is discussed.

Before taking up the method in detail it seems not inappro-

---

[1] *Journ. Amer. Chem. Soc.*, **37** (1915), 1636–8.

[2] The presence of the copper oxide obviously makes it impossible to estimate halogen or sulfur at the same time as the carbon and hydrogen, as has been worked out by Dennstedt.

[3] *Journ. Amer. Chem. Soc.* **40**, (1918), 460.

[4] Presented by the author at the Cleveland meeting of the American Chemical Society, September, 1918.

[5] That is, as compared with the ordinary "anhydrous" granular calcium chloride. Compare, A. T. McPherson, "*Granular* calcium chloride as a drying agent," *Journ. Amer. Chem. Soc.*, **39** (1917), 1317–9; and Dover and Marden, "A comparison of the efficiency of some common desiccants," *ibid.*, **39** (1917), 1609. Also Baxter and Starkweather, *ibid.*, **38** (1916), 2038.

priate to give the following quotation from Liebig's original directions, as translated by Gregory:[1]

> "*The essential conditions for performing a good analysis are the greatest accuracy in weighing and the strictest conscientiousness in the execution of all the preparatory steps of the process. Let us not flatter ourselves that we can obtain an accurate result if anything be neglected that can secure it. All the time and labor we bestow are thrown away, if we omit any one of the precautions which are recommended.*"

## II. List of Apparatus and Chemicals Required for the Determination of Carbon and Hydrogen

### *Apparatus*

1. Electric combustion furnace (p. 230).
2. Electric pre-heater (pp. 228–9).
3. Tank of oxygen with gauges and iron stand (p. 225).
4. Pyrex combustion tube, 76 cm. long and 15 mm. inside diameter, for combustion furnace (pp. 231–2).
5. Pyrex combustion tube, 36 cm. long and 15 mm. inside diameter, for pre-heater (p. 228).
6. Asbestos paper for lining trough of the furnace and of the pre-heater (pp. 229, 231).
7. Copper gauze, 40 mesh, 1 square foot (pp. 228, 235–6).
8. Copper wire, No. 16, 3 feet long (pp. 228, 235).
9. Bubble counter or gas bubble indicator (p. 227).
10. Six red rubber stoppers, one holed; four of them size 1 or 0, depending upon diameter of combustion tube; and two for calcium chloride tube connections (pp. 228, 242, 245).
11. Rubber pressure tubing (pp. 227, 230, 244).
12. Two U-tubes, with ground-glass stoppers, 12.5 cm. (5 inches) (p. 229).
13. Two Fisher absorption bottles (new style) (p. 237).
14. One calcium chloride tube, as a guard (p. 245).
15. One small bottle for palladious chloride solution (p. 245).

---

[1] "Instructions for the Chemical Analysis of Organic Bodies (1839), 3.

16. Glass tube for palladious chloride bottle (p. 245).
17. One porcelain or quartz boat (p. 236).
18. One special weighing tube, boat tube ("piggie") (p. 251).
19. Two quartz dishes, 7.5 cm. in diameter (p. 238), or one large one 11.5 cm. in diameter, depending upon conditions for heating.
20. Crucible tongs.
21. One pair of pliers.
22. Desiccator.
23. Six pine splinters, 5 to 6 inches, as aids in filling and emptying the absorption bottles (pp. 240 (foot-note), 245).
24. One pair of forceps (long and narrow, curved near the end, somewhat like those used in biological work) for handling the cotton, and for use in filling and emptying the absorption bottles (p. 240).

*Chemicals*

1. 35 grams soda lime, 20 mesh, 2 per cent water (about one filling of U-tube (p. 229) and absorption bottle) (p. 243).
2. 10 grams soda lime, 12 mesh, 15 per cent water (about one filling of absorption bottle) (p. 243).
3. 100 grams aluminium chloride, crystals ($AlCl_3.6H_2O$) (p. 238).
4. 1 ounce of absorbent cotton.
5. 5 grams cerium nitrate (p. 234).
6. 120 cc. pumice, 12 mesh (pp. 234, 238).
7. One vial stop-cock grease, E. & A. (p. 229).
8. Conc. sulfuric acid for bubble counter and desiccator.
9. 100 grams cupric oxide, wire form (p. 236).
10. 20 cc. palladious chloride solution (p. 245).

## III. Topical Outline of the General Method of Procedure

1. Set up the electric combustion furnace (p. 230).
2. Select the combustion tube, and if necessary cut to proper length and "round" the edges (p. 231).
3. Prepare the pumice and cerium nitrate mixture and place in the tube (p. 234).

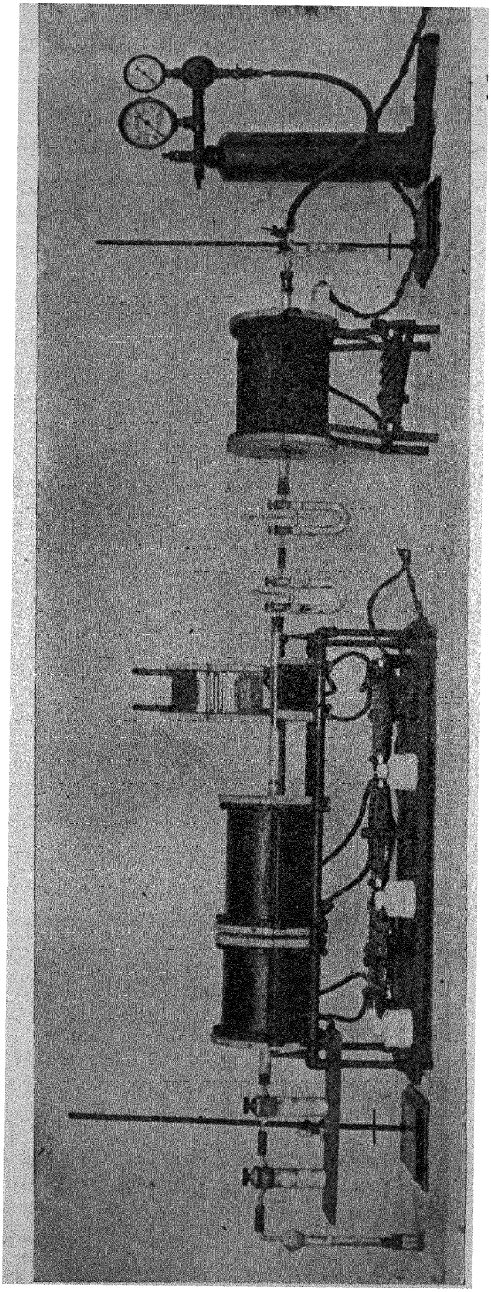
4. Get ready the oxygen apparatus, pre-heater, and purifying train (pp. 225–30).
5. Complete the preparation of the cerium dioxide on pumice in the tube (pp. 234–5).
6. Prepare the guard tube for protecting the combustion tube when the absorption train is not attached (pp. 246–7).
7. Prepare the rolls of copper gauze (p. 235), the copper wire with hook, and fill the remainder of the combustion tube (p. 236).
8. Make the preliminary heating (" glowing out ") (p. 246).
9. During the preliminary heating, prepare the entire absorption train (pp. 236–46).
10. Run a blank determination (p. 246), and weigh out the sample of dry substance (pp. 250–3).
11. The combustion proper (p. 253).
12. Calculate the results (p. 257).
13. Run a " check " determination (p. 256).

## IV. The Apparatus and How to Put it Together with Notes on Manipulation

**1. Tank of Compressed Oxygen with Stand and Pressure Gauges.**—The combustion is carried out in oxygen, which is most conveniently supplied in a tank or cylinder, equipped with the usual gauges,[1] and supported in an iron stand (see Fig. 14, p. 226, and Fig. 16, p. 233). The large gauge registers the pressure in the cylinder and the small one registers the pressure at which the oxygen is delivered. This delivery pressure is regulated by means of a thumbscrew which holds a spring in place upon an internal diaphragm. A small stop-cock is added beyond this gauge in order that the gas supply can be regulated further or shut off quickly when necessary. The operating pressure is generally from 1 to 4 pounds, but this varies greatly with the resistance offered throughout the combustion system. It is

---

[1] While this book is being published, Prof. S. W. Parr has described " A needle valve with delicate adjustment for high-pressure gases," *Journ. Ind. and Eng. Chem.*, **11** (1919), 768, by means of which the gas can be delivered directly from the cylinder without the use of gauges.



*Courtesy of Electric Heating Apparatus Co.*

FIG. 14.—Apparatus for the Determination of Carbon and Hydrogen.

(See, also, diagram Fig. 16.)

regulated in accordance with the gas bubbling. Ordinarily the gas bubbles should come through the bubble counter so fast that they can just be counted, about *three to four* a second. This rate of course varies with the substance being burned.

**2. The Bubble Counter.**[1]—The bubble counter (Figs. 15 and 16) is placed next to the supply of oxygen and is connected with the outlet from the pressure gauges by means of heavy-walled rubber pressure tubing. Only a very small amount of concentrated sulfuric acid is required in this apparatus, usually not over 0.3 cc.[2] A larger amount of the acid gives irregular bubbling on account of the depth of the liquid. The liquid is run in through a small tube or dropped into the *outlet* tube of the apparatus. The apparatus is constructed in such a manner that this small amount of sulfuric acid cannot run out, even though it be turned upside down, and cannot flow back in case of back pressure.[3]

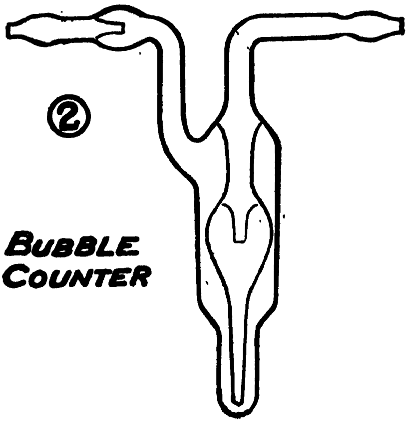


FIG. 15.

---

[1] Also called " Gas bubble indicator."

[2] About 15 drops as counted when dropped from the tip of a small tube, drawn out to a thin-walled opening, 1 mm. in diameter, such as would be used for filling the apparatus.

[3] If some other style of bubble counter is used which is not so constructed that provision is made for possible back flow, then arrangements should be made for attaching an inlet tube containing a bulb like a small pipette which will act as a reserve reservoir for the liquid in case of back pressure.

As stated in connection with the pressure of oxygen under the preceding heading the rate of gas bubbling should ordinarily be so fast that the bubbles can just be counted, three to four a second, although this rate will vary more or less with different substances.

The object of the bubble counter is not only to give one an idea as to how fast the gas is passing into the apparatus, but also to show a comparison between the amount of gas entering the train and the amount of gas leaving the system through the palladious chloride solution (see No. **5c**, p. 245). This will be discussed in detail later (pp. 245, 254).

The bubble counter is connected with the glass tube in the pre-heater by means of a good red rubber stopper. On the side near the oxygen tank it should be supported with a clamp to prevent sagging of the tube in the pre-heater when it is hot.

**3. Gas Purifying Apparatus, including the Pre-heater.**—*The Pre-heater.*—The compressed oxygen generally contains small amounts of impurities and it has been found that it is best and easiest to purify it by passage over hot copper oxide or cerium dioxide on pumice in a "pre-heater" before running the gas through the regular drying train.[1] After this treatment blank determinations will show that the apparatus is ready for use right after the preliminary heating of the combustion tube. Otherwise the percentage of hydrogen will be too high.

Round off the ends of a Pyrex combustion tube, 36 cm. long and 15 mm. inside diameter, in a blast flame. Then put inside a 12 cm. roll of copper gauze or a 12 cm. layer of copper oxide in wire form. The roll of copper gauze or copper "spiral" as this is sometimes called, is made by tightly rolling a piece of copper gauze (40 mesh to the square inch), 12 cm. wide and about 18 cm. long, around a length of No. 16[2] copper wire and bending the projecting ends of the wire into *short* loops close to the gauze.

---

[1] This has been found necessary when the oxygen is manufactured by electrolysis, as demonstrated in our laboratory by Miss Alice R. Thompson. It contains small amounts of hydrogen (0.3 to 1.0 per cent).

[2] Brown & Sharpe gauge.

This tube is heated to dull redness in a 20 cm. (8 in.) electric furnace provided for this purpose. It consists of one of the sections of an electric combustion furnace, mounted like the regular furnace itself, with trough and its own rheostat for temperature control. In order to prevent the glass, if it should melt, from adhering to the trough, place under it a strip of asbestos paper. The ends of the glass tube are allowed to project more than usual beyond the furnace, since all precautions must be taken to prevent the rubber stoppers from burning.

*The Purifying Train.*—The oxygen must be freed from any possible traces of carbon dioxide and water, and therefore it is next passed through a 12.5 cm. (5 in.) U-tube[1] containing soda lime (20-mesh size and containing 2 per cent of moisture) and then through another U-tube containing alumina-pumice.[2] These U-tubes should be fitted with ground glass stoppers[3] and should have glass braces[4] to give strength and to prevent breakage. The stoppers must be greased with a good stop-cock grease[5] in such a way that they present a clear surface showing good contact. Too little grease makes a stopper stick or leak; too much often stops up the openings and also makes the stopper so loose that the gas pressure may force it out of the tube. Never turn a stop-cock by using only one hand. Use the other hand at the same time to hold the U-tube, then you can be sure that the stopper is in tight and that there are no channels. The stoppers should be kept closed when the apparatus is not in use. This applies particularly to the alumina-pumice U-tube.

---

[1] A small funnel of thin glass with a wide stem is very useful in filling the apparatus.

[2] See p. 238 for preparing the alumina-pumice.

[3] Fasten these stoppers loosely with wire or twine, otherwise, if excessive pressure is developed, they may be forced out and the stoppers broken. This causes much inconvenience. Do not use rubber bands. On account of their elasticity they often alter the position of the stopper after it has been set.

[4] R. Nowicki, *Chem. Ztg.*, **28** (1904), 622; McIntire, *Journ. Amer. Chem. Soc.*, **33** (1911), 450–1 (like the ones shown in the figure). For other similar types, see Abderhalden's "Handbuch der Biochemischen Arbeitsmethoden," VIII (1915), 400–1.

[5] Do not use vaseline, since the stoppers are likely to stick. Eimer & Amend, N. Y., furnish a good stop-cock grease in handy soft metal tubes.

Place a wad of absorbent cotton on top of the material in each arm of the U-tubes to keep the stop-cocks free from dust particles.

Connect the U-tubes by means of rubber pressure tubing. It is well to support these U-tubes by means of a clamp around the rubber connection. This prevents any sagging of the tubes in both pre-heater and combustion furnace when they are hot.

The preparation of the aluminium oxide on pumice is described in connection with the absorption bottle for water (see **5a,** p. 238). The same kind of material must be used here for drying the gas as is used for absorbing the water in the absorption train, otherwise there will be discrepancies in the percentage of hydrogen.[1]

Instead of the U-tubes any variety of absorption apparatus may be used. No weighing is necessary and therefore the shape does not require consideration. The same type of absorption bottles as described in the absorption train can be used if desired.

If many combustions are to be run, the purifying train should consist of more U-tubes, or of larger apparatus according to conditions.

**4a. The Electric Combustion Furnace.**—The multiple unit type of electric combustion furnace is the most convenient to use.[2] Each heating section is regulated by its own rheostat placed underneath and is fitted with replaceable heating units. The upper part of each section can be lifted and the tube examined *at any time* during the course of the combustion. The maximum current requirement is from 12 to 18 amperes, depending upon the model. The units are so well insulated that parts of the tube may be heated to redness while other parts remain cool fairly close to the unit. This insulation to prevent loss of heat is a boon to the manipulator also because it makes it possible to run combustions in a small room even in summer time

---

[1] See, also, Morse, " Exercises in Quantitative Chemistry" (1905), pp. 340–2, 353–4, where data are given to illustrate the difference in the absorption capacity of warm and of cold calcium chloride, and of conc. sulfuric acid.

[2] Multiple unit electric organic combustion furnace, Type 122–S, manufactured by the Electric Heating Apparatus Co., Newark, N. J., is built in accordance with the specifications given in this description.

with no more discomfort than in carrying out ordinary work. The trough for supporting the combustion tube is made of nickel and therefore it does not corrode appreciably even in the high heat. A strip of asbestos paper is placed in this trough and then, if the glass melts, it will not stick to the metal and crack on cooling. In case the tube does crack, turn off the current and when the furnace is cold remove any copper oxide wire that might get among the wires of the heating units when the glass is taken away, otherwise short circuits will result later.

The electric combustion furnace is ordinarily supplied with three heating sections of unequal lengths. Each of these can heat the tube to redness. The longest section (No. 2)[1] should be in the center. The heat regulation of the smallest section (No. 1) should be such that when the current is on and all resistance in, the temperature should not be above 40°–50°. When necessary, it should be possible to keep the section of medium length (No. 3) at 300°–320°, since this is the temperature required when the lead peroxide mixture is used in the combustion of substances containing nitrogen and sulfur. (See p. 265.)

Each rheostat is generally arranged in such a way that when the handle is at the right all the resistance is in and therefore this position gives the lowest temperature. The heat is increased by moving the handle toward the left.

The temperature must be carefully watched when the coils of wire are red, since it gradually rises and thus may cause the tube to melt after a time. In a well-lighted room it is difficult to tell the temperature by the color of the wires. However, if you lift the upper half just a little so that the inside is shaded, you can then obtain a good idea of the color and be able to judge the temperature properly.

The handles on the upper section should be wound with asbestos cord to make it possible to touch them with the fingers at any time. A piece of heavy white rubber tubing serves well in place of the asbestos cord.

**4b. The Combustion Tube and How to Fill It.**—For combustion tubing, Pyrex glass is generally better than Jena or Bo-

---

[1] The sections are numbered correspondingly on the diagram, Fig. 16, p. 233.

hemian glass since it does not vitrefy and become opaque at the required high temperature.[1] Select a combustion tube of 15 mm. inside diameter and of such a length (about 76 cm.) that it will extend 3–4 cm.[2] beyond the ends of the nickel trough.[3] Usually this amount of extension is sufficient to prevent the burning of the rubber stoppers. The end next to the absorption train should not be so long that much water can condense since it is difficult to drive this water through.

Round off the edges of the tube by gentle heating first and then with a blast flame, so that they will not cut the rubber stoppers. Do not change the bore of the tube!

Clean the combustion tube, and fill it as indicated in the diagram, Fig. 16, making sure that the positions of the materials, etc., are in proper relation to the sections of the furnace. The dimensions given are for the 72 cm. (28½ in.) furnace. Even if a longer furnace is used, the positions of the cerium dioxide and the boat should be relatively the same as described here, the extra length being taken up simply with more copper oxide wire.

---

[1] Where many combustions are to be run, a quartz tube with a transparent section where the boat is placed is both advantageous and economical. Levene and Bieber, *Journ. Amer. Chem. Soc.*, **40** (1918), 460.

[2] A longer extension is necessary when a gas furnace is used.

[3] Pyrex combustion tubing is cut with a narrow grinding wheel. The ordinary methods cannot always be used, since the expansion of the glass on heating is so small. Some of these methods, however, do work sometimes and are given here for sake of convenience.

1. Make a short file mark at the desired length and then heat the tube at this point by giving a piece of twine two turns at the mark and drawing the twine up and down rapidly several times while the tube is held securely by another person on the desk with the edge for a guide. Then immediately put the tube under cold water, or apply a wet cloth.

2. A second method of cutting the glass tube is to make the file mark as above and then heat this mark very carefully with the *slanting* tiny flame from a capillary tube. This tube can be made of glass, although a metal one is of course preferable. As soon as a crack is formed follow it with the tiny flame until it extends clear around. Do not point the flame directly at the tube, always slant it, otherwise the crack may extend longitudinally.[1]

3. Another method consists in winding a platinum or nichrome wire around the tube and then heating it to redness by means of an electric current.

[1] K.H. Parker, *Journ. Amer. Chem. Soc.*, **40** (1918), 195, described "A new glass cutting tool,"—a small gas-heated iron for which he claims excellent results.

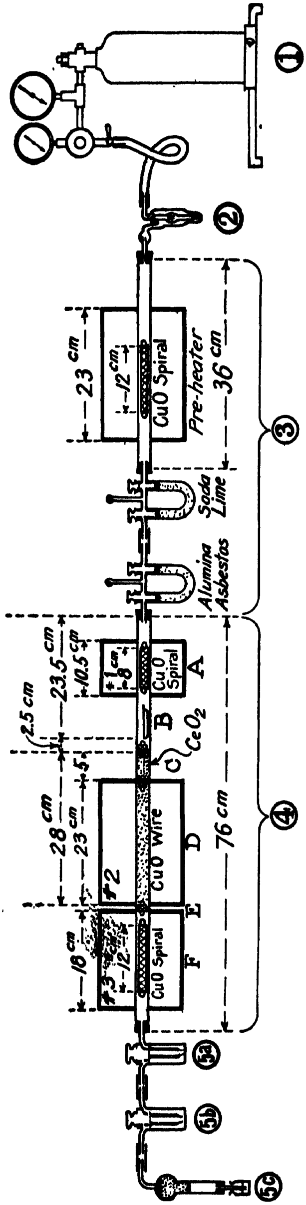


FIG. 16.—Diagram of Apparatus for the Determination of Carbon and Hydrogen.

Prepare the cerium dioxide *first*. Use enough pumice[1] of 12-mesh size to fill 5–6 cm. of the tube. Dissolve 5 grams of pure white crystals of cerium nitrate in enough water (about 12 cc.) to cover the pumice in a quartz or porcelain dish. Evaporate this mixture to dryness on the steam-bath, with frequent stirring to prevent formation of a cake. Then transfer this impregnated pumice to the tube and put the asbestos wads in place by means of a long glass rod flattened at one end. The asbestos wads should not be over 0.5 cm. in width, and the asbestos must not be so tightly packed that the oxygen gas will not go through it. This can be remedied when it is in place by putting in tiny holes, if necessary, with a long glass rod drawn out to a point. Support the asbestos wads in position by using a roll of copper gauze, 0.5 cm. in width. This prevents them from crumbling and from being moved out of position by the force of the gas, etc. It is important for proper heating that the cerium dioxide be placed in the relative position shown in the diagram (*C*) and also that the end of the boat be not more than 2.5 cm. distant, in order to prevent the formation of explosive mixtures of gases. Therefore the size of the asbestos wad and the short rolls of copper oxide gauze must not be greater than mentioned above. Complete the drying by heating the tube at a *low* temperature and at the same time passing a current of pure dry oxygen through the tube. As soon as no more moisture collects in the cool end of the tube gradually raise the temperature while the oxygen is still passing and finally complete the decomposition of the cerium nitrate at dull red heat.[2] Allow to cool in the current of dry oxygen or attach a drying tube to the open end of the combustion tube. When hot, the

---

[1] Pumice is used instead of asbestos, then the material does not crumble and "sag." Fisher and Wright, *Journ. Amer. Chem. Soc.*, **40** (1918), 869.

[2] This procedure is used in accordance with the suggestion of Levene and Bieber, *Journ. Amer. Chem. Soc.*, **40** (1918), 460, who found that when the decomposition was carried out over a gas burner the oxide was not always so good a catalyst as when prepared as above.

If the material is heated too much at first some of it is driven out of the pumice and deposited upon the inner walls of the tube, where it will remain when dry and form an opaque layer. No special harm is done if this happens.

cerium dioxide is deep yellow, but this color changes to a straw yellow when the material is cold. Complete the preparation of the cerium dioxide *before* putting any of the other substances into the tube. Otherwise the copper nitrate which is formed may cause trouble later by slowly being decomposed and giving off oxides of nitrogen which are caught in the absorption train. The small rolls of gauze next to the asbestos need not be considered in this. Once the cerium dioxide has been prepared it will remain ready for use at any time provided, of course, that the combustion tube is kept stoppered when not in use.

For position *A* prepare a roll of copper oxide gauze, 8 cm. long, by rolling a piece of copper gauze (40 mesh to the square inch), 8 cm. wide and about 18 cm. long, around a length of No. 16 copper wire (B. & S. gauge) and bending the short projecting ends of the wire into *short* loops close to the gauze. It should be rolled tightly. Let it remain in the tube overnight if possible and become molded to the proper shape and size. When oxidized it should fit the tube snugly but not so snugly that it sticks and cannot readily be withdrawn. After it has remained in the tube overnight cut off some of the gauze if necessary. The gauze usually is covered with more or less grease and dirt and if directly oxidized in the tube the inner walls of the glass often become coated with a black layer of fine copper oxide which makes the tube opaque. Therefore it is best to oxidize the roll of gauze (or copper " spiral " as it is sometimes called) in a large blast flame or over a Meker burner, before heating it in the tube.

The copper oxide gauze is moved back and forth in the tube by means of a stout copper wire with a *short* hook bent at *right* angles.

The object of this roll of gauze is twofold: In the first place it acts as an " oxidation buffer," that is, it oxidizes any gases that may go backward, and thus prevents them from getting so far back that the determination is spoiled. Furthermore, by its very shape, size, and position it causes the oxygen to flow through its interstices more rapidly than in the open spaces of the tube before and after and in this way tends to keep any unoxidized gases which may go backward from getting beyond it before they are completely oxidized.

The intervening space of 12 cm. between the roll of gauze at *A* and the cerium dioxide at *C* is reserved for the boat *B*. As stated above (p. 234), the boat should be placed within about 2.5 cm. of the cerium dioxide. A greater distance will allow the formation of explosive mixtures of oxygen and the gases from the substance.

Ordinarily a porcelain or quartz boat 7 cm. long is used. Clean it with dilute nitric acid, heat in a blast flame and allow to cool in a desiccator. A longer boat is used for very light and fluffy materials. A boat with little compartments aids the burning of a substance which decomposes readily. The compartments prevent that portion of the substance that has melted from mixing with the unmelted portion.

For weighing out sample, see p. 250.

Beyond the cerium dioxide in space *D* put a 23 cm. layer of cupric oxide [1] in wire form and keep it in place with a short roll of copper oxide gauze *E*. Cupric oxide is very hygroscopic.

The 12-cm. space at *F* is reserved for the lead peroxide mixture which is used when substances containing nitrogen and sulfur are burned. (See p. 265.) Otherwise it may be filled with copper oxide wire.

**5. The Absorption Train.**—The absorption train is made up of two absorption bottles, the first one for collecting the water and the second one for the carbon dioxide, and a guard tube and bottle of palladious chloride solution. The absorption apparatus selected should be one that is capable of being readily and thoroughly cleaned, easily filled and emptied, handled without difficulty, of a moderate capacity, and when filled not weighing over 100 grams. For carbon dioxide absorption, it should have two chambers which can be entirely shut off one from the other when the apparatus is not in actual use. It is believed that the

---

[1] Cupric oxide which has been used in the determination of nitrogen cannot be used for carbon and hydrogen since it contains some carbon dioxide, unless it has been heated for several hours in a stream of oxygen or in the open air. Compare foot-note, p. 284.

absorption bottle[1] shown in Fig. 17, fulfills these requirements.

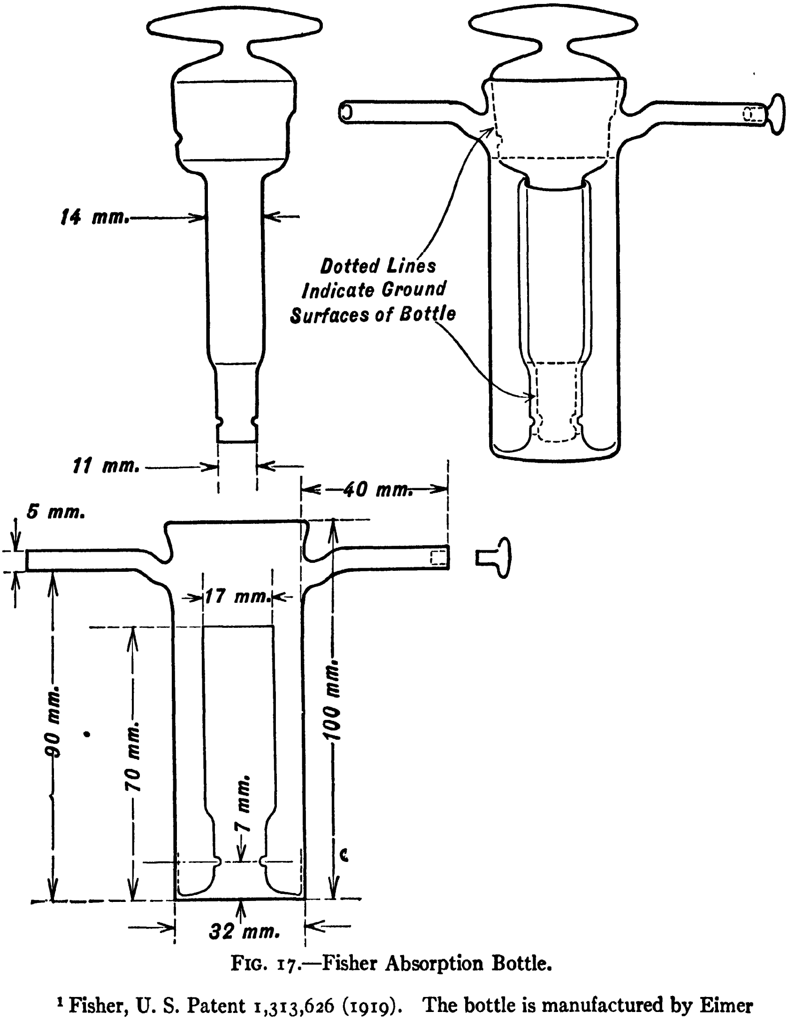


FIG. 17.—Fisher Absorption Bottle.

---

[1] Fisher, U. S. Patent 1,313,626 (1919). The bottle is manufactured by Eimer & Amend, New York. The forerunner of this particular bottle had no means of shutting off the two chambers, and the stopper was ground in to fit the top of the inner standing tube instead of the bottom. See Fisher, " A new form of absorption bottle for use with either calcium chloride or soda lime in the elemental analysis of carbon and hydrogen in organic substances," *Journ. Ind. and Eng. Chem.* **8** (1916), 368.

Other forms of absorption bottles and tubes can be found in the apparatus catalogues.

The bottle is literally a U-tube turned partially inside out. The available capacity of the stopper and its extension tube is 25 cc., and of the outer chamber of the bottle, 25–30 cc., making a total available capacity of 50–55 cc. By way of comparison it is of interest to note that an ordinary 5-inch U-tube has a total available capacity of only 20–25 cc.

**a. The First Absorption Bottle.**—Aluminium oxide (alumina) is used for absorbing the water formed in the combustion. It is mixed with pumice to make it more porous. The use of alumina is described first. Following this, on p. 239, is a description of the use of calcium chloride for the absorption of water. It should be borne in mind that whatever absorbing agent for water is used here, the same one must also be used in the soda lime bottle and in the drying train (compare p. 230).

**Preparation of Aluminium Oxide (Alumina) for the Absorption Bottle.**—Dissolve 50 grams of hydrated aluminium chloride ($AlCl_3 \cdot 6H_2O$) in 100 cc. of warm water in a 11.5 cm. quartz or porcelain dish and stir in 50 cc. (about 24 grams) of 12-mesh pumice.[1] Boil down this mixture over a wire gauze or asbestos disk with a free flame. Stir well with a stout glass rod after most of the water has disappeared, since it foams a good deal and will also form a cake. The particles of pumice should be kept separated as far as possible. Continue the heating and stirring until there is no danger of later fusion of the hydrated salt and agglomeration of the small lumps of impregnated pumice. Transfer this material to a 7.5 cm. quartz or porcelain dish and heat in an electric muffle furnace to 700°–750°[2] until no more hydrogen chloride is given off. A higher temperature should not be used. The time can be shortened to thirty to forty-five minutes if a stream of air is blown or drawn through the heating

---

[1] These amounts are for the first absorption bottle. Double them or make up a second batch in order to have enough for all requirements. On account of the foaming, the evaporation is best done in this larger dish. The final heating can also be done in this same dish, but it is too large for the ordinary muffle furnace, which has an opening only 10 cm. wide.

[2] *Approximately* these same conditions can be obtained by heating the mixture in the dish on a nichrome gauze at the tip of a non-luminous flame 5 cm. high, for 1½ to 2 hours.

chamber to remove the gaseous products. Traces of hydrogen chloride can of course be detected with the nose or by means of ammonium hydroxide. At the end of the heating the dishes should be cooled in a desiccator which has no other substance in it. A vacuum desiccator is convenient to use since the pressure inside from the heated atmosphere can be released with the stop-cock. If the heating is too long or too high the alumina will no longer cling to the pumice, but will drop off as a fine powder. It will do this to some extent under any conditions.

According to Johnson[1] the alumina is an excellent drying agent up to the time that it has absorbed about 18 per cent of its weight of water at ordinary temperature. Fifty grams of hydrated aluminium chloride theoretically yields about 10.7 grams of aluminium oxide, and this amount ought to absorb about 1.92 grams of water under ideal conditions. If we consider the average organic substance as containing about 5 per cent of hydrogen, then a 0.2 gram sample will yield approximately 0.09 gram of water, and on this basis the aluminium oxide theoretically ought to suffice for twenty-one combustions. In practice the mixture can safely be used for four to five combustions.

NOTE.—Originally the author used asbestos instead of pumice in order to give plenty of surface, and prepared the reagent by heating 10 grams of pure aluminium hydroxide with 2 grams of asbestos, as described above. The aluminium hydroxide must be free from alkali. When mixed with neutral water it should give only the faintest color with phenolphthalein (compare curve on p. 1500 in article by Blum, "The Constitution of Aluminates," *Journ. Amer. Chem. Soc.*, **35** (1913)). The alumina-asbestos mixture is very efficient as shown in this laboratory by Mr. Henry L. Faust, but it packs very readily and then it requires three to four hours for the complete passage of carbon dioxide through it, in some cases. The material can be regenerated by re-heating, but after a time the asbestos crumbles to a powder. Pumice was being considered in place of the asbestos when Mr. Geo. H. Walden suggested the use of hydrated aluminium chloride as the source of alumina instead of the aluminium hydroxide.

**The Use of Calcium Chloride.** Calcium chloride should be in a granular porous form (size about 8-mesh) and free from dust particles, when used in the absorption train. The ordinary "anhydrous" material as obtained on the market can be made much more efficient by heating it to 260°–275° in a current

---

[1] *Journ. Amer. Chem. Soc.*, **34** (1912), 911–2.

of air dried over phosphorus pentoxide.[1] Even this porous material, however, which contains some surface moisture, is better than the fused calcium chloride. Calcium chloride generally contains basic substances and these absorb carbon dioxide. On that account it must be saturated while in the absorption bottle with carbon dioxide by passing a stream of the *dry* gas through it for two hours and then displacing this with *dry* air or oxygen. Or, better, after driving out all the original air with dry carbon dioxide (one-half hour), let it stand overnight, and then displace the gas with dry air or oxygen.[2]

The amount of moisture absorbed by calcium chloride varies with the temperature even around the temperature of ordinary working conditions.[3] This is sometimes very important since the temperature of the calcium chloride in the drying train is seldom the same as that of the calcium chloride in the absorption train.

*To fill*[4] *the absorption bottle:* Remove the stopper and its extension tube. Place a flat wad of cotton over the hole in the inside of the stopper[5] and *rapidly* fill the stopper and its extension tube with some of the alumina-pumice. Put in a plug of absorbent cotton near the end. Place this filled part of the bottle immediately into a desiccator over fresh conc. sulfuric acid. Without any delay, put some cotton at the bottom of the outer

---

[1] A. T. McPherson, "Granular Calcium Chloride as a Drying Agent," *Journ. Amer. Chem. Soc.*, **39** (1917), 1317–9.

[2] Morse, "Exercises in Quantitative Chemistry" (1905), 340, 354, states that these methods are open to objections since the conversion into the carbonate is only superficial, and when the moisture comes in new surfaces are exposed. He also states that calcium chloride may be obtained in a neutral condition, that is, free from oxide, by evaporating a solution of the chloride with ammonium chloride and heating the residue until the latter salt has been expelled.

[3] Morse, *ibid.*, 340–1.

[4] A long narrow pair of forceps with slightly curved ends, such as are used in biological work, and a pine splinter, will be found very convenient as aids in filling and also emptying the bottle. The pine splinter is used instead of a piece of metal since a scratch on the inside of the bottle will almost invariably cause a crack. Similarly a glass rod with a sharp end should not be used. If a wire is used, be sure that the end is protected with cotton.

[5] But do not fill the entire stopper with cotton, since the space is needed for the drying agent.

chamber of the main part of the bottle to keep particles from sifting through the holes and getting upon the ground surface. Insert a plug of cotton or a cork in the top of the inner standing tube in the center of the bottle, and then *quickly* fill the outer chamber with the alumina-asbestos mixture. Pack in some cotton above it near the top of the tube. This keeps the fine particles from getting upon the ground surfaces of the stopper and also from being blown out into the side arm. Take out the cotton or cork from the top of the inner standing tube, quickly remove all dust particles from the ground surfaces in the bottom of the bottle and at the top by means of cotton held in the forceps, carefully grease with a good stop-cock grease[1] and insert the stopper. Do not use vaseline, since it has no "body" and is too " thin," and causes sticking of the stopper. The ground surfaces, when properly greased, will appear clear, showing that the joints are gas tight. Great care should be used in greasing the lower ground joint. Too little grease will make it stick and too much may close the holes. If this ground joint becomes " frozen " there is little hope of being able to open the bottle. Keep the cotton from coming in contact with the ground surfaces.

This bottle ought to be provided with a small ground stopper[2] in one arm, and this arm is the one that is next to the combustion tube. Then when the combustion is over and the rubber stopper removed, the ground stopper is inserted and any water that may remain in the arm cannot evaporate during further manipulations. Only a very small amount of grease, if any, should be put on this stopper on account of the danger of rubbing it off and thus causing loss of weight.

The side arms of the bottle are bent slightly upward near

---

[1] See footnote, p. 229.

[2] In case the absorption bottle is not provided with a small ground stopper, attach a short piece of rubber tubing and plug up the open end with a piece of glass rod. This serves to prevent the evaporation of any moisture that may remain in the arm. Since the rubber may vary in weight under the different conditions of treatment it should be removed and the arm carefully cleaned before the bottle is weighed.

the neck in order that any droplets of water that may collect will remain in the depression and not tend to run along the arm during subsequent handling. The side arms should be free from any dust particles which might be lost during the operation and change the weight. The cotton inside the bottle is used partly to prevent any particles from being carried by the gas into these side arms.

Connect the arm prepared for the small stopper *directly* with the combustion tube by means of a good rubber stopper.[1] In doing this do not grasp the bottle itself—take hold only of the side arm. Otherwise the arm may be broken off. *Do not use any intermediate tube since water will collect in it and stay there.* The ordinary rubber stopper is about 25 mm. long and tapers considerably. Since a snug fit is necessary and since precautions must be taken in order that the rubber stopper can easily and quickly be removed from the absorption bottle at the end of the combustion, cut off the ends of the stopper in such a way that it will be about 12–13 mm. long and that it will fit in the tube without leaving any spaces for the collection of water between the stopper and the tube. A longer stopper is very difficult to remove from the absorption bottle after the arm has been heated by the hot gases. Red rubber stoppers are the best. They should be thoroughly cleaned and all moisture removed. Sodium hydroxide will help to remove any sulfur.

The gases can be passed through either the inner or outer chamber first by changing the position of the large stopper. Since some heat is evolved in the absorption of the water, it is better to pass the gas through the outer chamber first. In subsequent combustions the gas must be passed *in the same manner*, otherwise there is the possibility of the gas leaving the bottle with some moisture which it has taken up from the part already more or less saturated in a previous run.

This absorption bottle and the one described next, when not in use, should be kept in a box packed with cotton for proper protection from breakage and dirt.

---

[1] *Carefully* breathe through the stopper for a moment and then it will slip over the tube more readily. Do not allow any excess of moisture to remain.

Before emptying the bottle, remove the grease from the ground surfaces with cotton.

**b. The Second Absorption Bottle.** The carbon dioxide absorption bottle is filled with moist soda lime in the outer chamber and with alumina-pumice in the inner chamber. The alumina must be used since the gas becomes moiast fter passing through the soda lime, and it must of course leave the bottle in as dry a condition as that in which it entered. The absorption bottle for this work is constructed with the idea of preventing the alumina from absorbing moisture from the soda lime when it is not in use. The only time that the two chambers are in communication is when the stopper is in " running " position.

Place some cotton in the outer chamber at the bottom of the bottle around the holes at the base of the tube, insert a plug of cotton or a cork in the top of the inner standing tube, and fill the outer chamber with three layers of moist soda lime.[1] The bottom layer and the top layer should consist of soda lime with 2 per cent of water and of 20-mesh size, the middle layer of soda lime with 15 per cent of water and of 12-mesh size. Cover the top with cotton to keep it in place. Then quickly fill the inner stopper and its extension tube with the alumina-pumice, and properly protect it with cotton, as in the case of the first absorption bottle (p. 240, see footnote 5). Be sure that the flat wad of cotton covers the hole in the stopper and that most of the stopper is filled with the drying agent. This can conveniently be done if it is filled while the stopper is inclined

---

[1] Soda lime is a mixture of sodium hydroxide and calcium hydroxide, and comes on the market in granular form of different sizes as anhydrous material and with different amounts of moisture. The anhydrous soda lime does not give rapid and complete absorption. (Compare Lamb, Wilson and Chaney, " Gas Masks Absorbents," *Journ. Ind. and Eng. Chem.*, **11** (1919), 437–8.) A simple method of distinguishing between the anhydrous material and that containing moisture is to heat the sample in a test-tube and note whether moisture condenses on the upper walls. The absorption bottle described above will hold a total weight of about 20 grams of the moist soda lime.

" Soda asbestos," a mixture of sodium hydroxide and asbestos in granular form, is recommended by G. L. Kelly, *Journ. Ind. and Eng. Chem.*, **8** (1916), 1038. See, also, Stetser and Norton, *Iron Age*, **102** (1918), 443–5; and Rogers, *Canadian Chem. Journ.*, **3** (1919), 122.

with the hole underneath. Rapidly clean the ground surfaces, and grease and put together as described above. See that the cotton does not get on the greased ground surfaces and also that the arms are free from particles. The glass stopper for one arm is, of course, not necessary in this bottle.

Connect this absorption bottle with the first absorption bottle by means of 3.5 to 4 cm. of heavy-walled rubber pressure tubing.[1] Here also do not grasp the bottle itself, but take hold only of the arm (compare p. 242). In order to avoid loss of gas the arms of the two bottles should almost meet, but care is necessary to prevent the edge of one from rubbing against the other since the glass is easily chipped off when they are brought together inside the heavy tubing. Sometimes it is advisable to wire these joints with No. 16 copper wire.

The gas must be passed into the *outer* chamber first.

One charge of soda lime (about 20 grams) is good for two combustions. Sometimes it can be used for one or two more, but then there is always a risk that the absorption may not be complete. Soda lime, when moist, absorbs carbon dioxide very rapidly and gives off considerable heat. Sometimes the soda lime is of a light yellowish-brown color which is due to the presence of some compound of iron from the pots in which it is prepared. As the absorption progresses, the color changes to white and thus it gives a measure of how much soda lime is being used. It is noticed that the color changes evenly as the absorption takes place. The presence of iron also helps by accelerating the rate of absorption, according to Guareschi.[2]

On account of the heat generated during the absorption, droplets of water will sometimes collect on the walls in the upper part of the outer chamber. This, of course, will do no harm.

In cases where many combustions are being run, and especially where extreme accuracy is required, it is desirable to add another

---

[1] *Carefully* breathe through the tubing. Compare note on the rubber stopper, p. 242.

[2] " Supp. ann. all'enciclopedia di chimica," Aug., 1915, *Chem. Abstracts,* **10** (1916), 25.

absorption bottle filled like the one described above with both soda lime and alumina-asbestos. This is weighed also and its weight indicates when the first bottle will no longer absorb carbon dioxide completely. Or instead, the second bottle of the train may be filled only with soda lime and the third one only with the alumina-asbestos. When the blank run (p. 246) is made with this latter combination, the third bottle should gain as much as the second bottle loses. In both of these combinations the *sum* of the gains of *each* bottle at the end of a combustion represents the total increase in weight due to carbon dioxide.

*Note on emptying the bottle.*—The soda lime becomes hard and caked on standing after the absorption of carbon dioxide and care must be exercised in removing it. A pine splinter[1] is useful in breaking up the mass. Often it becomes necessary to moisten the mass to soften it. Too much water must not be used and it must be poured off at once, otherwise the bottle may be cracked on account of the heat and expansion of the mass. Dilute hydrochloric acid will remove the particles adhering to the walls. The alumina-pumice must also be renewed.

**c. Guard Tube and Palladious Chloride Solution.**—To the carbon dioxide absorption bottle attach an ordinary calcium chloride tube which has the small end bent at 90°, and which has been half filled with the alumina-pumice mixture kept in place with plugs of cotton. At the wide end of the tube arrange a short glass tube, with a narrow opening, for leading the gas into a very dilute solution of palladious chloride. By leaving the drying tube half empty, we have a reservoir for any of the palladious chloride solution that might be drawn back, and thus it is prevented from entering the absorption bottle.

The palladious chloride solution is used for detecting any carbon monoxide from an incomplete combustion and also for indicating the rate of absorption of the products of combustion by comparing the bubbling here with that in the bubble counter. This will be discussed later (see p. 255). The solution is of a light-yellow color, and is prepared by mixing 1 cc. of a

---

[1] See foot-note, p. 240.

5 per cent solution of palladious chloride with 200 cc. of distilled water. From this very dilute solution carbon monoxide precipitates metallic palladium, which appears as black colloidal particles. The solution should be protected from any carbon monoxide in the room, especially when the laboratory is supplied with water gas. When in use the bottle should have a stopper through which passes the glass tube and which has a channel cut in the side to allow the gases to escape.

The short glass tube mentioned above leading into the palladious chloride solution, should be drawn out into a narrow opening like the one in the bubble counter, in order that the comparison of the rate can be made. Since the viscosity of the sulphuric acid is different from that of the palladious chloride solution and since the gas pressures are also different in each case, the rate of bubble formation will not be exactly the same, but a good idea of the "normal" rates can be obtained by comparing the bubbling before the substance begins to burn.

Instead of the small bottle for the palladious chloride solution a bubble counter can be used. In this case the drying tube preceding it is placed in a horizontal position. It is difficult to clean the bubble counter. If metallic palladium is precipitated it can be dissolved in nitric acid.

### V. Method of Running Blank Determinations

Since there is the possibility of many errors in the apparatus and chemicals; no combustion should be run until the operator is certain that everything is all right. The only satisfactory method of finding this out is to run a blank determination.

After the apparatus is all set up (without the boat and the absorption train), heat the combustion tube to the same temperature that will be used later in the determination, that is, to a cherry red, and pass in purified oxygen gas at the proper rate during the course of about two hours. This procedure is sometimes called "glowing out." At first, moisture will condense near the open end of the tube. After this moisture has disappeared attach an ordinary calcium chloride drying tube filled with granular anhydrous calcium chloride, which is properly protected at each end with plugs of cotton. Later a drying tube filled with the alumina-pumice can advantageously be used. The combustion tube should now be in good condition but the final proof is made as follows:

Remove the drying tube from the end of the combustion tube, and, without changing the heating or the oxygen gas,[1] attach the entire absorption train as if for a regular combustion. The bottles can be supported by means of copper wire hooks hung from a rod, or simply allowed to stand on a platform arranged at the proper height. They can be protected from the heat of the furnace by means of an asbestos shield. After thirty or forty minutes, disconnect the absorption train, replace the drying tube, and immediately weigh the absorption bottles. See p. 248 for weighing these bottles. Then re-attach the absorption train and allow it to remain under the same conditions as before for another thirty or forty minutes.[2] Weigh again in the same order as before. If the difference in each case is *not* greater than 0.0002 to 0.0003 gram the entire apparatus may be considered as all ready for the combustion. If necessary try another blank run. If the first absorption bottle continues to gain, then the purifying train is probably not doing its work and the alumina should be renewed. If the second absorption bottle containing the soda lime loses weight then the alumina-pumice has become saturated with moisture and must be renewed, or it is insufficient in amount.

Be sure to attach the drying tube to the end of the combustion tube, every time the absorption train is removed.

The error as shown by the blank determination should be a minimum, not more than the error in weighing. Other errors due to burning the sample, to improper weighing, etc., are likely to occur, but these can be more readily remedied provided the apparatus itself is all right.

---

[1] Do not allow the absorption bottles to remain long stoppered up after attaching since the pressure of the oxygen will become so great that the stoppers will be blown out. The stoppers can be put in " running " position *just* before attachment and then there will be no chance for trouble.

[2] During this time the substance can be weighed out. See p. 250.

In a later chapter the relative weight of the small variations in the blank runs are discussed (p. 259).

## VI. Weighing the Absorption Bottles

It has often been found that the greatest of all the errors lies in the weighing of the absorption bottles. The method given here is not claimed to be perfect but in our experience it gives excellent results. When it is considered how many changes the absorption bottle goes through, changes due to the passage of hot gases, handling in making the connections, deposits from the laboratory atmosphere of dirt and moisture, etc., it is no wonder that concordant results cannot be obtained unless great care and consistent treatment is given.

In the first place, the absorption bottles should be weighed each time right after being removed from the combustion tube.[1] Then general conditions will always be as nearly the same as practicable. The only alternative would be to let the bottles stand for many hours, but this of course cannot usually be done.

The bottles must be scrupulously clean when being weighed, otherwise surface conditions would vary too much. Wipe them very carefully with a clean dry cloth which is free from sizing and starch. A towel or handkerchief which has been washed many times is suitable. Good quality lens cloth is excellent for this purpose. It should only be used a few times. Make sure that all excess of grease around the stopper is removed by the first wiping in order that later cleanings will not change the weight on this account. Wipe very thoroughly *every part* of the bottle.[2] Be careful not to break off the side arms. It may be necessary to rub hard at first, but afterwards this should not be done since rubbing with a dry cloth induces a static charge of electricity and this apparently has much to do with discordant results when the apparatus is weighed under these conditions.[3]

---

[1] Dudley and Pease, *Journ. Amer. Chem. Soc.*, **15** (1893), 541; Levene and Bieber, *Journ. Amer. Chem. Soc.*, **40** (1918), 462.

[2] A disadvantage of many kinds of absorption apparatus is that they cannot be cleaned properly.

[3] H. K. Miller, in an article on " Electrical Disturbance in Weighing" (*Journ. Amer. Chem. Soc.*, **20** (1898), 428), states that " Careful experiments led to the

A change of several milligrams is a common occurrence. In order to dissipate this static charge some analysts allow the absorption apparatus to remain for a definite time (four minutes, for example, on the balance pan after wiping before taking the final weight[1]). However, there is a question whether the conditions are always the same since the wiping is not always the same. The bottle cannot be left too long before weighing, because as the charge is slowly being dissipated, and the apparent weight becoming less, it will begin to gain on account of the deposit of moisture, and no constant weight will be found.[2]

Another method to obtain a constant weight after the wiping is to pass the thumb and one finger down opposite sides of the bottle at the same time, and then immediately set the bottle on the balance pan and weigh. Repeat the alternate wiping and passage of the thumb and finger and weighing until the weight is constant or does not vary in two consecutive weighings by more than 0.0002 gram. This may require from four to ten complete repetitions. Perhaps the use of the fingers on the bottle just before weighing is open to question, but the method gives such good concordant results and is so rapid that we are willing to recommend it. The fingers should be clean, and are usually

---

conclusion that in wiping the flask it became electrified, and that this static charge, acting on the floor of the balance, induced on it a charge of opposite character, and that the mutual attraction between these two charges of electricity had the effect of apparently increasing the weight of the flask. The potential of the charge would vary with the atmospheric conditions and with the manner of wiping the flask. By using a linen cloth in very dry weather, it was found possible to produce a charge on a 100 cc. flask which would require 0.08 gram additional weight to restore equilibrium. A high charge like this, however, would be rapidly dissipated and the flask would appear to lose weight. It was found that a charge which apparently caused an increase in weight of about 0.01 gram would be retained quite a long time, and one might readily overlook the error which would thus be introduced. It was further found that a small charge would be retained many days on a flask kept in a desiccator. In damp weather a charge would readily pass off and not give rise to an error, but on a very dry day the practice of wiping glassware just before weighing is liable to cause serious errors."

[1] L. E. Wise, *Journ. Amer. Chem. Soc.*, **39** (1917), 2062. Small apparatus in connection with micro-analysis was used in this work, and the error is not so large.

[2] See also article by Rae and Reilly, *Chem. News*, **114** (1916), 187–9, 200–3. Prof. T. W. Richards has recommended the use of uranium oxide or radium bromide in the balance case to dissipate these charges.

slightly moist while handling the cloth and the bottle, and the very small amount of moisture and grease from the skin that may be left upon the surface of the bottle is no doubt fairly constant and involves an error far less than that caused by the static charge. The bottle should not, of course, be touched by the fingers except as directed.

Difficulty is sometimes experienced in obtaining concordant results on damp days,[1] but with proper precautions good results can be obtained without much trouble.

Since the absorption bottles are often shut off and disconnected under different pressures of oxygen, it is well to release the pressure within the bottle by *momentarily* opening the stopcock, before weighing.

A fine analytical balance must of course be used, and it should have a capacity of 100 grams for accurate work. The absorption bottles, when filled, seldom weigh much over 90 grams.

For an excellent discussion of and careful directions for weighing, calibration of weights, etc., you are referred to an article by Rae and Reilly, in *Chem. News*, **114** (1916), 187–9, 200–3, and to the forthcoming book on quantitative analysis by Professors H. T. Beans and Harold A. Fales of the Department of Chemistry, Columbia University.

A counterbalance weight or bottle is sometimes used by some analysts in weighing the absorption apparatus. A similar piece of apparatus is made to weigh approximately the same by adding lead shot, and is kept beside the absorption apparatus all the time and treated just the same in every way, as far as possible.

### VII. Weighing the Substance

Since organic substances are generally hygroscopic and since it is necessary to keep all moisture away from the substance up to the very time it is put into the combustion tube,

---

[1] Dudley and Pease, *Journ. Amer. Chem. Soc.*, **15** (1893), 540, state, "If we may trust our experience it is almost impossible to make satisfactory combustions in showery weather." These authors just weighed the apparatus direct from the furnace, without wiping. Their combustion consisted of determining carbon in steel.

the sample should be weighed in a closed tube and kept[1] there until transferred to the combustion tube. This is done in the boat tube illustrated in Fig. 18. On account of its shape it is known in laboratory parlance as the "piggie" in order to distinguish it from the other types of weighing tubes. The legs are placed in the center in order that the tube will rest securely on the balance pan. If they are near the stopper, as in some models, they are likely to slip off the edge of the ordinary balance pan and then the tube will roll and the boat will be upset.

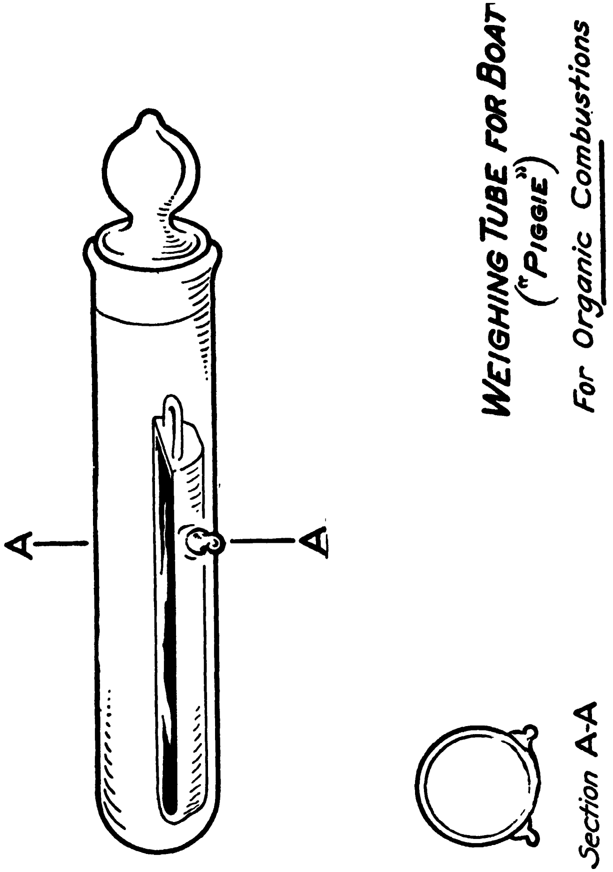


FIG. 18.

---

[1] If the substance readily sublimes, it should be weighed out just before beginning the combustion and not kept in the boat tube for any length of time.

The porcelain or quartz boat,[1] properly cleaned, heated in a non-luminous flame, and cooled in a desiccator, is placed in the "piggie" and both weighed together. Then the boat is removed with tongs or forceps, the substance added, and all weighed together again. The difference in weight is therefore the weight of sample used. Similar precautions should be taken here in cleaning the outside of the "piggie" and in handling it, as given for the absorption bottles, see p. 248. When not in use both the boat tube and the boat should be kept in the desiccator.

For weighing out liquids, see p. 267.

Ordinarily the amount of substance used for a combustion should be about 0.2 gram, with an allowance of about 0.02 gram above or below, since the actual weight need not be exactly 0.2 gram. With too small an amount of substance the proportional errors are greater and with a larger amount too much time is consumed in running the combustion. The weight should be carefully taken to the fourth decimal place, and properly recorded.

The substance should be perfectly *dry*. If necessary spread it upon a clean dry weighed watch glass, determine the total weight and set aside in a desiccator over fresh conc. sulfuric acid for at least twenty-four hours. Then weigh again. If the weight has changed put the substance back again for another period. The drying can be hastened by first placing it on the watch glass as above and setting it in an oven heated to 110° C. and after several hours allowing it to cool in a desiccator. This treatment cannot be given to all organic substances since many sublime, melt or decompose at that temperature. The latter can be dried in a vacuum oven at about 50°, or in a vacuum apparatus[2] provided with a drying agent and kept at the temperature of boiling acetone (56°).

In case it should be necessary to determine the hydrogen in a substance containing moisture, whose moisture content is

---

[1] See p. 236.

[2] Abderhalden's "Handbuch der Biochmischen Arbeitsmethoden," I (1910), 296; also, in Eimer & Amend, N. Y., catalogue, under the name, "Vaccum Drying Apparatus, Abderhalden's."

known, the hydrogen cannot be directly calculated to the dry basis like the carbon since the hydrogen has been obtained from the *total* weight of water absorbed in the first bottle. Therefore, the amount of *water* in the sample must *first* be subtracted from the weight of water absorbed, and the hydrogen calculated in the remaining weight of water. The percentage can then be obtained using the weight of *moisture-free* sample.

## VIII. The Combustion Proper

After it has been shown by the blank determination (p. 246) that the entire apparatus is all right, turn off the heat in the small section (No. 1) of the furnace and allow this end of the tube near the purifying train to cool to room temperature. Raise the upper half to hasten the cooling, At the same time push back the two other heating sections in order that the space for the boat will become cool.

When the forward end is cool, turn off the oxygen, shut off the stop-cock in the adjacent drying tube, disconnect the purifying train from the combustion tube and pull out the roll of oxidized copper gauze by means of the copper wire with hook already prepared for this purpose, making sure that the roll is placed upon some clean surface where it will not be in contact with any organic material. Then carefully remove the boat containing the weighed amount of substance from the boat tube ("piggie") by means of forceps, put it into the tube, and shove it back with the copper wire into its proper position about 2.5 cm. from the cerium dioxide. Replace the roll of oxidized gauze, connect the purifying train, and let the oxygen pass through.

Remove the guard tube from the other end of the combustion tube and attach the entire absorption train (p. 247, including footnote). If the substance is readily distilled out of the boat the absorption train should be attached *before* the boat is put into the tube. As a rule this is not necessary, and it is easier to attach the absorption train afterwards.

Regulate the passage of the oxygen in such a manner that the bubbles passing through the sulfuric acid in the bubble-counter can just be counted—that is, at the rate of about three to four a second.

It is very difficult to describe in detail the actual method of burning an organic substance, since each substance has its own peculiarities and therefore only a general description can be given. An idea as to how the substance behaves on heating should be gained beforehand, if sufficient is available, by gently heating it and gradually burning it in a boat over a small flame.[1] Gradually move the large heating section (No. 2) a centimeter at a time, toward the boat, until most of the cerium dioxide-pumice is heated to redness. At the same time, provided the substance is not too volatile, turn on the switch and allow the small heating section (No. 1) to become warm and finally hot, but not to red heat, except in special cases. Also heat up the last section (No. 3) so that no water will condense in that end of the combustion tube. These operations ordinarily require about ten minutes. Then move the large heating section (No. 2) closer to the boat until the cerium dioxide-pumice is all being heated, and the asbestos plate on the end of the heating section is over the asbestos plug between the cerium dioxide-pumice and the boat. Now *very slowly*, just a little (0.5 cm.) at a time, move the small heating section (No. 1) toward and finally over the boat. With substances that sublime readily, it may only be necessary to bring the small heating section (No. 1) to a moderate temperature to drive all of the sample over the cerium dioxide-pumice. With an active catalyst the forward points of the impregnated pumice will glow.[2] The glow cannot always be seen on account of the asbestos. With some substances the forward part of the pumice mixture will appear gray as the decomposition begins. This is probably due to particles of carbon which are later burned completely. The burning of the substance ordinarily requires from ten to twenty-five minutes, depending upon how rapidly the substance can be distilled and burned. It

---

[1] Weyl, "Die Methoden der organischen Chemie," I (1909), 17; and Wise, *Journ. Amer. Chem. Soc.*, **39** (1917), 20.

[2] In some cases the little roll of copper oxide gauze in front of the asbestos appears to act catalytically since it also glows under certain conditions.

is well to take the longer time specified for burning the substance the first time in order to learn any of its peculiarities.

During the course of the combustion the operator must be on the alert and watch not only the burning of the substance but also the temperature (compare p. 231) which will gradually rise, and the rate of flow of the oxygen gas coming in and of the gases leaving the apparatus through the palladious chloride solution. Bubbles of gas should *always* be coming through the palladious chloride solution. If their number is diminishing so rapidly that it appears they may stop then more oxygen should *immediately* be turned on in order that there may be an adequate supply for complete combustion. The presence of a black precipitate (colloidal palladium) in the palladious chloride solution indicates that carbon monoxide has been coming through the absorption train, and therefore that the combustion is incomplete and the determination no good (p. 245).

Soon after the combustion begins, moisture will condense in the forward arm of the alumina bottle, and then the soda lime bottle will become warm. The general operation should be continued until this latter absorption bottle is practically the same as the first one in temperature, as shown by the hand. The absorption bottles can be protected from the heat of the furnace which is not very great, by means of an asbestos shield.

After all the particles of carbon have disappeared from the boat the passage of the oxygen should be continued for at least forty-five minutes in order that all the products of combustion will be swept out and properly absorbed. During this time the temperature may gradually be reduced. Little care is needed after all the substance has disappeared and the boat is clean, except to see that the gas is passing all right and the temperature does not go so high that the tube is melted. Sometimes particles of black cupric oxide are found in the boat, having been swept along from the roll of oxidized gauze by the oxygen.[1]

---

[1] Levene and Bieber, *Journ. Amer. Chem. Soc.*, **40** (1918), 461, recommend that a small coil of fine platinum gauze be placed between the roll of oxidized copper gauze and the boat to prevent the particles of cupric oxide from getting into the boat. This is very important when the ash of the substance is to be weighed or analyzed.

This of course gives the appearance of unburned carbon and its presence is annoying since the end of the combustion is indicated by the absence of black carbon particles. That the particles do consist of cupric oxide can sometimes be established by the fact that they do not disappear after prolonged heating. Later, when the boat has been removed, the proof can be made definite by seeing if they are soluble in nitric acid. It should be noted however, that carbon particles formed under certain conditions are very difficult to burn (so-called "graphitic" carbon).

If moisture collects in the combustion tube just in front of the absorption apparatus and persists even for some time after the substance has been burned, it should be driven through by slowly drawing the tube further into the furnace. Considerable care is necessary for this gradual heating to prevent the burning of the rubber stopper and also the cracking of the tube.[1]

After the tube has been "swept out" for the forty-five minutes from the disappearance of the last particles of carbon in or around the boat, the absorption bottles are closed, disconnected and immediately weighed (p. 250). The guard tube should be replaced and the combustion apparatus is then ready for another determination without further treatment.

The time from putting the boat into the tube until the absorption bottles are taken to the balance usually is from an hour and ten minutes to an hour and a half. A little experience soon makes it possible to cut this down to an hour, or to forty-five minutes, provided no special difficulty is encountered in burning the substance.

Two combustions should always be run on the same substance whenever possible, and they should check up within narrow limits. See discussion of results, p. 258.

## NOTE

If no cerium dioxide is used the layer of cupric oxide wire must be much longer, 40–70 cm., and the substance must be burned very

---

[1] If a gas furnace is employed, the water may be driven over by holding one of the hot tiles under the tube. Some operators use a small flame, but great care is necessary to prevent cracking the tube and burning the stopper.

slowly. At least forty minutes is required just for the burning alone, and some substances are not completely oxidized even when the time is considerably extended.

## IX. Calculations, and Discussion of Results

Since the ratio of $H_2$ to $H_2O$ is $\frac{2.016}{18.016}$,[1] which is equal to 0.1119, the weight of hydrogen in the weight of water found can be calculated by multiplying the weight of water by 0.1119. The percentage of hydrogen is equal to the weight of hydrogen multiplied by 100 and divided by the weight of the substance used. Or the following formula may be used:

$$\text{Per cent H} = \frac{\text{Weight } H_2O \times 2.016 \times 100}{\text{Weight substance} \times 18.016}.$$

For logarithmic calculation:

$$\begin{array}{lll} & \left\{\begin{array}{l} \text{Log. wt. } H_2O \\ \text{Log. } 100 \\ \text{Log. } 0.1119 \end{array}\right. & \begin{array}{l} = \\ = \\ = \underline{9.0487 - 10} \end{array} \\ \text{Add} & & \\ \text{Subtract} & \text{Log. wt. subs.} & = \underline{\qquad\qquad} \\ & \text{Log. per cent H} & = \end{array}$$

Similarly, since the ratio of C to $CO_2$ is $\frac{12}{44}$ or $\frac{3}{11}$, which is equal to 0.2727, the weight of carbon in the weight of carbon dioxide found can be calculated by multiplying the weight of the carbon dioxide by $\frac{3}{11}$ or 0.2727. The percentage of carbon is equal to the weight of the carbon multiplied by 100 and divided by the weight of the substance used. Or,

$$\text{Per cent C} = \frac{\text{Weight } CO_2 \times 3 \times 100}{\text{Weight substance} \times 11}.$$

---

[1] Using $H = 1.008$.

For logarithmic calculation:

$$\text{Add}\ \begin{cases}\text{Log. wt. } CO_2 & = \\ \text{Log. } 100 & = \\ \text{Log. } 0.2727 & = \underline{9.4357-10}\end{cases}$$

$$\text{Subtract}\quad \text{Log. wt. subs.} = \underline{\qquad\qquad}$$

$$\text{Log. per cent C} =$$

For ease in calculation, a table of four-place logarithms is given on pages 308–11.

The figures showing the percentage of carbon and hydrogen should not be extended beyond the second decimal place. The figures beyond the second decimal place in this work are not significant.

**Limit of Error.**—In order to be able to compare the results of analyses to see whether they are what they should be, some standard is necessary for the limit of error. The criterion for the limit of error in good analytical work is one part in one thousand. Many examples can be given to show that the determination of carbon approaches this limit, although the hydrogen is not so good. The number of parts per thousand error, $X$, can be calculated by using the following ratio: Difference of percentages : percentage :: $X$ : 1000; or

$$X = \frac{\text{Diff. of per cents} \times 1000}{\text{per cent}};$$

where one percentage, often the theoretical, is taken for the basis of comparison. This is made more clear by means of the examples which follow:

A sample of cane sugar ($C_{12}H_{22}O_{11}$) was analyzed with the following results: C = 42.05%; H = 6.48%.[1] The theoretical percentages for this substance are C = 42.09%; H = 6.46%. The

---

[1] This analysis was made by Mr. R. T. Feliciano. His check analysis was C = 42.14% and 42.15%; H = 6.46% and 7.00%. Similar results were obtained on the same substance by Mr. H. R. Pyne: C = 42.19% and 42.07%; H = 6.23% and 6.26%. Alumina-asbestos mixture was used in the first instance, and alumina-pumice in the second.

difference between the theoretical value for C and the value actually obtained is 0.04. Therefore the error, expressed as parts per thousand, is $\frac{0.04 \times 1000}{42.09}$ which equals 0.95 (approximately one part per thousand). Correspondingly, for H, the difference between the theoretical value and the value actually found is 0.02; and $\frac{0.02 \times 1000}{6.46} = 3.1$ parts per thousand. This is an excellent analysis. The same comparison can of course be made, and should be made, between any two percentages found.

An example with a very high percentage of carbon: Analysis of anthracene ($C_{14}H_{10}$): Found, $C = 94.17\%$; $H = 5.71\%$;[1] the theory being $C = 94.34\%$; $H = 5.66\%$. The error for C is $\frac{(94.34 - 94.17) \times 1000}{94.34} = 1.8$ parts per thousand; for H, the error is $\frac{(5.71 - 5.66) \times 1000}{5.66} = 8.8$ parts per thousand.

The "allowed" error for carbon ought not to be more than 2.5 parts per thousand, and never over 5 parts per thousand. For hydrogen, the "allowed" error ought not to be more than 20 parts per thousand, and never over 30 parts per thousand.

Now it is possible to tell the extent of the errors which are found in connection with the blank runs (p. 247). If an increase of 0.0010 gram is noted in the case of the first absorption bottle, this means that in a regular combustion, which would ordinarily require about twice the time of the blank run, the increase would probably be about 0.0020 gram. On the basis of using a 0.2 gram sample, this gain, counted as water, would be equal to 0.11% H; and if the substance contained 5.0% H, the error due to this cause alone would be 22 parts per thousand, which is

---

[1] This analysis was made by Mr. Henry L. Faust and is the first one which showed us that alumina could be used in organic combustions. The same substance was later analyzed by Mr. David I. Hitchcock with the following results: $C = 94.36\%$ per cent and $94.12\%$; $H = 5.57\%$ and $5.53\%$.

For the sake of comparison, the very first results obtained by using the alumina-pumice mixture are added: Salicylic acid; found, $C = 60.77\%$ and $60.82\%$; $H = 4.47\%$ and $4.38\%$; theory, $C = 60.84\%$; $H = 4.38\%$. This work was done by Mr. Geo. H. Walden.

about the "allowed" error. Correspondingly, if the same gain of 0.0010 gram is noted in the case of the second absorption bottle, meaning about 0.0020 gram for a combustion, on the basis again of a 0.2 gram sample, this would be equivalent to 0.27% C, and supposing the C = 60%, the error on this account alone would be 4.5 parts per thousand, which is beyond the ordinary "allowed" limit of error. Any other error in the work would in each case put the determination way beyond what it should be.

The limit of error of 0.0002 gram in weighing alone would, under the conditions mentioned above, be equal to 4.4 parts per thousand for the hydrogen and 0.9 parts per thousand for the carbon.

These figures are given in order to show that the greatest care at all times must be exercised in carrying out the work.

Two combustions should always be run whenever possible, and they should check up within the limit of error specified above.

## NOTES

1. For calculating the hydrogen in a sample which contains some moisture and whose moisture content is known, see p. 252.

2. The percentage of C and H in a hydrocarbon should add up to 100±0.3 per cent.

3. The percentage of oxygen in a compound is found by difference. This method of calculating throws all the error upon the figure for this element. (For a method of determining oxygen directly, see Boswell, *Journ. Amer. Chem. Soc.*, **35** (1913), 284–90; **36** (1914), 127–32.)

4. The empirical formula of a compound is found by dividing the percentage of each element by the atomic weight of the element, and the ratio is then expressed in whole numbers by dividing each term by the lowest value or by some simple fraction of this value. Since these numbers as found by analysis seldom are whole numbers, the formula which has been found in this way should always be checked up by calculating the percentage composition of each element from the formula so obtained and comparing the values with those found experimentally. They should agree within the limit of error set forth above.

The molecular formula can only be obtained after a molecular weight determination has been made.

Sometimes the empirical formula cannot be selected since the results are too close to several possibilities. In this case some derivative of the substance should be made and then an analysis carried out on this new product. Usually the figures so obtained will settle the question. (An interesting case is the determination of the formula of cholesterol, see Glikin, " Chemie der Fette, Lipoide und Wachsarten," I (1912), 334–5, where Reinitzer's work is quoted from *Monatshefte*, **9** (1888), 421.)

## X. Some Common Errors and How to Avoid Them

Many of the errors have already been discussed in connection with different parts of the apparatus, the method of running the combustion, etc., and many errors are perfectly obvious. Yet it has been our experience that direct attention must often be drawn to some errors before they are corrected, and it is the most obvious error which is sometimes committed. Therefore all that have been noticed in actual work are mentioned.

Read over once again Liebig's advice which is quoted at the end of the historical introduction (p. 223).

### *The Apparatus*

1. Do not use too much sulfuric acid in the bubble counter. It may suck back or be splashed over and cause trouble with the rubber tubing and stopper (p. 227).
2. The pre-heater should not be heated to such an extent that the glass tube melts. Watch the temperature (p. 231).
3. Use heavy-walled " pressure " rubber tubing. Other kinds are not gas tight and do not fit snugly. Wire joints, if necessary, with No. 16 copper wire, and use a pair of pliers to tighten them (p. 244).
4. See that the glass stoppers are properly greased (p. 229). Attach a piece of twine to prevent them from being blown out in case of excess of pressure (p. 229, (footnote)).
5. Use red rubber stoppers, and clean them well, inside as well as out (p. 242).

6. Cut the rubber stopper properly for connecting the first absorption bottle to the combustion tube (p. 242).
7. Do not use a piece of glass or rubber tubing to connect the first absorption bottle with the combustion tube (p. 242).
8. Do not fill the stoppers of the absorption bottles with cotton. The space is needed for the drying agent, especially in the soda lime bottle (p. 243).
9. Do not allow the two absorption bottles to come so close that the ends of the arms are chipped (p. 244).
10. See that there is space provided above the palladious chloride solution for any emergency in case of back pressure (p. 245.)

### *The Chemicals*

1. Purify all oxygen by passing it through the pre-heater (p. 228).
2. Use the specified soda lime for both drying and absorption trains (pp. 229, 243). See that it is of proper size and moisture content.
3. Use the same drying agent in the drying train that is used in the absorption train (p. 230).
4. Do not expect the materials in the drying train to last forever.
5. Keep the stop-cocks of the U-tubes in the drying train closed when not in use (p. 229).
6. See that the copper spirals are properly made and fit all right (p. 235).
7. Do not use cupric oxide wire for carbon and hydrogen that has been used for determining nitrogen, unless it has been re-treated (p. 236).
8. Do not use alumina that has been heated too long or too high (p. 238).
9. Keep the palladious chloride solution stoppered except when in use (p. 246).

### *Weighing*

1. Use a proper analytical balance and, if you use a rider, see that it is the right one for your balance.

2. The absorption bottles should not have anything on them when weighed. Detach rubber stopper and tubing.
3. Wipe each absorption bottle carefully and do not record the weight until you are satisfied that it is all right and that you can duplicate it (p. 249).
4. Weigh the bottles in the same order each time and try to take approximately the same time in weighing. A slightly different weight is found when the bottle has been standing and is cold.
5. Wipe off all grease from around the stopper of the bottle before you begin to weigh. After that be careful not to wipe off any more in all other weighings (p. 248).
6. Make proper record of all weighings in a neat manner so that all figures are known. Do not leave anything to guess work. Do not throw away any papers until the work is completed and accepted.

### *Blank Runs*

1. Continued findings of gain in weight of first absorption bottle shows that drying train needs attention, or that rubber stoppers are burning.
2. Loss in weight of first absorption bottle usually means that (1) grease has been wiped off the stopper, (2) particles of the drying agent have been blown out of the bottle, or (3) the drying agent is " spent " and moisture is being removed from it by the dry gas from the drying train.
3. Loss in weight of either bottle may be due to chipping the glass at the end of the arms (p. 244).
4. Loss in weight of the soda lime bottle is usually due to " spent " *drying* agent, or not enough of the good material. Fill up the stopper (p. 243). Sometimes it is necessary to add a third bottle (p. 244).
5. Loss in weight may be due to the fact that the gas is being passed through the bottle in the wrong direction. (p. 242).
6. Loss in weight may be due to loss of particles from side arms. See that these are scrupulously clean (p. 242).
7. Gain in soda lime bottle is generally due to the burning of

rubber stoppers in the pre-heater or forward end of the combustion tube. If the rubber stopper next to the drying train in the pre-heater tube is burned, some of the gases may go through the drying train incompletely absorbed, and then they will be burned in the combustion tube. The rubber stopper should not become spongy.

### *The Combustion*

Some of the troubles mentioned under the previous heading apply here also.

1. Do not fail to prove your apparatus by running a blank determination.
2. Keep enough oxygen in the apparatus to supply the needs all the time. See that it is always bubbling through the palladious chloride solution (p. 255).
3. Do not try to burn the substance too fast before you are fully acquainted with the apparatus.
4. Remember that the combustion needs attention all the time. Do not try to do too many other things at the same time. Too much effort will be lost.
5. Black particles in the boat near end of the combustion may be carbon or cupric oxide (p. 255).
6. Do not let the small section become too hot, especially at the beginning (p. 254).
7. If you weigh the absorption bottle with the little stopper for one arm, do not fail to keep it safe and weigh it again with the bottle later.
8. It is most desirable as a rule to run a blank determination between two consecutive combustions, since all the moisture and carbon dioxide may not have been removed, especially if the time after the substance has been burned is cut short.
9. If the percentage of hydrogen in a determination is high and the carbon low, this may be due to the fact that the gases have not been completely driven through the first bottle. Attach the absorption train to the drying train, pass the oxygen through for twenty minutes and weigh again.

## XI. Combustion of Substances Containing Nitrogen, Sulfur, Halogens, Phosphorus, Sodium, etc.

**Nitrogen.**—With an active catalyst and plenty of oxygen, the nitrogen is oxidized to nitrogen dioxide. This is true even with substances containing nitrogen in the so-called "unoxidized" form, as in amines, amides, etc. Nitrogen dioxide is absorbed more or less by the drying agent and completely absorbed by soda lime. Therefore it is necessary to keep it from going into the absorption train. Lead peroxide ($PbO_2$)[1], kept at 300°–320°, is the best means of "fixing" the nitrogen dioxide and preventing it from leaving the combustion tube. The temperature must be tried out ahead of time to find out the working conditions. Too high a temperature (above 350°) will cause the decomposition of the lead nitrate which is formed, and also will convert the $PbO_2$ into $Pb_3O_4$. Since water vapor acts upon lead nitrate giving a basic nitrate and liberating nitric acid which is not all reabsorbed by the lead peroxide, it is necessary to mix an equal amount of $Pb_3O_4$ (minium) with the lead peroxide. Some $Pb_3O_4$ for use can readily be obtained by heating some of the lead peroxide in a tube or open dish to 400°–450°.

The lead peroxide mixture (7–8 grams) is placed in a tube of hard glass, Fig. 19, which fits the combustion tube snugly, and put in position *F* as shown on the general diagram, p. 233 (see also p. 236). Or it is placed in a large boat, 14 cm. long, preferably with the end open (broken off) toward the catalyst.[2]

Lead peroxide is very hygroscopic and care must be used in handling it and proving it in the blank run. It must be very pure, free from any organic particles such as dust, fibers from

---

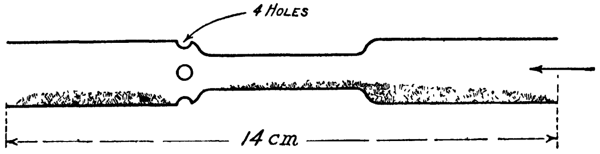
[1] Lead peroxide was used by Liebig and contemporary workers in organic combustions to absorb acidic gases, and in 1876 by Köpfer, when he introduced the catalytic method (p. 219), but Dennstedt has done the best work on how to use it. See his "Anleitung zur vereinfachten Elementaranalyse," 3 Aufl. (1910), 66–70, 90.

[2] Levene and Bieber, *Journ. Amer. Chem. Soc.*, **40** (1918), 460, recommend putting the lead peroxide directly into the tube with alternate layers of a mixture of it with asbestos.

filter paper, etc. It must also be free from lead oxide since this absorbs carbon dioxide at a high temperature.[1]

The combustion must be run slower than when the substance contains no nitrogen.[2]

Cupric oxide also absorbs nitrogen dioxide. The copper nitrate formed is only slowly decomposed around 300°, and if the latter part of the cupric oxide just preceding the lead peroxide mixture is not well heated between combustions, the nitrate may accumulate to such an extent that it will entirely block the combustion tube.[3]



*TUBE FOR LEAD PEROXIDE MIXTURE*

FIG. 19.

NOTES

1. For the electrolytic preparation of the lead peroxide you are referred to Dennstedt's book mentioned above, p. 265; and to Kingscott and Knight, " Methods of Quantitative Organic Analysis " (1914), 35.

2. For other methods of combusting organic substances containing nitrogen, see Gattermann, " Practical Methods of Organic Chemistry," 3d Amer. Ed., (1914), and especially, F. G. Benedict, " Elementary Organic Analysis " (1900), 59–64.

3. For estimating carbon, hydrogen, and nitrogen simultaneously, see Dennstedt and Hassler, *Ber.*, **41** (1908), 2778.

**Sulfur.**—For determining carbon and hydrogen by the catalytic method when the substance contains sulfur, the same procedure is used as above when nitrogen is present. The sulfur is fixed as lead sulfate.

---

[1] Lassar-Cohn, " Arbeitsmethoden," Allgemeine Theil, 4 Aufl. (1906), 286.

[2] Reimer, " On Rapid Organic Combustions," *Journ. Amer. Chem. Soc.*, **37** (1915), 1636–8.

[3] Fisher and Wright, *Journ. Amer. Chem. Soc.*, **40** (1918), 868.

Other methods, when a catalyst is not used, are discussed in the books mentioned in the foreword.

**Halogens.**—The lead peroxide mixture also serves for fixing chlorine and bromine, but not iodine. A roll of silver gauze or a long boat containing so-called " molecular silver," prepared by treating silver halide residues with granular zinc, is used for all the halogens.

**Phosphorus, Sodium, Mercury, etc.**—Only notes and references will be given for these.

Phosphorus is often converted into phosphoric acid which, on account of its physical state, holds back particles of carbon. It is then necessary to use an alundum boat, which is removed after most of the carbon has been burned, dialyzed to get rid of the phosphoric acid, dried, and put back with the carbon in it for complete conbustion.

Sodium and other basic elements retain carbon in the ash as carbonate. F. G. Benedict, " Elementary Organic Analysis" (1900), 70, recommends the admixture of lead chromate and potassium dichromate with the substance to expel the carbon dioxide. Or the ash can be analyzed by the ordinary methods. See also Kuzirian, " The estimation of $CO_2$ in the ash of plant and animal substances," *Journ. Ind. and Eng. Chem.*, **8** (1916), 89, who uses sodium paratungstate.

**Mercury.**—" The simultaneous determination of carbon, hydrogen, and mercury," V. Grignard and A. Abelman, *Bull. soc. chim.*, **19** (1916), 25–7.

## XII. Combustion of Liquids, Gases, and Explosive Substances

**Liquids.**—If the liquid substance has a boiling-point above about 170°, it may generally be weighed directly in the boat as if it were a solid. There should be no delay, of course, after weighing—the boat should be put directly into the combustion tube.

Lower boiling liquids are weighed in a sealed bulb with a capillary tube.[1] This tube is then carefully broken off at a

---

[1] Liebig, " Instructions for the Chemical Analysis of Organic Bodies." Trans by Gregory (1839), 20.

file mark, and the bulb and the piece are put into the boat in such a way that the tube will rest on the end of the boat near the cerium dioxide, and immediately placed in the combustion tube. It is slowly distilled out and burned in the usual manner. Particles of glass in the bulb aid in the distillation (suggested by M·. E. M. Slocum). The substance should not, of course, be allowed to be carbonized within the bulb.

A small thin-walled glass bulb,[1] 3–5 mm. in diameter, such as is often employed for molecular weight determinations by the vapor density method, is used. It is filled by placing it with the open capillary tube dipping into the liquid to be analyzed, contained in a dish, inside a vacuum desiccator. The suction is then turned on and after a few minutes air is allowed to re-enter the desiccator. This causes the liquid to be drawn into the bulb. The bulb should be weighed before, and again after sealing.

Very low-boiling liquids must be driven into the combustion tube somewhat as in the case when a gas is analyzed. They often form explosive mixtures.

### REFERENCES

Benedict, *loc. cit.*, 73–9; Clarke, "Note on the combustion of volatile organic liquids." *Jour. Amer. Chem. Soc.*, **34** (1912), 746–7.

**Gases.** Since gases form explosive mixtures with oxygen, the oxygen must always be in very great excess when the gas is slowly being driven into the combustion tube. The gas is held in a gas burette in which it is measured, and slowly sent through a *capillary* tube into the combustion tube. A long cupric oxide spiral near the entrance helps to cause thorough mixing and to prevent "back firing."

---

[1] This small bulb can be made as follows: Heat and draw out a piece of ordinary glass tubing, and cut off one end of the narrow tube at the shoulder. Then soften in the flame the end which has been cut off, and, with the other end as a mouthpiece, blow a bulb. It is completed by cutting the narrow tube at the desired length.

**Explosive Substances.** These are weighed out as usual in a boat and then mixed with three or four volumes of cupric oxide (which is free from moisture, etc.) or quartz sand.

## DIVISION B

## THE DETERMINATION OF NITROGEN

### I. Historical Introduction[1]

Gay-Lussac and Thénard (1810) were the first to determine nitrogen in organic substances. Their method consisted in burning the substance in the presence of potassium chlorate and analyzing the gases evolved (compare carbon and hydrogen, p. 218). Later (1815) cupric oxide was introduced by them and is still used up to the present time. Liebig used this same method, improving it so that he could collect and weigh the water and carbon dioxide, and measure the nitrogen as a gas. Dumas[2] burned the substance in an atmosphere of carbon dioxide, prepared from lead carbonate in the end of the closed tube, and collected the nitrogen in a eudiometer over mercury and a solution of potassium hydroxide to absorb the carbon dioxide. He also used reduced copper to reduce any oxides of nitrogen which may be formed. Thus he laid the complete foundation of the method which is the most general and, when properly carried out, as accurate for nitrogen as any yet devised.

Erdmann and Marchand[3] used an outside generator for the carbon dioxide, and Hugo Schiff[4] devised the azotometer which has been such a great help in handling the gases. It is of considerable interest to note how the azotometer was developed and modified. The references for the different forms (and each reference contains a sketch of the apparatus for which the author is sponsor), are found in Dennstedt's history, p. 40, and

---

[1] Dennstedt, "Die Entwickelung der organischen Elementaranalyse," Ahren's "Sammlung chemischer und chemisch-technischer Vorträge," IV (1899), 29.

[2] *Ann. Chim. phys.*, **2** (1831), 198; Dennstedt's history, p. 35.

[3] *J. pr. Chem.*, **14** (1838), 213.

[4] *Zeitschr. anal. Chem.*, **7** (1868), 430.

Richter's "Organische Chemie," 11 Aufl., I (1909), 7. Magnesite (magnesium carbonate) later displaced the lead and other carbonates and is most generally used when the substance is burned in a closed tube.[1]

Many organic substances when heated, expecially in the presence of soda lime, give up their nitrogen as ammonia, or some simple amine. This method was used for the determination of nitrogen by Varrentrapp and Will[2] in 1841. The ammonia formed is absorbed in a known amount of standard acid and the excess of acid titrated back with alkali. From this, the amount of acid neutralized by the ammonia is obtained and the ammonia and nitrogen can then be calculated. This method is not applicable to substances in which the nitrogen is in such combination as in the nitro-group, azo-group, etc.

Some forty years later, in 1883, Kjeldahl[3] brought forth another method which on account of its ease of manipulation and applicability to many substances which are analyzed for nitrogen in great numbers, has been of inestimable service. The Kjeldahl method consists of heating the substance with conc. sulfuric acid usually in the presence of a catalyst, such as a mercury salt, potassium permanganate or cupric sulfate. This procedure converts the nitrogen into ammonium sulfate. The mixture is then diluted, made strongly alkaline with sodium hydroxide, and distilled. The solution of ammonia which constitutes the distillate is collected in a definite amount of standard acid and the analysis completed by back titration, etc., as outlined in the previous paragraph. Some substances, especially those with the nitrogen in the ring are not completely decomposed by the method. Otherwise, by different modifications for increasing the temperature by adding potassium hydrogen sulfate, by reducing nitro-compounds just previously, etc., the method has found wide application.

Within very recent years micro-methods for determining

---

[1] This is the method outlined in Gattermann, "Practical Methods of Organic Chemistry," 3d Amer. Ed. (1914), 90.

[2] *Ann. Chem. Pharm.*, **39** (1841), 257.

[3] *Zeitschr. anal. Chem.* **22** (1883), 366.

nitrogen by both the Dumas and Kjeldahl methods have been devised by Pregl.[1]

Since the Dumas or absolute method is so generally applicable even though it is slow and must be carefully watched, it is the one selected and described in the following pages. The chief difficulties are in obtaining pure carbon dioxide and in preparing the cupric oxide so that it will not continue to give off occluded gases. These points are fully discussed later and need not be repeated here. The modifications used bring the results within a fair limit of error (compare p. 302). One must work with gases and with pressures above and below atmospheric. On this account many stop-cocks are necessary to make the apparatus efficient. However, although the array of stop-cocks may appear formidable at first you will rapidly become familiar with their uses and then good results will soon follow.

## II. List of Apparatus and Chemicals for the Determination of Nitrogen

### *Apparatus*

1. * Electric combustion furnace (p. 283).
2. * Pyrex combustion tube, 76 cm. long and 15 mm. inside diameter, for 72 cm. combustion furnace (p. 283).
3. * Asbestos paper for lining trough of the furnace (p. 231.)
4. * Copper gauze, 40 mesh, 1 square foot (pp. 283-4).
5. * Copper wire, No. 16, 3 feet long.
6. Two red rubber stoppers, one-holed, size 1 or 0 depending upon the diameter of the combustion tube; one rubber stopper, one-holed, for the dropping-funnel; one rubber stopper, three-holed, for the generator flask; one rubber stopper, two-holed, for the safety bottle connected with the generator; and one rubber stopper, three-holed, for the Erlenmeyer filtering flask in connection with the manometer.

---

[1] Pregl, Abderhalden's "Handbuch der biochemischen Arbeitsmethoden," V (1912), 1332. See also Fisceman, *Rend. accad. sci. fis. et mat. Napoli,* [3], **21** (1915), 135-42.

7. * Rubber pressure tubing (p. 283).
8. * One U-tube, with ground glass stoppers, 12.5 cm. (5 inches) (p. 282).
9. Glass beads for the U-tube (p. 282).
10. * One porcelain or quartz boat (pp. 284, 292).
11. * One special weighing tube, boat tube ("piggie") (p. 251).
12. Azotometer, 50 cc., graduated to 0.1 cc., and reservoir (p. 285).
13. Carbon dioxide generator (p. 275), consisting mainly of:
    - *a.* Erlenmeyer filtering flask, 750 cc.
    - *b.* Dropping-funnel, 200 cc.
    - *c.* Stout safety bottle, about 200 cc.
    - *d.* Bulbed test-tube, 6 inches.
    - *e.* Capillary tube.
14. Seven stop-cocks.
15. Erlenmeyer filtering flask (in connection with manometer) (p. 282).
16. Manometer stand (p. 281).
17. One length of glass tubing for manometer, about 140 cm.
18. Water pump or oil vacuum pump (p. 282).
19. Thermometer (p. 298).
20. * Crucible tongs.
21. * One pair of pliers.
22. * Desiccator.
23. Mercury, 450–500 grams (pp. 275, 281, 286).
24. One test-tube of Pyrex glass, for the reduced copper spiral (p. 285).
25. Glass wool or asbestos for the above (p. 285).
26. * Stop-cock grease, E. & A. (p. 283).

### *Chemicals*

1. 100 grams of cupric oxide, *wire form.*
2. Pure sodium bicarbonate, 100 grams for each determination.
3. Conc. sulfuric acid, for use in generator and U-tube.

* Those pieces of apparatus which are starred (*) are the same as on the list for the carbon and hydrogen determination and given on pp. 223–4.

4. Potassium hydroxide (100 grams dissolved in 100 cc. water makes a solution which is good for two determinations).

### III. Topical Outline of General Method of Procedure

1. Set up the electric combustion furnace (p. 283).
2. Select the combustion tube, and if necessary cut to proper length and " round " the edges (p. 284).
3. Fill the combustion tube (p. 284).
4. Assemble the carbon dioxide generator (p. 275), the manometer (p. 281), and accompanying stop-cocks and U-tube (p. 282).
5. Clean, attach and test the azotometer (nitrometer), (p. 285).
6. Prepare the carbonate mixture and 1 : 1 sulfuric acid for the generator (p. 277), and the mercury and the 1 : 1 potassium hydroxide solution for the azotometer (pp. 286–7).
7. Prepare the cupric oxide wire in the combustion tube by heating it under diminished pressure and allowing it to cool in an atmosphere of carbon dioxide (p. 288).
8. Test the entire apparatus (p. 293).
9. Prepare the reduced copper spiral and allow it to cool (p. 285).
10. Weigh out the substance (p. 292).
11. The combustion proper (p. 294); the furnace can be cold or hot at the beginning (p. 294).
    - *a.* Insert the boat containing the substance (pp. 294–5).
    - *b.* Insert the reduced copper spiral (pp. 294–5).
    - *c.* Connect up the entire apparatus, evacuate, and flood with carbon dioxide (p. 295).
    - *d.* Heat the reduced copper spiral to redness for about five minutes in order to drive out occluded gases (p. 295).
    - *e.* Test with azotometer full of the potassium hydroxide solution to see if all non-absorbable gases have been removed from the apparatus, or reduced to a minimum (pp. 295–6).
    - *f.* Heat the layer of cupric oxide wire to redness, being careful not to burn the substance (p. 295), and at the same time

*g.* Reduce the flow of carbon dioxide to such an extent that it will just keep the products of combustion moving toward the azotometer, using the stopper in the U-tube for regulating the gas (p. 282), and allowing the excess of carbon dioxide to escape through No. 2 (p. 276).

*h.* Slowly heat the oxidized copper spiral, and then combust the substance (p. 296).

*i.* Drive over all the remaining nitrogen gas with carbon dioxide by gradually increasing its flow (p. 297).

*j.* Close stop-cock No. 6 (between the azotometer and the combustion tube), wash the gas in the azotometer with one portion of the potassium hydroxide solution, while the reservoir is in the low position (I), and then wash with cold distilled water, which has been recently boiled to drive out dissolved air, until all the potassium hydroxide solution is out of the azotometer and the reservoir (p. 297).

*k.* Level the liquid in the reservoir and the azotometer, place a thermometer in the water in the top of the azotometer, and after twenty to thirty minutes record the volume of the gas by reading the lower meniscus, the temperature, and the corrected barometer reading (p. 298).

*l.* Calculate the percentage of nitrogen (p. 300).

12. In order to have the tube ready for another combustion, remove the reduced copper spiral, draw air through the tube while it is still hot in order to oxidize the copper that has been reduced in the combustion, then flood the apparatus with carbon dioxide. Now it may be used again at once, or it can be closed off and the cupric oxide allowed to cool in the atmosphere of carbon dioxide (p. 299).

## IV. The Apparatus and How to Put it together, with Notes on Manipulation

**1. The Carbon Dioxide Generator.**—Since the substance is burned in an atmosphere of carbon dioxide and since the nitrogen gas itself is measured directly, the carbon dioxide must be as free as possible from any impurities which will not be absorbed by the potassium hydroxide solution in the azotometer. The carbon dioxide can be prepared from sodium bicarbonate [1] or from normal potassium carbonate. On account of the expense involved in the use of the potassium carbonate, the sodium bicarbonate is generally used and unless otherwise stated is always referred to in the following discussion. The same style of generator can be used in either case.

The generator must be one that can be used with pressures above or below atmospheric. Many are the styles of generators that have been used and published, and the one described herein contains no new features. It has simply been selected as one that can easily be assembled from ordinary apparatus. At the end of this chapter an innovation is described in connection with the stop-cock (see p. 278).

A glance at the general diagram of apparatus, Fig. 20, shows that an Erlenmeyer filter flask (about 750 cc.) is surmounted by a dropping-funnel of about 200-cc. capacity. In order to equalize the pressures in the two chambers an outside connection is made from the top of the dropping-funnel through stop-cock No. 11 [2] to the top of the filter flask. A three-holed rubber stopper is used in the filter flask and the third hole is connected with a stout empty bottle and this with a stop-cock (No. 2) leading into a bulbed test-tube containing about 8 cc. (108

---

[1] Sodium bicarbonate was chosen by Bradley and Hale (*Journ. Amer Chem. Soc.*, **30** (1908), 1090) who prepared carbon dioxide which was of extreme purity containing only one part of impurity (that is, gas not absorbed by potassium hydroxide solution) in 30,000 to 40,000 parts of the gas.

[2] Stop-cock No. 11 is added to close off the acid and prevent it from absorbing $CO_2$ from the lower chamber and forming a partial vacuum. This is particularly true in the case of potassium carbonate when that is used. It is also added in order that the reservoir of the dropping-funnel may be recharged without allowing much air to get into the lower part of the generator.

grams) of mercury. This acts as a safety outlet for the excess of carbon dioxide. Generally the tube from the stop-cock should dip about 3.5–4 cm. into the mercury. The bulb in the test-tube prevents the mercury from splashing out of the tube. The top of the test-tube should be loosely packed with cotton to prevent fine particles of mercury from being thrown out. The empty bottle serves as a safety bottle to prevent any of the mercury from being drawn into the generator in case the stop-cock is not closed at the proper time. Whenever carbon dioxide

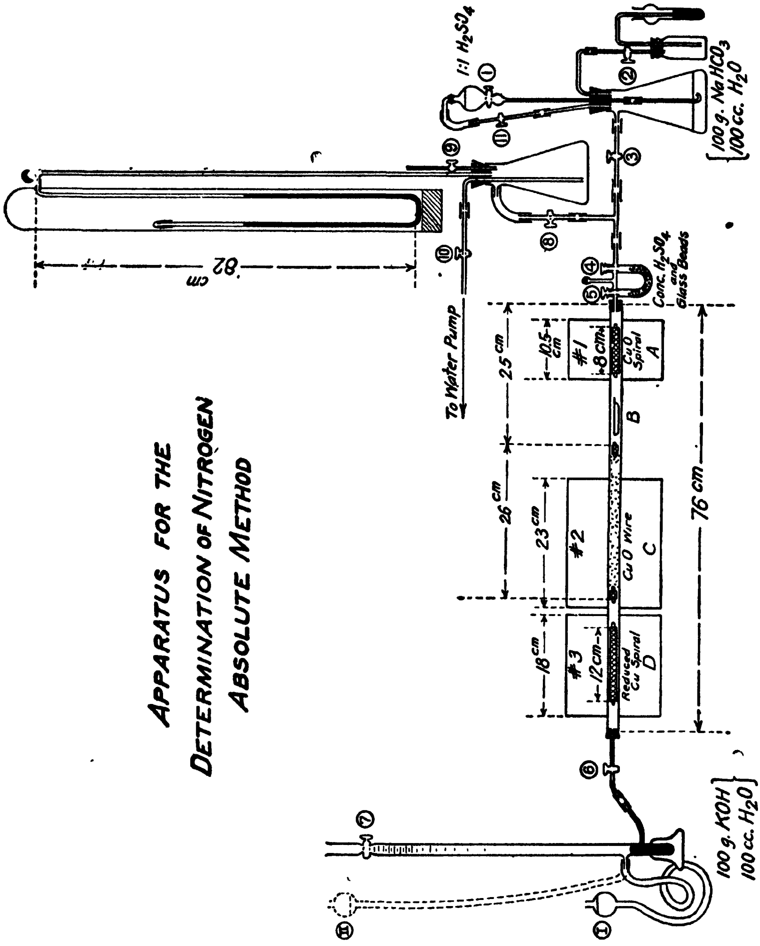


FIG. 20.

is being passed through the apparatus under its own pressure, stop-cock No. 2 should always be left open in order that any excess of pressure can be taken care of.

A capillary tube, 1 mm. inside diameter, bent upwards at the lower end, is attached to the stem of the dropping-funnel,[1] and is arranged to deliver the acid beneath the surface of the bicarbonate mixture. This insures a more even generation of carbon dioxide and better control than when the acid is allowed to drop from the stem. The upward bend prevents the carbon dioxide from going up the stem of the dropping-funnel. Modifications will, of course, suggest themselves to each operator for his convenience.

One hundred grams of pure sodium bicarbonate and 100 cc. of recently boiled and cooled water are used as a single charge for the generator. This is not enough water to dissolve all the bicarbonate, but is sufficient for the purpose. *The bicarbonate mixture should be removed and fresh material put in after each combustion.* Otherwise the supply of carbon dioxide may fail at a critical time when there is no possibility of making the change. One hundred and fifty cc. of a mixture of one part of conc. sulfuric acid and one part of distilled water in the dropping-funnel will serve for at least two combustions.

Sodium bicarbonate and water react to give carbon dioxide even at the ordinary temperature, and at elevated temperatures the bicarbonate is rapidly converted into the normal carbonate. Reduction of the pressure produces the same reaction at lower temperatures, as will be noticed during the operation.

Potassium carbonate has an advantage over sodium bicarbonate as a source of $CO_2$ in that it can be used in a fairly concentrated *solution*. The solution of the carbonate is made up with a specific gravity (1.45–1.5) somewhat greater than that of the sulfuric acid (1.4) and the carbonate solution is put into the dropping-funnel instead of the filter flask of the generator described above. The carbonate solution of sp.gr. 1.45–1.5

---

[1] The joints should be wired, since the rubber gradually swells and becomes loose.

contains 43–47 per cent of potassium carbonate and is prepared by dissolving about 85–90 grams of dry pure normal potassium carbonate in 100 cc. of recently boiled water, and the sulfuric acid solution is prepared by mixing 100 cc. of conc. sulfuric acid and 100 cc. of water. The relative specific gravity of the carbonate solution, when cold, can be tested if a hydrometer is not at hand by seeing if a drop of brombenzene (1.496/16°) or of chloroform (1.498/15°) sinks and a drop of ethyl bromide (1.468/13°) just floats in it, provided, of course, the influence of surface tension is guarded against by stirring. Since the carbonate solution dissolves carbon dioxide with the formation of the bicarbonate which is much less soluble than the normal carbonate and crystallizes out, and since this absorption produces a partial vacuum, the surface of the solution should be covered with a thin layer of petroleum oil[1] to prevent access of the carbon dioxide to the liquid.

A generator with a special stop-cock[2] for dropping the liquid arranged for equalizing the pressure above and below the outlet in the stop-cock is shown in Fig. 21. The equalizing is done through a connection made by means of the annular groove in the key of the stop-cock. No matter which position the key occupies there is always communication between the atmosphere in the lower flask and that in the upper flask. One arm of the stop-cock is extended until it opens above the liquid in the upper container. No outside connection is necessary. The liquid enters at an aperture in the lower part of the extended arm and is delivered through a small glass tube sealed in at this opening. Two styles of stop-cocks are shown in the diagram, using the same general principle in each.

If the flasks are used as shown they must be securely fastened by clamps close to the lips. The upper flask can be filled through

---

[1] Compare Watson Smith, Jr., "Quantitative determination of the carbonyl group in Aldehydes, Ketones, etc." *Chem. News*, **93** (1906), 83; where paraffin oil is used to protect Fehling's solution from absorbing carbon dioxide. Also given in H. Meyer, "Analyse und Konstitutionsermittelung organischer Verbindungen," 2. Auflage, p. 683.

[2] Fisher, *Journ. Ind. and Eng. Chem.*, **10** (1918), 1014.

a funnel attached by means of a piece of rubber tubing. The liquid will flow down the inside walls and not drop into the extended tube. The arrangement and kind of flasks can be changed as desired.

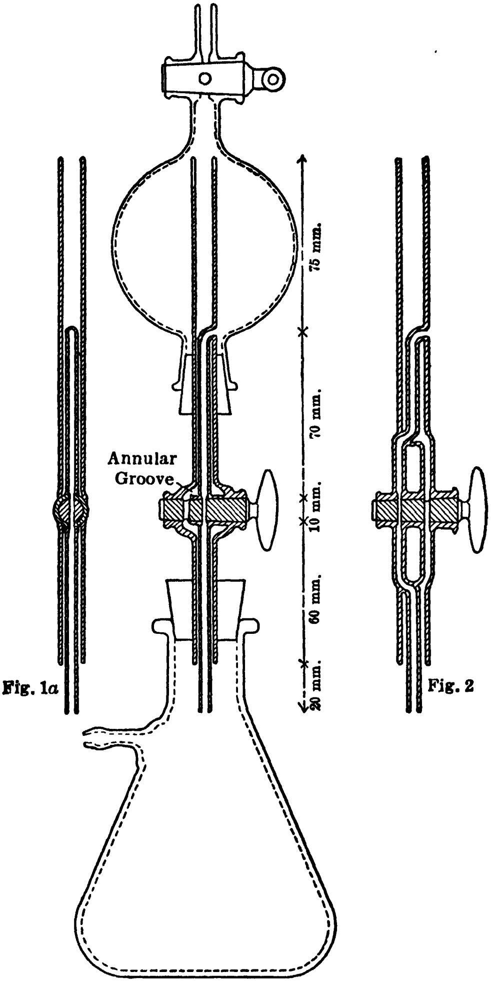


Fig. 1a

Fig. 2

Fig. 1

*Reproduced, with permission, from the Journal of Industrial and Engineering Chemistry.*

FIG. 21.

## Further Notes and References

F. Blau[1] used the potassium carbonate and sulfuric acid as described above. He found that 50–100 cc. of the carbonate solution was needed to drive the air out of the apparatus and only about 20 cc. was needed for the combustion proper. This latter amount in a blank run yielded only 0.07–0.1 cc. of unabsorbed gas in the azotometer, and the author's experience has been similar. Blau remarks that it is not necessary to boil the concentrated carbonate solution since it absorbs a much smaller amount of air than an equal volume of water and only a small volume is used. He adds that a more dilute solution cannot be used without having been boiled, since it absorbs a large amount of air and moreover greater amounts of the solution must be used.

Young and Caudwell[2] used potassium carbonate also in their generator. They found that "the carbon dioxide formed in this manner does not contain 0.1 cc. of air per 5 litres," which means an impurity of less than 1 part in 50,000 (compare below and p. 275). Fieldner and Taylor[3] used this method, and state that "there was little difficulty in clearing the cold tube of air so that the $CO_2$ was completely absorbed," and yet in reply to a letter from the author, Dr. Fieldner said that they tried three samples of potassium carbonate before they obtained carbon dioxide that gave only a minimum of tiny bubbles which were never totally absorbed.

The purest carbon dioxide that has ever been obtained and accurately analyzed and recorded was prepared by Bradley and Hale[4] in connection with work on physical constants of the gas. They used sodium bicarbonate in the form of a paste and conc. sulfuric acid. In guarding against impurities from the air they found it even necessary to place mercury jackets around all rubber connections since air diffuses in as well as carbon dioxide diffuses out through the rubber. In their article other recorded attempts to prepare pure $CO_2$ are given and discussed.

Sodium bicarbonate in the form of dry powder has been used in connection with nitrogen determinations in the open-tube method.

---

[1] *Monatshefte für Chemie*, **13** (1892), 277.

[2] "Apparatus for the Supply of Carbon Dioxide in the Determination of Nitrogen in Organic Compounds by the Absolute Method," *Journ. Soc. Chem. Ind.*, **26** (1907), 184.

[3] *Journ. Ind. and Eng. Chem.*, **7** (1915), 109.

[4] *Journ. Amer. Chem. Soc.*, **30** (1908), 1090.

It is heated in a separate tube. Dennstedt[1] selected this substance for his work. Gattermann[2] also describes how to use it. However, it is difficult to handle and contains occluded air.

Thudichum and Wanklyn[3] recommend a mixture of potassium bichromate and sodium carbonate for yielding carbon dioxide by direct heating.

Magnesite ($MgCO_3$) is used as the source of $CO_2$ in the closed-tube method[4] (see p. 270), but it usually contains small amounts of occluded air.

Carbon dioxide from a Kipp generator cannot be used even when the marble lumps have been boiled with water on account of the occluded air.

The tanks of liquid $CO_2$ as obtained on the market contain considerable amounts of air and therefore cannot be used.

**2. The Manometer, Accompanying Stop-cocks, U-tube, etc.—**—Since diminished pressures are used in the nitrogen determination, it is necessary to have a manometer in connection with the apparatus in order that the operator will be able to understand what to do. The U-form is recommended as shown in the general diagram (p. 276). It is made of ordinary glass tubing and is attached to a wooden stand provided for this purpose. The long arm should be *at least* 82 cm. in length and the short arm at least 55 cm. The short arm is surmounted with an inverted small test-tube with a plug of cotton at the bottom to prevent dust particles from getting into the tube and to prevent mercury from splashing out. With the ordinary glass tubing of about 5 mm. bore, approximately 250 grams of mercury is required. The column of mercury when at rest should extend in each arm 40–41 cm. from the lower bend. If it is much higher than this, it may be drawn over the top when a good vacuum is being obtained. A meter stick may be attached to the board to measure the difference in heights of the two columns,[5] if the actual

---

[1] Dennstedt, " Anleitung zur vereinfachten Elementaranalyse," 3 Auflage, 129.

[2] Gattermann, " Practical Methods of Organic Chemistry," trans. by Schober and Babasinian, 3d Amer. Ed. (1914), p. 101.

[3] *Journ. Chem. Soc.*, **22** (1869), 293.

[4] Gattermann, *loc cit.*, p. 94.

[5] Or short paper scales can be used. Select *any* point, *x*, not less than 38 cm. above the lowest bend in the glass tubing, and attach a narrow strip of paper near

pressure is desired. The pressure within the apparatus may be calculated by subtracting this difference in height from the barometer reading at the time.

The manometer is connected with an Erlenmeyer heavy-walled filtering flask and this is provided with an outlet stop-cock (No. 9) and another stop-cock (No. 10) leading to a suitable pump. When a water pump is used the connection is made to go to the bottom of the filtering flask in order that any water which may come over on account of unequal pressure in the water main will be sucked right out as soon as the greater water pressure returns. A good water pump will give a pressure in the apparatus as low as the vapor tension of the water at its particular temperature. In winter when the temperature of the water may be 8°, at which the vapor tension of the water is 7.99 mm., the pressure within the apparatus may approach 8 mm., but in summer when the temperature of the water may be as high as 23° a pressure cannot be obtained lower than 21 mm., which is the vapor tension of the water at that temperature. A good oil pump can be substituted for the water pump with much advantage.

The outlet of the Erlenmeyer filtering flask is connected by means of a stop-cock (No. 8) to a T-tube which joins the generator and a U-tube with ground stoppers. The U-tube is filled with glass beads and just enough conc. sulfuric acid is added to make a seal at the bottom and no more. The glass beads serve to prevent the acid from being splashed upon the stop-cocks. The acid attacks the grease and causes leakage as well as sticking of the stoppers. The acid is used to prevent an excess of moisture from the carbon dioxide from getting into the combustion tube and it also shows which way the gases are flowing. The amount

---

the top and one near the bottom of the stand. Measuring from the point $x$, mark on the papers numbers showing 28 to 38 cm. up and down, respectively. The numbers may vary according to the positions of the papers. Ruled centimeter paper is very convenient, and when this is used it should not be attached until a definite point opposite a centimeter line has been located. In order to calculate the pressure within the apparatus, add the numbers on the lower and upper scales opposite the top of the mercury meniscus and subtract the sum of these numbers from the barometer reading at the time.

of carbon dioxide flowing into the combustion tube is regulated by one of the stoppers (No. 5).

All connections are made with short lengths of heavy-walled rubber " pressure " tubing.

All stop-cocks should be carefully cleaned and greased with a good stop-cock grease, such as that prepared by Eimer & Amend, New York (see p. 229). Do not plug up the opening in the key with grease. Too much grease is worse than too little. Also do not use vaseline, since it has no " body." *Great care should always be exercised in turning the keys in the stop-cocks to see that they fit tightly and do not leak.* Never turn the key by using only one hand. Support the other side of the stop-cock with the other hand and use just a little pressure when turning the key. Fasten the keys with wire or twine, not with elastic bands, to avoid possible breakage (compare p. 229). The parts of all stop-cocks should be numbered in order that they will be properly assembled.

An alternative method of preparing the manometer is to use a straight glass tube, about 85 cm. long, dipping directly into mercury. The bottle containing the mercury should be of such a size that when the excess of $CO_2$ is passing out of the tube the pressure will be all right for the conditions involved, that is, the layer of mercury through which the gas must pass will be somewhat greater than that in the azotometer. Otherwise the gas would pass out at this opening instead of going into the azotometer. The method has the advantage of less apparatus, but the pressure in the generator cannot so easily be regulated as in the method described above, and there is more space to be emptied of air and kept filled with $CO_2$ all the time the combustion is being run, since stop-cock No. 8 cannot be shut off.

3. **The Electric Combustion Furnace.**—An electric combustion furnace of the multiple unit type is the most convenient furnace to use for heating the combustion tube in the determination of nitrogen. The arrangement of the heating sections and the heat control should be the same as described for the carbon and hydrogen combustion (p. 230).

### NOTE

Water formed in the reaction sometimes collects in the end of the combustion tube near the azotometer, especially if an extra long extension is used. Since the water is not needed no provision is made for getting rid of it. However, if it is allowed to collect, it will cause some combustion tubes to crack. In order to keep it from flowing back along the heated portion of the tube and causing the tube to crack, the tube may be slanted somewhat by blocking up the other end of the furnace 2–3 cm. above the level of the desk.

**4. The Combustion Tube and How to Fill It.**—The combustion tube itself should be the same in every way as the one described in connection with the determination of carbon and hydrogen (pp. 232–3).

The method of filling is indicated in the general diagram (p. 276). An 8-cm. roll of cupric oxide gauze (see p. 235) is prepared and placed at *A*, near the end to which the U-tube is connected. It serves the same purpose as the one in the carbon and hydrogen combustion, that is, mainly as an " oxidation buffer " in preventing any gases which may go backward from getting so far back that the determination is spoiled (see p. 235).

About 25 cm. from this same end of the combustion tube, place a short roll of copper gauze, fitting snugly; follow this with a layer of cupric oxide [1] in *wire* form, and keep this in place with another snugly fitting short roll of copper gauze. This entire layer, including the short " spirals " should measure approximately 26 cm. The open space, *B*, between the long cupric oxide " spiral " and the long layer of cupric oxide, is reserved for the boat.

For the far end of the combustion tube which is heated by section No. 3, prepare a 12-cm. roll of copper gauze, *D*. This is always used in the reduced condition in order that any oxides of nitrogen that may be formed will be converted into elemental

---

[1] Cupric oxide, which has been used for the determination of carbon and hydrogen, can be used for the determination of nitrogen, although the opposite is not the case on account of the possible retention of carbon dioxide, unless it has been heated in the open for a long time and allowed to cool in the air. The cerium dioxide catalyst cannot be used in the nitrogen determination.

nitrogen before passing into the azotometer. The reduction is carried out as follows: Select a Pyrex test-tube of such a size that the roll of copper gauze will fit in it loosely. Place a wad of asbestos or glass wool at the bottom, add not more than 1 cc. of methyl alcohol, and support it in a stand. Heat the spiral to redness over a Meker burner or in a very large blast flame. In order to avoid melting the copper the lower end of the spiral is slowly swung to and fro while the upper end is securely held in its position by the little loop with a pair of tongs. In this way the entire gauze is evenly heated. Then quickly drop it into the test-tube, and ignite the issuing vapors. Do not breathe the fumes, since they consist largely of formaldehyde. If the heating has been done properly the copper soon looks beautiful in the reduced condition. When the flame dies down and just as it recedes into the tube, put in the cork loosely, and set aside until it becomes cold before placing the spiral into the combustion tube. If the tube is not stoppered, the hot spiral will be reoxidized as air follows the flame down the tube.

5. **The Azotometer.**[1]—The nitrogen is collected and measured in a Schiff azotometer.[2] It is illustrated in the general diagram on p. 276, and as shown it consists of a graduated tube surmounted with a stop-cock and extension cap, and near the bottom arranged as indicated for a gas inlet protected by mercury and a

---

[1] The term "azotometer" is used instead of "nitrometer," as the apparatus is sometimes called, since the latter refers more directly to the measurement of nitric oxide formed in the analysis of nitric acid by reduction with mercury in presence of sulfuric acid, while azotometer literally means the nitrogen measure. (French, azote; Greek, μετρον (metron)). Schiff speaks of it in his original article, *Zeit. anal. Chem.*, **7** (1868), 430, as an "azotometer." Lunge, *Ber.*, **11** (1878), 434, named his nitrometer from the fact that he desired it for analyzing "nitrose," which is defined by Patterson in his "German-English Dictionary for Chemists" as "a solution of nitrosylsulfuric acid in sulfuric acid, formed in the lead-chamber process." This material is known in English as "nitrous vitriol" and described in the "Century Dictionary" as "strong sulfuric acid charged with nitrosulphonic acid. It runs off from the bottom of the Gay-Lussac absorbing tower in the manufacture of sulfuric acid by the lead-chamber process." Lunge also mentions "Gay-Lussac-Thurm-säure" (Gay-Lussac tower acid). Compare also Lunge, "Technical Methods of Analysis," trans. by Keane (1908), Vol. I, Pt. I, 125 and 131.

[2] Schiff, *Zeit. anal. Chem.*, **7** (1868), 430.

connection by means of a rubber tube to a reservoir which holds the solution of potassium hydroxide. An adjustable ring (not shown in the diagram) is attached for holding the reservoir in any position desired. The tube proper should be about 7–8 mm. inside diameter, 48 cm. long (measured from the reservoir outlet to the stop-cock) with a capacity of 50 cc. of gas and graduated in one-tenths. Enough mercury (about 10 cc. or 135 grams) should be put into the bottom to make a good seal for the inlet tube [1] but not enough to splash over into the tube leading to the reservoir. The distance between these inlet and outlet tubes should be not less than 3 cm. Furthermore the inlet tube should be bent upwards to such an extent (about 8 cm.) that the mercury will not run over when the reservoir full of KOH solution is raised to the top of the azotometer.

Some azotometers are made without the cup sealed on top, but have a narrow tube for connecting with a eudiometer for transferring the gas. A cup can be put on one of this type by attaching a wide tube by means of a rubber stopper. Some azotometers are provided with water jackets, but it does not appear necessary to use this for general work.

The stop-cock should be well ground and all directions given for handling stop-cocks should be used in handling this part of the azotometer (see pp. 229 and 283). Be sure that all parts of both key and barrel are dry before putting on the grease. Except when the apparatus is actually in use the key of the stop-cock should not be allowed to remain in its proper position, since it is very likely to become "frozen" even on standing overnight if there is any of the potassium hydroxide solution in the grease.[2] Attach it with a piece of twine.

---

[1] Dennstedt in his "Anleitung zur vereinfachten Elementaranalyse," 3 Auflage, 125–8, describes a modified azotometer which has a capillary inlet tube ending in an internal projection which delivers a fine stream of gas, and which also has an enlarged portion below the graduated part to serve as a reservoir in case a large amount of gas is suddenly delivered into the azotometer.

[2] An excellent method of removing "frozen" stop-cocks is given by V. C. Allison, *Journ. Ind. and Eng. Chem.*, **11** (1919), 468. The handle of the key is slipped into a socket in a block of hard wood while the opening of the block rests as a collar on the shoulder of the barrel of the stop-cock. A plug of wood is placed against the other end of the key, and easy regular pressure brought to bear by

The potassium hydroxide[1] solution is prepared by dissolving 100 grams of solid potassium hydroxide in 100 cc. of water. Since much heat is developed a porcelain or quartz casserole should be used. The solution should be clear and free from foreign particles. It can be filtered through an ordinary wet fluted[2] filter paper if the solution is added slowly. The amounts given are sufficient for the azotometer described above, and are enough for at least two " runs." The solution may become colored from contact with the rubber tubing but this seems to do no harm.

The mercury can be purified by washing, and then, after removing most of the water, filtering it through a dry filter paper containing a few tiny holes in the bottom. Repeat several times if necessary.

**Testing the Azotometer.**—Clean it thoroughly, properly grease the stop-cock, and add the mercury and the potassium hydroxide solution. Attach stop-cock No. 6, open it and also No. 7, the one on the azotometer (see general diagram, p. 276). Lift up the reservoir slowly from position I to position II, and note the rise of the mercury in the inlet tube. It should not go into the tube of the stop-cock, although this will do no particular harm, but it should never go beyond the stop-cock. Lower the reservoir until there is 4–5 cc. of air in the tube, then close the stop-cock (No. 7). Now lower the reservoir to position I and after allowing two to three minutes for drainage take the reading and record it. Allow the apparatus to stand for twenty to thirty minutes, take the reading under the same conditions, and compare with the previous reading. If there is no decided change and no chance for temperature fluctuation, the stop-cock is tight, but if the volume has increased there is something wrong with the stop-cock or with the greasing.

---

means of a vise. Different sizes are given for the ordinary stop-cocks in use. The scheme is rapid and it works!

[1] Sodium hydroxide cannot be used, since the carbonates formed crystallize out and cause much trouble.

[2] See foot note, p. 128.

## V. The Final Preparation of the Cupric Oxide[1]

Cupric oxide when heated and cooled in an atmosphere of oxygen or air adsorbs some of these gases. The cupric oxide thus

[1] NOTES AND REFERENCES

Cupric oxide has been used in organic combustions for the determination of carbon and hydrogen and nitrogen since 1815 (see p. 218), and the method for determining nitrogen separately was worked out especially by Dumas in 1831 (see p. 269). That cupric oxide absorbs gases and gives them up on heating was noticed as early as 1842, when Erdmann and Marchand, *J. für prakt. Chem.*, **26** (1842), 466–7, working "On the atomic weight of hydrogen," showed that 100 grams of cupric oxide when heated in an atmosphere of carbon dioxide after "pure carbonic acid" had been passed through the tube for many hours, gave 5.5. cc. of air unabsorbed by potassium hydroxide solution. In 1868 Frankland and Armstrong, in an article "On the Analysis of Potable Waters," *J. Chem. Soc.*, **21** (1868), 89 and 93, described their method of determining carbon and nitrogen in very small amounts of organic material by burning it in a combustion tube after complete evacuation with a Sprengel pump and analyzing the gases evolved. They state, "Cupric oxide prepared from the nitrate should on no account be used, since, even after being actually fused, it evolves considerable quantities of carbonic anhydride and nitrogen when ignited *in vacuo*." Eight years later Thudichum and Kingzett, *J. Chem. Soc.*, **30** (1876), 363, confirmed these findings in general. Hilditch, *Chem. News*, **49** (1884), 37, mentions the fact that cupric oxide occludes air, and Morley, *Amer. J. Sci.*, **41** (1891), 281, shows that cupric oxide slowly gives off gas in a vacuum. T. W. Richards, in revising the atomic weight of copper, *Proc. Amer. Acad. Arts and Sci.*, **26** (1891), 281, and *Zeit. anorg. Chem.*, **1** (1892), 196; proved that several of the formerly accepted results were incorrect on account of the error involved due to gas adsorbed by the cupric oxide which had been used for the determinations. In his later systematic work on this particular subject, "On the Cause of the Retention and Release of Gases occluded by the Oxides of Metals," *Amer. Chem. J.*, **20** (1898), 701, he states (page 711), "When the imprisoned gas (in cupric oxide) has once begun to be set free, at temperatures above 850°, the time is an essential factor, and that when sufficient time has been allowed, the expulsion of the gas is almost complete." Furthermore (p. 727), "Two grams of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting-point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed." Cupric oxide begins to lose "structural oxygen" even in the air at about 1000°, but this is above the melting-point of the hard glass used. Cuprous oxide was found in the residue. The observation is then made (p. 728):

"Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide prepared on being heated again *slowly* gives off the adsorbed gas. Since the gas which is slowly given off is not absorbed by the

as a displacing medium in the Dumas method, probably disposes of the error, however, for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide." (NOTE.—It should be emphasized that this latter statement refers only to the liberation of gas from the actual decomposition of the cupric oxide and not to the liberation of occluded gases.)

The gas occluded in the cupric oxide is only slowly given off by heating to redness, and the error involved in the nitrogen determination amounts to +0.2 to 0.5 per cent[1] (usually nearer the *higher* figure) when 0.2 gram of the sample is used. Diminishing the time of the combustion of course diminishes this error, and usually there are compensating errors, which vary a great deal, in general practice which also sometimes keep the final error down to the ordinary amount, that is, 0.2 per cent. When a substance with a high content of nitrogen is analyzed the "percentage error" is of course decreased, but with a low content of nitrogen it is very serious. None of the text-books on practical organic chemistry to which one would ordinarily go for a description of the Dumas method, such as those by Gattermann, W. A. Noyes, and J. B. Cohen, say anything about this error, Neither is it mentioned by Clarke, "A Handbook of Organic Analysis;" Kingscott and Knight, "Quantitative Organic Analysis;" nor even by Lassar-Cohn "Arbeitsmethoden," allgemeine Teil, 4 Auflage (1906); and Weyl, "Die Methoden der organischen Chemie," allgemeine Teil (1909). All these authors do generally speak of the "minimum amount of foam" that always collects in the top of the azotometer and which Thudichum and Kingzett, *J. Chem. Soc.*, **30** (1876), 366, characterized as "*that obstinate bubble in the gas-tube which has puzzled so many of the best experimentalists.*"

In 1915 Fieldner and Taylor, *J. Ind. and Eng. Chem.*, **7** (1915), 106, attempted to check up their results of the analysis of some samples of coal for nitrogen, made by modifications of the Kjeldahl method, with the Dumas method since "it is generally regarded as fundamental and applicable to most classes of organic compounds." Since the coal contained only very small amounts of nitrogen, approximately 1 per cent, they naturally tested their apparatus and method, as given in the usual references, by blank runs, and found what many others have also found, that varying amounts of gas were given off, for example, 6.6 cc. after six hours' heating followed by 1.4 cc. when the tube was re-heated the next day. They then noted the following remarks by H. Meyer in his "Analyse und Konstitutionsermittelung organischen Verbindungen," 2 Auflage (1909), 187, "The chief source of error lies in the impossibility of freeing the fine copper oxide from air, and therefore most of the results are too high by 0.1 to 0.2 per cent." Also, in Fresenius-Cohn, "Quantitative Chemical Analysis," 6th Ed., II (1904), 68, "The results are generally somewhat too high, viz., by about 0.2 to 0.5 per cent," and that in a blank experiment with sugar the quantity of unabsorbed gas "should not exceed 1 or 1.5 cc." H. N. Morse, "Exercises in Quantitative Chemistry" (1905), provides in part for the difficulty by heating both coarse and fine cupric oxide for 1½ hours at full red heat in a current of oxygen which is followed, without

---

[1] F. Blau, *Monatschefte*, **13** (1892), 277.

potassium hydroxide solution in the azotometer. it causes a serious error in the determination of nitrogen.

To prepare the cupric oxide for the analysis, it must be heated strongly to a good red heat, just as in the combustion itself, in a vacuum for about six hours, the gases being removed and replaced by " flooding " the apparatus two or three times with pure carbon dioxide. Finally the cupric oxide is allowed to cool in an atmosphere of pure carbon dioxide. In this manner the gas adsorbed is one that will cause no trouble in the analysis.

After the entire apparatus[1] is set up and the generator properly filled, according to the description in Chapter IV, p. 275, set the stop-cocks as follows: Nos. 1, 2, 6 and 9 closed, and 3, 4, 5, 7, 8, 10, and 11 open; then turn on the pump, and also begin the heating. It is not necessary that the heating be done without interruption, but if it is interrupted the cupric oxide must be allowed to cool in an atmosphere of carbon dioxide, otherwise little will have been accomplished.

Soon after the apparatus has been evacuated, occluded and

---

cooling, by carbon dioxide for an hour or more, and the oxide is allowed to cool in $CO_2$. Finally in an obscure journal, in an article published in 1898 by F. C. Phillips, on the " Fluctuation in the composition of Natural Gas," *Proc. Eng. Soc. Western Pa.*, **14**, 299, they found an account of similar difficulties overcome: " In beginning a series of determinations several days were often required for the purpose. The porcelain tube was strongly heated, while a slow stream of carbon dioxide was maintained; the CuO was not considered to be in proper condition until the escaping $CO_2$ was absorbed without residue. It was found that the CuO when once impregnated with $CO_2$, while strongly heated, could be reoxidized by air current with little tendency to occulsion of air, but if the copper oxide was allowed to cool in contact with air much time was lost in removing the air by carbon dioxide even when strong heat was applied." Fieldner and Taylor then proceeded to shorten the time for the final preparation of the cupric oxide by heating it *in vacuo*. It is well worth one's while to go over their recorded experiments as given in their original article mentioned above. They concluded that, " Errors in the Dumas method due to nitrogen from the CuO were minimized by previously heating the oxide for several hours *in vacuo*, cooling it in $CO_2$, and using ' wire form ' oxide pulverized to pass through a 40-mesh screen and remain on 100 mesh." These results are incorporated in the present work.

[1] The boat filled with CuO wire should be in place (p. 284), but the reduced copper spiral should, of course, not be in the tube during the preliminary heating (pp. 294-5). Also, it is not absolutely necessary to have the azotometer attached at this time.

dissolved air and finally some $CO_2$ will begin to come out of the materials in the generator. In order to help get rid of as much air in the generator as possible, allow a little sulfuric acid to flow into the carbonate mixture. After the vacuum has been maintained for about half an hour, close No. 3 and leave the generator under these conditions until you are ready to flood the apparatus with $CO_2$.

To flood the apparatus with $CO_2$: Close No. 10, *then* turn off the pump. If No. 3 has been closed during the heating, gradually open it. The mercury in the manometer will fall somewhat. Now allow the sulfuric acid to flow slowly into the carbonate mixture.[1] Carefully watch the fall of the mercury, and when the two columns are level quickly open No. 2 in order that the excess of $CO_2$ may pass out. By opening No. 6 (leaving No. 7 open also if the azotometer is attached) the gas can sweep out the entire apparatus. Then close No. 6 and No. 3, turn on the pump, and open No. 10, and continue the heating as before.

When the six hours' heating is at an end, flood the apparatus once again in the same way as before, making certain that No. 2 has been closed before No. 3 is opened. Now turn off the heat and allow the cupric oxide to cool in the atmosphere of $CO_2$. The tube may be left alone to cool after closing Nos. 5 and 6 If you have time, pass $CO_2$ through the tube while it is cooling; but this is probably not necessary. When you leave the apparatus for the night, see that Nos. 5, 6, 1, 2, 10, and 11 are closed; and that 3, 8, and 9 are open.

In order to avoid contaminating the carbon dioxide in the generator with air from possible leaks when the generator is under diminished pressure, it is well to keep it under a little pressure practically all the time and especially during the combustion, allowing the excess to pass out through stop-cock No. 2 and the mercury trap. By exercising a little care you will find it possible to keep the generator under pressure even when connecting it with the apparatus that has been evacuated. After stopcock No. 10 has been closed and while a good stream of gas is

---

[1] Too much acid at one time will cause the mixture to foam over into other parts of the apparatus.

going out through the mercury trap, partially open stop-cock No. 3, watching the overflow all the time. As soon as the mercury begins to rise in the outlet tube close stop-cock No. 3, and then gradually open it again. Frequent glances at the manometer will show how the operation is going on. In this way the apparatus will soon be filled with carbon dioxide and the generator always kept under pressure and free from contaminating air.

After the cupric oxide has been heated and cooled in $CO_2$, it can be handled in the open but not without adsorbing air that will cause a small error. For example, Fieldner and Taylor[1] found that when 100 grams of the cupric oxide "was subjected to alternate vacuum and carbon dioxide for several hours at 850° C., until no further nitrogen was evolved, and was then cooled in $CO_2$, exposed to air and again heated, the 40–100 mesh 'wire' oxide gave off only 0.7–0.9 cc. of nitrogen, while the 200-mesh material gave off 1.9–2.2 cc."

When a combustion has been run it is necessary to reoxidize some of the copper, and have it ready for another determination. Before turning off the heat (or after allowing to cool in $CO_2$), remove the reduced copper spiral, and while the tube is hot pass air or oxygen through it until all the copper has been oxidized. Then while the tube is still hot, replace the air or oxygen with pure $CO_2$ in the usual manner, keeping up the passage of the carbon dioxide for an hour, and allow to cool in the atmosphere of $CO_2$ while the tube is closed. It is not necessary to heat again for six hours as is the case when the cupric oxide has been *cooled* in air

## VI. Weighing the Substance

The substance is weighed in a porcelain or quartz boat inside the special boat tube ("piggie") and all precautions as to moisture, state of division, etc., mentioned in connection with weighing the substance for the carbon and hydrogen determination must be observed in this case also (see p. 252). After the substance has been weighed, and the weight recorded, it is not

---

[1] *Journ. Ind. and Eng. Chem.*, **7** (1915), 111.

essential in most cases that moisture be so rigidly excluded as for the carbon and hydrogen determination. However, it is unfortunate for one to let down on the good practice of keeping moisture from weighed samples, and thus spoil a good habit.

The amount of substance used should ordinarily be about 0.2000 gram. If the nitrogen content is approximately known, use enough substance to give about 15–20 cc. of nitrogen. Some substances have a high percentage of nitrogen, and 0.2 gram would give more nitrogen than the azotometer could hold. Then the amount of sample should be cut down accordingly. Correspondingly, the amount of sample of a substance with a very low content of nitrogen should be increased, even to 0.5 gram, if necessary, and provided this much can be spared.

### VII. General Method of Procedure for the Combustion Proper

**Testing the Apparatus.**—After the cupric oxide has been prepared and the tube filled with carbon dioxide as already described (p. 288), test out the entire apparatus to see if the cupric oxide is all right, the carbon dioxide is pure enough, and all joints are in good condition. Have all of the apparatus connected and heat the combustion tube as for a regular combustion. Pass carbon dioxide through it and into the azotometer for five to ten minutes.[1] In order not to exhaust the potassium hydroxide solution, drop the reservoir to position I, and have stop-cock No. 7 in the azotometer open. At the end of the time specified, while the gas is still passing, carefully raise the reservoir to position II when the solution will flow through the stop-cock and into the cup on top. Now close the stop-cock and slowly lower the reservoir to its former position in order to reduce the pressure against the inflowing gas. Pass the gas through at a fair rate for about five minutes. The bubbles should not be so large and come so fast that they fill the entire azotometer tube and force all the potassium hydroxide solution into the reservoir. After the five minutes note whether the volume of unabsorbed gas which collects at the top is more than 0.1 cc. It is difficult to

---

[1] In order to take care of any excess of pressure in the generator, be sure to have stop-cock No. 2 open (see p. 277).

formulate any rule for how much unabsorbed gas should be allowed, since the rate varies, etc., but if much gas collects, then the stop-cock (No. 7) should be opened again to let the solution flow down and carbon dioxide run through freely for another five minutes, and a second trial made for almost complete absorption as before. If the gas is not passing too rapidly the bubbles diminish to the size of pin-points as they float upward. If much unabsorbed gas is collected again either the cupric oxide has not been properly prepared or the generator and joints leak or the carbonate is impure, and these must be attended to. This operation shows the chief error involved in the determination of nitrogen and therefore the error in the final result will be in almost direct relation to the amount of gas unabsorbed in these blank tests.

If there is any doubt as to the proper condition of the apparatus a complete blank run should be carried out, using, for example, 0.2 gram of sucrose (cane sugar) in place of a nitrogenous substance.

When the test is satisfactory let that part of the combustion tube which is to contain the boat, and several centimeters each side of it, cool down to room temperature. During the cooling reduce the rate of the carbon dioxide, or close stop-cocks Nos. 5 and 6 to prevent any of the potassium hydroxide solution from being drawn into the combustion tube. If a combustion is not to be made immediately, let the entire tube cool down in an atmosphere of carbon dioxide (see p. 291).

**The Combustion.**—The following arrangements are made for beginning the combustion proper depending upon whether the furnace is *cold* or *heated* in part:

*a.*[1] If the furnace is *cold*, disconnect both ends of the combustion tube, carefully remove the cupric oxide spiral, insert the boat containing the substance,[2] replace the cupric
*b.* oxide spiral, and then insert the *cold* reduced copper spiral

---

[1] These letters in the margin refer to the corresponding parts in the Topical Outline, section 11, p. 273.

[2] If the substance burns with difficulty it should be covered with some of the cupric oxide wire already prepared for this purpose (p. 290).

in the position reserved for it beyond the layer of cupric
c. oxide. Connect up the apparatus again, remove the air
by evacuation and flood with pure $CO_2$ by the usual proce-
d. dure. While the reservoir of the azotometer is in position
I and stop-cocks Nos. 6 and 7 are open, and carbon dioxide
is slowly passing through the apparatus, heat the reduced
copper spiral to redness in order to drive out any occluded
gases, such as hydrogen and air, and then heat the adjacent
cupric oxide, making certain that the substance in the
boat is not heated at all. This can be done if the long
heating section, No. 2, is pushed over toward the *reduced*
spiral (see general diagram, p. 276).

e. While the tube is thus being heated, test the apparatus
to see if the amount of unabsorbed gas is at a minimum, as
f. described at the beginning of this chapter. If the sub-
stance decomposes readily the heating of the cupric oxide
should be delayed until after the final test.

If the combustion tube has been *heated* and only that part
which is to contain the boat and several centimeters on each
side of it including the cupric oxide spiral have been allowed
to cool down practically to room temperature, then, in order
to make the final preparations, disconnect both ends of the
combustion tube, carefully remove the cupric oxide spiral,
a insert the boat containing the substance,[1] and quickly
replace the spiral. Connect up this end only, leaving
the other end open, and pass $CO_2$ rapidly through the tube.
When you are reasonably certain that the air has been
b. driven out, insert the cold reduced copper spiral into the
c. heated part of the tube and quickly connect the azotometer,
making sure beforehand that stop-cocks Nos. 6 and 7 are
d. open and the reservoir is in low position I. In this way
the reduced spiral will not become oxidized, provided there
is a good flow of $CO_2$. Any occluded gases in the reduced
spiral will be driven out in about five minutes of strong
e. heating. Now test the apparatus to see if the amount of

---

[1] As stated above, if the substance burns with difficulty it should be covered with some of the cupric oxide wire already prepared for this purpose (p. 290).

unabsorbed gas is at a minimum, as described at the beginning of this chapter.

*f.* It must be borne in mind that these preliminary operations should be varied in accordance with the properties of the substance. If it has a high vapor pressure and sublimes readily or is easily melted, the time factor must be reduced, the heating regulated, etc. Furthermore, it cannot be overemphasized that good judgment and familiarity with the method are always very necessary to give reliable results.

As soon as it has been found that the amount of unabsorbed gas has been reduced to the proper minimum *g.* amount, reduce the flow of carbon dioxide to such an extent that it will just keep the products of combustion moving toward the azotometer, using the stopper (No. 5) in the U-tube for regulating the gas, and allowing the excess of carbon dioxide in the generator to escape regularly through stop-cock No. 2 and the safety bottle.

Raise up the reservoir and when it is opposite the stopcock (No. 7), open the stop-cock to allow the small amount of unabsorbed gas that may have collected to pass out, carefully close the stop-cock, leaving some of the solution in the cup above, and lower the reservoir to position I. If there has been any indication that the substance has begun to decompose then the small amount of unabsorbed gas should not be driven out of the azotometer lest some nitrogen from the substance be driven out too.

***h.*** Now gradually heat more of the cupric oxide by drawing the long heating section (No. 2) toward the boat a centimeter at a time, and at the same time begin to heat slowly the cupric oxide spiral on the other side of the boat with section No. 1.

As mentioned in connection with the carbon and hydrogen determination (p. 254), it is very difficult to describe in detail the actual method of burning the substance, since each one has its own peculiarities, and therefore only a general description can be given. Here also an idea as to how the substance behaves on heating should be gained beforehand, if sufficient is available, by heating it and gradually burning it in a boat over a small flame. Notice whether it gradually burns, sublimes, or suddenly decomposes.

The substance is slowly burned by *gradually* drawing the two adjacent sections closer and closer in alternate turns toward the boat. When the large heating section (No. 2) is over all the cupric oxide do not draw it any further. Use the small heating section (No. 1) to heat and slowly and completely decompose the substance in the boat. Since the substance chars and the carbon is not completely burned in the presence of carbon dioxide, the amount and appearance of the black deposit does not give a very good indication of the course of the combustion. But the amount of gas which enters the azotometer, and, passing upward, is only partially absorbed, does give a good idea as to how the combustion is progressing. The gas should not come through so fast that the bubbles will be very large and rapidly fill the azotometer tube, since there is danger that all the potassium hydroxide solution will be driven over into the reservoir and then the gas will follow!

After about twenty minutes the substance will all be decomposed and the rate of the gas entering the azotometer will then decrease to that of the carbon dioxide itself.
*i.* Now drive over the remaining nitrogen with carbon dioxide by gradually increasing the flow of the latter, and continue this until the bubbles of unabsorbed gas are very tiny just as was noticed before the combustion was begun. If the volume of nitrogen in the azotometer is large the bubbles will not have very much liquid through which to travel and on this account it is sometimes not so easy to make a proper comparison. In such a case the gas is run through for about ten minutes after it appears that all the nitrogen has been driven over.

*j.* Then close stop-cock No. 6 (between the azotometer and the combustion tube), and wash the nitrogen in the azotometer with one portion of the potassium hydroxide solution. This is done while the reservoir is in the low position (I), the stop-cock being carefully and partially opened to allow the solution to run easily down the inside walls to absorb any traces of carbon dioxide that may be present, and closed before all the solution has left the cup. Now wash the gas in a similar manner with successive portions of cold distilled water which has been recently boiled to drive out dissolved air,[1] until all the potassium hydroxide solution is out of the azotometer and the reservoir also. Always keep some liquid in the cup. While the washing is being done do not let the potassium hydroxide solution overflow. It should be poured out and saved for a second combustion unless it is " spent," and when you pour it out be sure not to pour all of it at a time, since air may get into the rubber tube and then into the azotometer!

*k.* Raise up the reservoir until the liquid in it is on a level with the liquid in the azotometer in order that the nitrogen will remain at atmospheric pressure, thus preventing any error from leakage, etc., and clamp the holder of the reservoir in this position. Place a thermometer in some water in the cup above, or hang it beside the azotometer, and allow the apparatus to remain untouched in a room of uniform temperature for at least twenty to thirty minutes. Then record the volume of the gas, as read by the bottom of the meniscus, the temperature, and also the barometric reading and the temperature of the barometer.

*l.* From these results and the weight of 1 cc. of *moist* nitrogen (given in milligrams) as found in the accompanying tables, for the proper temperature and pressure, you can calculate the weight of nitrogen obtained and then the percentage of nitrogen in the substance (see section on Calculations, p. 300).

---

[1] Otherwise this air will be liberated when the water mixes with the potassium hydroxide solution which does not dissolve as much air as water does.

## NOTES

1. Some operators prefer to measure the nitrogen over the potassium hydroxide solution. The weight of the nitrogen is different from what it is when measured over water on account of the difference in vapor pressure of the two liquids. One of the difficulties, however, in reading the volume over the alkaline solution is that it is practically impossible to get rid of the foam.

2. If only a small amount of water is used for the washing, not enough to displace all the potassium hydroxide solution, the column of liquid in the reservoir and its connecting tube will be of a greater density than the water in the azotometer tube. This means that the volume of nitrogen will be somewhat compressed when the two columns are leveled for the reading. This error would of course aid in reducing the "normal" error which is always too much, but any *known* error in manipulation should not be tolerated.

3. Some azotometers are made in such a way that water is retained at the top of the tube under the stop-cock. This changes the reading of the volume of nitrogen. By gently tapping the tube it can be made to run down the walls to the liquid below. Then allow it to stand, etc.

In order to have the tube ready for another combustion, the cupric oxide which has been partially reduced must be reoxidized. Do not allow the cupric oxide to cool with air in the tube if another combustion is to be made.[1] Without allowing the furnace to cool, disconnect the azotometer, remove the reduced copper spiral from the end near the azotometer, and while the tube is continued to be heated to redness draw air through it for several minutes. Then *without diminishing the heat* remove the remaining air and flood the apparatus with carbon dioxide in the usual manner. Now it may be used again at once, or it can be closed off and the cupric oxide allowed to cool in the atmosphere of carbon dioxide (p. 291).

---

[1] If there is not time to re-oxidize the cupric oxide, be sure to let the tube cool with carbon dioxide in it.

### General Notes

1. Some substances give off gases, such as methane, which are not oxidized by the cupric oxide in the absence of oxygen gas. These must be mixed with coarsely powdered lead chromate or freshly precipitated cuprous chloride, and the long layer of cupric oxide replaced with lead chromate.

2. In some cases the entire space occupied by the boat must be filled with cupric oxide mixed with the substance in order to get intimate contact.

3. If any nitric oxide, NO, has escaped the action of the reduced copper spiral its presence can be shown by the brown fumes formed when the nitrogen gas is allowed to come out into the air. Nitrogen as nitric oxide occupies only half the volume of the same amount of nitrogen in the free state.

## VIII. Calculations, and Discussion of Results

Having ascertained the volume of the nitrogen, $V$, its temperature, $t$, and the barometric reading and the temperature of the barometer (p. 298), correct the barometric reading to zero by using the following formula and table.[1]

$$H_0 = h - at$$

where $H_0$ = corrected reading;
$h$ = observed reading;
$a$ = coefficient;
$t$ = temperature;

| $h$ | $a$ | $h$ | $a$ | $h$ | $a$ | $h$ | $a$ |
|---|---|---|---|---|---|---|---|
| 720 | .1170 | 736 | .1196 | 752 | .1221 | 768 | .1248 |
| 722 | .1173 | 738 | .1199 | 754 | .1224 | 770 | .1251 |
| 724 | .1176 | 740 | .1202 | 756 | .1228 | 772 | .1254 |
| 726 | .1180 | 742 | .1205 | 758 | .1231 | 774 | .1257 |
| 728 | .1183 | 744 | .1208 | 760 | .1235 | 776 | .1261 |
| 730 | .1186 | 746 | .1212 | 762 | .1238 | 778 | .1264 |
| 732 | .1189 | 748 | .1215 | 764 | .1241 | 780 | .1267 |
| 734 | .1192 | 750 | .1218 | 766 | 1245 | | |

---

[1] This table gives the correction for a brass scale. The correction is approximately 8 per cent greater for a glass scale. It is very convenient to place a copy of this table for ready reference in the case surrounding the barometer.

The weight of the nitrogen can now be found by the formula:

$$\text{Wt. in grams} = 0.0012507 \times V \times \frac{(H_0 - p)}{760} \times \frac{273}{(273+t)};$$

where 0.0012507 is the weight of 1 cc. of pure dry nitrogen at normal temperature and pressure;

$V$ = volume of nitrogen in cubic centimeters;
$H_0$ = corrected barometric pressure;
$p$ = vapor pressure of water at $t°$;
$t$ = temperature.

TABLE OF VAPOR PRESSURE OF WATER[1]

| $t°$ | mm. | $t°$ | mm. | $t°$ | mm. | $t°$ | mm. |
|---|---|---|---|---|---|---|---|
| 0 | 4.6 | 9 | 8.6 | 18 | 15.5 | 27 | 26.7 |
| 1 | 4.9 | 10 | 9.2 | 19 | 16.5 | 28 | 28.4 |
| 2 | 5.3 | 11 | 9.8 | 20 | 17.5 | 29 | 30.1 |
| 3 | 5.7 | 12 | 10.5 | 21 | 18.7 | 30 | 31.8 |
| 4 | 6.1 | 13 | 11.2 | 22 | 19.8 | 31 | 33.7 |
| 5 | 6.5 | 14 | 12.0 | 23 | 21.1 | 32 | 35.7 |
| 6 | 7.0 | 15 | 12.8 | 24 | 22.4 | 33 | 37.7 |
| 7 | 7.5 | 16 | 13.6 | 25 | 23.8 | 34 | 39.9 |
| 8 | 8.0 | 17 | 14.5 | 26 | 25.2 | 35 | 42.2 |

The weight of nitrogen can more readily be obtained by using the accompanying tables (page 303), which give the weight of 1 cc. of *moist* nitrogen at different temperatures and pressures.

The percentage of nitrogen in the substance will be:

$$\text{Per cent N} = \frac{\text{Wt. nitrogen} \times 100}{\text{Wt. substance}}.$$

For logarithmic[2] calculation:

---

[1] From Scheel and Heuse, *Ann. Physik.*, **31** (1910), 731, as given in the Smithsonian Physical Tables, Third Reprint of Sixth Revised Edition (1918), 154-5.

[2] A table of four-place logarithms is given on p. 308.

$$\text{Add}\ \begin{cases}\text{Log. wt. 1 cc. N at } t^\circ \text{ and } H_0 = \\ \text{Log. } V \qquad\qquad\qquad\qquad = \end{cases}$$

$$\text{Add}\ \begin{cases}\text{Log. wt. total nitrogen} = \\ \text{Log. 100} \qquad\qquad\qquad = \end{cases}$$

$$\text{Subtract}\ \begin{cases} \\ \text{Log. wt. substance} \qquad = \end{cases}$$

$$\text{Log. per cent N} \qquad =$$

**The Limit of Error.**—This may be calculated in the same general way as given on p. 258. For results of analysis, obtained by the method described, the "allowed" error should ordinarily not be more than 10 parts per thousand, and never more than 20 parts per thousand. Check results should also come within these figures.

The following results are given as being typical of the possibilities in the method: *p*-nitro-toluene ($C_7H_7O_2N$) was analyzed for nitrogen by Mr. S. L. Handforth with the following results (only two analyses made): N = 10.29%, 10.30%; theory calls for N = 10.22%. The error here is 6.9 and 7.8 parts per thousand, respectively. The same substance was also analyzed by Miss Sophia Schulman, N = 10.09%, 10.23%, 10.18%; error, 12.7 (low), 0.9 and 3.9 (low) parts per thousand; and also by Mr. H. R. Pyne, N = 10.15%, 10.36%; error, 6.8 (low), 13.7 parts per thousand. Mr. T. C. Taylor obtained for nitrogen in diphenylamine ($C_{12}H_{11}N$), N = 8.28%, 8.32%; theory, N = 8.28%; one result is quite fortuitous, the error in the other is 4.8 parts per thousand. Mr. Geo. H. Walden obtained for acetanilide ($C_8H_9ON$); N = 10.32%, 10.43%; theory, N = 10.37%; error is 4.8 (low), and 5.8 parts per thousand. The greatest difference in the results in any of the sets of determinations mentioned is 0.21 (Mr. Pyne), and the error, based on the lower figure, is 20.7 parts per thousand.

# WEIGHT OF ONE CUBIC CENTIMETER OF MOIST NITROGEN IN MILLIGRAMS*

| t | b 692 | 694 | 696 | 698 | 700 | 702 | 704 | 706 | 708 | 710mm |
|---|---|---|---|---|---|---|---|---|---|---|
| 5° | 1.108 | 1.111 | 1.114 | 1.117 | 1.121 | 1.124 | 1.127 | 1.130 | 1.134 | 1.137 |
| | 04439 | 04565 | 04691 | 04817 | 04943 | 05068 | 05192 | 05317 | 05441 | 05564 |
| 6° | 1.103 | 1.106 | 1.109 | 1.113 | 1.116 | 1.119 | 1.122 | 1.125 | 1.129 | 1.132 |
| | 04251 | 04378 | 04504 | 04630 | 04755 | 04880 | 05005 | 05130 | 05254 | 05378 |
| 7 | 1.098 | 1.101 | 1.105 | 1.108 | 1.111 | 1.114 | 1.117 | 1.121 | 1.124 | 1.127 |
| | 04063 | 04190 | 04316 | 04442 | 04568 | 04693 | 04818 | 04943 | 05067 | 05191 |
| 8° | 1.093 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | 1.113 | 1.116 | 1.119 | 1.122 |
| | 03877 | 04003 | 04130 | 04256 | 04382 | 04507 | 04632 | 04757 | 04881 | 05005 |
| 9° | 1.089 | 1.092 | 1.095 | 1.098 | 1.101 | 1.105 | 1.108 | 1.111 | 1.114 | 1.117 |
| | 03691 | 03818 | 03944 | 04070 | 04196 | 04322 | 04447 | 04571 | 04696 | 04820 |
| 10° | 1.084 | 1.087 | 1.090 | 1.093 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | 1.113 |
| | 03499 | 03626 | 03752 | 03879 | 04005 | 04130 | 04255 | 04380 | 04505 | 04629 |
| 11° | 1.079 | 1.082 | 1.085 | 1.088 | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 |
| | 03300 | 03427 | 03554 | 03680 | 03806 | 03932 | 04057 | 04182 | 04307 | 04431 |
| 12° | 1.074 | 1.077 | 1.081 | 1.084 | 1.087 | 1.090 | 1.093 | 1.096 | 1.099 | 1.103 |
| | 03109 | 03236 | 03363 | 03490 | 03616 | 03741 | 03867 | 03992 | 04117 | 04241 |
| 13° | 1.069 | 1.073 | 1.076 | 1.079 | 1.082 | 1.085 | 1.088 | 1.091 | 1.095 | 1.098 |
| | 02912 | 03040 | 03167 | 03293 | 03420 | 03546 | 03671 | 03796 | 03921 | 04046 |
| 14° | 1.064 | 1.068 | 1.071 | 1.074 | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 | 1.093 |
| | 02709 | 02837 | 02964 | 03091 | 03217 | 03343 | 03469 | 03594 | 03719 | 03844 |
| 15° | 1.059 | 1.063 | 1.066 | 1.069 | 1.072 | 1.075 | 1.078 | 1.081 | 1.084 | 1.088 |
| | 02507 | 02635 | 02762 | 02889 | 03016 | 03142 | 03268 | 03393 | 03518 | 03643 |
| 16° | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 | 1.070 | 1.073 | 1.076 | 1.079 | 1.083 |
| | 02305 | 02433 | 02560 | 02687 | 02814 | 02940 | 03066 | 03192 | 03317 | 03442 |
| 17° | 1.050 | 1.053 | 1.056 | 1.059 | 1.062 | 1.065 | 1.068 | 1.071 | 1.074 | 1.077 |
| | 02097 | 02225 | 02353 | 02480 | 02607 | 02734 | 02860 | 02985 | 03111 | 03236 |
| 18° | 1.045 | 1.048 | 1.051 | 1.054 | 1.057 | 1.060 | 1.063 | 1.066 | 1.069 | 1.072 |
| | 01890 | 02018 | 02146 | 02273 | 02400 | 02527 | 02653 | 02779 | 02905 | 03030 |
| 19° | 1.039 | 1.042 | 1.046 | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 |
| | 01676 | 01805 | 01933 | 02060 | 02188 | 02314 | 02441 | 02567 | 02693 | 02818 |
| 20° | 1.034 | 1.037 | 1.040 | 1.043 | 1.046 | 1.049 | 1.053 | 1.056 | 1.059 | 1.062 |
| | 01457 | 01585 | 01713 | 01841 | 01969 | 02096 | 02222 | 02349 | 02475 | 02600 |
| 21° | 1.029 | 1.032 | 1.035 | 1.038 | 1.041 | 1.044 | 1.047 | 1.050 | 1.053 | 1.056 |
| | 01238 | 01367 | 01495 | 01623 | 01751 | 01878 | 02005 | 02131 | 02257 | 02383 |
| 22° | 1.024 | 1.027 | 1.030 | 1.033 | 1.036 | 1.039 | 1.042 | 1.045 | 1.048 | 1.051 |
| | 01019 | 01148 | 01276 | 01405 | 01532 | 01660 | 01787 | 01914 | 02040 | 02166 |
| 23° | 1.018 | 1.021 | 1.024 | 1.027 | 1.030 | 1.034 | 1.037 | 1.040 | 1.043 | 1.046 |
| | 00788 | 00917 | 01046 | 01174 | 01302 | 01430 | 01557 | 01684 | 01811 | 01937 |
| 24° | 1.013 | 1.016 | 1.019 | 1.022 | 1.025 | 1.028 | 1.031 | 1.034 | 1.037 | 1.040 |
| | 00557 | 00686 | 00815 | 00944 | 01072 | 01200 | 01328 | 01455 | 01582 | 01708 |
| 25° | 1.008 | 1.011 | 1.014 | 1.017 | 1.020 | 1.023 | 1.026 | 1.029 | 1.032 | 1.035 |
| | 00326 | 00456 | 00585 | 00714 | 00843 | 00971 | 01099 | 01226 | 01353 | 01480 |
| 26° | 1.002 | 1.005 | 1.008 | 1.011 | 1.014 | 1.017 | 1.020 | 1.023 | 1.026 | 1.029 |
| | 00083 | 00213 | 00342 | 00472 | 00600 | 00729 | 00857 | 00985 | 01112 | 01239 |
| 27° | 0.996 | 0.999 | 1.002 | 1.005 | 1.008 | 1.011 | 1.014 | 1.017 | 1.020 | 1.023 |
| | 99840 | 99970 | 00100 | 00230 | 00359 | 00488 | 00616 | 00744 | 00872 | 00999 |
| 28° | 0.991 | 0.994 | 0.997 | 1.000 | 1.003 | 1.006 | 1.009 | 1.012 | 1.015 | 1.018 |
| | 99590 | 99721 | 99851 | 99981 | 00110 | 00220 | 00368 | 00497 | 00625 | 00752 |
| 29° | 0.985 | 0.988 | 0.991 | 0.994 | 0.997 | 1.000 | 1.003 | 1.006 | 1.009 | 1.012 |
| | 99341 | 99472 | 99603 | 99733 | 99863 | 99994 | 00121 | 00250 | 00378 | 00506 |
| 30° | 0.079 | 0.982 | 0.985 | 0.988 | 0.991 | 0.994 | 0.997 | 1.000 | 1.003 | 1.006 |
| | 99079 | 99211 | 99341 | 99472 | 99602 | 99732 | 99861 | 99990 | 00119 | 00247 |
| t | b 692 | 694 | 696 | 698 | 700 | 702 | 704 | 706 | 708 | 710mm |

---

* From the Third American Edition of Gatterman's "Practical Methods of Organic Chemistry," published by The Macmillan Company, reprinted by permission.

## WEIGHT OF ONE CUBIC CENTIMETER OF MOIST NITROGEN IN MILLIGRAMS

| t | b 712 | 714 | 716 | 718 | 720 | 722 | 724 | 726 | 728 | 730mm |
|---|---|---|---|---|---|---|---|---|---|---|
| 5° | 1.140 | 1.143 | 1.146 | 1.150 | 1.153 | 1.156 | 1.159 | 1.163 | 1.166 | 1.169 |
| | 05688 | 05811 | 05933 | 06055 | 06177 | 06299 | 06420 | 06541 | 06662 | 06782 |
| 6° | 1.135 | 1.138 | 1.142 | 1.145 | 1.148 | 1.151 | 1.154 | 1.158 | 1.161 | 1 164 |
| | 05501 | 05624 | 05747 | 05869 | 05991 | 06113 | 06234 | 06355 | 06476 | 06596 |
| 7° | 1.130 | 1.133 | 1.137 | 1.140 | 1.143 | 1 146 | 1.149 | 1.153 | 1.156 | 1.159 |
| | 05314 | 05437 | 05560 | 05682 | 05804 | 05926 | 06048 | 06169 | 06289 | 06410 |
| 8° | 1.125 | 1.129 | 1.132 | 1 135 | 1.138 | 1.141 | 1.145 | 1.148 | 1.151 | 1.154 |
| | 05128 | 05251 | 05374 | 05497 | 05619 | 05741 | 05862 | 05983 | 06104 | 06225 |
| 9° | 1.121 | 1.124 | 1.127 | 1.130 | 1.133 | 1.137 | 1.140 | 1.143 | 1.146 | 1.149 |
| | 04943 | 05067 | 05190 | 05312 | 05434 | 05556 | 05678 | 05796 | 05920 | 06041 |
| 10° | 1.116 | 1.119 | 1.122 | 1.125 | 1.128 | 1.132 | 1.135 | 1.138 | 1.141 | 1.144 |
| | 04752 | 04876 | 04999 | 05121 | 05244 | 05366 | 05488 | 05609 | 05730 | 05851 |
| 11° | 1.111 | 1.114 | 1.117 | 1 120 | 1.123 | 1.126 | 1 130 | 1.133 | 1.136 | 1.139 |
| | 04555 | 04679 | 04802 | 04925 | 05047 | 05169 | 05291 | 05412 | 05534 | 05654 |
| 12° | 1 106 | 1.109 | 1.112 | 1 115 | 1.118 | 1.122 | 1.125 | 1.128 | 1.131 | 1.134 |
| | 04365 | 04489 | 04612 | 04735 | 04857 | 04980 | 05101 | 05223 | 05344 | 05465 |
| 13° | 1.101 | 1 104 | 1.107 | 1.110 | 1.113 | 1.117 | 1.120 | 1.123 | 1.126 | 1 129 |
| | 04170 | 04293 | 04417 | 04540 | 04662 | 04785 | 04907 | 05029 | 05150 | 05271 |
| 14° | 1.096 | 1.099 | 1.102 | 1.105 | 1.108 | 1.111 | 1.114 | 1.118 | 1.121 | 1.124 |
| | 03968 | 04092 | 04215 | 04339 | 04461 | 04584 | 04706 | 04828 | 04949 | 05070 |
| 15° | 1.091 | 1.094 | 1.097 | 1.100 | 1.103 | 1 106 | 1.109 | 1.113 | 1 116 | 1 119 |
| | 03767 | 03891 | 04015 | 04138 | 04261 | 04384 | 04506 | 04628 | 04750 | 04871 |
| 16° | 1.086 | 1.089 | 1.092 | 1.095 | 1.098 | 1 101 | 1 104 | 1.107 | 1.111 | 1.114 |
| | 03567 | 03691 | 03815 | 03938 | 04061 | 04184 | 04306 | 04428 | 04550 | 04672 |
| 17° | 1.081 | 1.084 | 1 087 | 1.090 | 1.093 | 1 096 | 1 099 | 1.102 | 1 105 | 1.108 |
| | 03361 | 03485 | 03609 | 03733 | 03856 | 03979 | 04101 | 04224 | 04345 | 04467 |
| 18° | 1.075 | 1.078 | 1.082 | 1.085 | 1.088 | 1 091 | 1 094 | 1 097 | 1 100 | 1.103 |
| | 03155 | 03279 | 03403 | 03527 | 03650 | 03774 | 03896 | 04019 | 04141 | 04262 |
| 19° | 1.070 | 1 073 | 1.076 | 1.079 | 1.082 | 1 086 | 1.089 | 1 092 | 1 095 | 1.098 |
| | 02943 | 03068 | 03192 | 03316 | 03440 | 03563 | 03686 | 03808 | 03931 | 04053 |
| 20° | 1.065 | 1.068 | 1.071 | 1.074 | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 | 1.092 |
| | 02725 | 02850 | 02975 | 03099 | 03223 | 03346 | 03469 | 03592 | 03715 | 03837 |
| 21° | 1.060 | 1.063 | 1.066 | 1.069 | 1.072 | 1.075 | 1.078 | 1 081 | 1.084 | 1.087 |
| | 02509 | 02634 | 02758 | 02883 | 03007 | 03130 | 03254 | 03377 | 03499 | 03621 |
| 22° | 1.054 | 1.057 | 1.060 | 1 063 | 1.066 | 1.069 | 1.073 | 1.076 | 1.079 | 1 082 |
| | 02292 | 02417 | 02542 | 02666 | 02791 | 02914 | 03038 | 03161 | 03284 | 03406 |
| 23° | 1.049 | 1.052 | 1.055 | 1.058 | 1 061 | 1.064 | 1.067 | 1.070 | 1.073 | 1.076 |
| | 02063 | 02189 | 02314 | 02439 | 02563 | 02687 | 02811 | 02934 | 03057 | 03180 |
| 24° | 1.043 | 1.046 | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 | 1.070 |
| | 01834 | 01960 | 02085 | 02210 | 02335 | 02459 | 02583 | 02707 | 02830 | 02953 |
| 25° | 1.038 | 1.041 | 1.044 | 1.047 | 1.050 | 1 053 | 1 056 | 1 059 | 1 062 | 1 065 |
| | 01606 | 01732 | 01858 | 01983 | 02108 | 02233 | 02357 | 02481 | 02604 | 02727 |
| 26° | 1.032 | 1 035 | 1.038 | 1.041 | 1 044 | 1.047 | 1 050 | 1.053 | 1.056 | 1.059 |
| | 01366 | 01492 | 01618 | 01743 | 01868 | 01993 | 02118 | 02242 | 02366 | 02489 |
| 27° | 1.026 | 1 029 | 1.032 | 1 035 | 1.038 | 1.041 | 1.044 | 1.047 | 1.050 | 1.053 |
| | 01126 | 01252 | 01378 | 01504 | 01630 | 01755 | 01879 | 02004 | 02128 | 02251 |
| 28° | 1.020 | 1.023 | 1.026 | 1.029 | 1.032 | 1.035 | 1.038 | 1.041 | 1.044 | 1.047 |
| | 00879 | 01006 | 01133 | 01259 | 01384 | 01510 | 01635 | 0 759 | 01884 | 02008 |
| 29° | 1.015 | 1.018 | 1.021 | 1 024 | 1.027 | 1 030 | 1.033 | 1 036 | 1.039 | 1.042 |
| | 00634 | 00761 | 00887 | 01014 | 01140 | 01265 | 01391 | 01516 | 01640 | 01764 |
| 30° | 1.009 | 1.012 | 1.015 | 1.018 | 1.021 | 1.024 | 1.027 | 1.029 | 1.032 | 1.035 |
| | 00375 | 00502 | 00629 | 00756 | 00882 | 01008 | 01134 | 01259 | 01384 | 01509 |
| t | b 712 | 714 | 716 | 718 | 720 | 722 | 724 | 726 | 728 | 730mm |

## WEIGHT OF ONE CUBIC CENTIMETER OF MOIST NITROGEN IN MILLIGRAMS

| *t* | *b* 732 | 734 | 736 | 738 | 740 | 742 | 744 | 746 | 748 | 750mm |
|---|---|---|---|---|---|---|---|---|---|---|
| 5° | 1.172 | 1.176 | 1.179 | 1.182 | 1.185 | 1 188 | 1.192 | 1.195 | 1.198 | 1.201 |
|  | 06902 | 07021 | 07141 | 07259 | 07378 | 07496 | 07614 | 07732 | 07849 | 07966 |
| 6° | 1.167 | 1.170 | 1.174 | 1.177 | 1.180 | 1.183 | 1.187 | 1.190 | 1.193 | 1.196 |
|  | 06716 | 06835 | 06955 | 07074 | 07192 | 07311 | 07429 | 07546 | 07664 | 07781 |
| 7° | 1.162 | 1.166 | 1.169 | 1.172 | 1.175 | 1.178 | 1.182 | 1.185 | 1.188 | 1.191 |
|  | 06530 | 06650 | 06769 | 06888 | 07007 | 07125 | 07243 | 07361 | 07479 | 07596 |
| 8° | 1.157 | 1.161 | 1.164 | 1 167 | 1.170 | 1.173 | 1.177 | 1.180 | 1.183 | 1.186 |
|  | 06345 | 06465 | 06584 | 06703 | 06822 | 06941 | 07059 | 07177 | 07294 | 07411 |
| 9° | 1 152 | 1.156 | 1.159 | 1.162 | 1.165 | 1.168 | 1.172 | 1.175 | 1.178 | 1.181 |
|  | 06161 | 06281 | 06400 | 06520 | 06638 | 06757 | 06875 | 06993 | 07111 | 07228 |
| 10° | 1.147 | 1.151 | 1.154 | 1.157 | 1 160 | 1.163 | 1.166 | 1 170 | 1.173 | 1.176 |
|  | 05971 | 06091 | 06210 | 06330 | 06449 | 06567 | 06686 | 06804 | 06922 | 07039 |
| 11° | 1 142 | 1.145 | 1.149 | 1 152 | 1.155 | 1.158 | 1 161 | 1 164 | 1.168 | 1.171 |
|  | 05775 | 05895 | 06015 | 06134 | 06253 | 06372 | 06490 | 06609 | 06726 | 06844 |
| 12° | 1.137 | 1.140 | 1.144 | 1.147 | 1.150 | 1.153 | 1 156 | 1 159 | 1.163 | 1.166 |
|  | 05586 | 05706 | 05826 | 05945 | 06064 | 06183 | 06302 | 06420 | 06538 | 06656 |
| 13° | 1.132 | 1.135 | 1 139 | 1.142 | 1.145 | 1 148 | 1.151 | 1.154 | 1.157 | 1 161 |
|  | 05392 | 05512 | 05632 | 05751 | 05871 | 05990 | 06108 | 06227 | 06345 | 06463 |
| 14° | 1.127 | 1.130 | 1.133 | 1.136 | 1 140 | 1 143 | 1.146 | 1 1 9 | 1.152 | 1.155 |
|  | 05191 | 05312 | 05432 | 05552 | 05671 | 05790 | 05909 | 06028 | 06146 | 06264 |
| 15° | 1 122 | 1.125 | 1.128 | 1.131 | 1.134 | 1.137 | 1 141 | 1.144 | 1.147 | 1.150 |
|  | 04992 | 05113 | 05233 | 05353 | 05472 | 05592 | 05711 | 05829 | 05947 | 06065 |
| 16° | 1.117 | 1.120 | 1.123 | 1.126 | 1.129 | 1.132 | 1 135 | 1.138 | 1.142 | 1.145 |
|  | 04793 | 04913 | 05034 | 05154 | 05274 | 05393 | 05512 | 05631 | 05749 | 05867 |
| 17° | 1 111 | 1.115 | 1.118 | 1.121 | 1 124 | 1 127 | 1 130 | 1.133 | 1.136 | 1.139 |
|  | 04588 | 04709 | 04830 | 04950 | 05070 | 05189 | 05308 | 05427 | 05546 | 05664 |
| 18° | 1.106 | 1.109 | 1.112 | 1 116 | 1.119 | 1 122 | 1 125 | 1 128 | 1.131 | 1.134 |
|  | 04384 | 04505 | 04625 | 04746 | 04866 | 04986 | 05105 | 05224 | 05343 | 05461 |
| 19° | 1.101 | 1.104 | 1.107 | 1 110 | 1 113 | 1 116 | 1.119 | 1.122 | 1.126 | 1.129 |
|  | 04174 | 04295 | 04416 | 04537 | 04657 | 04777 | 04896 | 05015 | 05134 | 05253 |
| 20° | 1.095 | 1.099 | 1.102 | 1 105 | 1.108 | 1 111 | 1 114 | 1.117 | 1.120 | 1.123 |
|  | 03958 | 04080 | 04201 | 04321 | 04442 | 04562 | 04682 | 04801 | 04920 | 05039 |
| 21° | 1.090 | 1.093 | 1.096 | 1.099 | 1.102 | 1 105 | 1 108 | 1.111 | 1.115 | 1.118 |
|  | 03743 | 03865 | 03986 | 04107 | 04228 | 04348 | 04468 | 04587 | 04707 | 04825 |
| 22° | 1.085 | 1 088 | 1 091 | 1.094 | 1.097 | 1 100 | 1.103 | 1 106 | 1.109 | 1.112 |
|  | 03528 | 03650 | 03772 | 03893 | 04013 | 04134 | 04254 | 04374 | 04493 | 04612 |
| 23° | 1.079 | 1.082 | 1.085 | 1.0 8 | 1 091 | 1 094 | 1.097 | 1.100 | 1.103 | 1.106 |
|  | 03302 | 03424 | 03546 | 03667 | 03788 | 03909 | 04029 | 04149 | 04268 | 04388 |
| 24° | 1.073 | 1 076 | 1.080 | 1.083 | 1.086 | 1 089 | 1 092 | 1.095 | 1 098 | 1.101 |
|  | 03076 | 03198 | 03320 | 03441 | 03562 | 03683 | 03804 | 03924 | 04044 | 04163 |
| 25° | 1.068 | 1.071 | 1.074 | 1 077 | 1 080 | 1.083 | 1.086 | 1.089 | 1 092 | 1.095 |
|  | 02850 | 02972 | 03094 | 03216 | 03338 | 03459 | 03579 | 03700 | 03820 | 03940 |
| 26° | 1.062 | 1.065 | 1.068 | 1.071 | 1 074 | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 |
|  | 02612 | 02735 | 02857 | 02979 | 03101 | 03222 | 03343 | 03464 | 03584 | 03704 |
| 27° | 1 056 | 1.059 | 1.062 | 1.065 | 1 068 | 1.071 | 1.074 | 1 077 | 1.080 | 1 083 |
|  | 02375 | 02498 | 02620 | 02742 | 02864 | 02986 | 03107 | 03228 | 03349 | 03469 |
| 28° | 1.050 | 1.053 | 1.056 | 1.059 | 1.062 | 1.065 | 1.068 | 1.071 | 1.074 | 1.077 |
|  | 02131 | 02254 | 02377 | 02500 | 02622 | 02744 | 02865 | 02986 | 03107 | 03228 |
| 29° | 1.044 | 1.047 | 1.050 | 1 053 | 1 056 | 1.059 | 1.062 | 1.065 | 1.068 | 1.071 |
|  | 01888 | 02012 | 02135 | 02258 | 02380 | 02502 | 02624 | 02745 | 02867 | 02987 |
| 30° | 1.038 | 1.041 | 1.044 | 1.047 | 1.050 | 1 053 | 1.056 | 1.059 | 1.062 | 1.065 |
|  | 01633 | 01757 | 01880 | 02003 | 02126 | 02248 | 02370 | 02492 | 02614 | 02735 |
| *t* | *b* 732 | 734 | 736 | 738 | 740 | 742 | 744 | 746 | 748 | 750mm |

## WEIGHT OF ONE CUBIC CENTIMETER OF MOIST NITROGEN IN MILLIGRAMS

| *t* | *b* 752 | 754 | 756 | 758 | 760 | 762 | 764 | 766 | 768 | 770mm |
|---|---|---|---|---|---|---|---|---|---|---|
| 5° | 1.205 | 1.208 | 1.211 | 1.214 | 1.218 | 1.221 | 1.224 | 1.227 | 1.230 | 1.234 |
|  | 08083 | 08199 | 08315 | 08431 | 08546 | 08661 | 08776 | 08891 | 09005 | 09119 |
| 6° | 1.199 | 1.203 | 1.206 | 1.209 | 1.212 | 1.216 | 1.219 | 1.222 | 1.225 | 1.228 |
|  | 07898 | 08014 | 08130 | 08246 | 08361 | 08477 | 08592 | 08706 | 08820 | 08934 |
| 7° | 1.194 | 1.198 | 1.201 | 1.204 | 1.207 | 1.210 | 1.214 | 1.217 | 1.220 | 1.223 |
|  | 07712 | 07829 | 07945 | 08061 | 08177 | 08292 | 08407 | 08522 | 08636 | 08750 |
| 8° | 1.189 | 1.193 | 1.196 | 1.199 | 1.202 | 1.205 | 1.208 | 1.212 | 1.215 | 1.218 |
|  | 07528 | 07645 | 07761 | 07877 | 07993 | 08108 | 08223 | 08338 | 08452 | 08566 |
| 9° | 1.184 | 1.188 | 1.191 | 1.194 | 1.197 | 1.200 | 1.203 | 1.207 | 1.210 | 1.213 |
|  | 07345 | 07462 | 07578 | 07694 | 07810 | 07925 | 08040 | 08155 | 08270 | 08384 |
| 10° | 1.179 | 1.182 | 1.186 | 1.189 | 1.192 | 1.195 | 1.198 | 1.201 | 1.205 | 1.208 |
|  | 07156 | 07273 | 07389 | 07505 | 07621 | 07737 | 07852 | 07967 | 08081 | 08196 |
| 11° | 1.174 | 1.177 | 1.180 | 1.183 | 1.187 | 1.190 | 1.193 | 1.196 | 1.199 | 1.202 |
|  | 06961 | 07078 | 07195 | 07311 | 07427 | 07542 | 07658 | 07773 | 07887 | 08002 |
| 12° | 1.169 | 1.172 | 1.175 | 1.178 | 1.181 | 1.185 | 1.188 | 1.191 | 1.194 | 1.197 |
|  | 06773 | 06890 | 07007 | 07123 | 07239 | 07355 | 07470 | 07585 | 07700 | 07814 |
| 13° | 1.164 | 1.167 | 1.170 | 1.173 | 1.176 | 1.179 | 1.182 | 1.186 | 1.189 | 1.192 |
|  | 06580 | 06697 | 06814 | 06930 | 07046 | 07162 | 07278 | 07393 | 07508 | 07622 |
| 14° | 1.158 | 1.161 | 1.165 | 1.168 | 1.171 | 1.174 | 1.177 | 1.180 | 1.183 | 1.187 |
|  | 06381 | 06498 | 06615 | 06732 | 06848 | 06964 | 07080 | 07195 | 07310 | 07425 |
| 15° | 1.153 | 1.156 | 1.159 | 1.162 | 1.166 | 1.169 | 1.172 | 1.175 | 1.178 | 1.181 |
|  | 06183 | 06300 | 06417 | 06534 | 06650 | 06767 | 06882 | 06998 | 07113 | 07228 |
| 16° | 1.148 | 1.151 | 1.154 | 1.157 | 1.160 | 1.163 | 1.166 | 1.170 | 1.173 | 1.176 |
|  | 05985 | 06103 | 06220 | 06336 | 06453 | 06569 | 06685 | 06801 | 06916 | 07031 |
| 17° | 1.142 | 1.146 | 1.149 | 1.152 | 1.155 | 1.158 | 1.161 | 1.164 | 1.167 | 1.170 |
|  | 05782 | 05900 | 06017 | 06134 | 06251 | 06367 | 06483 | 06599 | 06714 | 06829 |
| 18° | 1.137 | 1.140 | 1.143 | 1.146 | 1.149 | 1.153 | 1.156 | 1.159 | 1.162 | 1.165 |
|  | 05579 | 05697 | 05814 | 05931 | 06048 | 06165 | 06281 | 06397 | 06512 | 06627 |
| 19° | 1.132 | 1.135 | 1.138 | 1.141 | 1.144 | 1.147 | 1.150 | 1.153 | 1.156 | 1.159 |
|  | 05371 | 05489 | 05607 | 05724 | 05841 | 05957 | 06074 | 06190 | 06305 | 06421 |
| 20° | 1.126 | 1.129 | 1.132 | 1.135 | 1.138 | 1.141 | 1.145 | 1.148 | 1.151 | 1.154 |
|  | 05157 | 05275 | 05393 | 05510 | 05627 | 05744 | 05861 | 05977 | 06093 | 06208 |
| 21° | 1.121 | 1.124 | 1.127 | 1.130 | 1.133 | 1.136 | 1.139 | 1.142 | 1.145 | 1.148 |
|  | 04944 | 05062 | 05180 | 05298 | 05415 | 05532 | 05649 | 05765 | 05881 | 05997 |
| 22° | 1.115 | 1.118 | 1.121 | 1.124 | 1.127 | 1.130 | 1.133 | 1.136 | 1.139 | 1.143 |
|  | 04731 | 04849 | 04967 | 05085 | 05203 | 05320 | 05437 | 05553 | 05669 | 05785 |
| 23° | 1.109 | 1.112 | 1.115 | 1.119 | 1.122 | 1.125 | 1.128 | 1.131 | 1.134 | 1.137 |
|  | 04507 | 04625 | 04744 | 04862 | 04979 | 05097 | 05214 | 05330 | 05447 | 05563 |
| 24° | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 | 1.119 | 1.122 | 1.125 | 1.128 | 1.131 |
|  | 04282 | 04401 | 04520 | 04638 | 04756 | 04873 | 04991 | 05108 | 05224 | 05341 |
| 25° | 1.098 | 1.101 | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 | 1.119 | 1.122 | 1.125 |
|  | 04059 | 04178 | 04297 | 04415 | 04533 | 04651 | 04769 | 04886 | 05002 | 05119 |
| 26° | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 | 1.119 |
|  | 03823 | 03943 | 04062 | 04180 | 04299 | 04417 | 04534 | 04652 | 04769 | 04886 |
| 27° | 1.086 | 1.089 | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 | 1.110 | 1.113 |
|  | 03589 | 03708 | 03828 | 03946 | 04065 | 04183 | 04301 | 04419 | 04536 | 04653 |
| 28° | 1.080 | 1.083 | 1.086 | 1.089 | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 |
|  | 03348 | 03468 | 03587 | 03706 | 03825 | 03944 | 04062 | 04180 | 04297 | 04415 |
| 29° | 1.074 | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 | 1.092 | 1.095 | 1.098 | 1.101 |
|  | 03108 | 03228 | 03348 | 03467 | 03586 | 03705 | 03823 | 03941 | 04059 | 04177 |
| 30° | 1.068 | 1.071 | 1.074 | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 | 1.092 | 1.095 |
|  | 02855 | 02976 | 03096 | 03216 | 03335 | 03454 | 03573 | 03691 | 03809 | 03927 |
| *t* | *b* 752 | 754 | 756 | 758 | 760 | 762 | 764 | 766 | 768 | 770mm |

# WEIGHT OF ONE CUBIC CENTIMETER OF MOIST NITROGEN IN MILLIGRAMS

| *t* | *b* 772 | 774 | 776 | 778 | 780 mm |
|---|---|---|---|---|---|
| 5° | 1.237 | 1.240 | 1.243 | 1.247 | 1.250 |
| | 09233 | 09346 | 09459 | 09572 | 09684 |
| 6° | 1.232 | 1.235 | 1.238 | 1.241 | 1.245 |
| | 09048 | 09162 | 09275 | 09387 | 09500 |
| 7° | 1.226 | 1.230 | 1.233 | 1.236 | 1.239 |
| | 08864 | 08977 | 09090 | 09203 | 09316 |
| 8° | 1.221 | 1.224 | 1.228 | 1.231 | 1.234 |
| | 08680 | 08794 | 08907 | 09020 | 09133 |
| 9° | 1.216 | 1.219 | 1.223 | 1.226 | 1.229 |
| | 08498 | 08612 | 08725 | 08838 | 08951 |
| 10° | 1.211 | 1.214 | 1.217 | 1.220 | 1.224 |
| | 08310 | 08423 | 08537 | 08650 | 08763 |
| 11° | 1.206 | 1.209 | 1.212 | 1.215 | 1.218 |
| | 08116 | 08230 | 08343 | 08456 | 08569 |
| 12° | 1.200 | 1.203 | 1.207 | 1.210 | 1.213 |
| | 07929 | 08043 | 08156 | 08269 | 08383 |
| 13° | 1.195 | 1.198 | 1.201 | 1.204 | 1.208 |
| | 07737 | 07851 | 07964 | 08078 | 08191 |
| 14° | 1.190 | 1.193 | 1.196 | 1.199 | 1.202 |
| | 07539 | 07653 | 07767 | 07881 | 07994 |
| 15° | 1.184 | 1.187 | 1.190 | 1.194 | 1.197 |
| | 07342 | 07457 | 07571 | 07684 | 07798 |
| 16° | 1.179 | 1.182 | 1.185 | 1.188 | 1.191 |
| | 07146 | 07260 | 07374 | 07488 | 07601 |
| 17° | 1.173 | 1.177 | 1.180 | 1.183 | 1.186 |
| | 06944 | 07058 | 07173 | 07287 | 07400 |
| 18° | 1.168 | 1.171 | 1.174 | 1.177 | 1.180 |
| | 06742 | 06857 | 06971 | 07085 | 07199 |
| 19° | 1.162 | 1.166 | 1.169 | 1.172 | 1.175 |
| | 06536 | 06651 | 06765 | 06879 | 06993 |
| 20° | 1.157 | 1.160 | 1.163 | 1.166 | 1.169 |
| | 06324 | 06439 | 06553 | 06668 | 06782 |
| 21° | 1.151 | 1.154 | 1.157 | 1.160 | 1.163 |
| | 06112 | 06227 | 06342 | 06457 | 06571 |
| 22° | 1.146 | 1.149 | 1.152 | 1.155 | 1.158 |
| | 05901 | 06016 | 06131 | 06246 | 06360 |
| 23° | 1.140 | 1.143 | 1.146 | 1.149 | 1.152 |
| | 05679 | 05794 | 05909 | 06024 | 06139 |
| 24° | 1.134 | 1.137 | 1.140 | 1.143 | 1.146 |
| | 05457 | 05572 | 05688 | 05803 | 05917 |
| 25° | 1.128 | 1.131 | 1.134 | 1.137 | 1.140 |
| | 05235 | 05351 | 05467 | 05582 | 05697 |
| 26° | 1.122 | 1.125 | 1.128 | 1.131 | 1.134 |
| | 05002 | 05118 | 05234 | 05349 | 05465 |
| 27° | 1.116 | 1.119 | 1.122 | 1.125 | 1.128 |
| | 04770 | 04886 | 05002 | 05118 | 05233 |
| 28° | 1.110 | 1.113 | 1.116 | 1.119 | 1.122 |
| | 04531 | 04648 | 04764 | 04880 | 04996 |
| 29° | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 |
| | 04294 | 04411 | 04527 | 04644 | 04759 |
| 30° | 1.098 | 1.101 | 1.104 | 1.107 | 1.110 |
| | 04045 | 04162 | 04278 | 04395 | 04511 |
| *t* | *b* 772 | 774 | 776 | 778 | 780 mm |

| Natural Numbers. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Proportional Parts. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 10 | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 | 4 | 8 | 12 | 17 | 21 | 25 | 29 | 33 | 37 |
| 11 | 0414 | 0453 | 0492 | 0531 | 0569 | 0607 | 0645 | 0682 | 0719 | 0755 | 4 | 8 | 11 | 15 | 19 | 23 | 26 | 30 | 34 |
| 12 | 0792 | 0828 | 0864 | 0899 | 0934 | 0969 | 1004 | 1038 | 1072 | 1106 | 3 | 7 | 10 | 14 | 17 | 21 | 24 | 28 | 31 |
| 13 | 1139 | 1173 | 1206 | 1239 | 1271 | 1303 | 1335 | 1367 | 1399 | 1430 | 3 | 6 | 10 | 13 | 16 | 19 | 23 | 26 | 29 |
| 14 | 1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | 27 |
| 15 | 1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 3 | 6 | 8 | 11 | 14 | 17 | 20 | 22 | 25 |
| 16 | 2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 3 | 5 | 8 | 11 | 13 | 16 | 18 | 21 | 24 |
| 17 | 2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 2 | 5 | 7 | 10 | 12 | 15 | 17 | 20 | 22 |
| 18 | 2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 2 | 5 | 7 | 9 | 12 | 14 | 16 | 19 | 21 |
| 19 | 2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 2 | 4 | 7 | 9 | 11 | 13 | 16 | 18 | 20 |
| 20 | 3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
| 21 | 3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 22 | 3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 15 | 17 |
| 23 | 3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 15 | 17 |
| 24 | 3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 16 |
| 25 | 3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 15 |
| 26 | 4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 2 | 3 | 5 | 7 | 8 | 10 | 11 | 13 | 15 |
| 27 | 4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 13 | 14 |
| 28 | 4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 29 | 4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 12 | 13 |
| 30 | 4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 11 | 13 |
| 31 | 4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 12 |
| 32 | 5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| 33 | 5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 12 |
| 34 | 5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
| 35 | 5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 1 | 2 | 4 | 5 | 6 | 7 | 9 | 10 | 11 |
| 36 | 5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 37 | 5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5786 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| 38 | 5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5866 | 5877 | 5888 | 5899 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| 39 | 5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 |
| 40 | 6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 |
| 41 | 6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 42 | 6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 43 | 6335 | 6345 | 6355 | 6365 | 6375 | 6385 | 6395 | 6405 | 6415 | 6425 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 44 | 6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 6503 | 6513 | 6522 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 45 | 6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 46 | 6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 8 |
| 47 | 6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 48 | 6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| 49 | 6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 6981 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| 50 | 6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| 51 | 7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | [illegible] |
| 52 | 7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 | 7 |
| 53 | 7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 54 | 7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |

| Natural Numbers. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Proportional Parts. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 55 | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 56 | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 57 | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 58 | 7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| 59 | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| 60 | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 61 | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 62 | 7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 6 |
| 63 | 7993 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 64 | 8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 65 | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 8176 | 8182 | 8189 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 66 | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 67 | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 68 | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 69 | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| 70 | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| 71 | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 72 | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 73 | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 74 | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 75 | 8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| 76 | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| 77 | 8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 78 | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 79 | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 80 | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 81 | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 82 | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 83 | 9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 84 | 9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 85 | 9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 86 | 9345 | 9450 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 87 | 9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 88 | 9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 89 | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 90 | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 91 | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 92 | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 93 | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 94 | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 95 | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 96 | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 97 | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 98 | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 99 | 9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |

| Log. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | PROPORTIONAL PARTS. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .00 | 1000 | 1002 | 1005 | 1007 | 1009 | 1012 | 1014 | 1016 | 1019 | 1021 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .01 | 1023 | 1026 | 1028 | 1030 | 1033 | 1035 | 1038 | 1040 | 1042 | 1045 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .02 | 1047 | 1050 | 1052 | 1054 | 1057 | 1059 | 1062 | 1064 | 1067 | 1069 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .03 | 1072 | 1074 | 1076 | 1079 | 1081 | 1084 | 1086 | 1089 | 1091 | 1094 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .04 | 1096 | 1099 | 1102 | 1104 | 1107 | 1109 | 1112 | 1114 | 1117 | 1119 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .05 | 1122 | 1125 | 1127 | 1130 | 1132 | 1135 | 1138 | 1140 | 1143 | 1146 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .06 | 1148 | 1151 | 1153 | 1156 | 1159 | 1161 | 1164 | 1167 | 1169 | 1172 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .07 | 1175 | 1178 | 1180 | 1183 | 1186 | 1189 | 1191 | 1194 | 1197 | 1199 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .08 | 1202 | 1205 | 1208 | 1211 | 1213 | 1216 | 1219 | 1222 | 1225 | 1127 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 3 |
| .09 | 1230 | 1233 | 1236 | 1239 | 1242 | 1245 | 1247 | 1250 | 1253 | 1256 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 3 |
| .10 | 1259 | 1262 | 1265 | 1268 | 1271 | 1274 | 1276 | 1279 | 1282 | 1285 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 3 |
| .11 | 1288 | 1291 | 1294 | 1297 | 1300 | 1303 | 1306 | 1309 | 1312 | 1315 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| .12 | 1318 | 1321 | 1324 | 1327 | 1330 | 1334 | 1337 | 1340 | 1343 | 1346 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| .13 | 1349 | 1352 | 1355 | 1358 | 1361 | 1365 | 1368 | 1371 | 1374 | 1377 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .14 | 1380 | 1384 | 1387 | 1390 | 1393 | 1396 | 1400 | 1403 | 1406 | 1409 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .15 | 1413 | 1416 | 1419 | 1422 | 1426 | 1429 | 1432 | 1435 | 1439 | 1442 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .16 | 1445 | 1449 | 1452 | 1455 | 1459 | 1462 | 1466 | 1469 | 1472 | 1476 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .17 | 1479 | 1483 | 1486 | 1489 | 1493 | 1496 | 1500 | 1503 | 1507 | 1510 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .18 | 1514 | 1517 | 1521 | 1524 | 1528 | 1531 | 1535 | 1538 | 1542 | 1545 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .19 | 1549 | 1552 | 1556 | 1560 | 1563 | 1567 | 1570 | 1574 | 1578 | 1581 | 0 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3 |
| .20 | 1585 | 1589 | 1592 | 1596 | 1600 | 1603 | 1607 | 1611 | 1614 | 1618 | 0 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3 |
| .21 | 1622 | 1626 | 1629 | 1633 | 1637 | 1641 | 1644 | 1648 | 1652 | 1656 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 |
| .22 | 1660 | 1663 | 1667 | 1671 | 1675 | 1679 | 1683 | 1687 | 1690 | 1694 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 |
| .23 | 1698 | 1702 | 1706 | 1710 | 1714 | 1718 | 1722 | 1726 | 1730 | 1734 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| .24 | 1738 | 1742 | 1746 | 1750 | 1754 | 1758 | 1762 | 1766 | 1770 | 1774 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| .25 | 1778 | 1782 | 1786 | 1791 | 1795 | 1799 | 1803 | 1807 | 1811 | 1816 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| .26 | 1820 | 1824 | 1828 | 1832 | 1837 | 1841 | 1845 | 1849 | 1854 | 1858 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| .27 | 1862 | 1866 | 1871 | 1875 | 1879 | 1884 | 1888 | 1892 | 1897 | 1901 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| .28 | 1905 | 1910 | 1914 | 1919 | 1923 | 1928 | 1932 | 1936 | 1941 | 1945 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .29 | 1950 | 1954 | 1959 | 1963 | 1968 | 1972 | 1977 | 1982 | 1986 | 1991 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .30 | 1995 | 2000 | 2004 | 2009 | 2014 | 2018 | 2023 | 2028 | 2032 | 2037 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .31 | 2042 | 2046 | 2051 | 2056 | 2061 | 2065 | 2070 | 2075 | 2080 | 2084 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .32 | 2089 | 2094 | 2099 | 2104 | 2109 | 2113 | 2118 | 2123 | 2128 | 2133 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .33 | 2138 | 2143 | 2148 | 2153 | 2158 | 2163 | 2168 | 2173 | 2178 | 2183 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .34 | 2188 | 2193 | 2198 | 2203 | 2208 | 2213 | 2218 | 2223 | 2228 | 2234 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .35 | 2239 | 2244 | 2249 | 2254 | 2259 | 2265 | 2270 | 2275 | 2280 | 2286 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .36 | 2291 | 2296 | 2301 | 2307 | 2312 | 2317 | 2323 | 2328 | 2333 | 2339 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .37 | 2344 | 2350 | 2355 | 2360 | 2366 | 2371 | 2377 | 2382 | 2388 | 2393 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .38 | 2399 | 2404 | 2410 | 2415 | 2421 | 2427 | 2432 | 2438 | 2443 | 2449 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .39 | 2455 | 2460 | 2466 | 2472 | 2477 | 2483 | 2489 | 2495 | 2500 | 2506 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| .40 | 2512 | 2518 | 2523 | 2529 | 2535 | 2541 | 2547 | 2553 | 2559 | 2564 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| .41 | 2570 | 2576 | 2582 | 2588 | 2594 | 2600 | 2606 | 2612 | 2618 | 2624 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| .42 | 2630 | 2636 | 2642 | 2649 | 2655 | 2661 | 2667 | 2673 | 2679 | 2685 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| .43 | 2692 | 2698 | 2704 | 2710 | 2716 | 2723 | 2729 | 2735 | 2742 | 2748 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| .44 | 2754 | 2761 | 2767 | 2773 | 2780 | 2786 | 2793 | 2799 | 2805 | 2812 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| .45 | 2818 | 2825 | 2831 | 2838 | 2844 | 2851 | 2858 | 2864 | 2871 | 2877 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .46 | 2884 | 2891 | 2897 | 2904 | 2911 | 2917 | 2924 | 2931 | 2938 | 2944 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .47 | 2951 | 2958 | 2965 | 2972 | 2979 | 2985 | 2992 | 2999 | 3006 | 3013 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .48 | 3020 | 3027 | 3034 | 3041 | 3048 | 3055 | 3062 | 3069 | 3076 | 3083 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| .49 | 3090 | 3097 | 3105 | 3112 | 3119 | 3126 | 3133 | 3141 | 3148 | 3155 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |

| Log. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Proportional Parts. 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .50 | 3162 | 3170 | 3177 | 3184 | 3192 | 3199 | 3206 | 3214 | 3221 | 3228 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| .51 | 3236 | 3243 | 3251 | 3258 | 3266 | 3273 | 3281 | 3289 | 3296 | 3304 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| .52 | 3311 | 3319 | 3327 | 3334 | 3342 | 3350 | 3357 | 3365 | 3373 | 3381 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| .53 | 3388 | 3396 | 3404 | 3412 | 3420 | 3428 | 3436 | 3443 | 3451 | 3459 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| .54 | 3467 | 3475 | 3483 | 3491 | 3499 | 3508 | 3516 | 3524 | 3532 | 3540 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| .55 | 3548 | 3556 | 3565 | 3573 | 3581 | 3589 | 3597 | 3606 | 3614 | 3622 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 | 7 |
| .56 | 3631 | 3639 | 3648 | 3656 | 3664 | 3673 | 3681 | 3690 | 3698 | 3707 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| .57 | 3715 | 3724 | 3733 | 3741 | 3750 | 3758 | 3767 | 3776 | 3784 | 3793 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| .58 | 3802 | 3811 | 3819 | 3828 | 3837 | 3846 | 3855 | 3864 | 3873 | 3882 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| .59 | 3890 | 3899 | 3908 | 3917 | 3926 | 3936 | 3945 | 3954 | 3963 | 3972 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| .60 | 3981 | 3990 | 3999 | 4009 | 4018 | 4027 | 4036 | 4046 | 4055 | 4064 | 1 | 2 | 3 | 4 | 5 | 6 | 6 | 7 | 8 |
| .61 | 4074 | 4083 | 4093 | 4102 | 4111 | 4121 | 4130 | 4140 | 4150 | 4159 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .62 | 4169 | 4178 | 4188 | 4198 | 4207 | 4217 | 4227 | 4236 | 4246 | 4256 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .63 | 4266 | 4276 | 4285 | 4295 | 4305 | 4315 | 4325 | 4335 | 4345 | 4355 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .64 | 4365 | 4375 | 4385 | 4395 | 4406 | 4416 | 4426 | 4436 | 4446 | 4457 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .65 | 4467 | 4477 | 4487 | 4498 | 4508 | 4519 | 4529 | 4539 | 4550 | 4560 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .66 | 4571 | 4581 | 4592 | 4603 | 4613 | 4624 | 4634 | 4645 | 4656 | 4667 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 9 | 10 |
| .67 | 4677 | 4688 | 4699 | 4710 | 4721 | 4732 | 4742 | 4753 | 4764 | 4775 | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 |
| .68 | 4786 | 4797 | 4808 | 4819 | 4831 | 4842 | 4853 | 4864 | 4875 | 4887 | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 |
| .69 | 4898 | 4909 | 4920 | 4932 | 4943 | 4955 | 4966 | 4977 | 4989 | 5000 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| .70 | 5012 | 5023 | 5035 | 5047 | 5058 | 5070 | 5082 | 5093 | 5105 | 5117 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 9 | 11 |
| .71 | 5129 | 5140 | 5152 | 5164 | 5176 | 5188 | 5200 | 5212 | 5224 | 5236 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| .72 | 5248 | 5260 | 5272 | 5284 | 5297 | 5309 | 5321 | 5333 | 5346 | 5358 | 1 | 2 | 4 | 5 | 6 | 7 | 9 | 10 | 11 |
| .73 | 5370 | 5383 | 5395 | 5408 | 5420 | 5433 | 5445 | 5458 | 5470 | 5483 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
| .74 | 5495 | 5508 | 5521 | 5534 | 5546 | 5559 | 5572 | 5585 | 5598 | 5610 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 12 |
| .75 | 5623 | 5636 | 5649 | 5662 | 5675 | 5689 | 5702 | 5715 | 5728 | 5741 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 10 | 12 |
| .76 | 5754 | 5768 | 5781 | 5794 | 5808 | 5821 | 5834 | 5848 | 5861 | 5875 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| .77 | 5888 | 5902 | 5916 | 5929 | 5943 | 5957 | 5970 | 5984 | 5998 | 6012 | 1 | 3 | 4 | 5 | 7 | 8 | 10 | 11 | 12 |
| .78 | 6026 | 6039 | 6053 | 6067 | 6081 | 6095 | 6109 | 6124 | 6138 | 6152 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| .79 | 6166 | 6180 | 6194 | 6209 | 6223 | 6237 | 6252 | 6266 | 6281 | 6295 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 11 | 13 |
| .80 | 6310 | 6324 | 6339 | 6353 | 6368 | 6383 | 6397 | 6412 | 6427 | 6442 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 12 | 13 |
| .81 | 6457 | 6471 | 6486 | 6501 | 6516 | 6531 | 6546 | 6561 | 6577 | 6592 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| .82 | 6607 | 6622 | 6637 | 6653 | 6668 | 6683 | 6699 | 6714 | 6730 | 6745 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| .83 | 6761 | 6776 | 6792 | 6808 | 6823 | 6839 | 6855 | 6871 | 6887 | 6902 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 13 | 14 |
| .84 | 6918 | 6934 | 6950 | 6966 | 6982 | 6998 | 7015 | 7031 | 7047 | 7063 | 2 | 3 | 5 | 6 | 8 | 10 | 11 | 13 | 15 |
| .85 | 7079 | 7096 | 7112 | 7129 | 7145 | 7161 | 7178 | 7194 | 7211 | 7228 | 2 | 3 | 5 | 7 | 8 | 10 | 12 | 13 | 15 |
| .86 | 7244 | 7261 | 7278 | 7295 | 7311 | 7328 | 7345 | 7362 | 7379 | 7396 | 2 | 3 | 5 | 7 | 8 | 10 | 12 | 13 | 15 |
| .87 | 7413 | 7430 | 7447 | 7464 | 7482 | 7499 | 7516 | 7534 | 7551 | 7568 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 16 |
| .88 | 7586 | 7603 | 7621 | 7638 | 7656 | 7674 | 7691 | 7709 | 7727 | 7745 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 16 |
| .89 | 7762 | 7780 | 7798 | 7816 | 7834 | 7852 | 7870 | 7889 | 7907 | 7925 | 2 | 4 | 5 | 7 | 9 | 11 | 13 | 14 | 16 |
| .90 | 7943 | 7962 | 7980 | 7998 | 8017 | 8035 | 8054 | 8072 | 8091 | 8110 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 15 | 17 |
| .91 | 8128 | 8147 | 8166 | 8185 | 8204 | 8222 | 8241 | 8260 | 8279 | 8299 | 2 | 4 | 6 | 8 | 9 | 11 | 13 | 15 | 17 |
| .92 | 8318 | 8337 | 8356 | 8375 | 8395 | 8414 | 8433 | 8453 | 8472 | 8492 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 15 | 17 |
| .93 | 8511 | 8531 | 8551 | 8570 | 8590 | 8610 | 8630 | 8650 | 8670 | 8690 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| .94 | 8710 | 8730 | 8750 | 8770 | 8790 | 8810 | 8831 | 8851 | 8872 | 8892 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| .95 | 8913 | 8933 | 8954 | 8974 | 8995 | 9016 | 9036 | 9057 | 9078 | 9099 | 2 | 4 | 6 | 8 | 10 | 12 | 15 | 17 | 19 |
| .96 | 9120 | 9141 | 9162 | 9183 | 9204 | 9226 | 9247 | 9268 | 9290 | 9311 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
| .97 | 9333 | 9354 | 9376 | 9397 | 9419 | 9441 | 9462 | 9484 | 9506 | 9528 | 2 | 4 | 7 | 9 | 11 | 13 | 15 | 17 | 20 |
| .98 | 9550 | 9572 | 9594 | 9616 | 9638 | 9661 | 9683 | 9705 | 9727 | 9750 | 2 | 4 | 7 | 9 | 11 | 13 | 16 | 18 | 20 |
| .99 | 9772 | 9795 | 9817 | 9840 | 9863 | 9886 | 9908 | 9931 | 9954 | 9977 | 2 | 5 | 7 | 9 | 11 | 14 | 16 | 18 | 20 |

# LIST OF APPARATUS FOR GENERAL ORGANIC CHEMISTRY[1]

## Box I—Articles Returnable

| | | Cat. No.[2] | |
|---|---|---|---|
| 1 | Addition tube | Emil Greiner | |
| 1 | Adapter tube | E. & A. | 110 |
| 1 | Beaker, lipped, Griffin's low form, 50 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 100 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 150 cc | E. & A. | 737 |
| 1 | Beaker, lipped (Pyrex), Griffin's low form, 250 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 400 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 600 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 800 cc | E. & A. | 737 |
| 1 | Beaker, lipped, Griffin's low form, 1000 cc | E. & A. | 737 |
| 6 | Bottles, sq., G. S., for handing in liquid preparations, 15 cc | E. & A. | 926 |
| 6 | Bottles, wide-mouthed, glass-stoppered, round, 10 cc., for handing in solid preparations | E. & A. | 934 |
| 2 | Bottles, tincture, narrow mouth, G. S., 250 cc | E. & A. | 918 |
| 3 | Bottles, wide mouth, 250 cc | E. & A. | 910 |
| 1 | Calcium chloride tube, 6-inch | E. & A. | 7052 |
| 1 | Condenser, sealed joints, bulbed inner tube, 12 inches long | E. & A. | 2246 |
| 1 | Condenser, straight inner tube | E. & A. | 2243 |
| 1 | Condenser, inner tube, "air condenser," 15-inch | E. & A. | 2240 |
| 1 | Watch glass, 3-inch (cover glass) | E. & A. | 7382 |
| 1 | Watch glass, 4½-inch (cover glass) | E. & A. | 7382 |
| 1 | Bottle, sealing tube, 15 cc. | | |
| 1 | Cylinder, graduated, 100 cc. | E. & A. | 2512 |
| 1 | Cylinder, graduated, 10 cc | E. & A. | 2512 |
| 1 | Evaporating dish, porc., 6 cm. diam. (Coors) | E. & A. | 501 |
| 2 | Flasks, distilling, round bottom, 30 cc. (Pyrex) | E. & A. | 3065 |
| 2 | Flasks, distilling, B. & C., round bottom, 50 cc. (Pyrex) | E. & A. | 3065 |
| 2 | Flasks, distilling, B. & C., round bottom, 125 cc. (Pyrex) | E. & A. | 3065 |
| 1 | Flask, distilling, B. & C., round bottom, 250 cc. (Pyrex) | E. & A. | 3065 |
| 2 | Flasks, Erlenmeyer, 150 cc | E. & A. | 3027 |
| 2 | Flasks, Erlenmeyer, 50 cc | E. & A. | 3027 |
| 1 | Flask, Erlenmeyer, 250 cc | E. & A. | 3027 |
| 1 | Flask, heavy glass, for filtering, with side neck, 500 cc | E. & A. | 3090 |
| 1 | Glass evaporating-dish, 5 cm | E. & A. | 2624 |
| 1 | Flask, round bottom, 125 cc | E. & A. | 3050 |
| 1 | Flask, round bottom, 250 cc | E. & A. | 3050 |
| 1 | Flask, round bottom, 300 cc., short neck | E. & A. | 3057 |
| 1 | Flask, round bottom, 500 cc | E. & A. | 3050 |
| 1 | Flask, round bottom, 1000 cc | E. & A. | 3050 |
| 1 | Funnel, 4 cm. diam. | E. & A. | 3216 |

---

[1] See preface, p. v.

[2] These are given for the sake of convenience only.

| | Cat. No. |
|---|---|
| 1 Funnel, 7.5 cm. diam., short stem, special | E. & A. 3216 |
| 1 Funnel, dropping, 60 cc | E. & A. 3302 |
| 1 Funnel, separatory, Squibb's, 250 cc | E. & A. 3300 |
| 1 Funnel, Buchner, porcelain, 5 cm. diam. (Coors) | E. & A. 630 |
| 1 Gooch perforated plate | |
| 1 Set of three thermometers, short scale, with case (Fisher) | E. & A. |
| 1 Thermometer, milk glass scale, 360° C. | E. & A. 6746 |
| 6 Test-tubes, 4"×½" | E. & A. 7210 |
| 12 Test-tubes, 6"×¾" | E. & A. 7216 |
| 3 Test-tubes, 8"×1" | E. & A . 7216 |
| 2 Test-tubes, side neck, 6"×1" | E. & A. 7218 |
| 1 Melting-point apparatus | |
| 1 Hard glass test-tube, Pyrex, special, 10 cm.×9 mm. | |
| 1 Mortar, glass lipped, 2¾ inches | E. & A. 4616 |
| 1 Pestle for above, glass | E. & A. 4616 |
| 1 Spatula and spoon combined, porc., 12 cm. | Coors, 553 |
| 1 Glass stop-cock, 2 mm. | E. & A. 6468 |

### BOX II — ARTICLES RETURNABLE

| | Cat. No. |
|---|---|
| 2 Burette clamps, iron | E. & A. 2006 |
| 2 Burners, Tirrill | E. & A. 1462 |
| 1 Burner chimney | E. & A. 1586 |
| 1 Burner, star support for chimney | E. & A. 1608 |
| 2 Condenser clamps, iron, large | E. & A. 2020 |
| 2 Condenser clamps, iron, medium | E. & A. 2016 |
| 4 Clamp holders, for 9/16-inch rods | E. & A. 2044 |
| 1 Set of rings for steam-bath | |
| 1 Filter pump with special Columbia coupling medium, 4¾ inches | E. & A. 5624 |
| 1 Oil bath, iron, 6-inch, modified | E. & A. 616 |
| 2 Ring stands, medium, iron, modified in shop | E. & A. 6540 |
| 1 Ring for iron stand, 2 inches | E. & A. 6010 |
| 1 Ring for iron stand, 3 inches | E. & A. 6010 |
| 1 Set cork borers, Nos. 1–9 brass (Old Cat.) | E. & A. 2841 |
| 1 Screw clamp | E. & A. 2080 |
| 1 Test-tube rack, copper | |
| 1 Tripod, 4½ inches diam. | E. & A. 7000 |
| 1 Wing top for burner | E. & A. 1616 |
| 1 Set weights, rental .75 (Columbia Style B) | |

The following pieces of apparatus are too large to go into the packing box, but the student will need them immediately, therefore he should go to the Stockroom and draw them at once on a new debit card.

2 Ring stands, large, iron, extra heavy, modified in shop . E. & A. 6040

The following and other apparatus may be obtained at the Stockroom at any time as needed:

Manometer stand
Hot-water funnel
Porcelain casseroles
Evaporating dishes

Funnels, Nos. 5 and 6 (12 cm. and 15 cm.)
Electric motor
Stirring apparatus
Desiccators
Wind shields
Special distilling-flasks
Instruments
Glass stop-cocks
Large condensers, bulbed or straight inner tubes

Etc.

### Box II—Articles Non-returnable

| | | Cat. No. |
|---|---|---|
| 4 | Lengths glass tubing, 6 mm. bore, $2\frac{1}{2}$ ft. | E. & A. 3730 |
| 2 | Lengths glass rod, 4 mm. bore, $2\frac{1}{2}$ ft. | E. & A. 3726 |
| 3 | Porous tiles | |
| 1 | File, rat tail, 5 inches | E. & A. 2864 |
| 1 | File, rat tail, 7 inches | E. & A. 2864 |
| 1 | File triangular, 5 inches | E. & A. 2866 |
| 1 | Wire gauze, 4 inches square | E. & A. 7450 |
| 1 | Steel spatula, 7.5 cm | E. & A. 6272 |
| 1 | Sodium knife (common knife) | E. & A. 2300 |
| 1 | Test-tube brush, sponge end | E. & A. 1210 |
| 1 | Test-tube cleaner | E. & A. 1214 |
| 1 | Package filter paper, $12\frac{1}{2}$ cm., Whatman No. 2 | E. & A. 5001 |
| 2 | Boxes matches | |
| 1 | Test-tube holder, nickel | E. & A. 2068 |
| 1 | Sponge | E. & A. 6378 |
| 1 | Box labels, square | E. & A. |
| 2 | Towels | |
| 8 | Feet black rubber tubing, $\frac{3}{16}$ inch I. D | E. & A. 6054 |
| 12 | Feet white rubber tubing, $\frac{1}{4}$ inch I. D., heavy walled | E. & A. 6048 |
| 1 | Pair goggles, wire gauze protectors | E. & A. 3794 |
| 2 | Dozen assorted corks, sizes 1–15 | E. & A. 2284 |
| 1 | Suberite ring, $2\frac{3}{8}$ inches I. D | E. & A. 6020 |
| 1 | Cake Pummo soap | |
| 1 | Tin pail | |
| 2 | Locks with keys, Eagle Lock Co. | |
| 1 | Vial litmus paper, neutral, Squibb's | |
| 1 | Pocket ruler | |
| 1 | Rubber stopper No. 7, 3 holes, to fit 250-cc. bottle | E. & A. 6040 |
| 1 | Rubber stopper No. 5, 1 hole, to fit test-tube, with side neck | E. & A. 6040 |
| 1 | Rubber stopper, 3 holes to fit 250-cc. short neck R. B. flask | E. & A. 6040 |
| 1 | Rubber stopper, No. 5, 2 holes to fit test-tube with side neck | E. & A. 6040 |
| 1 | Scissors | E. & A. 6104 |
| 1 | Cork screw, Williamson Wire Novelty Co. | $9\frac{1}{2}$ |
| 1 | Rubber washer | |
| 1 | Perfection sand paper holder | H. & S. 1017 |
| 1 | Package sand paper, $4\frac{1}{2}'' \times 4\frac{1}{2}''$ [1] | |

---

[1] For keeping Alberene desk top clean.

# LIST OF CHEMICALS FOR LONG COURSE[1]

## FIRST SEMESTER

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 1 | Acetone | 30 cc. | G. S. B.[2] |
| 2 | Acetophenone | 10 gms. | G. S. B. |
| 3 | Alcohol, 95% | 2×300 cc.[3] | G. S. B. |
| 4 | Amyl alcohol (iso) | 1 cc. | G. S. B. |
| 5 | Aniline from sulfate for B. P. determination | 15 cc. | G. S. B. |
| 6 | Anisic acid, powdered, for M. P. determination | 0.1 gm. | Vial |
| 7 | Anthracene, powdered, for M. P. determination | 0.1 gm. | Vial |
| 8 | Anthraquinone, powdered, for M. P. determination | 0.1 gm. | Vial |
| 9 | Benzine, 70–80° | 15 cc. | G. S. B. |
| 10 | Benzoic acid | 1 gm. | Vial |
| 11 | Benzoic acid, powdered, for M. P. determination | 0.1 gm. | Vial |
| 12 | Bromine | 1 oz. | G. S. B. |
| 13 | Bromine water | 25 cc. | G. S. B. |
| 14 | Bromine, 5% in carbon tetrachloride | 20 cc. | G. S. B. |
| 15 | Calcium chloride, anhyd., gran. | 100 gms. | C. S. B.[2] |
| 16 | Calcium carbide, lumps | 15 gms. | C. Vial |
| 17 | Calcium oxide | 150 gms. | WM., G. S. B.[2] |
| 18 | Carbazol, powdered, for M. P. determination | 0.1 gm. | Vial |
| 19 | Chloroform | 10 cc. | G. S. B. |
| 20 | Copper oxide, powder | 2 gms. | Vial |
| 21 | Copper sulfate, anhyd | 5 gms. | C. Vial |
| 22 | Copper sulfate, crystals | 1 gm. | Vial |
| 23 | Copper sulfate, $\frac{1}{80}$ molar | 3 cc. | C. S. B. |
| 24 | Copper turnings | 5 gms. | Vial |
| 25 | Copper wire | 2 ft. | Vial |
| 26 | Cotton, absorbent | 2 gms. | Vial |

---

[1] See preface, p. v.

[2] Abbreviations: G. S. B. = glass stoppered bottle; C. S. B. = cork stoppered bottle; WM. = wide-mouthed.

[3] The amounts of such reagents as alcohol, ether, sulfuric acid are only nominal. These must be added to later in the work.

## LIST OF CHEMICALS FOR LONG COURSE—*Continued*

### First Semester

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 27 | Di-nitrobenzoic acid (1 : 3 : 5) | 1 gm. | Vial |
| 28 | Ether, Merck's | $2 \times \frac{1}{4}$ lb. | Cans |
| 29 | Ethyl bromide | 35 cc. | C. S. B. |
| 30 | Fehling's solution A [1] | 5 cc. | G. S. B. |
| 31 | Fehling's solution, B | 5 cc. | G. S. B. |
| 32 | Formalin | 25 cc. | G. S. B. |
| 33 | Glass wool | 20 cc. | Vial |
| 34 | Glycerol | 10 cc. | C. S. B. |
| 35 | Hydrochloric acid, conc. | 35 cc. | G. S. B. |
| 36 | Hydroxylamine hydrochloride | 3.5 gms. | WM., G. S. B. |
| 37 | Iodine | 17 gms. | WM., G. S. B. |
| 38 | Lime water | 10 cc. | C. S. B. |
| 39 | Magnesium (Grignard's) | 5 gms. | Vial |
| 40 | Menthol | 5 gms. | C. Vial |
| 41 | Methylal | 2 cc. | S. T.[2] |
| 42 | Methyl alcohol | 2 cc. | C. S. B. |
| 43 | Naphthalene, powder, for M. P. determination | 0.1 gm. | Vial |
| 44 | Phenolphthalein, sol | 5 cc. | C. S. B. |
| 45 | Phosphoric acid (1.7) | 40 cc. | G. S. B. |
| 46 | Phosphorus pentachloride | 1 gm. | S. T. |
| 47 | Phosphorus, red | 2 gms. | Vial |
| 48 | Pinene | 15 cc. | C. S. B. |
| 49 | Porous tile, gran | 10 gms. | Vial |
| 50 | Potassium carbonate, fused | 15 gms. | C. Vial |
| 51 | Potassium hydroxide | 5 gms. | C. Vial |
| 52 | Potassium hydroxide, purified by alcohol | 3 gms. | C. Vial |
| 53 | Potassium permanganate | 2 gms. | Vial |
| 54 | Quinoline (synthetic) for B. P. determination | 15 cc. | G. S. B. |
| 55 | Rapeseed oil | 300 cc. | C. S. B. |
| 56 | Resorcinol solution, 0.5% | 2 cc. | C. S. B. |
| 57 | Salicylic acid, powder, for M. P. determination | 0.1 gm. | Vial |
| 58 | Schiff's aldehyde reagent (fuchsine sulfurous acid) | 10 cc. | G. S. B. |
| 59 | Soda lime, dry | 20 cc. | C. Vial |
| 60 | Sodium bicarbonate | 5 gms. | Vial. |

---

[1] The ground part of the glass stopper of the bottle containing the "alkaline half" of Fehling's solution is dipped in melted paraffin before being used. This prevents the stopper from becoming "frozen." Cork and rubber stoppers cannot be used.

[2] S. T. = sealed tube.

## LIST OF CHEMICALS FOR LONG COURSE—*Continued*

### FIRST SEMESTER

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 61 | Sodium bichromate | 45 gms. | Vial |
| 62 | Sodium bisulfite, sat. sol | 5 cc. | C. S. B. |
| 63 | Sodium carbonate, dry | 5 gms. | Vial |
| 64 | Sodium chloride, sat. sol | 50 cc. | C. S. B. |
| 65 | Sodium hydroxide | 50 gms. | C. Vial |
| 66 | Sodium, metallic | 12 gms. | WM., G. S. B. (in can) |
| 67 | Sulfuric acid, conc | 300 cc. | G. S. B. |
| 68 | Sulfuric acid, fuming | 15 cc. | S. T. |
| 69 | Vaseline | 10 cc. | Vial |
| 70 | Zinc dust | 10 gms. | Vial |

## LIST OF CHEMICALS FOR LONG COURSE[1]

### SECOND SEMESTER

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 1 | Acetic acid (glacial) | 75 cc. | G. S. B.[1] |
| 2 | Acetic anhydride | 12 cc. | G. S. B. |
| 3 | Acetylacetone | 1 cc. | G. S. B. |
| 4 | Acetacetic ester | 1 cc. | G. S. B. |
| 5 | Acetone | 25 cc. | C. S. B. |
| 6 | Alcohol, 95% | 2×300 cc.[1] | C. S. B. |
| 7 | Aluminium chloride (anhyd.) | 5 gms. | C. Vial |
| 8 | Ammonium acetate (dry) | 15 gms. | C. Vial |
| 9 | Ammonium hydroxide, conc | 50 cc. | G. S. B. |
| 10 | Ammonium molybdate reagent | 25 cc. | G. S. B. |
| 11 | Aniline I | 5 cc. | G. S. B. |
| 12 | Animal charcoal | 5 gms. | Vial |
| 13 | Anthracene | 2.5 gms | Vial |
| 14 | Benzene, 80°–82° | 115 cc. | C. S. B. |
| 15 | Benzene, thiophene free | 3 cc. | G. S. B. |
| 16 | Benzaldehyde | 5 cc. | C. S. B. |
| 17 | Benzyl chloride | 15 cc. | S. tube |
| 18 | Bleaching powder | 5 gms. | C. vial |
| 19 | Bromine | 1 oz. | G. S. B. |
| 20 | Bromine water | 10 cc. | G. S. B. |
| 21 | Bromine in $CCl_4$, 5% | 1 cc. | G. S. B. |
| 22 | Butter | 10 gms. | |
| 23 | Cane sugar | 5 gms. | Vial |
| 24 | Carbon disulfide | 1 cc. | C. S. B. |
| 25 | Catechol | 0.1 gm. | Vial |
| 26 | Chloroform, U.S.P. | 20 cc. | C. S. B. |
| 27 | Chromium trioxide | 4.5 gms. | C. vial |
| 28 | Cinnamic acid | 0.1 gm. | Vial |
| 29 | Copper carbonate (basic) | 0.5 gm. | Vial |
| 30 | Copper sulfate N | 7 cc. | C. S. B. |
| 31 | Corn cob (ground) | 1 gm. | Vial |
| 32 | Cotton (absorbent) | 0.5 gm. | Vial |
| 33 | Dimethylaniline | 2 cc. | G. S. B. |
| 34 | Dimethyl sulfate | 30 gms. | S. tube |
| 35 | Diphenyl-thiourea | 0.01 gm. | Vial |
| 36 | Egg | 1 | Shell |
| 37 | Ether (Merck's) | 2×½ lb.[1] | Cans |
| 38 | Ether ("over sodium") | 90 cc. | C. S. B. |
| 39 | Ethyl ammonium chloride | 2 cc. | C. S. B. |

---

[1] See foot-notes, p. 315.

## LIST OF CHEMICALS FOR LONG COURSE—*Continued*

### SECOND SEMESTER

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 40 | Ethyl bromide.......................... | 20 cc. | C. S. B. |
| 41 | Fehling's solution "A"................ | 35 cc. | G. S. B.[1] |
| 42 | Fehling's solution "B"................ | 35 cc. | G. S. B. |
| 43 | Ferric chloride, $\frac{1}{6}$ molar................ | 5 cc. | C. S. B. |
| 44 | Ferric chloride, N.................... | 2 cc. | C. S. B. |
| 45 | Ferrous sulfate........................ | 1 gm. | Vial |
| 46 | Ferrous sulfide........................ | 20 gms. | Vial |
| 47 | Gallic acid............................ | 0.01 gm. | Vial |
| 48 | Gelatine............................... | 1 gm. | Envelope |
| 49 | Gum arabic............................. | 0.5 gm. | Vial |
| 50 | Hydrochloric acid, conc............... | 125 cc. | G. S. B. |
| 51 | Hippuric acid.......................... | 1 gm. | Vial |
| 52 | Iron powder............................ | 5 gms. | Vial |
| 53 | Iron nails (small).................... | 3 gms. | Vial |
| 54 | Lactose................................ | 12 gms. | Vial |
| 55 | Lead acetate, N........................ | 10 cc. | C. S. B. |
| 56 | Magnesium sulfate, cryst............. | 6 gms. | Vial |
| 57 | Methyl iodide.......................... | 1 cc. | S. tube |
| 58 | Michler's ketone....................... | 0.1 gm. | Vial |
| 59 | Monomethyl aniline, commercial....... | 1 cc. | G. S. B. |
| 60 | Nitric acid, conc...................... | 60 cc. | G. S. B. |
| 61 | Nitric acid, fuming................... | 1 cc. | S. tube |
| 62 | Nitrobenzene, commercial............. | 20 cc. | C. S. B. |
| 63 | Phenol................................. | 13 gms. | Vial |
| 64 | Phthalic anhydride.................... | 0.2 gm. | Vial |
| 65 | Phenylhydrazine....................... | 2 cc. | G. S. B. |
| 66 | Phosphorus oxychloride................ | 2 cc. | S. tube |
| 67 | Phosphorus trichloride................ | 5 cc. | S. tube |
| 68 | Potassium carbonate (fused)........... | 25 gms. | C. vial |
| 69 | Potassium cyanate..................... | 0.5 g. | Vial |
| 70 | Potassium fluoride.................... | 0.5 g. | Vial |
| 71 | Potassium iodide, N/10................ | 2 cc. | C. S. B. |
| 72 | Potassium permanganate............... | 10 gms. | Vial |
| 73 | Potassium ethyl sulfate............... | 0.5 gm. | Vial |
| 74 | Pyridine, commercial.................. | 5 cc. | G. S. B. |
| 75 | Quinoline.............................. | 2 cc. | G. S. B. |
| 76 | Resorcinol............................. | 0.1 gm. | Vial |
| 77 | Salicylic acid......................... | 0.1 gm. | Vial |
| 78 | Schiff's aldehyde reagent............. | 20 cc. | Amb. G. S. B. |

---

[1] See foot-note, p. 316.

## LIST OF CHEMICALS FOR LONG COURSE—*Continued*

### SECOND SEMESTER

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 79 | Silver nitrate, N/10 | 10 cc. | Amb. G. S. B. |
| 80 | Sodium, metallic | 12 gms. | WM., G. S. B. (in can) |
| 81 | Sodium bisulfite, sat. sol. | 10 cc. | C. S. B. |
| 82 | Sodium carbonate, cryst. | 4 gms. | Vial |
| 83 | Sodium chloride, commercial | 4 lbs. | Bag |
| 84 | Sodium chloride, sat. sol. | 50 cc. | C. S. B. |
| 85 | Sodium dichromate | 15 gms. | C. vial |
| 86 | Sodium hydroxide | 50 gms. | C. vial |
| 87 | Sodium nitrite | 8 gms. | Vial |
| 88 | Sodium nitroprusside | 0.1 gm. | Vial |
| 89 | Starch, soluble | 5 gms. | Vial |
| 90 | Sulfanilic acid | 1 gm. | Vial |
| 91 | Sulfuric acid (fuming) | 6 cc. | S. tube |
| 92 | Tannin (tannic acid) | 2 gms. | Vial |
| 93 | Tin, granulated | 35 gms. | Vial |
| 94 | Toluene, commercial | 110 cc. | C. S. B. |
| 95 | Toluidine (ortho) | 5 cc. | G. S. B. |
| 96 | Triphenyl-chlor-methane | 0 5 gm. | Vial |
| 97 | Xylene, commercial | 30 cc. | C. S. B. |
| 98 | Zinc chloride, N | 10 cc. | C. S. B. |
| 99 | Zinc dust, commercial | 5 gms. | Vial |
| 100 | Zinc, powdered | 1 gm. | Vial |

## LIST OF CHEMICALS FOR SHORT COURSE[1]

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 1 | Acetic acid, glacial | 100 cc. | G. S. B.[1] |
| 2 | Acetic anhydride | 13 cc. | G. S. B. |
| 3 | Acetacetic ester | 1 cc. | G. S. B. |
| 4 | Acetylacetone | 1 cc. | G. S. B. |
| 5 | Acetone | 25 cc. | C. S. B.[1] |
| 6 | Alcohol, 95% | 2×300 cc.[1] | G. S. B. |
| 7 | Ammonium acetate | 15 gms. | C. vial |
| 8 | Ammonium hydroxide, conc | 50 cc. | G. S. B. |
| 9 | Ammonium molybdate, sol | 25 cc. | G. S. B. |
| 10 | Amyl alcohol (iso) | 1 cc. | G. S. B. |
| 11 | Aniline I | 15 cc. | G. S. B. |
| 12 | Aniline from sulfate, for B. P. determination | 15 cc. | G. S. B. |
| 13 | Animal charcoal | 15 gms. | Vial |
| 14 | Anthracene, powdered, for M. P. determination | 0 1 gm. | Vial |
| 15 | Benzene, 80°–82° | 15 cc. | C. S. B. |
| 16 | Benzene (thiophene free) | 3 cc. | C. S. B. |
| 17 | Benzine 70°–80° | 15 cc. | G. S. B. |
| 18 | Benzaldehyde | 5 cc. | C. S. B. |
| 19 | Benzoic acid | 1 gm. | Vial |
| 20 | Bleaching powder | 5 gms. | Vial |
| 21 | Bromine | 5 cc. | G. S. B. |
| 22 | Bromine water | 25 cc. | G. S. B. |
| 23 | Bromine, 5% in carbon tetrachloride | 20 cc. | G. S. B. |
| 24 | Butter | 10 gms. | |
| 25 | Calcium chloride, anhydrous, gran | 35 gms. | C. S. B. |
| 26 | Calcium carbide, lumps | 15 gms. | Vial |
| 27 | Calcium oxide | 150 gms. | WM., C. S. B. |
| 28 | Cane sugar | 5 gms. | Vial |
| 29 | Catechol | 0.5 gm. | Vial |
| 30 | Chloroform | 50 cc. | G. S. B. |
| 31 | Cinnamic acid | 0.1 gm. | Vial |
| 32 | Copper carbonate, basic | 0.5 gm. | Vial |
| 33 | Copper oxide, powder | 5 gms. | Vial |
| 34 | Copper sulfate, anhyd | 5 gms. | C. vial |
| 35 | Copper sulfate, cryst | 1 gm. | Vial |
| 36 | Copper sulfate, N sol | 5 cc. | C. S. B. |
| 37 | Copper turnings | 5 gms. | Vial |
| 38 | Copper wire, No. 16 | 2 ft. | Vial |
| 39 | Cotton, absorbent | 2 gms. | Vial |

---

[1] See preface, p; v. and also foot-notes, p. 315.

## LIST OF CHEMICALS FOR SHORT COURSE—*Continued*

| Reagent No. | Name and Specification. | Amount. | Kind of Container. |
|---|---|---|---|
| 40 | Dimethyl aniline | 2 cc. | G. S. B. |
| 41 | Diphenyl-thiourea | 0.01 gm. | Vial |
| 42 | Egg | 1 | Shell |
| 43 | Ether (Merck's) | 2×½ lb. | Cans |
| 44 | Ethyl ammonium chloride, sol | 2 cc. | C. S. B. |
| 45 | Ethylene dibromide | 2 cc. | C. S. B. |
| 46 | Fehling's solution, "A" [1] | 20 cc. | G. S. B. |
| 47 | Fehling's solution, "B" | 20 cc. | G. S. B. |
| 48 | Ferric chloride, $\frac{1}{5}$ molar | 20 cc. | C. S. B. |
| 49 | Ferrous sulfate | 1 gm. | Vial |
| 50 | Ferrous sulfide | 20 gms. | Vial |
| 51 | Gallic acid | 0.1 gm. | Vial |
| 52 | Glass wool | 20 cc. | Vial |
| 53 | Hippuric acid | 1 gm. | Vial |
| 54 | Hydrochloric acid, conc | 150 cc. | G. S. B. |
| 55 | Hydroxylamine hydrochloride | 1.5 gms. | WM., G. S. B. |
| 56 | Iodine, resublimed | 17 gms. | WM., G. S. B. |
| 57 | Iron powder | 5 gms. | Vial |
| 58 | Lead acetate, N sol | 10 cc. | C. S. B. |
| 59 | Lime water | 10 cc. | C. S. B. |
| 60 | Methyl iodide | 1 cc. | Seal T |
| 61 | Michler's ketone | 0.1 gm. | Vial |
| 62 | Monomethyl aniline | 1 cc. | C. S. B. |
| 63 | Naphthalene, powdered, for M. P. determination | 0.1 gm. | Vial |
| 64 | Nitric acid, conc | 50 cc. | G. S. B. |
| 65 | Nitric acid, fuming | 1 cc. | Seal T |
| 66 | Nitrobenzene, commercial | 20 cc. | C. S. B. |
| 67 | Nitrobenzene, for B. P. determination | 15 cc. | C. S. B. |
| 68 | Phthalic anhydride | 0.2 gms. | Vial |
| 69 | Phenolphthalein sol | 5 cc. | C. S. B. |
| 70 | Phenylhydrazine | 5 cc. | G. S. B. |
| 71 | Phosphorus, red | 2 gms. | Vial |
| 72 | Phosphorus pentoxide | 4 gms. | C. vial |
| 73 | Phosphorus oxychloride | 2 cc. | Seal T |
| 74 | Phosphorus trichloride | 7.5 cc. | Seal T. |
| 75 | Pinene | 15 cc. | C. S. B. |
| 76 | Porous tile, small broken pieces | 20 cc. | C. vial |
| 77 | Potassium carbonate, anhyd | 20 gms. | C. vial |
| 78 | Potassium hydroxide | 5 gms. | C. vial |
| 79 | Potassium hydroxide, purified by alcohol | 3 gms. | C. vial |

---

[1] See foot-note, p. 316.

## LIST OF CHEMICALS FOR SHORT COURSE—*Continued*

| Reagent No. | Name and Specification. | Amount | Kind of Container. |
|---|---|---|---|
| 80 | Potassium flouride | 0.5 gm. | Vial |
| 81 | Potassium iodide, N/10 sol | 2 cc. | C. S. B. |
| 82 | Potassium permanganate | 5 gms. | Vial |
| 83 | Pyridine, commercial | 5 cc. | G. S. B. |
| 84 | Quinoline | 2 cc. | G. S. B. |
| 85 | Rapeseed oil | 300 cc. | C. S. B. |
| 86 | Resorcinol | 0.2 gm. | Vial |
| 87 | Salicylic acid | 0.1 gm. | Vial |
| 88 | Salicylic acid, for M. P. determination | 0.1 . | Vial |
| 89 | Schiff's aldehyde reagent | 20 . | Amb. G. S. B. |
| 90 | Silver nitrate sol., N/10 | 25 cc. | Amb. G. S. B. |
| 91 | Sodium bisulfite, sat. sol | 15 cc. | C. S. B. |
| 92 | Sodium dichromate, commercial | 20 gms. | C. vial |
| 93 | Sodium chloride, sat. sol | 50 cc. | C. S. B. |
| 94 | Sodium chloride | 100 gms. | C. S. B. |
| 95 | Sodium carbonate, cryst | 10 gms. | Vial |
| 96 | Sodium hydroxide | 25 gms. | C. vial |
| 97 | Sodium nitrite | 8 gms. | Vial |
| 98 | Sodium nitroprusside | 0.01 gm. | Vial |
| 99 | Starch, soluble | 5 gms. | Vial |
| 100 | Sulfanilic acid | 1 gm. | Vial |
| 101 | Sulfuric acid, conc | 100 cc. | G. S. B. |
| 102 | Sulfuric acid, fuming | 10 cc. | Seal T |
| 103 | Tin, gran | 35 gms. | Vial |
| 104 | Toluidine (ortho) | 5 cc. | G. S. B. |
| 105 | Vaseline | 10 cc. | Vial |
| 106 | Zinc chloride, N/10 | 10 cc. | C. S. B. |
| 107 | Zinc dust, commercial | 10 gms. | Vial |

# GENERAL INDEX

NOTE.—Substances with a prefix such as *l*-menthone, *p*-tolunitrile, etc., are indexed under the name of the substance regardless of the prefix.

# Wiley Special Subject Catalogues

For convenience a list of the Wiley Special Subject Catalogues, envelope size, has been printed. These are arranged in groups—each catalogue having a key symbol. (See special Subject List Below). To obtain any of these catalogues, send a postal using the key symbols of the Catalogues desired.

**1—Agriculture. Animal Husbandry. Dairying. Industrial Canning and Preserving.**

**2—Architecture. Building. Masonry.**

**3—Business Administration and Management. Law.** **Industrial Processes:** Canning and Preserving; Oil and Gas Production; Paint; Printing; Sugar Manufacture; Textile.

## CHEMISTRY

**4a** General; Analytical, Qualitative and Quantitative; Inorganic; Organic.

**4b** Electro- and Physical; Food and Water; Industrial; Medical and Pharmaceutical; Sugar.

## CIVIL ENGINEERING

**5a** Unclassified and Structural Engineering.

**5b** Materials and Mechanics of Construction, including; Cement and Concrete; Excavation and Earthwork; Foundations; Masonry.

**5c** Railroads; Surveying.

**5d** Dams; Hydraulic Engineering; Pumping and Hydraulics; Irrigation Engineering; River and Harbor Engineering; Water Supply.

(Over)

## CIVIL ENGINEERING—*Continued*

**5e** Highways; Municipal Engineering; Sanitary Engineering; Water Supply. **Forestry. Horticulture, Botany and Landscape Gardening.**

**6—Design. Decoration. Drawing:** General; Descriptive Geometry; Kinematics; Mechanical.

## ELECTRICAL ENGINEERING—PHYSICS

**7**—General and Unclassified; Batteries; Central Station Practice; Distribution and Transmission; Dynamo-Electro Machinery; Electro-Chemistry and Metallurgy; Measuring Instruments and Miscellaneous Apparatus.

**8—Astronomy. Meteorology. Explosives. Marine and Naval Engineering. Military. Miscellaneous Books.**

## MATHEMATICS

**9**—General; Algebra; Analytic and Plane Geometry; Calculus; Trigonometry; Vector Analysis.

## MECHANICAL ENGINEERING

**10a** General and Unclassified; Foundry Practice; Shop Practice.

**10b** Gas Power and Internal Combustion Engines; Heating and Ventilation; Refrigeration.

**10c** Machine Design and Mechanism; Power Transmission; Steam Power and Power Plants; Thermodynamics and Heat Power.

**11—Mechanics.**

**12**—Medicine. Pharmacy. Medical and Pharmaceutical Chemistry. Sanitary Science and Engineering. Bacteriology and Biology.

## MINING ENGINEERING

**13**—General; Assaying; Excavation, Earthwork, Tunneling, Etc.; Explosives; Geology; Metallurgy; Mineralogy; Prospecting; Ventilation.

# INTERNATIONAL ATOMIC WEIGHTS, 1920.

| | Symbol. | Atomic weight. |
|---|---|---|
| Aluminium | Al | 27.1 |
| Antimony | Sb | 120.2 |
| Argon | A | 39.9 |
| Arsenic | As | 74.96 |
| Barium | Ba | 137.37 |
| Bismuth | Bi | 208.0 |
| Boron | B | 10.9 |
| Bromine | Br | 79.92 |
| Cadmium | Cd | 112.40 |
| Caesium | Cs | 132.81 |
| Calcium | Ca | 40.07 |
| Carbon | C | 12.005 |
| Cerium | Ce | 140.25 |
| Chlorine | Cl | 35.46 |
| Chromium | Cr | 52.0 |
| Cobalt | C | 58.97 |
| Columbium | | 93.1 |
| Copper | Cu | 63.57 |
| Dysprosium | Dy | 162.5 |
| Erbium | Er | 167.7 |
| Europium | Eu | 152.0 |
| Fluorine | F | 19.0 |
| Gadolinium | Gd | 157.3 |
| Gallium | Ga | 70.1 |
| Germanium | Ge | 72.5 |
| Glucinum | Gl | 9.1 |
| Gold | Au | 197.2 |
| Helium | He | 4.00 |
| Holmium | Ho | 163.5 |
| Hydrogen | H | 1.008 |
| Indium | In | 114.8 |
| Iodine | I | 126.92 |
| Iridium | Ir | 193.1 |
| Iron | Fe | 55.84 |
| Krypton | Kr | 82.92 |
| Lanthanum | La | 139.0 |
| Lead | Pb | 207.20 |
| Lithium | Li | 6.94 |
| Lutecium | Lu | 175.0 |
| Magnesium | Mg | 24.32 |
| Manganese | Mn | 54.93 |
| Mercury | Hg | 200.6 |
| Molybdenum | Mo | 96.0 |

| | Symbol. | Atomic weight. |
|---|---|---|
| Neodymium | Nd | 144.3 |
| Neon | Ne | 20.2 |
| Nickel | Ni | 58.68 |
| Niton (radium emanation) | Nt | 222.4 |
| Nitrogen | N | 14.008 |
| Osmium | Os | 190.9 |
| Oxygen | O | 16.00 |
| Palladium | Pd | 106.7 |
| Phosphorus | P | 31.04 |
| Platinum | Pt | 195.2 |
| Potassium | K | 39.10 |
| Praseodymium | Pr | 140.9 |
| Radium | Ra | 226.0 |
| Rhodium | Rh | 102.9 |
| Rubidium | Rb | 85.45 |
| Ruthenium | Ru | 101.7 |
| Samarium | Sa | 150.4 |
| Scandium | Sc | 44.1 |
| Selenium | Se | 79.2 |
| Silicon | Si | 28.3 |
| Silver | Ag | 107.88 |
| Sodium | Na | 23.00 |
| Strontium | Sr | 87.63 |
| Sulfur | S | 32.06 |
| Tantalum | Ta | 181.5 |
| Tellurium | Te | 127.5 |
| Terbium | Tb | 159.2 |
| Thallium | Tl | 204.0 |
| Thorium | Th | 232.15 |
| Thulium | Tm | 168.5 |
| Tin | Sn | 118.7 |
| Titanium | Ti | 48.1 |
| Tungsten | W | 184.0 |
| Uranium | U | 238.2 |
| Vanadium | V | 51.0 |
| Xenon | Xe | 130.2 |
| Ytterbium (Neoytterbium) | Yb | 173.5 |
| Yttrium | Yt | 89.33 |
| Zinc | Zn | 65.37 |
| Zirconium | Zr | 90.6 |