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New York : Wiley, 1912.

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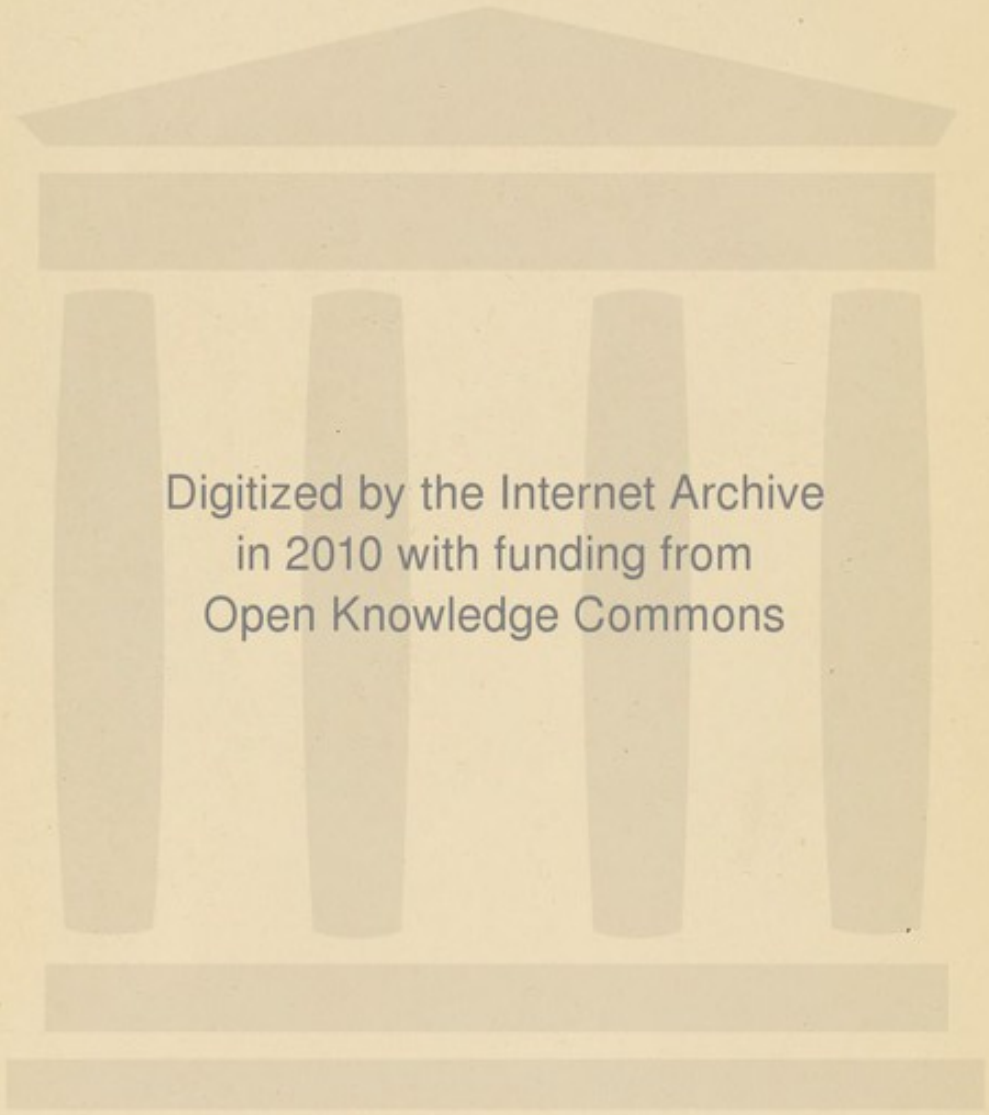
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LECTURE-NOTES

ON

CHEMISTRY

FOR

DENTAL STUDENTS

INCLUDING

DENTAL CHEMISTRY OF ALLOYS, AMALGAMS, ETC.

SUCH PORTIONS OF ORGANIC AND PHYSIOLOGICAL CHEMISTRY AS HAVE PRACTICAL BEARING ON THE SUBJECT OF DENTISTRY

AN INORGANIC QUALITATIVE ANALYSIS WITH SPECIALLY ADAPTED BLOWPIPE AND MICROSCOPICAL TESTS, AND THE CHEMICAL EXAMINATION OF URINE AND SALIVA

BY

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SECOND EDITION REVISED AND ENLARGED

FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

1912

C. Franklin MacDonald D. M.

RK 290
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1912

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H. CARLTON SMITH

Stanhope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

PREFACE TO FIRST EDITION.

THE arrangement of this book follows rather closely the lecture course in Dental Chemistry as given by the author at the Harvard Dental School. It has been the aim of these lectures to give the student, as concisely as possible, such portions of the various branches of chemistry as are most likely to be of value in practical work.

Simplicity of manipulation has in some cases been considered of greater practical value than extreme accuracy, especially in the chapter on Quantitative Analysis, the volumetric processes being given, as a rule, rather than the more exact but more difficult gravimetric methods.

The usual equipment of a dental laboratory has been borne in mind, and considerable prominence given to the simpler analytical tests made in the dry way by means of few reagents.

Recent text-books and current literature have been very generally consulted. New tests have been verified so far as possible — often modified — before being recommended to the student.

The U. S. Dispensatory and the Newer Materia Medica, as given in the Druggists' Circular, have been drawn upon in the sections on Local Anæsthetics and Hall's and Essig's Chemistries in the section on Alloys and Amalgams.

A chapter on Organic Chemistry has been introduced, designed to furnish an understanding of this branch of chemical science, which will enable the student to better comprehend the physiological chemistry which follows.

The chapter on the Analysis of Saliva is one which is, of

necessity, incomplete and imperfect. The investigations being at present carried on along the lines suggested by Dr. Joseph Michaels of Paris and Dr. Kirk of Philadelphia are opening up fields of research of the greatest magnitude and of utmost importance, and they can only be touched upon in this work.

The atomic weights given are from the international atomic weights for 1905. O = 16.

In the chapter on Physiological Chemistry the author wishes to particularly acknowledge his indebtedness to Professor Wm. B. Hills of the Harvard Medical School, who furnished the majority of the laboratory experiments for this portion of the work.

H. C. S.

PREFACE TO SECOND EDITION.

THE second edition of Chemistry for Dental Students is an almost new book, using the first edition as foundation only.

The chapter on Organic Chemistry has been considerably enlarged.

A number of new cuts, about ninety pages of text, and eighty-five experiments have been added, and the arrangement has been changed with the purpose of making the book useful to any teacher of Dental Chemistry. The laboratory work follows closely the outline of lectures.

An effort has been made to make the chapter on Saliva fairly complete to date, June, 1912, but of course every month brings its added contribution of experiment and much of valuable fact relative to this interesting and important subject.

The author wishes to acknowledge indebtedness to F. M. Rice, A.M., of the Chemical Department of Harvard Dental School for reviewing manuscript.

H. C. S.

TO THE STUDENT.

As the student of dentistry takes up the study of chemistry, it is necessary that he should realize that the course will be of value to him in the ability acquired to draw correct inferences from observed phenomena, and in the attainment of accuracy and delicacy in manipulation, fully as much as in amount of chemical knowledge obtained. In other words, he must do his own thinking, carry out his own processes and experiments, make his own analyses, or the time spent will be little better than wasted, for the chemical facts which he may happen to remember will be of slight benefit in the work to which every student, worthy of the name, aspires, that of developing, broadening, and elevating the profession which he has chosen as his own.

The course of study outlined in this book is designed to furnish the starting-points, which will be of practical value in solving the problems constantly presenting themselves for consideration in the various branches of chemistry. It is hoped that these starting-points may, in the future, serve as the basis for work along the lines of original research and that the best interests of dental science may be furthered thereby.

It is supposed that the student has had the advantage of a laboratory training in general chemistry and is conversant with the properties and methods of preparation of the so-called non-metallic elements, also with the fundamental principles and laws of theoretical and physical chemistry, that he is familiar with laboratory apparatus, such as test-tubes, beakers, crucibles, casseroles, evaporating-dishes, retorts, etc., and that

he has had some experience in the ordinary processes of precipitation, filtration, evaporation, distillation, sublimation, and crystallization.

If there is any feeling of insufficient preparation it is strongly advised that a short course of preliminary study be taken. Chemistry furnishes the groundwork of all branches of medical science to a much greater extent than we are apt to think, and even in the study of subjects which in times past have been carried on with little reference to chemistry, we now see the desirability if not the necessity of a good general knowledge of chemical science. The physiologist and the bacteriologist are to-day turning to chemistry for the utlimate solution of their most perplexing problems.

H. C. S.

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DENTAL CHEMISTRY

PART I.

SALTS OF THE METALS AND QUALITATIVE ANALYSIS

CHAPTER I.

INTRODUCTION.

EVERY science has a language peculiar to itself, a thorough understanding of which is an essential preliminary to the study of that science. Hence, before we take up the study of Dental Chemistry, it will be well to review a few definitions and perhaps a few of the facts of Physics which are closely related to our subject.

Elements. — An element is one of the simplest forms of matter — a substance which cannot by any means be resolved into matter differing from itself.

Compounds. — Compounds consist of two or more elements chemically combined.

Molecule. — The molecule is the smallest particle of matter that can exist and retain the properties of the original substance.

Atoms. — Atoms are the smaller particles of matter of which molecules are composed.

Statements regarding the size and shape of atoms or molecules are statements of theories, which are helpful in understanding certain chemical phenomena and some of which will be briefly considered in a subsequent lecture.

Chemical Affinity or Chemism is the attraction existing between atoms whereby they are held together as molecules.

Valence. — Valence is a property of atoms and represents their combining power relative to hydrogen. Valence is not always constant for the same elements; for example, sulphur has a combining power of six in sulphuric acid, of four in sulphur dioxide, and of two in hydrogen sulphide. Nitrogen has a combining power of three in ammonia gas and five in ammonium chloride. Valence is also indicated by the terms quantivalence and atomicity.

Bond. — The bond is used to indicate the relationship of atoms in a molecule and at the same time shows the valence of the atom.

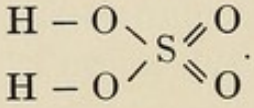
Example, H — O — H, the dash (bond) shows that oxygen has two combining points relative to the hydrogen which is considered to have one.

Symbols. — Symbols are used to designate the various elements. In some cases the initial letter of the element alone is used, as C for carbon. In other cases there is added a distinctive small letter of the name when there happen to be a number of elements with names beginning with the same letter such as Calcium, Ca; Cobalt, Co; Copper, Cu; etc.

Chemical Formula. — A chemical formula represents the molecule and is made up of the symbols of the several constituent elements. Chemical formulae may be empirical, dualistic or graphic. The empirical formula represents the molecule without reference in any way to its structure, i.e., H_2SO_4.

The dualistic formula indicates compounds which may enter into the composition of a molecule. By this sort of formula sulphuric acid would be represented by $H_2O.SO_3$.

The graphic formula attempts to show the probable relation of the atoms in the molecule by means of bonds, e.g.,



Ions. — The electrically charged particles or parts of molecules capable of attraction to either cathode or anode in the process of electrolysis have been called "ions" (Faraday's definition). Ions may consist of single atoms as in H^+Cl^- or of groups of atoms (radicals) as in water $H^+(OH)^-$ or ammonium hydrate $(NH_4)^+(OH)^-$.

Acid. — An acid is a compound containing positive hydrogen ions which may be replaced by a metallic element or radical. The more common acids are sour to the taste and act in characteristic manner upon a number of color compounds known as indicators.

Base. — A base is a substance containing negative hydroxyl ions which may be replaced by acid radicals. Bases in general characteristics oppose acids. The strongest bases are known as alkalies, e.g., KOH, NaOH.

A Salt. — A salt is a substance produced by the chemical union of an acid and a base.

In the formation of the salt the acid may not have been completely neutralized by the base and an *acid salt* results. In such a case the salt contains a part of the hydrogen ions of the acid, e.g., potassium acid sulphate, $KHSO_4$, the production of which may be represented by the equation

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

Acid salts may or may not have acid properties such as sour taste and power to give acid reactions with indicators. A salt may on the other hand be *basic* and contain a portion of the hydroxyl ions (or sometimes oxygen atoms) of the base.

Example: $Bi(OH)_3 + 2\,HNO_3 = BiOH(NO_3)_2 + 2\,H_2O$ or

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

If the acid is exactly neutralized by the base, *neutral salts* result.

$$2\,NaOH + H_2SO_4 = Na_2SO_4 + 2\,H_2O.$$

Reactions between chemical substances may be " completed " or " reversible."

A completed reaction is one which progresses in a definite way irrespective of changes in temperature or of the quantities of the reacting substances; or, a completed reaction is one in which one of the products is chemically inactive. This inactivity may be due to one of several causes, such as the production of an insoluble precipitate; e.g. AgCl in the reaction,

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

or the escape of the product as a gas and its consequent removal from solution — as when carbonates are dissolved by acid.

The reversible reaction is one in which the products remain to a greater or less degree in solution and a change of temperature or increase in quantity of one of the products may start a reverse reaction; for example, at the body temperature, dibasic sodium phosphate and uric acid may become monobasic sodium phosphate and acid sodium urate,

$$Na_2HPO_4 + H_2\overline{U} = NaH_2PO_4 + NaH\overline{U},$$

while at reduced temperature,

$$NaH_2PO_4 + NaH\overline{U} = Na_2HPO_4 + H_2\overline{U}.$$ (See page 237.)

Reversible reactions are often expressed by use of the sign $\rightleftarrows$; thus, $MgCl_2 + 2\ NH_4OH \rightleftarrows Mg(OH)_2 + 2\ NH_4Cl$. The reaction may be expressed as an equation if we know what substances take part in the reaction and what products are formed. The above reaction can be balanced at a glance and is therefore not well suited for illustration but the use of a little more complex equation will show how easily it can be balanced by a few algebraic combinations.

$$Cu + HNO_3 = Cu(NO_3)_2 + NO + H_2O.$$

Represent these all as unknown quantities.

$$x\,Cu + y\,HNO_3 = z\,Cu(NO_3)_2 + m\,NO + p\,H_2O,$$

then

$$\left.\begin{array}{l} x\,\mathrm{Cu} = z\,\mathrm{Cu} \\ y\,\mathrm{H} = p\,\mathrm{H_2} \\ y\,\mathrm{N} = z\,(\mathrm{N})_2 + m\,\mathrm{N} \\ y\,\mathrm{O_3} = z\,(\mathrm{O_3})_2 + m\,\mathrm{O} + p\mathrm{O} \end{array}\right\} \text{or} \quad \begin{array}{ll} x = z & (1) \\ y = 2p & (2) \\ y = 2z + m & (3) \\ 3y = 6z + m + p & (4) \end{array}$$

multiplying equation 3 by 3, $3y = 6z + 3m$ (5)

and by elimination (4 and 5) $2m = p$ (6)

and $4m = 2p$, then by eq. 2 $y = 4m$ (7)

assuming that $m = 1$, then, in 7, $y = 4$; in 6, $p = 2$; in 3, $2z = 3$, or $z = 1\frac{1}{2}$, in 1, $x = 1\frac{1}{2}$. Knowing that all equations must be expressed by whole numbers we double these values and have $x = 3, y = 8, z = 3, m = 2, p = 4$.

Upon substituting these values we shall find that the equation " balances."

Solution. — If we are to study physiological chemistry a clear understanding of the meaning of this term is desirable.

" Solution is the equal distribution of a body in a liquid, the resulting mass being in all parts homogeneous and fluid enough to form drops," according to an old definition quoted in " Colloids and the Ultra-microscope " by Dr. Richard Zsigmondy.

We can readily adopt this definition for present use provided our conception of homogeneity is sufficiently elastic to include " Colloidal " solutions, which as a class are of rapidly increasing importance.

The colloids are distinguished from crystalloids by their inability to pass through parchment membrane. In colloidal solutions the substance (colloid) may be considered as in suspension or a state of subdivision so nearly complete as to approach closely to the homogeneity of crystalloidal solution.

In many colloidal solutions the particles are large enough to interfere with the passage of light and the preparation is more or less opaque. In some, however, this is not noticeable except by use of polarized light and special apparatus.

There is no sharply defined line between the suspensions and the colloidal solutions, and it is often true that the homogeneity of a solution is dependent upon the " grossness of our means of observation." The separation of the solid particles from the liquid may be effected in several ways.

Sedimentation serves to remove the coarser particles from suspension: the liquid in this case may be decanted or turned off from the heavy sediment.

Filtration through paper will remove the finer particles of suspension or ordinary precipitates.

Some very fine precipitates, such as sulphur and barium sulphate, require special papers.

Colloidal substances as a class may be separated from the crystalloids by *Dialysis*, animal membrane suspended in distilled water being used as a separating medium. The crystalloids will pass through the membrane into the pure water, while the colloids remain behind. The use of the dialyzer as applied to saliva analysis is shown on page 327.

Osmosis signifies the passage of water only through a membrane, tending to correct inequalities of pressure produced by differences in molecular concentrations of two solutions.

This is usually illustrated by dropping potassium ferrocyanide solution into copper sulphate. The drop of potassium ferrocyanide becomes surrounded by a film of copper ferrocyanide, through which water alone will pass. Membrane of this character is known as semi-permeable.

Porous cups are prepared for demonstrations of osmosis by precipitating within the pores of the cup or cell the ferrocyanide of copper.

Osmotic pressure is the pressure produced within a semi-permeable cell by passage of water from the outside; or, as stated by Holland, it is " That push of the molecules of a solute upon its solvent which causes a flow through a membrane into the solution."

Measures. — The metric system of weights and measures and the centigrade thermometer are largely used in all scientific work. The dentist, however, has also considerable use for troy weights and apothecaries' measures if he considers at all the composition of his gold solders, dental alloys, mouth washes, local anæsthetics, etc. Hence, a few equivalents are here given.

The *metre* is the primary unit of the metric system and was originally calculated as one ten-millionth part of the quadrant from the equator to the pole.

1 metre = 100 centimeters = 1000 millimeters or 39.37 inches.
1 centimeter = 10/25 or 0.3937 of an inch.
1 cubic centimeter = 16.23 minims or 0.0338 of a fluid ounce.
1000 cubic centimeters (c.c.) 1 liter or 2.113 pts.

The weight of 1 c.c. of pure water at the temperature of its greatest density (4° C.) is taken as a unit of weight and called a gram (gramme).

1 gram = 15.43 grains.
1000 grams = 1 kilogram (kilo) = 35 oz. 120 grains or 2.2 lbs. avoir.
1 inch = 2.54 centimeters or 25.4 millimeters.
1 oz. av. = 28.3495 grams or 437.5 grains.
1 fluid oz. = 8 fluid drams, 29.57 c.c., or 456 grains of water.
1 fluid dram = 3.7 c.c.
1 troy oz. = 8 drams (ʒ) or 480 grains.
1 troy oz. = 24 scruples (℈) or 20 pennyweight (pwt. or dwt.)
1 scruple = 20 grains, 1 pennyweight = 24 grains.
1 grain = 64 milligrams.
1 pint = 473.11 c.c.
1 gallon = 8 pints, or 3785 c.c., or 231 cubic inches.
1 lb. avoir. = 7000 grains or 453.59 grams.

Measure of Temperature. — We shall constantly meet reference to both the Centigrade and Fahrenheit scales and an understanding of the relationship of the two methods is essential.

The thermometer is graduated by marking the point at which the mercury stands when the instrument is placed on melting ice; and again the point reached by the mercury when the thermometer is surrounded by dry steam under ordinary atmospheric conditions.

On the Centigrade thermometer, the lower or freezing point is marked 0, the upper or boiling point is marked 100, and the intervening space divided into 100 equal degrees. On the Fahrenheit scale, these points are marked respectively 32 and 212 and the scale is divided into 180°; hence, 1° C. equals 1.8° or 9/5° Fahrenheit, and 1° F. equals 5/9 of a Centigrade degree. Providing for the different freezing points (0° and 32°), we can formulate a rule for converting temperature records from one scale to the other, as follows:

To convert Centigrade to Fahrenheit, take 9/5 of the given number of degrees and add 32.

To convert Fahrenheit to Centigrade, subtract 32 from the given number and take 5/9 of the remainder; e.g.

$$20° \text{ C.} = 68° \text{ F.}$$
$$-5° \text{ C.} = +\ 23° \text{ F.}$$
$$77° \text{ F.} = 25° \text{ C.}$$
$$14° \text{ F.} = -10° \text{ C.}$$

Absolute Temperature.

According to the Law of Charles or of Gay-Lussac, gases (free molecules) contract 1/273 of their volume, measured at 0° C., for every Centigrade degree that the temperature falls; so it is assumed that, at a point 273° below the Centigrade zero, no further contraction would be possible, molecular motion

would cease and all things become solid. This temperature has been called the absolute zero and temperature recorded from this point absolute temperature; thus, water freezes at 273° C. absolute temperature.

Gravity Signifies Weight.

Specific gravity is the relative weight of equal bulks of different substances, one of which is taken as a standard.

The standard is usually water for liquids and solids.

The standard for gases may be air or hydrogen.

When gases are referred to hydrogen as a standard, the term density is often used instead of specific gravity, and, to avoid confusion, this usage is recommended; i.e., the density of carbon dioxide is 22, while its specific gravity compared with air is about 1.53.

The density of a gas will, according to the Law of Avogadro, be one-half its molecular weight.

The specific gravity of a liquid may be diminished by the solution of a gas, as in case of solution of ammonia; or it may be increased, as in case of solution of hydrochloric acid. Specific gravity is increased by solution of solid substances.

The boiling point of a liquid is raised by the solution of solids.

The freezing point of water is lowered by solution of either solids or gases.

Cryoscopy is a term applied to the determination of freezing points in their relations to conditions of concentration or of purity. In medicine, the body fluids, such as blood, milk, and urine, have been investigated in this way.

Precipitation signifies throwing out in solid form a substance previously held in solution.

Precipitation may be brought about in three ways:

First, by change of temperature, many substances being soluble at high temperature which will precipitate as the solution cools.

Second, by change in the character of the solvent; example, laboratory exercise 1, experiments 1 and 2.

These two may be regarded as physical methods, while the third is chemical and involves the production of a new and comparatively insoluble substance: example, laboratory exercise 1, experiments 5 and 7.

An old law of precipitation is, in effect, as follows: whenever two substances in solution can, by an interchange of radicals, produce a soluble and an insoluble, or a soluble and a less soluble substance, double decomposition always takes place and the less soluble substance will be precipitated.

Laboratory Exercise I.

Conditions Influencing Precipitation.

Write Reactions if possible.

Exp. 1. Mix equal volumes of an alcoholic solution of camphor and water. Explain precipitation.

Exp. 2. To concentrated HCl add a saturated solution of NaCl. Explain precipitation.

Exp. 3. To 2 c.c. of $HgCl_2$ solution, found on side shelf, add 2 c.c. of KI solution.

Exp. 4. To 2 c.c. of $HgCl_2$ used above add 5 c.c. of KI solution.

Exp. 5. To a mixture of $CuSO_4$ and $CdSO_4$ add H_2S water and filter. To the filtrate add more H_2S water and filter again if precipitate forms. Repeat till no further precipitation takes place.

Exp. 6. To a few cubic centimeters of strong HCl add one drop of $AgNO_3$ solution.

Exp. 7. To a few cubic centimeters of dilute HCl add one drop of $AgNO_3$ solution.

Exp. 8. Mix strong HNO_3 and H_2S water.

Exp. 9. Mix $(NH_4)_2S_x$ solution and HCl concentrated.

CHAPTER II.

THE METALS AND THEIR SALTS.

Qualitative Analysis.

The metals occur free in nature to quite an extent, but more often combined with other elements. These combinations are chiefly as oxids, sulphids, carbonates, and silicates, and in one or more of these four forms the great mass of metals contained in the earth's crust may be found.

Metallic sulphates are found to a considerable extent.

Other natural sources of the metals are phosphates and chlorids, also smaller amounts of nitrates and comparatively slight amounts of bromids, iodids, and fluorids. Metals are extracted from their ores chiefly by reduction with some form of carbon. In case of the oxids this reduction takes place directly, according to this reaction: $2\ CuO + C = 2\ Cu + CO_2$.

In case the metallic combination is a sulphid, the ore is first "roasted" in the air, whereby the sulphur is burned off and an oxid, which may then be reduced as above, is formed:

$$2\ CuS + 3\ O_2 = 2\ CuO + 2\ SO_2.$$

The native carbonates are reduced to oxids by calcination, as

$$CaCO_3 + \text{heat} = CaO + CO_2.$$

The silicates must first be changed to carbonates by fusion with alkali carbonates; then the reduction may be carried on as before:

$$MgSiO_3 + Na_2CO_3 = MgCO_3 + Na_2SiO_3;$$

then

$$MgCO_3 + \text{heat} = MgO + CO_2.$$

The metals, from certain physical properties, have been vari-

ously classified. Thus, in the older books we read of the *Noble* metals, those unaffected by heat, as gold, silver, and platinum; the *Base* metals, the *Bastard* metals, those easily crystallizable, as antimony and zinc; the *Metalloids*, sodium and potassium.

As the fact that the properties of metals were to a considerable extent dependent upon conditions of temperature and pressure became better understood, the old classifications were less and less used, until now we are very apt to group them according to the chemical behavior of their salts, irrespective of their properties as metals. Thus Ag, Pb, and Hg (Mercurous) form a group of metals whose chlorids are insoluble in water or dilute acids. These metals may consequently be thrown out of solution or precipitated by the addition of HCl to any solution of their salts. We therefore let Ag, Hg′, and Pb constitute the *First Analytical Group*, and HCl is the *First Group Reagent.*

In like manner we find a group of nine metals that are precipitated from dilute acid solution by hydrosulphuric acid (H_2S). These metals are Cu, Cd, Bi, Hg, As, Sb, Sn, Au, and Pt, and constitute the *Second Analytical Group*, and H_2S is the *Second Group Reagent.*

The fact that the sulphids formed by the first four of these metals are *insoluble* in ammonium sulphid, and those formed by the last five are soluble, furnishes a simple method of separating this group into two parts, *a* and *b*:

Pb,* Cu, Cd, Bi, and Hg constituting Group II (*a*) and
As, Sb, Sn, Au, and Pt, Group II (*b*).

Thus, the metals are divided into various analytical groups, each with its own peculiar group reagent. Different groupings are possible, and hardly any two analysts will employ exactly the same scheme for identifying all the metals, although the following group divisions are generally used:

* Lead is included in this group because it is not entirely separated as a chlorid in Group I, traces of it remaining in solution even after addition of HCl.

Analytical Groups.

Group I. — Ag, Pb, and Hg′. Metals that form insoluble chlorids and are precipitated from aqueous solution by HCl (the group reagent).

Group II (*a*). — Cu, Cd, Bi, Hg″, and Pb. Metals that form sulphids insoluble in dilute HCl solution and also insoluble in ammonium sulphid.

Group II (*b*). — As, Sb, Sn, Au, and Pt. Metals that form sulphids insoluble in dilute HCl but soluble in yellow ammonium sulphid, or alkaline hydrates.

Group III. — Fe, Al, and Cr. In solutions free from H_2S and which do not contain phosphates, oxalates, tartrates, or salts of certain other organic acids these three metals may be separated by ammonium hydrate, (NH_4OH).

Group IV. — Co, Ni, Mn, and Zn. Metals forming sulphids soluble in acid but insoluble in alkaline solution. Ammonium sulphid, $(NH_4)_2S$, is the group reagent.

Group V. — Ba, Sr, Ca, and Mg.* Metals forming carbonates, insoluble in alkaline solutions. The group reagent is ammonium carbonate, $(NH_4)_2CO_3$.

Group VI. — K, Na, Li, NH_4. Metals which cannot be precipitated by any single reagent and for which it is necessary to make individual tests.

It is our purpose to take up the study of the metals according to their analytical grouping: first, the deportment of their salts in solution; later, the metals themselves and their specific application to dentistry.

* In the process of analysis, magnesium is held in solution by the presence of NH_4Cl and is not thrown out as a carbonate with the other three members of the group.

CHAPTER III.

METALS OF GROUP I.

Silver, Ag (Argentum).

The Metal. — Atomic weight 107.93. Silver occurs free, as sulphids, such as silver glance, Ag_2S, and in combination with the sulphids of antimony, lead, and copper.

It occurs also as silver chlorid, AgCl, known as "Horn Silver."

Silver fuses at 954° C., forming a revolving globule on charcoal or plaster without oxidation.

Silver dissolves in hot H_2SO_4 with evolution of SO_2. It is readily soluble in nitric acid with formation of $AgNO_3$, colorless crystals, without water of crystallization.

Silver amalgamates readily, and the "amalgamation process" is one of the important methods for its reduction from the ore.

This process, briefly, is as follows: The ore is roasted with salt, producing chlorid of silver; this, in suspension in water, is reduced by metallic iron,

$$2\,AgCl + Fe = FeCl_2 + 2\,Ag.$$

The mixture treated with mercury forms an amalgam from which the mercury can be driven off by heat.

Alloys. — Important alloys of silver are United States coin silver, consisting of silver 90 parts, copper 10 parts; and Sterling silver consists of silver 92.5 parts, copper 7.5 parts. Dental or amalgam alloys contain 50 to 65% silver.

Compounds. — Salts of silver are liable to decomposition by action of light with reduction in greater or less degree to metallic

silver. The salts change from violet to black according to the amount of silver reduced. Such reduction is used in the preparation and use of the ordinary photographic plates.

Silver oxid (Ag_2O), a dark brown powder, may be produced in the wet way, i.e., by precipitation of soluble silver salts with hydroxids of the fixed alkalis.

$$2\,AgNO_3 + 2\,NaOH = Ag_2O + H_2O + 2\,NaNO_3.$$

Silver hydroxid (white) may be formed if the above reaction is brought about in alcoholic solution; but it is a very unstable compound, quickly changing to $Ag_2O + H_2O$. Silver thiosulphate, $Ag_2S_2O_3$, may be precipitated white from solution of silver nitrate and sodium thiosulphate. Excess of the thiosulphate produces a soluble double salt $NaAgS_2O_3$. This fact may be utilized in the removal of silver stains.

Fused silver nitrate in the form of pencils or small sticks is used as an escharotic, and is known as "Lunar Caustic." Dilute lunar caustic consists of equal parts of $AgNO_3$ and KNO_3 fused together in pencil form.

Analytical Reactions. — Make the following tests with a weak solution of $AgNO_3$ (about 2%). Write the reactions and enter color and solubility of each precipitate formed in laboratory note-book.*

$AgNO_3$ with HCl gives a white curdy precipitate of AgCl which darkens by action of sunlight. If Ag solution is very dilute, the precipitate will assume the curdy appearance and filter more easily if it is heated and rotated quite rapidly in the test-tube. Allow the precipitate to settle. Decant the liquid carefully, divide precipitate into two parts, and test its solubility in dilute nitric acid, also in ammonia water.

* The author uses mimeograph copies of these experiments with space for the reactions and colors of precipitates, which are filled out without reference to the book and handed in by the student at the close of the laboratory exercise.

These reactions have purposely been confined to such as may be applied to the process of analysis.

$AgNO_3$ with KBr gives a white precipitate of AgBr, less easily soluble in ammonia than the AgCl.

$AgNO_3$ with KI gives a pale yellow precipitate of AgI, insoluble in ammonia.

$AgNO_3$ with H_2S gives a black precipitate of Ag_2S. $AgNO_3$ with K_2CrO_4 gives a red precipitate of Ag_2CrO_4 in neutral solution. Test the solubility of Ag_2CrO_4 in NH_4OH, HCl, and HNO_3.

Mercury, Hg (Hydrargyrum).

The Metal. — Atomic weight 199.8. Occurs as red sulphid, cinnabar, and in small quantities amalgamated with silver or gold or combined with chlorin or iodin. It is the only metal which is liquid at ordinary temperatures, solidifying at -39° C.

It boils at 357.8° C. and this wide range of temperature throughout which the fluid form is maintained, together with its comparatively great coefficient of expansion (about 1/160), makes it particularly suitable for use in thermometers and other instruments for measuring temperature or pressure.

The molecule of mercury consists of a single atom.

Alloys of mercury are amalgams and will be considered under this head.

Compounds. — Mercury forms two series of salts; one, mercurous salts referable to the oxide Hg_2O, in which mercury exhibits a valence of one; and the other, mercuric, referable to HgO, the mercury having a valence of two.

(Mercuric compounds will be considered under group two.)

Mercurous chloride, or calomel, may be made by the reduction of $HgCl_2$ by a reducing agent, as SO_2. $2\ HgCl_2 + 2\ H_2O + SO_2 = 2\ HgCl + H_2SO_4 + 2\ HCl$; but the process commercially employed is usually to sublime a mixture of mercuric sulphate, sodium chloride and mercury.

$$HgSO_4 + 2\ NaCl + Hg = 2\ HgCl + Na_2SO_4.$$

Mercurous iodide, HgI, is a greenish colored unstable salt produced by double decomposition of $HgNO_3$ and KI.

Mercurous nitrate is an easily soluble salt produced by action of cold nitric acid on excess of mercury, a solution of which may be used for the study of mercurous precipitates.

Note. — The solution of mercurous nitrate, upon standing, will be found to contain more or less mercuric nitrate, unless care is taken to keep excess of mercury in the bottom of the bottle.

Analytical Reactions. — $HgNO_3$ with HCl gives a white precipitate of HgCl (calomel). After the precipitate has settled, decant the liquid, and test the solubility of the HgCl in ammonia water. Does it dissolve? How does its behavior differ from that of AgCl?

Alkaline hydroxids form with mercurous salts the black oxid Hg_2O; a preparation of which, made with lime-water and calomel, is known as "blackwash."

Lead, Pb (Plumbum).

The Metal. — Atomic weight 206.9. Melting-point from 325° to 335° C. Occurs as sulphid (galena), PbS, in lesser quantities as native carbonate (cerussite), also as phosphate and chromate.

Lead is reduced from the sulphid in a reverberatory furnace by a few simple reactions as follows: $3\ PbS + 5\ O_2 = 2\ PbO + PbSO_4 + 2\ SO_2$; then, by increasing the heat without access of air, the sulphur is driven off and the lead separates by two double decompositions,

$$2\ PbO + PbS = 3\ Pb + SO_2 \text{ and } PbSO_4 + PbS = 2\ Pb + 2\ SO_2.$$

Lead is soluble in nitric or acetic acid, forming $Pb(NO_3)_2$ or $Pb(C_2H_3O_2)_2$.

Lead is also dissolved to a very slight extent by pure water containing oxygen, or by water containing CO_2, mineral salts

or organic matter. It tarnishes in the air, with formation of a suboxide, Pb_2O.

Alloys. — Solders and fusible metals are among the important alloys.

Type metal consists of an alloy of lead and antimony.

Compounds. — Besides the suboxide of lead above mentioned, three more compounds of lead and oxygen are of interest.

Litharge, PbO, is the yellow oxide used in pharmacy as the base of "Diacylon plaster."

The black oxide, PbO_2, is used as an oxidizing agent. Red lead (minium), Pb_3O_4, is practically a mixture of PbO_2 and 2 PbO, and used as a source of PbO_2 by treatment with HNO_3.

$$Pb_3O_4 + 4\,HNO_3 = PbO_2 + 2\,Pb(NO_3)_2 + 2\,H_2O.$$

Lead carbonate, as prepared by precipitation of soluble lead salts by alkali carbonates, has the composition $(PbCO_3)_2Pb(OH)_2$.

The basic carbonate, prepared by exposure of the metal to fumes of acetic acid, CO_2, and moisture, is known as "White lead," and is used in manufacture of paint.

Lead acetate, or sugar of lead, formed by solution of the metal or the oxide PbO in acetic acid, is a white soluble salt crystallizing with three molecules of H_2O. The solution has an acid reaction to litmus paper.

Lead subacetate, or basic acetate of lead, a solution of which is known as Goulard's extract, is made by boiling lead acetate solution with litharge. It is used in medicine as an external application and in physiological chemistry as a reagent. It deteriorates by absorption of CO_2 and precipitation of a carbonate.

Lead chromate (chrome yellow) is a yellow insoluble salt used as a pigment.

Lead nitrate, an easily soluble white crystalline salt, may be used in the study of the analytical reactions of lead.

Lead arsenate, a poisonous salt, is quite largely used for spraying trees.

Analytical Reactions. — $Pb(NO_3)_2$ with 2 HCl gives white precipitate of $PbCl_2$. Test its solubility in hot water and in NH_4OH.

$Pb(NO_3)_2$ with NH_4OH gives white precipitate of $Pb(OH)_2$ insoluble in hot water.

$Pb(NO_3)_2$ with H_2S gives black PbS. Test solubility of precipitate in warm dilute HNO_3.

$Pb(NO_3)_2$ with H_2SO_4 gives white precipitate of $PbSO_4$, forming slowly in dilute solutions.

$Pb(NO_3)_2$ with K_2CrO_4 (or $K_2Cr_2O_7$) gives a yellow precipitate of $PbCrO_4$.

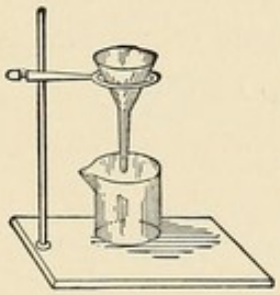
$Pb(NO_3)_2$ gives with KI a yellow precipitate, PbI_2. Avoid excess of the potassium iodid.

By application of the reactions of the salts of Ag, Pb, and Hg′, we may formulate a scheme for the separation and identification of the metals of Group I as follows:

Analysis of Group I.

(Ag, Pb, Hg′.)

To the clear solution to be tested add slowly dilute HCl as long as any precipitation occurs. Filter and wash the precipitate *once* with cold water, add this washing to filtrate to be tested for remaining groups, then wash precipitate on the paper with several small portions of *hot* water.



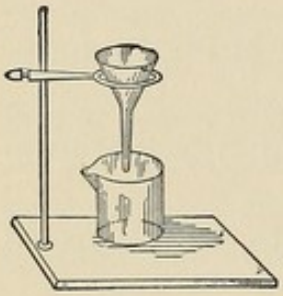
AgCl and HgCl remain undissolved.

$PbCl_2$ is in the hot-water solution.

Divide this hot-water solution into three parts and make three of the following tests for lead: *First*, with $K_2Cr_2O_7$, which

gives yellow precipitate of $PbCrO_4$. *Second*, with dilute H_2SO_4, giving a white precipitate of $PbSO_4$. *Third*, with H_2S water, giving black precipitate of PbS. *Fourth*, with KI solution, which forms a yellow precipitate of PbI_2. Write these reactions.

To undissolved residues of Hg and Ag chlorids add warm NH_4OH.



Hg remains on the paper, black, as $HgNH_2HgCl$.

Ag is dissolved by the NH_4OH and may be precipitated as AgCl by adding HNO_3 to acid reaction. Presence of Hg in the black residue may be confirmed as in Group II (page 38).

QUESTIONS ON GROUP I.

Why wash the precipitated chlorids only *once* with cold water?

Why is it necessary to wash the $PbCl_2$ out with hot water *before* using ammonia?

Why is the ammonia used?

How does HNO_3 reprecipitate silver *chlorid?*

Laboratory Exercises II and III.

Laboratory exercises 2 and 3 will consist of the analytical reactions of the first-group metals, a study of the solubility of the precipitates formed, and an analysis of an unknown solution containing a mixture of first-group metals.

CHAPTER IV.

METALS OF GROUP II.

Copper, Cu (Cuprum).

The Metal. — Atomic weight 63.3. Melting-point 1054° C. Occurs free in vicinity of Lake Superior, also in western United States, Chili, and Spain, as sulphids, copper pyrites, $CuFeS_2$, and copper glance, Cu_2S. Malachite green and malachite blue are native basic carbonates of Cu.

Copper dissolves easily in nitric acid and with difficulty in HCl; heated with H_2SO_4 it forms $CuSO_4$, with the evolution of SO_2.

Alloys of Copper are both numerous and important. The amalgam was formerly used in dentistry to a considerable extent.

Copper is used to harden silver and gold, used in the manufacture of coins, jewelry and the solders, and used in crown and bridge work.

Copper is also used in the preparation of bronze, brass, bell metal, dental gold, and German silver. Page 108.

Compounds. — Salts and solutions of copper are usually blue or green.

Copper forms two series of salts: the cuprous, of which there are but few important compounds, and the cupric. Cuprous oxid, Cu_2O, which is red in color (sometimes yellow through admixture of CuOH) and obtained by reduction of cupric salts by organic substances such as sugar, and cuprous chlorid, used as a reagent for the detection of acetylene, are perhaps the most important.

Cupric oxid, CuO, is a black powder formed by ignition of copper in the air or by boiling copper solution with the fixed alkali hydroxids.

Copper arsenate and aceto-arsenite, the latter known as Paris green, are both green powders which have been used as pigments and as insecticides.

Copper sulphate, $CuSO_4$, crystallizes with five molecules of water and is known as bluestone or blue vitriol. It is used extensively in the "Gravity Battery," and in copper plating.

Verdigris is a sub-acetate or oxy-acetate of copper composition, $Cu_2O(C_2H_3O_2)_2$.

Copper salts combine with NH_3, forming a series of "cuprammonium" compounds freely soluble and of intense blue color.

The chlorid nitrate and sulphate are the common soluble salts. A 1% solution of either of these will give the analytical reactions.

Analytical Reactions. — $CuSO_4$ with H_2S gives CuS, brownish-black sulphid. Test its solubility in $(NH_4)_2S$ and in warm dilute HNO_3.

$CuSO_4$ with NH_4OH (one or two drops of reagent) will precipitate $Cu(OH)_2$ bluish white. Add more NH_4OH to same test-tube and note the result. To this clear solution add a sufficient amount of dry KCN to completely decolorize the liquid. Then add to the mixture some H_2S water. Is the black CuS thrown out? The behavior of Cu solutions thus treated is due to the formation of double salts, the solution in ammonia being due to a compound of $CuSO_4$ and NH_3, and the decolorization of the blue solution to one of $Cu(CN)_2$ and KCN.

$CuSO_4$ with K_4FeCy_6 (potassium ferrocyanid) gives in acetic acid solution a red-brown precipitate of Cu_2FeCy_6.

Metallic zinc or iron will precipitate copper from solution. Hold a knife-blade in a solution of $CuSO_4$ for a few seconds.

Mercury in Mercuric Combination.

Compounds of Dyad Mercury. — Mercuric oxid, HgO, is a red powder obtained by ignition of mercury in the air. Mercuric oxid may also be prepared by precipitation of mercuric chlorid with alkaline hydroxids. A precipitate thus formed is yellow in color, and, when prepared by mixing mercuric chlorid and lime water, forms the "yellow wash" used to a considerable extent in pharmacy.

Mercuric chlorid, $HgCl_2$. This intensely poisonous salt is known by the fairly descriptive name of corrosive sublimate. It corrodes metals, such as zinc and iron; it coagulates albumin and acts as a corrosive poison when taken internally.

It is made in a manner analogous to that used for the preparation of calomel, i.e., by sublimation, the salts used in this instance being mercuric sulphate and sodium chlorid alone.

$$Hg_2SO_4 + NaCl = 2\,HgCl + Na_2SO_4.$$

Mercuric chlorid is antiseptic and a disinfectant in dilutions of 1 to 1000. Antiseptic tablets designed to give about this strength of solution by the addition of one tablet to one pint of water are made to contain 7.7 grains $HgCl_2$ and 7.3 grains NH_4Cl, with sufficient purple coloring to advertise the nature of the tablets and thus act as a safeguard against accidental poisoning.

Mercuric chlorid is soluble in water and in alcohol. It is used in the preparation of antiseptic gauze, sterile cotton, etc., but, on account of its corrosive properties, cannot be used to sterilize instruments.

Ammoniated mercury, mercur-ammonium chlorid, or white precipitate (NH_2HgCl) is a white powder obtained by slowly pouring a solution of $HgCl_2$ into ammonia water.

Mercuric iodid, red iodid (HgI_2), is made by reaction of mercuric chlorid with potassium iodid:

$$HgCl_2 + 2\,KI = 2\,KCl + HgI.$$

Mercuric iodid is soluble in excess of either reagent, also in alcohol.

Mercuric iodid combines with potassium iodid (KI) forming an iodo-hydrargyrate, used as a reagent in physiological chemistry (page 278), also as an alkaloidal precipitant.

An alkaline solution of potassium iodo-hydrargyrate, constitutes Nessler's reagent, used in analysis of water and of saliva as a test for ammonium compounds.

Analytical Reactions. — A 2% solution of corrosive sublimate ($HgCl_2$) may be used in demonstrating the reactions of dyad mercury.

$HgCl_2$ with H_2S gives first a white precipitate, turning yellow, brown, and finally black, as proportion of H_2S increases. The black precipitate *only* is mercuric sulphid, and care must be taken to add H_2S till this compound is produced.

Test the solubility of HgS in $(NH_4)_2S$ and HNO_3.

To $HgCl_2$ solution add $SnCl_2$. The mercuric chlorid is reduced to mercurous chlorid (HgCl, white) or metallic mercury (Hg, gray), according to proportion of the tin salt used:

$$2\,HgCl_2 + SnCl_2 = 2\,HgCl + SnCl_4$$

or

$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

$HgCl_2$ with KI gives red HgI_2, easily soluble in excess of either of the reagents.

$HgCl_2$ with NH_4OH gives white precipitate of $(NH_2Hg)Cl$, known as "white precipitate" (see ammoniated mercury). "Red precipitate" is a term sometimes used to designate the red oxid of mercury, HgO, made in the dry way.

Bismuth, Bi.

The Metal. — Atomic weight 208.5; melting-point 268° C. At higher temperatures Bi burns to Bi_2O_3. Bismuth does not occur in large quantities, but is usually found in the free state.

Small amounts are obtained from the oxid, Bi_2O_3, bismuth ochre, and from the sulphid, Bi_2S_3.

It is easily identified by means of the blowpipe test on plaster with S and KI (page 102).

Alloys. — The most important alloys from a dental standpoint are the fusible metals, Mellot's metal, Wood's metal, Rose's metal, etc. (page 126).

Compounds. — Salts of bismuth as a rule require excess of acid for permanent solution; and, by adding a considerable volume of water, they are easily thrown out of solution as insoluble basic or oxysalts, the reaction of the nitrate being as follows:

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2\,HNO_3.$$

This may be demonstrated by allowing a few drops of bismuth solution to fall into a comparatively large amount of H_2O (two to six ounces). A white cloud of insoluble oxysalt may be observed settling through the clear water. This may be employed as a final test for Bi in the course of systematic analysis.

The subnitrate and the subcarbonate of bismuth are both used in medicine. The latter is a common starting-point in the preparation of other bismuth salts.

Analytical Reactions. — The most available salt is the nitrate, insoluble in water unless strongly acidulated.

Use a 2% solution of $Bi(NO_3)_3$ in the following tests:

$Bi(NO_3)_3$ with NH_4OH gives white precipitate of bismuth hydroxid, $Bi(OH)_3$.

$Bi(NO_3)_3$ with H_2S precipitates Bi_2S_3, brownish black, insoluble in $(NH_4)_2S$, but soluble in warm dilute HNO_3.

Cadmium, Cd.

The Metal. — Atomic weight 112.4; melting-point 320° C. Occurs associated with Zn in zinc blende. It is more easily volatile than zinc, and advantage is taken of this fact in effecting its separation from that metal.

Alloys. — Cadmium is used as a constituent of fusible metals and rarely, in small proportion, in dental alloys. Its use in the latter case is objectionable on account of the yellow stain of CdS frequently produced (page 115, amalgam).

Analytical Reactions. — A 2% solution of the sulphate or nitrate may be used in studying the deportment of cadmium salts.

$CdSO_4$ with H_2S gives a bright yellow sulphid, CdS, soluble in dilute nitric acid.

$CdSO_4$ with $(NH_4)_2S$ also precipitates the yellow sulphid.

Cadmium sulphid forms slowly, and, in presence of Cu or other second-group metals, may escape precipitation if the reagent is added in insufficient quantity.

Arsenic, As.

Atomic weight 75.0. Occurs associated with copper and iron sulphids, as arsenical pyrites, $FeAs.FeS_2$; as native sulphids, orpiment, As_2S_3, and realgar, As_2S_2; also to some extent as the trioxid, As_2O_3.

Compounds. — Arsenic forms two series of salts, the arsenious, As''', and arsenic, As^v, and it also acts as an acid radical forming arsenious and arsenic acids. In the process of analysis, arsenic compounds whether acid or basic are reduced to arsenious by action of H_2S. It is most easily obtained in the form of the trioxid, As_2O_3, also known as arsenious acid or white arsenic.

White arsenic is intensely poisonous; but, nevertheless, it has been very freely used in curing the skin of fur-bearing animals and otherwise as a preservative. In dentistry white arsenic is used to devitalize pulp.

Arsenic is widely distributed in nature, occurring in soft coal, from which source it finds its way into the roadside dust or any substance capable of holding dust, such as the majority of fabrics, wall papers, etc. Arsenic is a common impurity in

mercury, zinc, and commercial acids. Inasmuch as these things are largely used in the preparation of filling material used by dentists, it is necessary that considerable pains be taken to prevent the presence of the poison in sufficient quantity to cause irritation.

The poisonous character of arsenic differs greatly with the combination in which it occurs. A gaseous hydrid of arsenic, AsH_3, being among the most poisonous of its compounds, while some of the organic compounds are claimed to be non-poisonous.

Arsenic forms an insoluble arsenate with ferric hydrate; hence, freshly precipitated ferric hydroxid is the official antidote for arsenical poisoning. This is prepared by mixing 150 c.c. of dilute ferric sulphate solution (containing 50 c.c. of the U. S. P. "Solution") with a well-shaken mixture of 10 grains of oxid of magnesium in about 750 c.c. of water:

$$Fe_2(SO_4)_3 + 3\,Mg(OH)_2 = Fe_2(OH)_6 + 3\,MgSO_4.$$

Fowler's solution containing 1% As_2O_3 dissolved by use of potassium bicarbonate. Solution of arsenious acid containing 1% As_2O_3 dissolved by aid of two parts of HCl. Donovan's solution containing 1% each of AsI_3 and HgI_2, and Pearson's solution containing 1% sodium arsenate are Pharmacopœial preparations of arsenic.

Analytical Reactions. — A solution for studying the reactions of arsenic (As‴) is conveniently made by dissolving about 15 grams of white arsenic in dilute NaOH solution by aid of heat, then diluting to one liter and acidifying slightly with HCl.

To an arsenious solution, which may be represented by $AsCl_3$, add H_2S water. A lemon-yellow precipitate of As_2S_3 will be thrown down. Test the solubility of this precipitate in yellow ammonium sulphid and in ammonium carbonate.

To the alkaline solution of the sulphid add excess of HCl: As_2S_3 is precipitated.

To an arsenious solution add $(NH_4)_2S$ in repeated small portions.

In neutral solution, as of sodium arsenite, Na_3AsO_3, silver nitrate will throw down yellow silver arsenite, soluble in excess of nitric acid or ammonia.

SPECIAL TESTS FOR ARSENIC.

REINSCH'S TEST for arsenic, applicable to any solution whether organic or not, and very valuable for a preliminary test, is made as follows: place the solution or mixture to be tested in a porcelain dish, acidify strongly with HCl, and add a small strip of bright copper foil (cleaned in dilute HNO_3 and thoroughly washed in distilled H_2O) and boil for ten or twenty minutes, adding sufficient water to replace loss by evaporation. Remove the copper foil; a dark gray to black coating is an indication of arsenic but not conclusive, as some other substances give similar deposits, mercury and antimony in particular.

To prove the presence of As roll the foil as tightly as possible and place it in the bulb of a small glass matrass (Fig. 1).



FIG. 1.

Heat the bulb over a very small luminous flame, when crystals of As_2O_3 (tetrahedral or octahedral) will deposit in the constricted portion of the tube, and which may be identified by microscopical examination. There will be sufficient air in the matrass for the formation of the oxid and the test becomes much more delicate than if heated in the ordinary open tube as often recommended.

GUTZEIT'S TEST is made by placing the suspected solution in a test-tube, acidifying with H_2SO_4, adding a few small pieces of arsenic-free zinc, and, as hydrogen begins to be given off, placing over the mouth of the tube a piece of filter-paper carry-

ing a drop of a strong solution of $AgNO_3$. The presence of arsenic is indicated by the darkening of the moistened filter-paper in accordance with the following reactions:

The nascent H liberated by action of the Zn upon the acid forms with any As present the gaseous AsH_3 which, in contact with the filter-paper wet with $AgNO_3$ solution, produces a brown or black stain of metallic Ag, while the As becomes arsenious acid, H_3AsO_3. The stain may possibly be yellow by formation of a compound of silver *arsenide* and silver nitrate, but, as a rule, moisture is present in sufficient amount to insure the decomposition of this compound.

Antimony will give a similar brown or black stain (not yellow), but presence of As may be conclusively demonstrated by making FLEITMANN'S TEST, which is conducted in the same way as the preceding, except that the hydrogen is evolved in alkaline solution, either by means of Zn and strong KOH solution ($Zn + 2\ KOH = K_2ZnO_2 + H_2$) or by sodium amalgam (made with arsenic-free mercury) and water ($NaHg_x + H_2O = NaOH + Hg + H$). In this case the SbH_3 is *not formed;* so a stain thus obtained constitutes a positive test for *arsenic.*

The MARSH-BERZELIUS TEST for arsenic is the most delicate of all and the one to which we resort in detecting As in the saliva or the urine. By this method one two-hundredth of a milligram or about 1/12800 of a grain can be easily shown as a brown deposit in the constricted tube at about the point *K*, Fig. 2. The apparatus used in this test is shown in Fig. 2, and consists of a small Erlenmeyer flask, or wide-mouth bottle, fitted as a hydrogen generator, *A*, and connected with a drying-tube, *B*, filled with fused calcium chlorid, then with a tube of hard glass, *C*, drawn out to a very small diameter for half its length.

The generator *A* is charged with arsenic-free zinc, and dilute sulphuric acid (1/5) introduced through the thistle-tube *E*. After *all air has been driven from the apparatus*, light the escaping H at *T*, then the Bunsen burner *D*, and allow the generator to

run for about twenty minutes, thus making a blank test of apparatus and reagents; if at the end of this time the hard glass is perfectly free from any deposit, the suspected liquid, which must have been freed from organic matter (process described in detail in chapter on Urine Analysis), may be introduced in portions of about 10 c.c. each.

The flame should be spread somewhat so as to heat at least 1 inch of the glass tube. This may be accomplished, in the

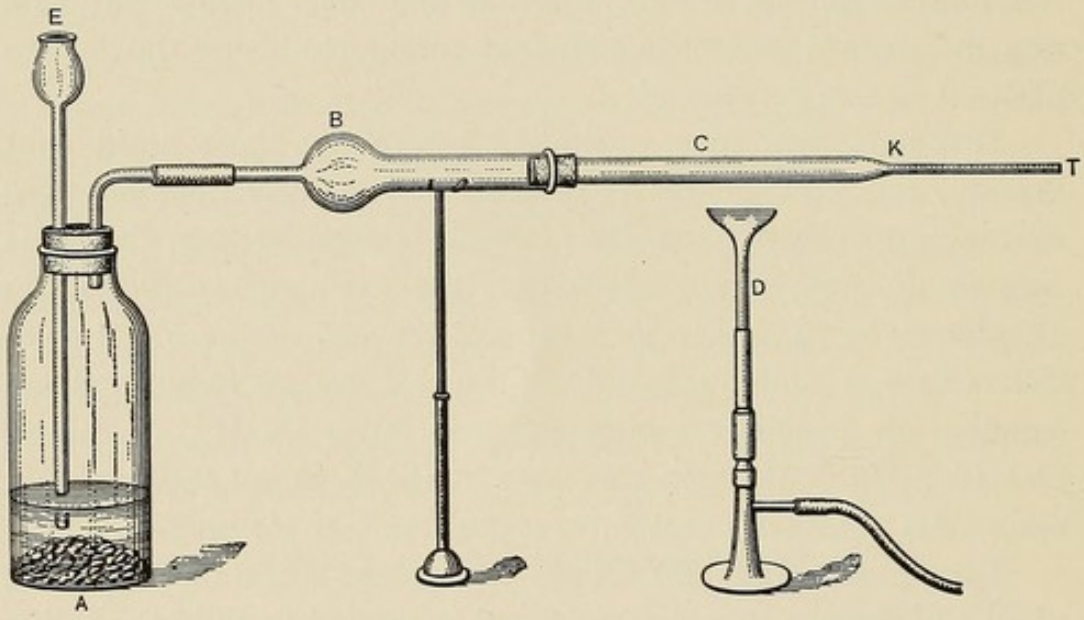


FIG. 2.

absence of a burner-tip, by placing an inverted V-shaped piece of asbestos board, 1 inch wide, over the heated part of the tube.

The presence of arsenic increases the evolution of hydrogen and, unless the solution is added gradually, the AsH_3 may be driven so rapidly past the flame as to escape decomposition, or the tube may become heated to such an extent that arsenic will not be deposited.

The escape of As at *T* may be noticed by the bluish color of the flame and by the characteristic garlic odor.

Antimony is similarly deposited as a dead-black stain instead of brown-black, and as Sb is less easily volatile than As

the deposit will be nearer the flame, possibly on both sides of the flame. (For further differences between As and Sb see tests given on page 32.)

A test, using an apparatus similar to the above and known as Gutzeit's test, has been investigated by Sanger and Black, (proceedings of the American Academy of Arts and Sciences, October, 1907).

AsH_3 is produced in the generator by use of Zn and HCl, and passed through the drying tube *B*; (Fig. 2) then through a tube of *uniform diameter C* containing strips of drawing paper sensitized with solution of $HgCl_2$.

The $HgCl_2$ paper is stained yellow to brown beginning at the end next the generator, and by carefully regulating conditions, the extent of the stain may have a quantitative value.

Arsenic compounds (As^v), as Na_2HAsO_4, are of but little interest from the dentist's standpoint.

All arsenic compounds are reduced by nascent H to arsenious combinations, then to elementary As, then to AsH_3 (arsine); hence the special tests given for arsenious compounds are applicable.

Free chlorin, nitric acid, and potassium ferricyanid oxidize arsenious compounds to arsenic, and in this condition the As is not easily volatilized and organic matter may be destroyed by deflagration (in presence of excess of nitrates) with but slight loss of arsenic.

Antimony, Sb (Stibium).

Atomic weight 120.2. Occurs native in Australia, and as the sulphid, Sb_2S_3, known as stibnite.

Alloys. — Antimony is used in making type metal, Britannia metal, and rarely in low-grade dental alloys.

Compounds. — The salts of antimony may be classified as antimony salts, referable to the hydroxid $Sb(OH)_3$, and antimonyl salts, referable to $SbO(OH)_3$.

Butter of antimony, antimony tri-chlorid, $SbCl_3$, when pure, is a colorless solid of buttery consistency, hence its name. It may be formed by direct union of constituent elements.

Salts of antimony tend to form oxycompounds and are held in solution by excess of acid. The antimonious chlorid, $SbCl_3$, in solution with HCl is precipitated by excess of water as a white oxychlorid, $Sb_4Cl_2O_5$, also known as "powder of Algaroth." The antimonic chlorid in like manner precipitates the antimonic oxychlorid, $SbOCl_3$. Demonstrate by turning 1 or 2 c.c. of $SbCl_3$ solution into a large excess of water.

Analytical Reactions. — The most common compound of antimony is the double tartrate of antimony and potassium ($KSbOC_4H_4O_6$), known as tartar emetic (an antimonyl compound). A 2% aqueous solution may be used in the following tests:

To an antimony solution represented by $SbCl_3$ add H_2S water: Sb_2S_3 is precipitated orange-red. Test solubility of the precipitate in $(NH_4)_2S$ and in $(NH_4)_2CO_3$.

How does it differ from arsenic?



FIG. 3.

Upon the addition of HCl in excess to the ammonium sulphid solution the Sb is reprecipitated, but not necessarily as Sb_2S_3, but more usually as Sb_2S_5 or a mixture of the two sulphids.

Marsh's test for As (or Sb) consists of a simple hydrogen generator with glass tip for burning the gas, as shown in Fig. 3. In this apparatus Sb and As are converted into the gaseous hydrides, AsH_3 and SbH_3; and, if a piece of cold porcelain is pressed down upon the flame, As or Sb will be deposited as metallic stains (mirrors) upon the porcelain. To distinguish between As and Sb spots the following tests will suffice:

Arsenic.	*Antimony.*
Brown-black, lustrous spots.	Dead brown or black surfaces.
Soluble in solution of hypochlorite of lime or soda.	Insoluble in solution of hypochlorite of lime or soda.
Easily volatilized.	Volatilized at red heat.

Antimony may be retained in the generator by the introduction of a piece of platinum-foil, the Sb being precipitated upon the platinum to which it adheres quite strongly.

Tin, Sn (Stannum).

The Metal. — Atomic weight 119.0; melting-point 238° C. Cassiterite, or tin-stone, nearly pure SnO_2, is by far the most important source. The free metal has been found associated with gold.

Banca tin from the East Indies and block tin from England are pure varieties of the commercial article. Pure tin will give a peculiar crackling sound when bent. Tin is very malleable at the ordinary temperature, being fourth in the list of malleable metals (see page 105), but becomes brittle when heated to about 200° C.

Alloys. — Pewter usually contains Sn, Pb, Cu, and Sb, sometimes Zn. Rees's alloy Sn 20 parts, gold 1 part, and silver 2 parts. Tin is also a constituent of solders, fusible metals, Babbitt's metal, bell metal, and bronze.

An alloy of tin and mercury (tin amalgam) is used for "silvering mirrors."

Compounds. — Metallic tin is not dissolved by HNO_3, but is converted into a white, insoluble metastannic acid. This acid, upon standing, changes to normal stannic acid which is easily soluble in acids; hence, in making use of this reaction in the analysis of amalgam alloys, it is not well to allow the nitric acid solution of the alloy to stand too long before filtering.

Metallic zinc thrown into a tin solution will precipitate the tin as follows: $SnCl_2 + Zn = ZnCl_2 + Sn$.

This reaction is used in the separation of tin from antimony in the second group; and, in order to obtain the tin in soluble form suitable for a final test, it is necessary to add HCl sufficient first to dissolve *all* the Zn present; otherwise it (Sn) may remain adhering to the zinc.

Tin, like arsenic and antimony, forms two series of salts, the stannous (Sn'') and the stannic (Sn^{IV}). A little HCl treated with excess of granulated tin till hydrogen is no longer given off furnishes a solution of stannous chlorid suitable for the following experiments:

Analytical Reactions. — $SnCl_2$ with H_2S gives brown precipitate of SnS, soluble in $(NH_4)_2S$, insoluble in $(NH_4)_2CO_3$.

$SnCl_2$ with $HgCl_2$ gives a white or gray precipitate, as explained on page 24 under "Mercury," and is used as a test for presence of mercury. It may also be used as an alkaloidal precipitant.

Strong solutions of $SnCl_2$ in presence of metallic Sn keep fairly well, but dilute solutions without an excess of tin oxidize very rapidly to stannic combinations and cease to be of value as reagents.

Gold, Au (Aurum).

Atomic weight 197.2; melting-point 1075° C. Usually found uncombined, but mixed with various impurities.

Alloys. — Gold is alloyed with copper to make it harder and more durable for use in the manufacture of jewelry, plate, and coin. It is alloyed with silver for the purpose of reducing its melting point. Copper and zinc, or copper, silver, and zinc may be used in this way. (See page 130 for formulæ for gold alloys.)

The term "carat" as applied to gold signifies 1/24 part and is used as a measure of purity of an alloy, 22 carat gold being 22/24 pure gold. Twenty carat gold is 20/24 pure, etc. The

amount of gold in a given alloy may be determined approximately by use of a device shown in Fig. 4, much used by jewelers, consisting of a series of standard alloys and a piece of stone upon which the test is made. The tips are standard alloys. Parallel markings are made on the stone with the alloy in question and with the tip supposed to correspond to it; then the addition of a drop of strong nitric acid to the marks and a careful comparison of their appearance will show if the two are of the same composition.

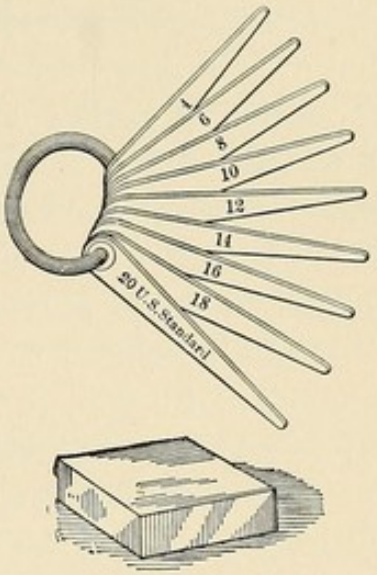


FIG. 4.

If the composition of an alloy is known, the value in carats may be determined by the following:

Rule to determine the carat of a given alloy: Multiply 24 by the weight of *gold* used and divide result by total weight of alloy. For instance, if an alloy is made containing 9 parts of gold and 3 of another metal, the total weight will be 12 and the calculations $24 \times 9 \div 12 = 18$. The alloy is an 18-carat gold.

Gold may be *raised* to a higher carat by the following rule: Multiply weight of alloy used by difference between *its* carat and that of the metal to be added. Then divide product by the difference between the carat of the metal added and that of the required alloy. The figure thus obtained represents the total weight of *required* alloy. Subtract from this weight of material taken and difference in weight of pure or alloyed gold to be added. (From Hall's Dental Chemistry.)

To *reduce* gold to a required carat Essig takes the following rule from Richardson's Mechanical Dentistry: "Multiply the weight of gold used by 24 and divide the product by the required carat. The quotient is the weight of the mass when reduced,

from which subtract the weight of the gold used, and the remainder is the weight of the alloy to be added."

Analytical Reactions. — Gold is insoluble in simple acids, but may be dissolved in nitrohydrochloric acid (aqua regia) with formation of auric chlorid. Gold also unites easily with Br or I, forming $AuBr_3$ or AuI_3. A one-half per cent solution of $AuCl_3$ may be used in the following tests:

H_2S with $AuCl_3$ gives dark brown Au_2S_3 (auric sulphid), soluble in yellow ammonium sulphid.

Gold is reduced to the metallic state by many of the other metals, as Pb, Cu, Ag, Sn, Al, Sb, Fe, Mg, Zn, and Hg; also by ferrous sulphate, stannous chlorid, and oxalic acid.

Add a freshly prepared solution of ferrous sulphate to a little acid solution of $AuCl_3$. Gold is precipitated as follows: $AuCl_3 + 3\ FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3$.

Stannous chlorid precipitates from gold solution the "purple of Cassius," consisting of a mixture of gold and oxid of tin in colloidal forms.

Gold is only slowly precipitated by oxalic acid; but, as Pt is not precipitated at all by this reagent, it is possible to separate Au and Pt in solution, as chlorids, by this means.

KI will give a dark-green precipitate of AuI_2 provided the KI is in excess; if the gold is in excess, the precipitate is apt to be the yellow AuI (aurous iodid). In the presence of a considerable excess of KI the AuI_3 is kept in solution as the potassio-auric iodid, $KIAuI_3$. The reduction of this double salt by sodium thiosulphate is made the basis of the method to determine the quantity of Au in a given alloy, as described in the chapter on Volumetric Analysis.

Platinum, Pt.

Atomic weight 194.8. Melting-point 2000° C. Platinum solubilities are similar to gold; aqua regia forms the chlorid $PtCl_4$.

Alloys. — Platinum alloys quite easily with other metals, particularly lead; and platinum utensils may be destroyed by heating in contact with the compounds of metals easily reduced. Sulphur and phosphorus also attack platinum.

Platinum 90% and iridium 10% give an alloy harder, more brittle, and more resistant to chemical action than pure platinum.

"Platinum Color," for coloring enamel, is made, according to Mitchell's Dental Chemistry, by precipitating platinum from a solution of $PtCl_4$ by boiling with KOH and grape sugar; then, grinding this finely divided platinum with feldspar in the proportion of 1 part Pt to 16 parts feldspar.

Analytical Reactions. — $PtCl_4 + H_2S$ gives a precipitate of sulphid of platinum almost black, soluble in yellow ammonium sulphid.

Platinum solution with NH_4Cl precipitates yellow ammonium platinic chlorid, $(NH_4)_2PtCl_6$, crystalline. Potassium chlorid also gives a yellow crystalline precipitate of K_2PtCl_6, isomorphous with the ammonium compound. (Plate III, Figs. 1 and 3.) These reactions may be made quantitative by using neutral, fairly concentrated solutions and adding an equal volume of alcohol.

Both of these double salts are soluble in excess of alkali, and reprecipitated by HCl.

Stannous chlorid reduces $PtCl_4$ to $PtCl_2$ but forms no precipitate. Metallic Zn will precipitate platinum as a fine black powder or spongy mass.

Analysis of Group II.

Separation of parts (a) and (b).

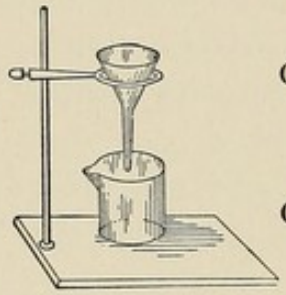
A portion of the clear filtrate, from Group I, containing a slight excess of HCl is tested for metals of Group II by the addition of H_2S water.*

* A preliminary test is made on a part of the solution because in the absence of Group II, the analysis of Group III can be made more easily without the presence of H_2S.

If a precipitate is obtained, warm the *whole* of the solution and pass in H_2S gas for from three to five minutes, which precipitates all metals of the group as sulphids. Filter.

Break point of filter-paper with glass rod and wash Group II into beaker with warm $(NH_4)_2S$; digest hot for a few minutes.

Filter and wash the precipitate till wash-water shows only traces of Cl. Throw away all wash-water except the first.

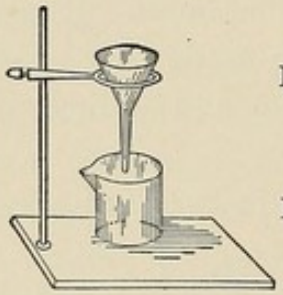


Group II (*a*). Cu, Cd, Bi, Hg, and Pb.

Group II (*b*). As, Sb, Sn, Au, and Pt.

Analysis of Group II (*a*).

Dissolve the precipitate off the paper with hot dilute HNO_3.



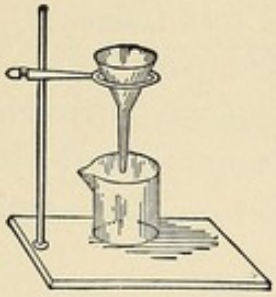
Hg, if present, will remain on paper, black.

Filtrate contains nitrates of Pb, Cu, Cd, and Bi.

Test black residue on paper for Hg'' by dissolving in aqua regia and precipitating with $SnCl_2$. For reaction between $SnCl_2$ and $HgCl_2$ see page 24. Aqua regia may be made by mixing two or three parts of HCl with one part of HNO_3. Free Cl is liberated which dissolves the HgS as $HgCl_2$.

$$3\,HCl + HNO_3 = NOCl + 2\,H_2O + Cl_2.$$

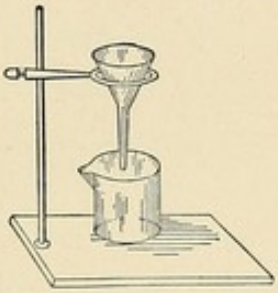
If lead is present in Group I, the filtrate above will contain traces which must be separated by adding a few drops of H_2SO_4 and allowing to stand at least fifteen minutes. Filter.



$PbSO_4$ remains on paper.

Filtrate contains Cu, Cd, Bi.

To the filtrate add NH_4OH till alkaline; Bi separates as $Bi(OH)_3$, white. Filter.



$Bi(OH)_3$.

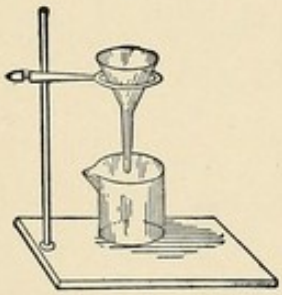
Cu and Cd.

Divide the filtrate (Cu and Cd) into two parts. A blue color indicates presence of Cu. With one part test for Cu by making it acid with acetic acid and adding K_4FeCy_6, which will give a brown precipitate of Cu_2FeCy_6. With the other part test for Cd by adding solid KCN very carefully till all blue color has disappeared; then a little H_2S water will give a yellow precipitate of CdS if cadmium is present.

Analysis of Group II (*b*).

To the ammonium sulphid add HCl till acid. A very fine white precipitate may be sulphur only.

Filter and wash. Throw away wash-water. Pierce filter and wash sulphids into large test-tube or small beaker. Add 10 c.c. of $(NH_4)_2CO_3$ and heat for a few minutes. Filter.

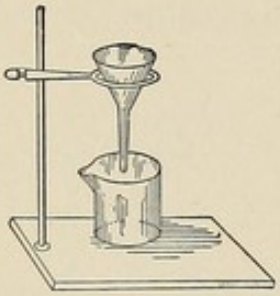


Sb, Sn, Au, Pt sulphids.

Arsenic sulphid.

Add HCl and Zn and make Gutzeit's test (page 28) and if necessary Fleitmann's (page 29) or Marsh's (page 32).

Dry this precipitate upon paper and place paper and precipitate in a porcelain evaporator, add concentrated HCl and heat. (This *must* be done under the hood.) Dilute and filter, when Au and Pt will remain undissolved.



Au and Pt.

Sb and Sn.

To the Sb and Sn solution add a *little* Zn and a piece of platinum-foil. The antimony and tin will both be reduced to the metallic state, the Sb being deposited on the Pt as a brown or black coating. Presence of Sb may be confirmed by removing the Pt, washing carefully, treating with $(NH_4)_2S$, and drying, when the coating will become Sb_2S_3, orange-red.

To the solution to be tested for Sn add HCl enough to dissolve *all* the Zn which has been added, filter, and test filtrate with $HgCl_2$ (page 38).

Dissolve the insoluble residue of Au and Pt (the residue will be dark-colored if either of these metals are present) in aqua regia and divide solution into two parts.

Test one part for gold with solution of $FeSO_4$, or a mixture of $SnCl_2$ and $SnCl_4$ (page 36).

Test the other part for Pt by adding NH_4Cl, allow to stand overnight adding a little alcohol, and precipitate of ammonium platinic chlorid will be obtained, yellow and crystalline (see Plate 3, Fig. 1).

QUESTIONS ON GROUP II.

Why is it necessary to wash the precipitate of Group II practically free from Cl before dissolving in warm HNO_3?

How does the Hg found in Group II differ from the Hg in Group I?

How does the Pb found in Group II differ from the Pb in Group I?

Before making the final test for Sn, why is it necessary to dissolve *all* the Zn which has been added?

In precipitating Group II why should the solution be made acid with HCl before adding H_2S?

Why is it better to use H_2S gas rather than H_2S water in precipitating metals of Group II?

Before testing for Cd why add KCN to decolorize the copper solution?

LABORATORY EXERCISE IV.

Analytical reactions of the copper group (pages 22–26).

LABORATORY EXERCISE V.

Analysis of copper and the silver groups.

LABORATORY EXERCISE VI.

Special tests for arsenic (pages 28–31).

LABORATORY EXERCISE VII.

Preliminary reactions of the arsenic group (pages 32–34) and analysis of unknown solutions.

LABORATORY EXERCISE VIII.

Unknown solutions.

Laboratory Exercises IX.

Experiments with metals of Groups I and II.

Exp. 10. Precipitate a little silver chlorid according to the following:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

Filter and allow the precipitate to become nearly dry. Mix a little of the precipitate with powdered charcoal, and heat before the blowpipe until a globule of metallic silver is obtained.

Exp. 11. Mix intimately a small quantity of litharge and powdered charcoal. Heat in a blowpipe flame and obtain a particle of metallic lead.

Exp. 12. In a solution of lead (acetate or nitrate) suspend a strip of zinc. Set aside for several hours and note the separation of metallic lead. Write the reaction.

Exp. 13. Put a small quantity of cinnabar (HgS) into a small, hard glass tube open at both ends. Hold the tube, slightly inclined, in a strong heat of the Bunsen flame; then examine the sublimate under the microscope. What becomes of the sulphur?

Exp. 14. Hold a strip of iron or steel (knife blade) for a few seconds in a solution of copper sulphate. Does the strip of iron dissolve? If so, in what combination?

Exp. 15. In an open, hard glass tube, heat strongly a mixture of charcoal and copper oxid. Explain the change of color.

Exp. 16. To a very small piece of copper foil in a test-tube, add a little ammonium chlorid solution and allow to stand.

CHAPTER V.

METALS OF GROUP III.

Iron, Fe (Ferrum).

The Metal. — Atomic weight 55.9.

Melting-point 1275° C. Iron occurs widely distributed in nature combined with oxygen as Fe_2O_3 or Fe_3O_4, with sulphur as FeS_2, and with carbon as $FeCO_3$.

The reduction of iron from its ores is typical of one of the four general methods, that is, reduction by carbon. This is carried out in the blast furnaces, which are so constructed that a supply of coal, iron ore, and fusible slag, introduced at the top of the furnace, are dissolved and hold impurities, while the purified molten metal is withdrawn from the bottom. This melted iron, cast in molds as it comes from the furnace, constitutes our cast iron, is brittle, and contains a considerable proportion of carbon and other impurities.

Wrought iron is produced by working melted iron in specially constructed furnaces so that the greater part of the impurities are removed. By the addition, to very pure iron after such treatment, of carbon, manganese, etc., steel is produced.

Reduced iron or "iron by hydrogen" is prepared by the reduction of the heated oxid or hydroxid in a stream of hydrogen gas.

Compounds. — Iron forms two classes of salts, ferrous, represented by ferrous sulphate, $FeSO_4$; and ferric, represented by ferric sulphate, $Fe_2(SO_4)_3$, or ferric chlorid, $FeCl_3$.

Ferric sulphate, also known as Monsel's salt, is used as a styptic.

Ferric chlorid, $FeCl_3$ or Fe_2Cl_6, is made by dissolving iron in hydrochloric acid, oxidizing the ferrous chlorid with nitric acid, and then driving off the nitric acid by evaporation. The resulting solution, however, contains traces of free nitric and considerable free hydrochloric acid. In the tincture of chlorid of iron these acids react with the alcohol forming various ethers, to which the peculiarities of the tincture may be due.

Copperas and green vitriol are commercial names for crystallized ferrous sulphate. $FeSO_47H_2O$ is used as a disinfectant and, to a slight extent, in medicine as an astringent.

Ferrous carbonate, $(FeCO_3)x(Fe(OH)_2)y$, prepared by double decomposition between $FeSO_4$ and potassium or sodium carbonate, is a medicinal preparation quite largely used as "Blaud's pills."

Analytical Reactions. — A solution for demonstrating the reactions of ferrous salts is best made by saturating cold dilute sulphuric acid with clean iron wire. A 3 to 5 per cent solution of fresh crystals of ferrous ammonium sulphate may be used. The ordinary ferrous sulphate or "copperas" is almost sure to contain some ferric salt. Use a 2 to 3 per cent solution of ferric chlorid and make the following tests, comparing the deportment of the ferrous and ferric solutions with each reagent. Write the reactions.

H_2S with pure ferrous salts gives no reaction; with ferric salts the iron is reduced to the ferrous combination, but gives no precipitate except sulphur.

$(NH_4)_2S$ gives with ferrous iron a black precipitate of FeS; with ferric salts it gives a precipitate containing FeS and S.

NH_4OH precipitates Fe″ as ferrous hydroxid, $Fe(OH)_2$; white if perfectly pure, but usually a dirty green from admixture of ferric compounds. The presence of NH_4Cl prevents a *complete* precipitation as $Fe(OH)_2$.

With ferric salts, NH_4OH completely precipitates the iron as brick-red ferric hydroxid, $Fe(OH)_3$.

K_4FeCy_6 gives with ferrous salts a bluish-white precipitate of potassium ferrous ferrocyanid, $K_2FeFeCy_6$.

With a solution of ferric salts the deep Prussian blue, ferric ferrocyanid, $Fe_4(FeCy_6)_3$, is thrown out.

With potassium ferricyanid, ferrous salts give a dark-blue precipitate of ferrous ferricyanid, $Fe_3(FeCy_6)_2$. With ferric salts no precipitation occurs, but the color may change to green or brown.

KCyS or NH_4CyS gives no reaction with pure ferrous salts, but with ferric salts a deep red solution of ferric thiocyanate, $Fe(CyS)_3$, is produced. This red color is destroyed by addition of $HgCl_2$, not affected by HCl, and may be extracted from the aqueous solution by shaking with ether in which the Fe $(CyS)_3$ is soluble.

Aluminum, Al.

Atomic weight 27.1. Melting-point 700° C. Aluminum as a constituent of clay, feldspar, mica, etc., constitutes a considerable part of the earth's crust.

Alloys. — Aluminum alloys are not difficult to produce, but few are of practical value. The pure metal is used in making plates. The following may be noted.

Aluminum alloys for bridge work. Dr. Richards, Paris, Dental Cosmos, March, 1912, page 378,

(1)		(2)	
Copper	5.5	Tin	7
Tin	2.0	Zinc	10
Aluminum	92.5	Aluminum	83

Number two is more elastic than number one and either makes a better appearance than pure aluminum.

Compounds. — The most important soluble salts of Al are ammonia alum, $NH_4Al(SO_4)_2\ 12\ H_2O$, potash alum, $KAl(SO_4)_2\ 12\ H_2O$, and aluminum sulphate, $Al_2(SO_4)_3$.

The term alum is applied to any salt of definite crystalline

form containing one molecule of a univalent sulphate, such as K_2SO_4 or Na_2SO_4, combined with one molecule of a trivalent sulphate, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ or $Cr_2(SO_4)_3$, and crystallized with twenty-four molecules of water. The formula of alum, as given above, comprises just one half of this combination. Alum need not contain any aluminium whatever so long as it conforms to the foregoing requirements, e.g., chrome alum may be $NH_4Cr(SO_4)_2$ 12 H_2O and ferric alum is usually $NH_4Fe(SO_4)_2$ 12 H_2O.

Analytical Reactions. — Use a 5% solution of either of these for the following tests:

$Al_2(SO_4)_3$ with $(NH_4)_2S$ and H_2O gives a white precipitate of $Al(OH)_3$. Write the reaction.

$Al(OH)_3$ is likewise produced by NH_4OH, Na_2CO_3, or NaOH; the precipitate is soluble in excess of fixed alkali hydroxids with formation of aluminates:

$$Al(OH)_3 + KOH = KAlO_2 + 2\ H_2O.$$

The alkaline aluminates may also be formed by fusion with Na_2CO_3 and KNO_3 and then may be dissolved in hot water.

From the solution of $KAlO_2$ the Al may be precipitated as $Al(OH)_3$ by excess of NH_4Cl (difference from Zn, page 55).

The presence of organic acids, tartaric, oxalic, etc., interferes with the precipitation of aluminium hydroxid and may entirely prevent it. The presence of ammonium chlorid favors its precipitation.

Chromium, Cr.

Atomic weight 52.1. Occurs as chrome iron ore or chromite, $FeOCr_2O_3$. Chromium forms two oxids, one basic in character, Cr_2O_3, which forms the basis of chromic salts, as $Cr_2(SO_4)_3$, $Cr_2Cl_6(CrCl_3)$,* etc.; the other, CrO_3, is an acid anhydrid, crystallizes as dark-red needles, and gives rise to two series of salts: neutral chromates, such as K_2CrO_4, and acid chromates or dichromates, $K_2Cr_2O_7$.

* There is a series of chromous salts, $CrCl_2$, $Cr(OH)_2$, etc., corresponding to a chromous oxid, CrO, but the oxid itself is not known

The soluble chromic salts most easily obtained are chrome alum, $KCr(SO_4)_2$, chromic sulphate, $Cr_2(SO_4)_3$, and chromic chlorid, $CrCl_3$. With a 5% solution of either of these the following may be demonstrated:

$Cr_2(SO)_3$ with $(NH_4)_2S$ gives greenish precipitate of $Cr(OH)_3$.

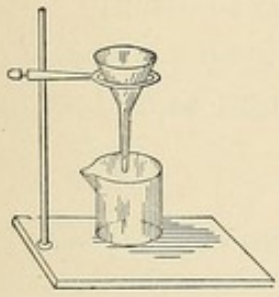
Similarly to Al, the chromium *hydroxid* is precipitated by the alkaline carbonates and the alkaline sulphids as well as by the hydroxids; and then by boiling the $Cr(OH)_3$ with NaOH or KOH, or by fusing with Na_2CO_3 and KNO_3, chromates of the alkalis are produced.

The solid dichromate $K_2Cr_2O_7$ with strong H_2SO_4 gives, in the presence of chlorids, the reddish-brown gas CrO_2Cl_2 (chlorochromic anhydrid or chromium dioxychlorid) used as a test for chlorids (page 90).

Analysis of Group III.

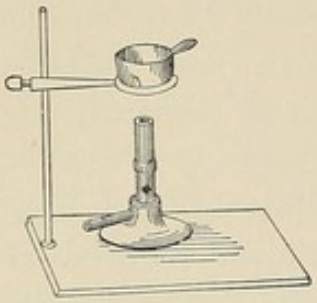
(Fe, Al, Cr. Phosphates and oxalates being absent.)

The filtrate from Group II must be freed from H_2S by boiling with a few drops of HNO_3 in a porcelain dish till a drop removed by a glass rod does not blacken filter-paper wet with a solution of lead acetate. This treatment also serves to oxidize the iron (reduced by H_2S) to ferric salt and at the same time concentrates the solution. To the clear solution thus obtained add 10 c.c. of NH_4Cl solution, then NH_4OH till alkaline, when the metals of this group will separate out as hydroxids: $Fe(OH)_3$ brick-red, $Al(OH)_3$ white, $Cr(OH)_3$ bluish-green. Filter, wash carefully, and dry precipitates, removing paper from funnel.

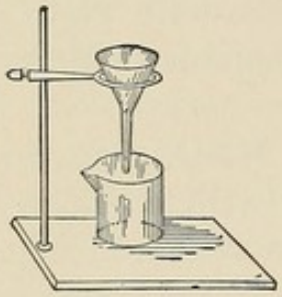


Group III.

Groups IV, V, and VI.



Scrape dried precipitate from paper in a crucible and cover well with a mixture of dry Na_2CO_3 and KNO_3 and fuse, keeping fusion liquid for at least three minutes. Cool. Boil the fused mass with H_2O. Filter.



Fe.

Al and Cr.

Iron will remain on the paper; Al and Cr will be in solution as alkaline aluminate and chromate.

Divide filtrate (Al and Cr) into two parts. Test one portion for Al, by acidifying with HCl, adding $(NH_4)_2CO_3$ till alkaline, and boiling, when Al will separate as a white flocculent precipitate of $Al_2(OH)_6$.

Test second portion of filtrate for Cr by acidifying strongly with *acetic* acid, boiling to expel CO_2, and adding a few drops of a solution of lead acetate. A yellow precipitate ($PbCrO_4$) indicates Cr.

Wash the precipitate remaining on the paper (Fe) and dissolve in dilute HCl. Divide resulting solution ($FeCl_3$) into two parts and confirm presence of Fe by testing one with K_4FeCy_6 (blue precipitate) and the other with KCyS (red solution).

If iron is found, determine in original substance whether ferrous or ferric, by use of tests described on pages 44 and 45.

QUESTIONS ON GROUP III.

Why boil off H_2S before precipitating the group with NH_4OH?

Why add HNO_3?

Of what use is the nitrate of potash (KNO_3) in the fusion of the hydroxids of Al and Cr?

In making the final test for Cr why is it necessary to add *acetic* acid, and why boil off the CO_2?

Why must HCl be added before making the final test for Al with $(NH_4)_2CO_3$?

Laboratory Exercise X.

Iron, Aluminum, and Chromium.

Exp. 17. (*a*) To 5 c.c. of dilute alum solution containing a little NH_4Cl, add NH_4OH solution and heat.

Note. — NH_4Cl aids in the complete separation of the $Al_2(OH)_6$.

Write reaction. Will the precipitate dissolve in an excess of the reagent?

(*b*) Repeat, using a chromium solution in place of the alum.

Exp. 18. Dissolve a few crystals of $FeSO_4$ in water. Filter, if necessary, and to a portion of the clear solution add a little ammonia water. To another portion add a few drops of HNO_3 and boil for two or three minutes. Carefully add ammonia water till a permanent precipitate is obtained.

To a solution of ferric alum add a little ammonia. What change is produced by the HNO_3 in the second part of the experiment.

$$FeSO_4 + NH_4OH = ?$$
$$3\,H_2SO_4 + 6\,FeSO_4 + 2\,HNO_3 = ?$$
$$Fe_2(SO_4)_3 + NH_4OH = ?$$

Note. — The addition of sulphuric acid is not necessary to the oxidation by HNO_3. It simplifies the reaction, as otherwise more or less ferric nitrate is formed.

Exp. 19. Make a little fresh solution of potassium ferricyanide, also a solution of ferrous sulphate, to which add a little H_2SO_4 and a piece of iron wire. After hydrogen ceases to be

evolved make the following tests, completing the reaction in each case:

$FeSO_4 + K_3FeCy_6 = ?$	$Fe_2Cl_6 + K_3FeCy_6 = ?$
$FeSO_4 + K_4FeCy_6 = ?$	$Fe_2Cl_6 + K_4FeCy_6 = ?$
$FeSO_4 + KCyS = ?$	$Fe_2Cl_6 + KCyS = ?$

Exp. 20. To a solution of chrome alum add a little NH_4OH. Filter, wash the precipitate once or twice and allow to dry.

$$Cr_2(SO_4)_3 + NH_4OH = ?$$

Exp. 21. To the dried precipitate obtained in Exp. 20 add a little dry sodium carbonate and potassium nitrate. Mix thoroughly, transfer to a porcelain crucible and heat strongly for several minutes, cool and note the color of the fused mass. Dissolve in water, acidify with acetic acid, and divide the solution into two parts; to the first add a few drops of a solution of $Pb(NO_3)_2$ or $Pb(C_2H_3O_2)_2$, and to the second a few drops of $BaCl_2$.

Exp. 22. To separate solutions of aluminum, iron, and chromium salts, add $(NH_4)_2S$. Iron alone forms a sulphid; the other two give precipitates of hydroxids. Write the reactions.

Laboratory Exercises XI and XII.

Analyses of unknown solutions containing metals of Groups I, II, and III.

CHAPTER VI.

METALS OF GROUP IV.

Cobalt, Co.

The Metal. — Atomic weight 59.0. Cobalt occurs in nature as an arsenide $CoAs_2$, smaltite; also CoAsS, cobaltite. These ores are poisonous and have in times past caused the miners so much trouble that the name cobalt was applied to them, the word meaning, "A demon or mountain sprite." Metallic arsenic has also been called cobalt. These facts are probably responsible for a reputation which is attached to the pure oxid of cobalt.

Analytical Reactions. — Use a 2% solution of nitrate. Crystalline salts of Co are usually of pink color; anhydrous salts are blue.

$Co(NO_3)_2$ with $(NH_4)_2S$ gives precipitate of CoS, black. Test solubility of this precipitate in HCl.

Make a borax bead by fusing a little borax on the looped end of a *clean* platinum wire. When a bead of clear "borax glass" has been obtained, dip it in a little of the CoS just formed, and fuse again. The color of the bead when cold is a deep blue.

Note. — Be sure and make the fusion complete; the use of an insufficient amount of heat will account for much of the trouble experienced by students in obtaining satisfactory bead tests.

$Co(NO_3)_2$ with KNO_2 forms a double nitrite, $Co(NO_2)_2$ 2 KNO_2, soluble in water; but if sufficient acetic acid is added to produce a strong acid reaction, the solution heated, and then allowed to stand overnight, the cobalt is completely precipitated as another double salt, $Co(NO_2)_3,3KNO_2$, yellow and crystalline.

Nickel, Ni.

Atomic weight 58.7. Occurs associated with Co, sometimes with Fe as sulphid.

The metal is white, hard, and has a high melting-point. It is soluble in dilute mineral acids, most easily in nitric. It is the least malleable of the common metals.

Alloys. — The principal alloys are German silver, containing copper, nickel, and zinc, and an alloy of 25% nickel and 75% copper, used by the United States Government in making five-cent pieces.

Nickel is largely used for plating steel and copper.

Analytical Reactions. — Use a 2% solution of the sulphate or nitrate. $NiSO_4$ with $(NH_4)_2S$ gives NiS, black. Test solubility in HCl.

The borax-bead test applied to NiS or other nickel salt gives a bead yellowish brown when cold, but the color is easily masked by other metals.

Ni salts with KNO_2 give the soluble double nitrite of similar composition to the Co salt, $Ni(NO_2)_2$, 2 KNO_2. The nickel salt, unlike the cobalt, is not easily decomposed, and is not precipitated by heating with acetic acid. Advantage is taken of this fact in effecting the separation of cobalt from nickel (page 56).

Manganese, Mn.

Atomic weight 55.0. Occurs chiefly as the dioxid, MnO_2, pyrolusite.

Compounds. — The black oxid, MnO_2, is commercially important in the production of chlorin. By Weldon's process, the chlorin is obtained from HCl, the pyrolusite acting as an oxidizing agent.

The oxidization of MnO_2 in the presence of KOH results in the formation of potassium permanganate, $KMnO_4$. This salt is a valuable disinfectant and is largely used. Its decomposition

furnishes 5 atoms of available oxygen from every double molecule ($K_2Mn_2O_8$).

Condy's fluid, a commercial disinfectant, is a solution of $KMnO_4$.

Manganese salts are usually flesh-colored.

Analytical Reactions. — A 3% solution of the sulphate may be used in the following tests:

$MnSO_4$ with $(NH_4)_2S$ gives flesh-colored precipitate of MnS. Test solubility in HCl. With a little of the precipitated MnS make a RED-LEAD TEST for Mn as follows:

Place in a test-tube a little red lead (Pb_3O_4). Add three or four cubic centimeters of a solution of nitric acid (about one part of concentrated HNO_3 and one of H_2O), and boil well. Add, by means of a glass rod, a little of the washed MnS to the mixture in the tube and boil again. Now dilute with water till the tube is about three-quarters full, and allow to stand till liquid is clear. If Mn is present, the supernatant fluid will be a pink to red color due to the formation of permanganic acid, $HMnO_4$.

Note. — HCl or chlorids, even in small quantities, interfere with the reaction; hence it is recommended to make the test on the sulphid. Reducing agents must likewise be absent. When these precautions are observed the test is a very simple and an extremely delicate one.

$MnSO_4$ with NaOH gives flesh-colored $Mn(OH)_2$ insoluble in excess of reagent (separation from Zn).

Upon fusion with a mixture of KNO_3 and Na_2CO_3, manganese salts produce green manganates, as Na_2MnO_4.

ZINC, Zn.

The Metal. — Atomic weight 65.4. Melting-point 420° C. (burns). Occurs chiefly as the carbonate, $ZnCO_3$, calamine. A native carbonate of zinc is also known as smithsonite. The sulphid, ZnS (zinc blende), and the silicate are also natural sources of the metal.

These ores of zinc, whether sulphate or carbonate, upon roasting in air are converted into oxide, and the oxide is easily reduced by carbon to metallic zinc. The metal is bluish white in color, melts at 420° C.; is brittle at ordinary temperatures, but malleable and ductile at 140° to 150° C. At 200° C., however, it again becomes brittle and fuses as above stated at 420° C. At 950° zinc boils and may be distilled; in air it ultimately burns to a white sulphate.

Alloy. — Zinc is of considerable importance from a dental standpoint, the metal itself being used in the manufacture of counter-dies and solders; and, according to Mitchells' Dental Chemistry, it may be advantageously used in the proportion of 1 to 1.5% in silver-tin amalgam alloys. "It tends to control shrinkage, imparts a 'buttery' plasticity to the amalgam, adds to the whiteness of the filling and assists in the maintaining of its color."

Compounds. — The oxide of zinc combines with phosphoric acid and is peculiarly adapted to the preparation of dental cements. Zinc salts with alkaline carbonates precipitate a white basic carbonate, $Zn_5(OH)_6(CO_3)_2$, which is used as a pigment in the preparation of paint and also as a source of pure oxide of zinc.

The sulphate, $ZnSO_4$, also known as white vitriol, is perhaps the most common salt. The chlorid is a constituent of many commercial liquid disinfectants and antiseptics. The nitrate also is easily obtained.

A 2 or 3 per cent solution of any of these soluble salts may be used in the following tests:

Analytical Reactions. — $ZnSO_4$ with $(NH_4)_2S$ gives a white precipitate of ZnS.

Sulphid of zinc is the only white *sulphid* formed in the course of analysis of ordinary solutions, but the following white precipitates are formed: Sulphid of manganese is flesh-colored or dirty white. Aluminum hydroxid resembles sulphid of zinc in

appearance and is precipitated by $(NH_4)_2S$. Yellow $(NH_4)_2S$ added to an acid solution will precipitate sulphur, white, very fine and difficult to filter out.

$ZnSO_4$ with NaOH (or KOH) gives a white gelatinous precipitate of zinc hydrate, $Zn(OH)_2$, soluble in excess of the reagent as Na_2ZnO_2 (sodium zincate).

Note. — Colorless gelatinous precipitates in slight amounts may escape detection, as it sometimes takes careful observation to see them, especially if the laboratory light happens to be poor.

Na_2ZnO_2 with H_2S or $(NH_4)_2S$ gives precipitate of ZnS.

From solution of Na_2ZnO_2 the Zn may be precipitated as $Zn(OH)_2$ by addition of NH_4Cl, but further addition of the NH_4Cl redissolves the precipitate (distinction from Al, page 46).

$ZnSO_4$ with K_4FeCy_6 gives white precipitate of zinc ferrocyanid (Zn_2FeCy_6), insoluble in NH_4OH.

Note. — The ferrocyanid and the sulphid are the only two zinc salts not soluble in NH_4OH. (Prescott and Johnson, page 179.)

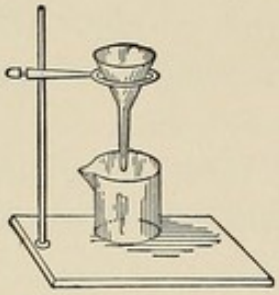
Soluble zinc salts, with oxalic acid or oxalates, give a precipitate of zinc oxalate sufficiently insoluble in alcohol and water to make it available for use in the quantitative separation of zinc from dental alloys. The crystals are of characteristic form, which may be recognized under a microscope (Plate II, Fig. 6, page 162).

Analysis of Group IV.

(Co, Ni, Mn, Zn.)

(In the presence of phosphates, oxalates, borates, etc., examine this group by the scheme given on page 80).

To the clear filtrate from Group III add $(NH_4)_2S$. A precipitate may be NiS, CoS, MnS, and ZnS. Wash the precipitate and treat with *cold dilute* HCl, which will dissolve MnS and ZnS only.



CoS and NiS, black.

$MnCl_2$ and $ZnCl_2$ in solution.

Make a borax-bead test (page 51) of the precipitates. If a clear red-brown bead is obtained, Ni alone is present. If the bead is blue, Co is present, Ni may or may not be.

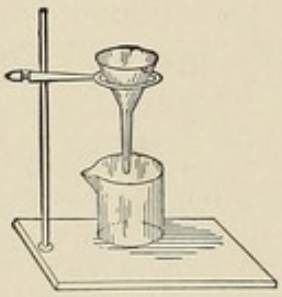
Separation of Cobalt and Nickel.

If Co is present, dissolve the black precipitate off the paper with aqua regia, evaporate in porcelain capsule practically to dryness, dissolve in H_2O, add excess of acetic acid and potassium nitrite (KNO_2). Allow to stand over night, when Co will separate out as a yellow crystalline precipitate (page 51).

Filter and test filtrate for Ni with NaOH, which gives a pale-green precipitate of $Ni(OH)_2$ insoluble in excess of the precipitant.

Separation of Manganese and Zinc.

Boil the HCl solution of Zn and Mn to expel the H_2S, then add a decided excess of KOH or NaOH and allow to stand ten minutes *without* heating. Mn will separate out as $Mn(OH)_2$, while Zn will remain in solution as K_2ZnO_2.



$Mn(OH)_2$.

K_2ZnO_2.

Test precipitate by the red-lead test for Mn, page 53. Test filtrate for Zn by adding H_2S or a few drops of $(NH_4)_2S$, which will precipitate ZnS, white.

QUESTIONS ON GROUP IV.

Why dissolve the MnS and ZnS in *cold* and *dilute* HCl?

Why is it necessary to separate *all* the Mn before testing for Zn?

If traces of Co or Ni are dissolved by the HCl, how does it affect the final test for Zn?

In this analysis (in absence of phosphates, etc.) what important difference between the behavior of salts of Zn and Al?

Why is it necessary to allow time for *complete* precipitation of Co with KNO_2?

Why expel H_2S before separating Mn?

Where does this H_2S come from?

LABORATORY EXERCISE XIII.

Cobalt, Manganese, Nickel and Zinc.

Exp. 23. Add to solutions of $Co(NO_3)_2$, $MnSO_4$, $Ni(NO_3)_2$ and $ZnSO_4$ a few drops of $(NH_4)_2S$ solution.

Note color of precipitate and write reaction in each case.

Exp. 24. On four separate filter papers collect the several precipitates formed in Exp. 23. Wash once with H_2O and make a borax-bead test with each precipitate as shown in the laboratory demonstration. To each precipitate add, on the paper, cold dilute HCl.

Exp. 25. (*a*) To a solution of $ZnSO_4$ add a little NH_4OH. Will the precipitate dissolve in excess of reagent?

(*b*) Repeat, adding NH_4Cl before using the NH_4OH.

(*c*) Repeat (*a*) using NaOH in place of NH_4OH.

Exp. 26. Precipitate a little MnS, filter and wash. Make red-lead test as described on page 53.

Exp. 27. (*a*) To a solution of $Co(NO_3)_2$ in a test-tube, add a drop or two of dilute NH_4OH. Now add an excess of NH_4OH and note if any change occurs.

(*b*) Repeat, using a solution of $NiSO_4$.

What are the precipitates formed?

Exp. 28. To a solution of zinc salt add a solution of Na_2CO_3. The precipitate is a basic carbonate of zinc.

Balance the equation

$$ZnSO_4 + Na_2CO_3 + H_2O = Zn_5(OH)_6(CO_3)_2 + Na_2SO_4 + CO_2.$$

Exp. 29. Shake in a test tube a little ZnO and water, filter and test filtrate for Zn as in Exp. 23.

Repeat using ammonium chloride solution instead of the water. Inference.

Laboratory Exercise XIV.

Analytical reactions of metals of the zinc group. (*Pages 51–56.*)

Laboratory Exercises XV and XVI.

Unknown solutions.

CHAPTER VII.

METALS OF GROUP V.

The Alkaline Earths Ba, Sr, Ca, Mg.

The common alkaline earth metals present similarity of properties which ally them more closely than the metals of some of the previous analytical groups. None of the metals occur free in nature. The metals themselves are isolated with considerable difficulty, with the exception of magnesium, and they all decompose water with evolution of hydrogen, calcium, strontium and barium producing the decomposition at ordinary temperatures; magnesium, at high temperatures only.

As a group they form insoluble carbonates, from which CO_2 is easily driven off by heat, leaving the oxid of the metal. This oxid unites with water, forming feebly soluble hydroxids. The solutions of the hydroxids are alkaline to litmus, and are used, to a considerable extent in medicine, as antacids.

There are two other metals belonging to this group. The first, glucinum, also called beryllium, has an atomic weight of 9.1. Soluble salts of glucinum are precipitated by ammonium hydroxid as white and gelatinous $Be(OH)_2$. The precipitate somewhat resembles aluminum hydroxid. Ammonium carbonate also precipitates the hydroxid which is easily soluble in excess of reagent. The solution, however, should not be boiled as prolonged boiling will cause the glucinum hydroxid to reprecipitate.

Beryllium oxid unites with phosphoric acid, forming a phosphate similar in its properties to the basic phosphate of zinc, and its use is claimed by some manufacturers to be essential to the preparation of artificial enamels. (See page 124.)

The second rare metal belonging to this group is radium; atomic weight 225. The metal itself has not as yet been isolated. Its compounds are obtained from uraninite or pitchblende, a source of uranium. It is bivalent, and the chlorids, bromids, nitrates, and hydroxids have been studied.

Radium compounds are luminous, and the active emanations emitted by them have been condensed at 150° below zero centigrade, forming new substances, among which helium has been identified. The discovery of this fact is responsible for our new conception of the possible divisibility or disintegration of what were once considered indivisible atoms, the "smoke ring" molecule, and the possible transmutation of the elements.

Barium, Ba.

Compounds. — Barium, the next metal to radium in this group in point of atomic weight, which is 137.4, occurs chiefly as a sulphate $BaSO_4$, heavy spar, and $BaCO_3$, witherite. Barium oxid may be formed by heating the carbonate or nitrate to red heat. It absorbs oxygen from the air with formation of the binoxid BaO_2. This in turn is decomposed, oxygen being given off and BaO being reproduced. The barium oxid hence becomes a source of oxygen of commercial importance. The cost of producing oxygen by this method is obviously small.

The peroxid of barium is also of particular importance to the dentist, in that it is an important source of peroxid of hydrogen. This substance is considered more fully in a chapter on mouth washes and local anæsthetics. (See page 171.)

Barium hydroxid, BaO_2H_2, slightly soluble in water, absorbs CO_2 very rapidly and may be used as a test for this gas. The solution is known as "Baryta Water."

Analytical Reactions. — Use a 2% solution of the chlorid for tests.

$BaCl_2$ with $(NH_4)_2CO_3$ gives white precipitate of barium

carbonate. Test solubility in acids. With soluble sulphates $BaCl_2$ produces $BaSO_4$ insoluble in HCl. (Test for sulphates.)

$BaCl_2$ with $K_2Cr_2O_7$ or K_2CrO_4 gives yellow precipitate of $BaCrO_4$. Barium salts moistened with HCl and held on a clean platinum wire give to the colorless flame of the Bunsen burner a green or yellowish-green color.

Strontium, Sr.

Atomic weight 87.6. Occurs as the carbonate, $SrCO_3$, strontianite, also as the sulphate.

Strontium salts are used commercially in the preparation of colored fires, strontium imparting a vivid red color to the flame. They are not used medically. Strontium oxalate crystallizes in practically the same forms and much more easily then calcium oxalate.

Analytical Reactions. — Use a 3 to 4% solution of the nitrate or chlorid for tests.

$Sr(NO_3)_2$ with $(NH_4)_2CO_3$ gives white precipitate of $SrCO_3$.

$Sr(NO_3)_2$ with H_2SO_4 or soluble sulphate gives white precipitate of $SrSO_4$, rather more soluble in water and more slowly formed than $BaSO_4$.

A saturated solution of $SrSO_4$ may be used to test for barium in presence of Sr salts.

$Sr(NO_3)_2$ with K_2CrO_4 gives precipitate of $SrCrO_4$, but with the acid chromate (dichromate) of potassium, $K_2Cr_2O_7$, no precipitate is formed except in concentrated solutions.

$Sr(NO_3)_2$ with oxalic acid gives a precipitate of strontium oxalate, SrC_2O_4, crystallizing in the so-called envelop form (Plate II, Fig. 3, page 162). Salts of Sr color the Bunsen flame crimson.

Calcium, Ca.

Atomic weight 40.1. Calcium is widely distributed and very abundant, limestone, chalk, marble, and calc-spar being

natural carbonates; $CaCO_3$, gypsum, and alabaster are sulphates.

Calcium phosphate occurs in the mineral apatite and is also a principal constituent of animal bones.

Calcium sulphate is of particular interest, occurring as gypsum, $CaSO_4.2\,H_2O$. Upon heating, the two molecules of water of crystallization may be driven off, leaving the anhydrous $CaSO_4$, or plaster of Paris, so largely used in dental laboratories. When water is added to the anhydrous powder, it reunites in the proportions of the original crystallized salt and thereby occasions the "setting" of the plaster. Essig states that if, in the preparation of plaster, the heat is allowed to exceed 127° C., its affinity for water is impaired or destroyed and this effect will not be produced.*

As plaster sets, more or less expansion takes place, and, if spread upon glass, the mass usually rises slightly in the center, producing a plate which is somewhat concave on the under surface. This tendency to expansion varies with different grades of plaster, as may easily be shown by a method suggested by Dr. George H. Wilson in the Dental Cosmos for August, 1905, page 940, which consists simply of filling small glass beakers with mixtures similarly prepared. Some samples were found to expand so slightly as not to injure the glass, others cracked, and some broke the beaker into fragments.

The method of mixing also affects the amount of expansion. In a valuable article on "Experiments in Plaster of Paris to Test Expansions," by Dr. Stewart J. Spence, in Items of Interest, 1902, page 721, it is shown that "not only do different plasters expand in differing degrees, but the same plaster expands very differently according to the stirring given it before pouring," and that long stirring increases the heat developed, the rapidity of setting, and the amount of expansion, but decreases the strength.

* American Text-book of Prosthetic Dentistry.

Various methods have been prepared to overcome the difficulties in manipulation of plaster, such as mixing the plaster with alum, marble-dust, or potassium sulphate. A compound on the market consists of a mixture of plaster and Portland cement. A mixture which has been very strongly recommended as an investment preparation consists of two-thirds plaster and one-third powdered pumice-stone.

Analytical Reactions. — Use a 3 or 4% solution of $CaCl_2$ for tests.

$CaCl_2$ with $(NH_4)_2CO_3$ gives white precipitate of $CaCO_3$, easily soluble in acids.

$CaCl_2$ with oxalic acid or soluble oxalates gives a white precipitate of CaC_2O_4, similar in form to the SrC_2O_4 but much more difficult to obtain in the crystalline condition.

$CaSO_4$ is not precipitated except from moderately concentrated solution.

A saturated solution of $CaSO_4$ may be used to test for strontium salts in presence of Ca.

Magnesium, Mg.

Atomic weight 24.36. Burns easily in the air, forming MgO. Principal sources are the carbonate, $MgCO_3$, magnesite, and a double carbonate, $CaMg(CO_3)_2$, dolomite. The sulphate $MgSO_4$ occurs in the mineral kieserite in the "Stassfurt deposit." "French chalk" (or talcum), soapstone, and meerschaum consist of magnesium silicate in varying states of purity.

Asbestos is a double silicate of magnesium and calcium.

Compounds. — Epsom salt, or magnesium sulphate, occurs as a constituent of laxative waters. The crystallized salt, $MgSO_4.7\ H_2O$ resembles oxalic acid in appearance, and has been mistaken in several instances for the poisonous acid.

Magnesium carbonate is used in pharmacy in two forms; viz., the light and the heavy. These are produced by precipi-

tating dilute or concentrated solution of magnesium sulphate with sodium carbonate.

The light and heavy magnesium oxides are produced by calcination of the light or heavy carbonates. Magnesium salts are quite generally distributed in the human system, but in small quantities. They occur in the bones, the teeth, and the various body fluids.

Analytical Reactions. — A 5% solution of the sulphate or nitrate may be used in the following tests:

Magnesium salts with $(NH_4)_2CO_3$ give a white precipitate of basic carbonate of variable composition. This precipitate forms *very* slowly in dilute solution, and in the presence of NH_4Cl the formation of soluble double salts prevents the precipitation altogether.

$MgCl_2$ with Na_2HPO_4 gives in fairly concentrated solution a white precipitate of $MgHPO_4$. In presence of NH_4Cl and NH_4OH the alkaline phosphates precipitate magnesium-ammonium-phosphate, $MgNH_4PO_4,6H_2O$, even from *very* dilute solution (Plate IV, Fig. 2).

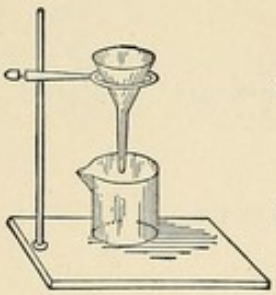
In case the precipitate has formed very slowly, it may separate as small, almost transparent, crystals clinging to the sides of the beaker.

Ammonium oxalate does not precipitate magnesium solutions.

Analysis of Group V.

(Ba, Sr, Ca, Mg.)

To the filtrate from Group IV containing NH_4Cl and NH_4OH, add $(NH_4)_2CO_3$. (If NH_4Cl and NH_4OH are not present, add 10 c.c. of NH_4Cl solution and NH_4OH till strongly alkaline before proceeding with the analysis.) Ba, Sr, and Ca will be precipitated as carbonates; Mg will be held in solution by the ammonium chlorid. Filter.



Ca, Ba, Sr carbonates.

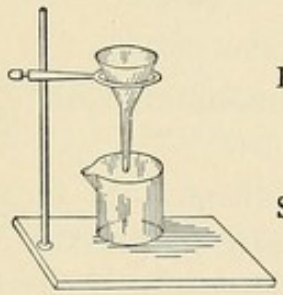
Mg. and metals of Group VI.

Test the filtrate for Mg by adding Na_2HPO_4, when a white crystalline precipitate is NH_4MgPO_4,6 H_2O.

To the carbonates on the paper add dilute acetic acid, which will dissolve the precipitate, forming acetates of the three metals.

Take a *portion* of the acetate solution in a test-tube and make a preliminary test for Ba by adding *acid* chromate of potassium ($K_2Cr_2O_7$). A yellowish precipitate will be $BaCrO_4$.

If *Ba is present*, add $K_2Cr_2O_7$ to the whole of the solution and filter out the $BaCrO_4$.

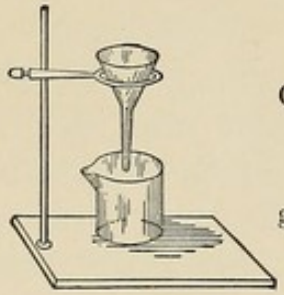


$BaCrO_4$.

Sr and Ca acetates, $K_2Cr_2O_7$, etc.

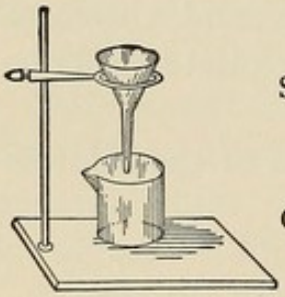
It is desirable to remove the excess of bichromate from the filtrate before testing for Ca and Sr.* To do this add NH_4OH till alkaline; then $(NH_4)_2CO_3$ will precipitate $SrCO_3$ and $CaCO_3$. Filter and dissolve off the paper with acetic acid as before.

* The object of removing the $K_2Cr_2O_7$ is to furnish a colorless solution wherein the Sr or Ca precipitates may be more clearly discerned. It is not absolutely necessary and, in case the amount of Sr and Ca is probably slight, might be omitted, as the operation is always attended with some loss.



$CaCO_3$ and $SrCO_3$, which when treated with acetic acid, will give a solution of the acetates of Ca and Sr.

Reserve about one-fourth of this acetate solution. To the remainder add dilute K_2SO_4 solution, which will precipitate $SrSO_4$. (If only slight amounts of Sr are present, it may take some time to complete the precipitation. If a large amount of Ca is present, some $CaSO_4$ may also be thrown down.) Filter.



$SrSO_4$.

$Ca(C_2H_3O_2)_2$ or $CaSO_4$.

Test filtrate for Ca by adding ammonium oxalate, which will precipitate calcium oxalate, white.

If there is any question about the precipitate thrown out by K_2SO_4 being Sr, make confirmatory test on reserved portion, either by flame test (page 61), or by adding $CaSO_4$, and allowing to stand twelve hours. $CaSO_4$ will precipitate Sr as $SrSO_4$, but of course cannot precipitate Ca.

QUESTIONS ON GROUP V.

Why add NH_4Cl before precipitating the group with $(NH_4)_2CO_3$?

Why dissolve the precipitated carbonates in acetic acid rather than HCl?

Why use the acid chromate of potassium ($K_2Cr_2O_7$) in testing for Ba rather than the neutral chromate (K_2CrO_4)?

Why precipitate Sr and Ca after separation of Ba with $K_2Cr_2O_7$?

LABORATORY EXERCISE XVII.

The Alkaline Earths.

Exp. 30. To a little clear lime water add a few drops of ammonium carbonate solution.

$$CaO_2H_2 + (NH_4)_2CO_3 = ?$$

Will an excess of reagent dissolve this precipitate? If CO_2 were used in place of $(NH_4)_2CO_3$ would the solubility of the precipitate be the same? Why?

Exp. 31. Take in separate test-tubes about 5 c.c. of each of the following dilute solutions: $CaCl_2$, $BaCl_2$, $Sr(NO_3)_2$, and $MgCl_2$. Add to each 1 or 2 c.c. of NH_4Cl solution, and then a little $(NH_4)_2CO_3$ solution.

Now add cautiously to each tube, containing a precipitate, dilute acetic acid till the precipitates are all dissolved. To each of these three tubes add a few drops of $K_2Cr_2O_7$ solution.

Write the reactions. Formulate a method for the separation of Ca, Ba, and Mg from a mixture containing all three.

Exp. 32. To a solution of magnesium chlorid add a little NH_4OH and NH_4Cl solution and lastly some sodium phosphate.

The formula for the precipitate is NH_4MgPO_4. Complete the reaction.

$$MgCl_2 + Na_2HPO_4 + NH_4OH =$$

Exp. 33. To each of the four solutions used in Exp. 31 add a little dilute H_2SO_4.

Which of the four metals forms the least soluble sulphate?

Which the most soluble?

Exp. 34. To a solution of $Sr(NO_3)_2$ add a solution of $CaSO_4$ and allow to stand.

Exp. 35. To a solution of a calcium salt add some ammonium oxalate solution. Write reaction.

Exp. 36. In a watch glass place a few drops of lime-water, in another place some baryta water. Set the two glasses aside for a while and explain any change that takes place.

Exp. 37. Make flame tests with solutions of barium, strontium, and calcium.

Laboratory Exercises XVIII, XIX, and XX.

Unknown solutions. Metals of the various groups thus far considered.

CHAPTER VIII.

METALS OF GROUP VI.

The Alkaline Metals, K, Na, NH, Li.

Potassium, sodium, and the hypothetical "metal" ammonium are the bases of a very large number of salts used in the arts and sciences.

As a class the metals may be distinguished from the alkaline earths by the ready solubility of their hydrates and carbonates. The hydrates of the alkaline earths are only sparingly soluble, and their carbonates are insoluble.

The salts of lithium are also soluble, but are used in relatively small amounts.

These bases are not precipitated by any group reagent and must be detected by individual tests.

Potassium, K (Kalium).

Atomic weight 39.15. Occurs as carbonate in wood ashes, as nitrate in the "nitre beds" of India, etc., as chlorid from the Stassfurt deposit in the Province of Saxony, Prussia, as the mineral sylvite, also in the double chlorid of Mg and K (carnallite).

The salts of potassium are generally soluble in water. Among the more important compounds is the hydroxid KOH. This is used very largely as a starting point in the preparation of many of the medicinal salts of potassium. It may be made by treating potassium carbonate with slaked lime, according to the following reaction:

$$CaO_2H_2 + K_2CO_3 = CaCO_3 + 2\,KOH.$$

The carbonate obtained from wood ashes is known as salts of tartar, and in the impure form as pearl ash. Potassium carbonate is also made in large quantities from the native chlorid found in the Stassfurt deposit.

The bicarbonate $KHCO_3$, or saleratus, may be obtained by saturating the carbonate with CO_2.

$$K_2CO_3 + CO_2 + H_2O = 2\ KHCO_3.$$

This salt, used in cooking, proves more or less irritating, and has been practically replaced by the corresponding sodium salt, $NaHCO_3$ or "cooking soda."

Potassium nitrate, KNO_3, also called nitre and saltpeter is used in medicine as a diuretic. It gives off oxygen easily, and is consequently a good oxidizing agent, and as such is a constituent of fireworks, gunpowder, etc.

KNO_3 may be prepared from the cheaper sodium nitrate by double decomposition with potassium chlorid.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Potassium bromid, used as a sedative, may be prepared by treating caustic potash, KOH, with bromin.

$$6\ Br + 6\ KOH = 5\ KBr + 3\ H_2O + KBrO_3.$$

The bromate, $KBrO_3$, is separated by crystallization.

Potassium iodid may be made in a similar manner by substituting iodin for the bromin. Potassium iodid is very soluble, being dissolved in less than its own weight of water. In the laboratory potassium iodid is used as a solvent for iodin, and as a reagent.

Potassium cyanid, KCN, an extremely poisonous compound, is used by jewelers for cleaning silver, etc., and in the arts for the preparation of double salts used in electro-plating. It is decomposed by CO_2, forming K_2CO_3 and liberating hydrocyanic acid.

Potassium chlorate may be prepared by treating a hot solution

of the hydroxid with chlorin gas. The reaction is the same as that given for the preparation of the bromid, and results in five molecules of the potassium chlorid to one of the chlorate.

Potassium sulphid, K_2S, is soluble in water and in common with other alkaline sulphids, is a solvent for sulphur, thereby forming a number of polysulphids.

The pentasulphid, K_2S_5, is known as liver of sulphur or sulphuret of potassium.

Potassium platinic chlorid, K_2PtCl_6, and potassium acid tartrate, $KHC_4H_4O_6$, are only sparingly soluble and may be precipitated by addition to the solution of an equal volume of alcohol, in which they are quite insoluble.

The potassium acid tartrate, or bitartrate, is also called cream of tartar, and is used in the manufacture of baking powder. This salt separates from wine vats, it being precipitated by the alcohol produced during the process of fermentation of the grape juice. In this impure form it is known as argols, or crude tartar.

Analytical Reactions. — The presence of potassium salts may be detected spectroscopically or by the violet color given to the flame observed through blue glass. Make comparative tests with known solutions of sodium and potassium salts, using blue glass of sufficient thickness to obscure the yellow (Na) ray.

Note. — In making the flame test the best results are obtained by evaporating a little of the *original* solution to dryness, moistening with HCl and then taking up on a loop of clean platinum wire.

The platinic chlorid test may be made as follows:

Add a few drops of HCl to a little of the solution, then evaporate to dryness. Keep at a low red heat till all ammonium salts have been driven off, cool, and take up in a little (not more than 5 c.c.) distilled water. Add a few drops of H_2PtCl_6 and about 5 c.c. of alcohol. Set aside for some time. K_2PtCl_6, yellow, will crystallize out recognizable under the microscope (Plate III, Fig. 3).

Sodium, Na (Natrium).

Atomic weight 23.05. Occurs principally as chlorid in sea-water and in mineral deposits, and to a lesser extent as nitrate, Chili saltpeter, and as cryolite, the double fluorid of Al and Na, (Na_3AlF_6), found in Greenland.

Compounds. — Sodium peroxid, or dioxid, Na_2O_2, may be prepared by simply heating metallic sodium in dry air. It is a yellowish white powder used somewhat in dental practice for the preparation of alkaline solutions of H_2O_2:

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2.$$

The alkaline peroxid is much more efficient as a bleaching agent than the neutral or acid preparations.

Sodium hydroxid, NaOH, is found in trade in several forms. The stick "caustic soda," used in chemical laboratories, contains anywhere from 5 to 30 per cent of water. In a powder form, less pure than the above, it is known as "concentrated lye," Babbitt's potash, etc., and is used for cleaning, and in the manufacture of soap. NaOH is caustic or escharotic in its action upon animal tissue. It may be made experimentally by experiment No. 39, page 78.

Sodium carbonate, Na_2CO_3, crystallizes with ten molecules of water. In this form it is known as "sal soda," or washing soda. It is used as a starting point in the manufacture of other sodium salts. Sodium carbonate is produced from NaCl by the LeBlanc process, in which the following reactions are involved:

(1) $2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$

(2) $Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2.$

(3) $Na_2S + CaCO_3 = Na_2CO_3 + CaS.$

The last two reactions are combined in the actual process of manufacture, and the mixture of sodium sulphate, carbon, and calcium carbonate are heated together with the resulting forma-

tion of "black ash" from which is produced pure sodium carbonate.

More recent processes are the Solvay or Ammonia process, depending on the following reaction:

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

and the cryolite process in which the source of the sodium is the double fluorid of sodium and aluminum, Na_3AlF_6. By this process the cryolite is heated with lime, forming calcium fluorid and sodium aluminate.

$$Na_3AlF_6 + 3\ CaO = 3\ CaF_2 + Na_3AlO_3.$$

Note. — According to Remsen the sodium aluminate probably consists of a variety similar in composition to the potassium aluminate given on page 46, ($NaAlO_2$ and Na_2O until water is added).

Sodium bicarbonate, $NaHCO_3$, also called cooking soda, is largely used like "saleratus" ($KHCO_3$) as a source of CO_2 in the leavening or aerating of bread.

Sodium bicarbonate is hydrolized by water, i.e., it dissociates in solution forming NaOH and H_2CO_3. The carbonic acid is a weak acid furnishing very few hydrogen ions, while the hydroxid is a strong base. It follows that the reaction of such a solution is alkaline to litmus, although the salt answers to our definition of an acid salt. This is true of Na_2CO_3 (the products of dissociation being NaOH and $NaHCO_3$), and in a similar manner of corresponding potassium salts.

Sodium chlorid, NaCl, common salt, exists in sea-water to the extent of 2.7%, and is, to some extent, obtained from this source, although the greater amount is produced by the salt mines. Salt is a constituent of all of the body fluids, and can be easily obtained as cubical crystals by the evaporation of urine or of dialyzed saliva.

Physiological, or normal salt solution, contains about 0.7% NaCl, and has practically the same osmotic pressure as blood.

The term "physiological" is to be preferred to the term "normal," as normal salt solution is also properly applied to a solution used in volumetric analysis containing exactly 5.85% NaCl (see page 149).

Sodium nitrate, $NaNO_3$, Chili saltpeter, is valuable as a fertilizer, but too hygroscopic to be used in the same way as potassium nitrate, in the preparation of gunpowder, fireworks, etc.

Sodium phosphate, trisodic phosphate, Na_3PO_4, is a crystalline salt, soluble in water, but of slight interest in Dental Chemistry. It is easily decomposed by CO_2, forming Na_2HPO_4 and Na_2CO_3.

$$2\,Na_3PO_4 + H_2O + CO_2 = 2\,Na_2HPO_4 + Na_2CO_3.$$

The disodic phosphate, Na_2HPO_4, also called neutral or orthosodium phosphate, is the sodium phosphate of the Pharmacopœia. It is faintly alkaline in reaction, and exists in the body fluids generally. The alkaline reaction (to litmus) of saliva is, in part, due to its presence.

The acid, or monobasic sodium phosphate, NaH_2PO_4, is a translucent crystalline salt found to some extent in the body fluids, particularly the urine, to the acidity of which it is probably a contributing factor, although to a much less extent than was formally supposed.

Sodium potassium tartrate, $KNaC_4H_4O_6$, Rochelle salt, is used in medicine as a mild laxative. It is the product of the double decomposition incident to raising bread with "cream of tartar and soda."

$$KHC_4H_4O_6 + NaHCO_3 = KN_2C_4H_4O_6 + CO_2 + H_2O.$$

Sodium sulphate crystallized with ten molecules of water ($Na_2SO_4 10\,H_2O$) is known as Glauber's salt.

Analytical Reactions. — Na may be detected by the use of the spectroscope or by the *persistence* of the yellow flame obtained with a *clean* platinum wire and a colorless Bunsen flame. Make a comparative test with small amount of known sodium salt.

Sodium salts are soluble with only a very few exceptions. The pyroantimonate, $Na_2H_2Sb_2O_7$, may be precipitated in the cold by a freshly prepared solution of *potassium* pyroantimonate. (Prescott and Johnson, p. 228.)

From a solution stronger than 3% and nearly neutral the double acetate of uranyl and sodium ($NaC_2H_3O_2,UO_2(C_2H_3O_2)_2$) may be precipitated. (Plate IV, Fig. 6.) As triple crystalline acetates may also be formed with Mg, Cu, Fe, Ni, and Co, it is recommended to first precipitate the bases of the first five groups and drive off ammonium salts, as in the test for K with H_2PtCl_6.*

Lithium, Li.

Atomic weight 7.03. The carbonate, citrate, bromid and chlorid are used in medicine.

The value of lithium salts as uric acid solvents is questionable, because of the insolubility of the phosphate (page 237).

The presence of lithium is easily shown after the precipitation of strontium by the intense carmine color given to the Bunsen flame.

The spectroscope furnishes a very delicate and positive test for this element.

Ammonium, NH_4.

Ammonia is obtained in large part from the ammoniacal liquor of the gas works, where illuminating gas is made by the distillation of coal. The liquor, charged with ammonia, is treated with hydrochloric or sulphuric acid, thus producing an impure salt which is subsequently purified or used as a source of NH_3 in the preparation of pure ammonium compounds.

$$(NH_4)_2SO_4 + CaO_2H_2 = CaSO_4 + 2\,NH_3 + 2\,H_2O.$$

* Behrens's Manual of Microchemical Analysis, page 32.

Compounds. — Ammonium hydroxid, NH_4OH, has never been separated as such, free from water. It undoubtedly exists, however, in aqueous solutions of ammonia gas.

$$NH_3 + H_2O = NH_4OH.$$

The negative hydroxyl ions of this ammonium base do not dissociate to the same degree as takes place in solutions of KOH; hence, it is a weaker base.

Aqua ammonia of the pharmacopœia contains 10% NH_3. The "stronger water of ammonia" contains 28% of the gas, which is about as strong a solution as it is safe to make for shipment, and containers should never be more than four-fifths full. The 28% solution is referred to as 26° ammonia, the degree indicating the specific gravity as taken by the Baumé hydrometer.

Ammonium carbonate exists in solution. The salt used in medicine under this name is really a mixture of ammonium bicarbonate, NH_4HCO_3, and the carbamate, $NH_4NH_2CO_2$.

This salt gives off NH_3 gas, and moistened with ammonia water and perfumed constitutes "smelling salts."

Ammonium chlorid, sal ammoniac (NH_4Cl), white crystalline, is made by neutralizing NH_4OH with hydrochloric acid. Ammonium chloride will sublime unchanged. It is freely soluble in water, and its solution acts as an electrolyte and will dissolve metals from an alloy. If a silver spoon or a 10-cent piece is allowed to remain for 10 or 12 hours in a dilute solution of NH_4Cl, an appreciable amount of copper will pass into solution, coloring it blue or green, according to the concentration of the copper solution. It also dissolves some metallic oxides, as ZnO.

As saliva is known to contain considerable NH_4Cl, the above facts should be studied carefully in considering the action of saliva on substances used for filling teeth, although the solvent action of NH_4Cl in saliva is nothing like what it is in water.

Ammonium nitrate, NH_4NO_3, crystallizes in large six-sided prisms without water of crystallization. It is very soluble in water. It melts at 165° C. Heated to 210° C., it decomposes into nitrous oxid and water. Above 250° C., other oxids of nitrogen are produced, so in the preparation of nitrous oxid for dental anesthesia, care should be taken to keep the temperature of the reaction between these limits.

Ammonium acetate, $NH_4C_2H_3O_2$. A solution of this salt, containing about 7%, is used in medicine as a diaphoretic. The solution is also known as Spirit of Mindererus. In analytical chemistry, it is used as a solvent for lead sulphate.

Ammonium sulphate, $(NH_4)_2SO_4$, is a white crystalline salt soluble in water, not used medicinally, but largely used as a reagent in physiological chemistry. It melts at 140° C., and at a higher temperature it decomposes.

Ammonium sulphid, $(NH_4)_2S$, is used as a solvent and reagent. It may be prepared by saturating ammonia water, NH_4OH, with H_2S, then adding an equal volume of ammonia water:

$$NH_4OH + H_2S = NH_4SH + H_2O,$$

and

$$NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$$

A polysulphid, made by dissolving sulphur in $(NH_4)_2S$ is the reagent used in dissolving the sulphids of Group II (*b*) and in precipitating the zinc group.

Ammonium phosphates. Ammonium, like other univalent bases, is capable of forming, with phosphoric acid, three different salts. $(NH_4)_3PO_4$ is very unstable. The diammonium phosphate has been used, to a slight extent, in medicine (BrP) and has been shown to be an energetic activator of lactic acid organisms.*

The importance of this fact, in relation to dental caries, has yet to be demonstrated.

* Dr. Percy Howe in Dental Cosmos, Jan., 1912.

Microcosmic salt is a name given to a double ammonium sodium phosphate ($NH_4NaHPO_4 \cdot 4\ H_2O$) used in blowpipe analysis.

Analytical Reactions. — Ammonium salts are generally soluble. H_2PtCl_6 precipitates the double chlorid $(NH_4)_2PtCl_6$, similar in appearance and crystalline form to the corresponding potassium salt (Plate III, Figs. 1 – 3).

Ammonium salts are most easily detected by the evolution of ammonia gas (NH_3) whenever they are heated with fixed alkali, NaOH or KOH.

The test may be made upon the original solution by boiling in a test-tube with a little 10% NaOH, and the escaping NH_3 may be detected by the odor or, better, by suspending in the upper part of the tube a piece of *moistened red* litmus paper,* which is promptly turned blue by the "volatile alkali." The litmus-paper test is more delicate than the odor test. Care should be taken that the paper does not touch the sides of the tube, as it may come in contact with traces of NaOH.

Many ammonium solutions give off NH_3 gas without the aid of any fixed alkali. Common examples are the carbonate, acid carbonate, hydrate, sulphid, and sulphydrate.

Laboratory Exercise XXI.

The Alkali Metals.

Exp. 38. In 10 or 15 c.c. of water contained in a porcelain dish, dissolve a small piece of metallic potassium.

Stand well away from the dish as the reaction may result in spattering hot water or hot metal.

Test resulting solution with red litmus paper. Write reaction.

Exp. 39. Take a little strong solution of carbonate of soda (about 20% of crystallized salt), heat nearly to boiling in a porcelain dish, then add about half as much milk of lime (made

* Blue paper may be reddened by leaving it a few hours in a wide-mouth bottle after wetting the under side of the stopper with a drop or two of acetic acid.

of one part $Ca(OH)_2$ to four parts water). Continue the boiling for several minutes, then allow to settle. Decant the clear liquid.

Test the liquid with various indicators. Is it acid or alkaline?

To a small portion of it add a few drops of HCl. Does it effervesce? Test in a similar manner the carbonate of soda solution

$$Na_2CO_3 + CaH_2O_2 = ?$$

Which of these two compounds used is a base?

Which an alkali?

Exp. 40. In separate test-tubes heat the following mixtures:

1. Solution of NH_4Cl and solution of NaOH.
2. Solution of $(NH_4)_2SO_4$ and solution of KOH.
3. Dry NH_4Cl and dry CaO_2H_2.

In each case note the odor of the gas evolved and test the VAPOR with moistened red litmus paper and write the reaction.

Exp. 41. Take three test-tubes and into one put about 5 c.c. of a dilute solution NaCl; into the second, KCl; and into the third, NH_4Cl; then to each add a few drops of platinic chlorid solution and allow to stand till the next exercise.

Exp. 42. Make flame tests according to directions given in the lecture room, with salts of sodium, potassium, and lithium.

Exp. 43. Place in an ignition tube one or two grams of potassium tartrate and heat till no further change takes place. Cool and dissolve in water. Test a portion of the resulting solution with a few drops of HCl. In like manner test the original tartrate.

Note. — In general, the ignition of salts of organic acids results in the formation of carbonates.

Exp. 44. Make a spectroscopic examination of solutions of Na, K, Li, Ba, Sr, and Ca, and describe the bands observed.

Note. — This experiment is only to be performed under the direction of an instructor. Opportunity will be given for this experiment during the next exercise if necessary.

Laboratory Exercises XXII and XXIII.

Analyses of Solutions Containing all Bases.

Analysis of Groups III, IV, and V.

When phosphates, borates, or oxalates are present.

To the filtrate from Group II add NH_4Cl and NH_4OH in slight excess. Heat to boiling and add $(NH_4)_2S$ slowly (always keeping the solution at the boiling-point) until precipitation is complete. Filter as rapidly as possible and wash with hot water, adding occasionally a little $(NH_4)_2S$.

The filtrate, which may contain the barium and potassium groups, must be concentrated by evaporation, filtered if necessary, and set aside.* The precipitate may contain MnS, ZnS, CoS, NiS, FeS, $Al(OH)_3$, and $Cr(OH)_3$ with phosphates or oxalates soluble in acids only. The color of the precipitate will give some indication of what is present. Test the precipitate for Mn by fusing a part with KNO_3 and Na_2CO_3.

Treat the precipitate with *cold dilute* HCl in which CoS and NiS alone are insoluble. Filter. Treat insoluble residue for Co and Ni according to directions on page 56.

The HCl solution, which may contain Mn, Zn, Fe, Cr, and Al as chlorids, and phosphates and oxalates soluble in acids, and which is green or violet if much Cr is present, is boiled with a few drops of HNO_3 until all the H_2S is expelled.

Test a *small* portion of the solution for Fe exactly as in analysis of Group III given on page 48. Of the remainder of the solution take about one-third, and add dilute H_2SO_4.

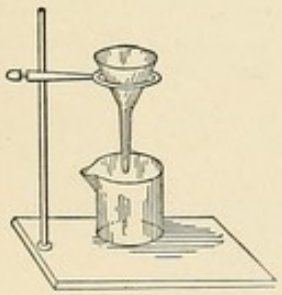
* If Ni is present, the filtrate is frequently brown or black, since NiS is somewhat soluble in an excess of $(NH_4)_2S$, especially if much NH_4OH is present. The NiS may be precipitated, after evaporation, by acidifying with HCl.

A white precipitate may contain $BaSO_4$, $SrSO_4$, and possibly $CaSO_4$. Filter, wash precipitate, and fuse with a mixture of Na_2CO_3 and K_2CO_3,

Note. — The mixture of the two carbonates in molecular proportions fuses at a lower temperature than either salt alone.

Filter and wash the carbonates thus formed, dissolve them in acetic acid and examine this solution for Ba, Sr, and Ca as directed under the Ba group. To the filtrate from the precipitate produced by H_2SO_4, or to the solution in which H_2SO_4 has failed to give a precipitate, add three times its volume of alcohol; Ca, if present, is precipitated as white $CaSO_4$, and its presence may be confirmed by dissolving the precipitate in water and adding $(NH_4)_2C_2O_4$, which precipitates CaC_2O_4, white.

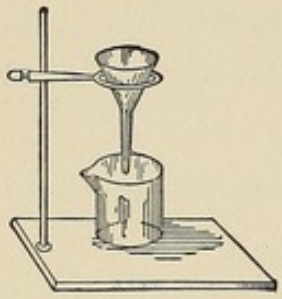
To the rest of the HCl solution add ferric chlorid, carefully, till a drop of the solution gives, when mixed with a drop of ammonic hydrate, a yellowish precipitate. To the solution add Na_2CO_3 or K_2CO_3 till the acid is nearly neutralized, then add excess of freshly precipitated $BaCO_3$, and allow to stand over night. Filter.



Cr and Al as hydrates. (Fe as phosphate or hydrate and $BaCO_3$.)

$MnCl_2$, $ZnCl_2$, and possibly members of Group V.

Transfer the precipitate to a small beaker and boil for some time with NaOH or KOH. The Al will be converted into the aluminate $KAlO_2$. The phosphate will be more or less completely changed to potassium or sodium phosphate. Filter.



$Cr(OH)_3$, $BaCO_3$, etc.

$KAlO_2$ and Na_2HPO_4.

Test precipitate for Cr as on page 48. Add HNO_3 to filtrate till acid, then divide into two parts; test one for P_2O_5 with $(NH_4)_2MoO_4$.

Test the other for Al by adding NH_4OH till alkaline, when precipitate will be $AlPO_4$, insoluble in acetic acid.

To the solution of Mn and Zn chlorids add a little HCl and boil. Then make alkaline with NH_4OH, add $(NH_4)_2S$, warm slightly and filter. The precipitate (MnS and ZnS) may be dissolved in cold dilute HCl and tested for Mn and Zn as in analysis of Group IV, page 56.

OUTLINE SCHEME FOR ANALYSIS OF GROUP I.

To about one-third of a test-tubeful of the unknown solution add a few drops of HCl.

Ppt. = AgCl, HgCl, $PbCl_2$. Add hot H_2O.

<table>
<tr><td colspan="2">Residue = AgCl, HgCl.
Add NH_4OH.</td><td rowspan="2">Solution = $PbCl_2$.
Test as on page 19.</td></tr>
<tr><td>Residue = HgCl.
Test, page 20.</td><td>Solution = AgCl.
Test with HNO_3.</td></tr>
</table>

OUTLINE SCHEME FOR ANALYSIS OF GROUP II.

To the warmed filtrate from Group I add H_2S. A ppt. may be sulphids of As, Sb, Sn, Au, Pt, Cu, Cd, Bi, Hg, and Pb.

Filter and treat with warm $(NH_4)_2S$.

<table>
<tr><td colspan="3">Residue is Group II (a), page 38, and consists of sulphids of Cu, Cd, Bi, Hg, and Pb. Treat on paper c̄ warm dil. HNO_3.</td><td colspan="3">Solution=As, Sb, Sn, Au, and Pt. Reprecipitate c̄ HCl, filter and treat ppt. c̄ strong $(NH_4)_2CO_3$ sol.</td></tr>
<tr><td rowspan="4">Residue is Hg. Dissolve in aqua regia and test c̄ $SnCl_2$ (page 38).</td><td colspan="2">Solution Cu, Cd, Bi, and Pb. Add H_2SO_4 and filter.</td><td colspan="2">Residue=Sb, Sn, Au, and Pt, sulphids. Treat c̄ conc. HCl, dilute and filter.</td><td rowspan="4">Solution. As. Make Gutzeit's or Fleitmann's test for As (page 28).</td></tr>
<tr><td>Ppt. is $PbSO_4$.</td><td>Solution is Cu, Cd, and Bi. Add NH_4OH and filter.</td><td rowspan="2">Residue. Au and Pt. Dissolve in aqua regia and divide.</td><td rowspan="2">Solution. Sb and Sn. Test for Sb c̄ Pt foil and Zn.</td></tr>
<tr><td>Ppt. is $Bi(OH)_3$</td><td>Solution is Cu and Cd.</td></tr>
<tr><td colspan="2"></td><td>Test for Cu c̄ HA and K_4FeCy_6.</td><td>Test for Cd c̄ KCN and H_2S. (page 39.)</td><td>Pt. I. Test for Au c̄ $FeSO_4$ (p. 40).</td><td>Pt. II. Test for Pt c̄ NH_4Cl and alcohol.</td><td>Test for Sn in filtrate c̄ $HgCl_2$ (p. 40).</td></tr>
</table>

OUTLINE SCHEME FOR ANALYSIS OF GROUPS III AND IV.

Take the clear solution in which H_2S fails to produce a precipitate and boil with a few drops of HNO_3 till H_2S is expelled. Add NH_4Cl and NH_4OH. Filter.

<table>
<tr><td colspan="3">Precipitate=Group III. Fe, Al, and Cr. Fuse c̄ Na_2CO_3 and KNO_3. Boil c̄ H_2O and filter.</td><td colspan="3">Solutions=Groups IV, V, and VI. Add $(NH_4)_2S$ and precipitate. Group IV — Co, Ni, Mn, and Zn. Treat with cold dilute HCl.</td></tr>
<tr><td rowspan="2">Residue=Fe. Test for Fe c̄ KCyS and K_4FeCy_6 (page 48).</td><td colspan="2">Solution=Al and Cr. Divide solution and</td><td rowspan="2">Residue=Co and Ni. Make borax-bead test. Separate Co by means of KNO_2 (page 56).</td><td colspan="2">Solution=Mn and Zn. Boil and treat c̄ KOH or NaOH.</td></tr>
<tr><td>Test for Al with HCl and $(NH_4)_2CO_3$ (page 48)</td><td>Test for Cr with acetic and lead acetate (page 48).</td><td>Precipitate=$Mn(OH)_2$. Make red-lead test for Mn (page 53).</td><td>Solution=K_2ZnO_2. Test for Zn c̄ H_2S or $(NH_4)_2S$ (page 57).</td></tr>
</table>

OUTLINE SCHEME FOR ANALYSIS OF GROUPS III, IV, AND V.

(Phosphates, oxalates, borates, etc., being present.)

To filtrate from Group II add NH_4Cl and NH_4OH. Heat and add $(NH_4)_2S$. Filter rapidly.

<table>
<tr><td colspan="5">*Precipitate* = MnS, ZnS, CoS, NiS, FeS, $Al(OH)_3$, $Cr(OH)_3$, also phosphates, etc., soluble in acids only. Fuse part of precipitate and test for Mn (page 57). Treat remainder c cold dilute HCl.</td><td>Filtrate, members of Ba and K groups.</td></tr>
<tr><td>*Residue* = CoS and NiS. Make borax-bead test and separate Co if necessary, c KNO_2 (page 56).</td><td colspan="4">*Solution* = Mn, Zn, Cr, and Al. Divide solution into three parts of about 1/8, 2/8, and 5/8, respectively, and treat as follows:</td></tr>
<tr><td></td><td>I. Test small portion for Fe (page 48).</td><td colspan="3">II. To second portion add dilute H_2SO_4.</td><td rowspan="3"></td></tr>
<tr><td></td><td></td><td>*Precipitate* may be $BaSO_4$, $SrSO_4$ or $CaSO_4$. Filter, wash, fuse c Na_2CO_3 and K_2CO_3. Dissolve fusion in HA and analyze for Group V.</td><td>*Solution* = $CaSO_4$. Add alcohol; if precipitate occurs, filter, dissolve in H_2O, and test with ammonium oxalate.</td></tr>
<tr><td colspan="5">III. To third portion add $FeCl_3$ to combine c H_3PO_4, etc., then add Na_2CO_3 or K_2CO_3, and $BaCO_3$ (page 81).</td></tr>
<tr><td colspan="3">*Precipitate* = Cr, Al, Fe, and $BaCO_3$. Boil precipitate c NaOH and filter.</td><td colspan="2" rowspan="2">*Solution* = Mn and Zn. Reprecipitate Mn and Zn as sulphids, and test according to page 56.</td></tr>
<tr><td colspan="2">*Residue* = Cr, $BaCO_3$, etc. Test for Cr as on page 48.</td><td>*Solution* = $KAlO_2$. Test for Al as on page 48.</td></tr>
</table>

OUTLINE SCHEME FOR ANALYSIS OF GROUPS V AND VI.

To the clear filtrate from Group IV add $(NH_4)_2CO_3$.

<table>
<tr><td colspan="2">*Precipitate* = Ba, Sr, and Ca. Add $K_2Cr_2O_7$ if necessary to precipitate Ba.</td><td rowspan="2">*Solution* = Mg and Group VI. Test for Mg with Na_2HPO_4 (page 65). Make separate tests for metals of Group VI according to pages 71, 74, and 78 of the text.</td></tr>
<tr><td>*Precipitate* = $BaCrO_4$.</td><td>*Solution* = Sr and Ca. Reprecipitate Sr or Ca with $(NH_4)_2CO_3$ and test, or $CaSO_4$. Remove Sr with K_2SO_4 and alcohol, and test filtrate for Ca with $(NH_4)_2C_2O_4$ (page 66).</td></tr>
</table>

CHAPTER IX.

ANALYTICAL REACTIONS OF THE ACIDS.

In the analytical processes thus far described we have considered only the separation and detection of the basic or metallic part of the salt, that is, we have analyzed a solution of ferric chlorid and found the iron only. It is necessary to find the chlorin. Before making any examination for acid, it will be possible to save a considerable amount of both time and labor by first carefully considering what acids are capable of forming soluble salts with the bases which have already been detected. To facilitate this consideration a table of solubilities will be found below and on the following page, by a careful study of which it will be possible to select such acids as are most likely to be present in the unknown solution under investigation, and also to neglect a number of acids which, from the solubility of their salts, together with the character of the solution (acid, alkaline, neutral and aqueous, or otherwise), will necessarily be absent.

TABLE SHOWING THE SOLUBILITY OF SALTS.

	K	Na	NH_4	Mg	Ba	Sr	Ca	Mn	Zn	Co	Ni	Fe	Fe_2
Acetate	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenate	w	w	w	a	a	a	a	a	a	a	a	a	a
Arsenite	w	w	w	a	wa	wa	a	a		a	a	a	a
Borate	w	w	w	wa	a	a	a	a	a	a	a	a	a
Bromid	w	w	w	w	w	w	w	w	w	w	w	w	w
Carbonate	w	w	w	a	a	a	a	a	a	a	a	a	a
Chlorate	w	w	w	w	w	w	w	w	w	w	w	w	w
Chlorid	w	w	w	w	w	w	w	w	w	w	w	w	w
Chromate	w	w	w	w	a	wa	wa	w	w	a	a		w
Cyanid	w	w	w	w	wa	w	w	a	a	ai	ai	ai	
Iodid	w	w	w	w	w	w	w	w	w	w	w	w	w
Nitrate	w	w	w	w	w	w	w	w	w	w	w	w	w
Oxalate	w	w	w	a	a	a	a	a	a	a	a	a	a
Oxid	w	w		a	w	w	w	a	a	a	a	a	a
Phosphate	w	w	w	a	a	a	a	a	a	a	a	a	a
Silicate	w	w		a	a	a	a	a	a	a	a	a	a
Sulphate	w	w	w	w	i	i	wi	w	w	w	w	w	w
Sulphid	w	w	w	wa	w	w	w	a	a	a	a	a	a
Sulphocyanate	w	w	w	w	w	w	w	w	w	w	w	w	w
Tartrate	w	w	w	wa	a	a	a	wa	a	w	a	wa	w

TABLE SHOWING THE SOLUBILITY OF SALTS.—*CONCLUDED*

	Cr_2	Al_2	Sb	Sn''	Sn^{IV}	Au	Ag	Hg_2	Hg	Pb	Bi	Cu	Cd
Acetate	w	w	w	w	w		wa	wa	w	w	w	w	w
Arsenate	a	a	a	a	a		a	a	a	a	a	a	a
Arsenite			a	a	a		a	a	a	a		a	
Borate	a	a		a			a			a	a	a	wa
Bromid	w	w	wa	w	w	w	i	ai	wa	wi	wa	w	w
Carbonate							a	a	a	a	a	a	a
Chlorate	w	w		w			w	w	w	w	w	w	w
Chlorid	w & i	w	wa	w	w	w	i	ai	w	wi	wa	w	w
Chromate	a		a	a			a	a	wa	ai	a	w	a
Cyanid	a					w	i		w	a	wa	a	a
Iodid	w	w	wa	w	w	a	i	a	a	wa	a	a	w
Nitrate	w	w		a	a		w	w	w	w	a	w	w
Oxalate	w	a	a	a	w		a	a	a	a	a	a	a
Oxid	a & i	a & i	a	a	a & i		a	a	a	a	a	a	a
Phosphate	a	a	a	a	a		a	a	a	a	a	a	a
Silicate	a	ai								a		a	a
Sulphate	w& a	w	a	w	w		wa	wa	wa	i	a	w	w
Sulphid			a	a	a	a	a	a	a	a	a	a	a
Sulphocyanate	w				w		i	a	w	a		a	wa
Tartrate	w	w	w	wa			a	a	a	a	a	wa	wa

w, soluble in water; a, insoluble in water, soluble in acids; i, insoluble in water or acids; wa, sparingly soluble in water, readily soluble in acids; wi, sparingly soluble in water and acids; ai, sparingly soluble in acids only.

In this connection it is well to remember that practically all nitrates and chlorates are soluble in water; sulphates are mostly soluble, except those of barium, strontium, and calcium. Phosphates (di- or trimetallic), silicates, oxalates, and borates are practically insoluble, except those of the alkaline metals. This latter statement is also true of carbonates, except that some of the carbonates will dissolve to an appreciable extent in water containing CO_2. Chlorids, bromids, and iodids are nearly all soluble except those of the first-group metals. Sulphids are insoluble except those of Groups V and VI. Acid salts are usually more soluble than neutral salts.

In making qualitative tests for the acids it is not necessary to separate them one from the other, as it is in the case of metals; hence the tests are individual ones, usually made upon the original substance or solution, and often require confirmation before conclusive evidence is obtained. The grouping is, therefore, simply for convenience, as it thus becomes possible to exclude a considerable number of acids by a single general test.

Acid Groups.

Group I may include such acids as give effervescence when their dry salts are treated with *dilute* H_2SO_4, as H_2CO_3, H_2S, $H_2S_2O_3$, H_2SO_3 and HCN.

Group II may include acids giving a precipitate with $AgNO_3$ in dilute HNO_3 solution, as HCl, HBr, HI, HCN, HCNS, HNO_2, HClO, H_4FeCy_6, H_3FeCy_6, $H_2S_2O_3$, H_2S and HPH_2O_2.

This second group may be further subdivided into three parts according to the color of the precipitate obtained (pages 89 and 91).

Group III may include acids forming insoluble salts with $BaCl_2$ or $CaCl_2$ and not found in Groups I or II, or H_2SO_4, $H_2C_2O_4$, H_3PO_4, H_3BO_3, H_2CrO_4 and H_2SiO_3.

Besides the acids found in these groups there are three others of common occurrence: nitric (nitrates), chloric (chlorates), and acetic (acetates).

Detection of Acids of Group I.

(Acids effervescing with dilute sulphuric acid. H_2CO_3, H_2S, H_2SO_3, $H_2S_2O_3$, HCN.)

To a test-tube a quarter full of the unknown solution, or a little dry substance on a watch-glass, add dilute H_2SO_4. If solution is very dilute, concentrate it before making test, as a slight amount of gas might be absorbed by the water. Watch carefully for any escape of gas and note any odor which may be given off.

Carbonates evolve CO_2, odorless, but if passed into lime-water or baryta-water will give white precipitate of $CaCO_3$ or $BaCO_3$.

Sulphids evolve H_2S, odor of rotten eggs. Confirm by adding a little dilute H_2SO_4 to the suspected powder (or solution) in a test-tube and holding over the mouth of the tube a piece of filter-paper wet with a solution of lead acetate. The test-tube may be warmed slightly to expel the gas, when a dark-colored stain will appear on the filter-paper, due to the formation of PbS.

Sulphites evolve SO_2, odor of burning sulphur. Sulphites in *neutral* solution may be further identified by the deep-red color produced with ferric chlorid. The color is discharged upon addition of dilute acids, HCl, or H_2SO_4 (difference from HCyS).

Thiosulphates *also* evolve SO_2, but at the same time the mixture becomes cloudy from precipitation of sulphur.*

Thiosulphates in neutral solution treated with ferric chlorid give a violet to purple color, fading (rapidly upon warming) to a colorless solution. In mixtures of sulphites and thiosulphates both acids may often be detected by the use of $FeCl_3$, the deep-red coloration of the mixed acids rapidly fading to the lighter red of $Fe_2(SO_3)_3$ (not to colorless solution).

Cyanids evolve HCN, odor of peach-stones. (Mercuric cyanid does not respond to this reaction.) Confirm by reactions given under Group II.

Preliminary Tests for Common Acids of Groups II and III.

(In preparatory courses the acids given in this list may be sufficient.)

From the acids of Group II and III it may be desirable to select for laboratory practice, at least at the beginning of the acid work, the more common members of the groups. These will be HCl, HBr, HI, HCN, and H_2S of Group II and H_2SO_4, $H_2C_2O_4$, and H_3PO_4 of Group III; and tests for them may be made as follows:

Chlorids give with $AgNO_3$ in presence of HNO_3 a white curdy precipitate of AgCl, much more freely soluble in ammonia than any other acid of the group here given except the cyanid AgCN, but HCN is a member of the *first* acid group and would have been previously detected.

* Sulphids may also precipitate sulphur in presence of compounds capable of oxidizing the H_2S, such as $FeCl_3$. In the absence of sulphates either H_2SO_3 or $H_2S_2O_3$ can be oxidized to H_2SO_4 by heating with HNO_3 and a precipitate of $BaSO_4$ obtained with $BaCl_2$.

Bromids with $AgNO_3$ and HNO_3 give a precipitate of AgBr similar in appearance to AgCl, but with a slightly yellowish color and only sparingly soluble in NH_4OH.

The tests, described on page 91, should also be made if bromids or iodids are suspected in the solution.

Cyanids, see Group I.

Sulphids will give a black precipitate with $AgNO_3$, and have been previously considered in Group I.

Sulphates may be detected by first acidifying the solution strongly with HCl (filtering out a precipitate if any occurs) and adding solution of $BaCl_2$; a white precipitate will then be $BaSO_4$, showing presence of sulphates in solution tested.

Phosphates in a solution containing HNO_3 and free or nearly free from HCl will give, with ammonium molybdate, a yellow crystalline precipitate of ammonium phosphomolybdate.

Oxalates may be detected, in a solution free from sulphates and which is slightly acid with acetic acid, by simple addition of calcium chlorid, which will precipitate CaC_2O_4, white and crystalline.

Detection of Acids of Group II.

(Giving precipitate with $AgNO_3$ in presence of dilute HNO_3.)

To the solution to be tested add a *very* slight amount of HNO_3 and a few cubic centimeters of $AgNO_3$ solution. A precipitate indicates acids of this group.

(*a*) If the precipitate is white, the presence of chlorids (HCl), cyanides (HCN), sulphocyanates (HCNS), ferrocyanates (H_4FeCy_6), hypochlorites (HClO),* or nitrites (HNO_2) is indicated.

* Precipitate is AgCl. Reaction is $3\ NaClO + 3\ AgNO_3 = 2\ AgCl + AgClO_3 + 3\ NaNO_3$.

To separate or identify these silver precipitates allow to settle, decant the supernatant fluid, and add NH_4OH. Shake thoroughly, when the chloride (AgCl), cyanide (AgCN), and nitrite ($AgNO_2$) will dissolve easily, the sulphocyanate (AgCyS) and the ferrocyanide (Ag_4FeCy_6) slowly or slightly.

If HCyS, or H_4FeCy_6 is indicated, test original solution with a few drops of $FeCl_3$. Sulphocyanates or thiocyanates (HCNS) give a deep blood-red solution. The color is soluble in ether and may be discharged by $HgCl_2$. Ferrocyanids (H_4FeCy_6) give a deep-blue precipitate. (See page 45.)

Acids forming white silver and precipitates, easily soluble in ammonia, may be distinguished as follows:

Chlorids (HCl) may be distinguished from HBr and HI by the ready solubility of the silver precipitate in NH_4OH. If bromids and iodids are present, liberate the halogens by means of MnO_2 and H_2SO_4 and pass the mixed gases into a solution of anilin in acetic acid (4 c.c. of saturated aqueous solution of anilin and 1 c.c. glacial acetic acid). Iodin gives no precipitate, bromin gives a white one and chlorin a black one. (Prescott and Johnson, page 336.)

This is a delicate and very satisfactory test for bromin but not so delicate for chlorin in the presence of bromids. For such cases the following *chloro-chromic anhydrid test* is recommended. Neutralize the solution if necessary, evaporate to dryness, transfer residue to a test-tube of rather small diameter, add a little solid $K_2Cr_2O_7$, then concentrated H_2SO_4. Decant the *fumes* into a wider test-tube containing a few centimeters of NH_4OH.

If the chloro-chromic anhydrid is evolved, ammonium chromate will be formed. Test by making acid with acetic acid, then adding acetate of lead. A yellow precipitate of lead chromate indicates chlorin in the original solution.

Hypochlorites liberate I from KI without the addition of acid.

Note. — Hypochlorite solutions are usually quite strongly alkaline, and in such cases a considerable amount of iodid is necessary to obtain the characteristic color in chloroform or with starch.

Nitrites liberate I from KI after the addition of acetic acid. They also give a brown coloration with acetic acid and a crystal of ferrous sulphate. (Nitrates require a stronger acid.)

Note. — This test is much more delicate than either of the others given, and if the solution is very dilute it is well to make it, even if the indigo color is not discharged.

Further mix a little of the solution with a few cubic centimeters of dilute indigo solution and shake. The indigo is decolorized by either hypochlorites (HClO) or by nitrites (HNO_2).

Cyanids may be tested for as under Group I. If this test is not conclusive, they may be converted into sulphocyanides by the addition of a few drops of $(NH_4)_2S$ and evaporation on the water-bath to dryness. It may then be dissolved in a little distilled H_2O, filtered and tested with $FeCl_3$.

(*b*) The precipitate is red-brown or orange, soluble in NH_4OH = H_3FeCy_6. *Ferricyanid* indicated.

(*c*) The precipitate is black or turns black upon warming: H_2S turns black immediately. HH_2PO_2 starts to precipitate white, but rapidly turns black, $H_2S_2O_3$ precipitates white and turns black slowly or upon heating.

Sulphids (H_2S) and **thiosulphates** ($H_2S_2O_3$) may also be detected as described under Group I, Acids.

(*d*) If the precipitate, originally obtained, is yellow and insoluble in NH_4OH, *iodids* are indicated; if yellowish white and slowly soluble in NH_4OH, *bromids* are probably present.

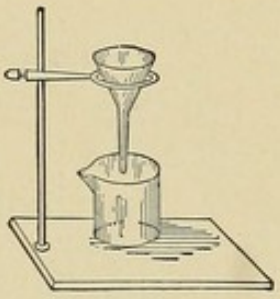
Iodids and **bromids** (HI and HBr) may be detected in the same solution by adding Cl water, very cautiously at first, and shaking with chloroform. The Cl liberates the iodin, which is dissolved by the chloroform with violet color. Excess of Cl decolorizes the iodin and liberates the bromin, which, in turn, is dissolved by the chloroform with yellow to red color.

Acid Group III.

(Acids forming insoluble barium or calcium salts, not included in the Acid Group I or II.)

The members of this group may be separated from each other, although this is not necessary unless several members are present. H_2SO_4, $H_2C_2O_4$, H_2CrO_4, H_2SiO_3, H_3BO_3, H_3PO_4, separated as follows: To a little of the unknown solution add 2 or 3 c.c. of HCl; a white or gelatinous precipitate which is not dissolved by dilution with water and warming is probably silicic acid. Make a bead test with microcosmic salt; the particles of SiO_2 remain undisturbed by the hot bead, forming the so-called silicon "skeleton." Filter out the silicic acid and add $CaCl_2$ or a mixture of $BaCl_2$ and $CaCl_2$; a white precipitate will be $BaSO_4$* (test for *sulphates*). The Ba and Ca salts of all remaining acids of the group being soluble in HCl.

Filter out the $BaSO_4$, and to the filtrate add NH_4OH, which will cause a precipitate of barium *oxalate*, *chromate*, *borate*, and *phosphate*. Filter, wash precipitate two or three times, reject wash-water, then transfer to test-tube by making a small hole in point of paper and forcibly washing through with the least possible amount of water; acidulate strongly with acetic acid, which will dissolve the phosphates and borates, leaving undissolved the oxalates (BaC_2O_4, white) and chromates ($BaCrO_4$, yellow.)



Oxalic and chromic acids as barium salts.

Phosphoric and boric acids.

* If the HCl is too strong, $BaCl_2$ may be precipitated as such, but the precipitate in this case will form more slowly than the $BaSO_4$; it will have a crystalline appearance and will dissolve upon addition of water.

Divide the filtrate into two parts, (*a*) and (*b*). Test one part, (*a*), for H_3PO_4 by adding to it an excess of ammonium molybdate* (in HNO_3), when a yellow precipitate (forming sometimes after several hours' standing) is ammonium phosphomolybdate (test for *phosphates*); the mixture may be warmed to hasten precipitation; the degree of heat should not exceed 40° C., as the ammonium molybdate might be decomposed, giving a yellow precipitate similar to the phosphomolybdate.

Note.— If As is present, it must be removed by H_2S before testing for H_3PO_4.

Test the other part, (*b*), for H_3BO_3 by evaporating to dryness in a porcelain dish; then moisten with strong H_2SO_4, cover with a little alcohol, and ignite. Boric acid will give to the flame (particularly the edge) of the burning alcohol a green color due to formation of ethyl borate. This color is more easily apparent if the dish is placed in a darkened corner.

A test for H_3BO_3 may also be made with turmeric paper, which if dipped into a solution of boric acid, or of a borate mixed with HCl or H_2SO_4 to slight but distinct acid reaction, and dried at 100°, becomes red; the red color becomes bluish black or greenish black when moistened with a solution of an alkali or an alkaline carbonate. If there is a suspicion that H_2CrO_4 and $H_2C_2O_4$ are both present, dissolve the precipitate of barium oxalate and chromate off the paper with dilute HCl; divide the filtrate into two parts and test one for H_2CrO_4 by addition of H_2O_2, which with chromates in presence of HCl produces a deep-blue solution and ultimately $CrCl_3$.

In the *absence* of chromates, the precipitate being white, oxalates may be confirmed by coloring the second part of the solution a faint pink with a dilute solution of $KMnO_4$ and warming, when the color will be discharged.

In the *presence* of chromates, the precipitate being yellow, it will be necessary to test the original solution for oxalates

* Preparation of ammonium molybdate solution, appendix p. 377.

as follows: To a few centimeters of the unknown add alcohol; warm. The chromate will be reduced to $CrCl_3$. Add NH_4OH till alkaline and filter out the precipitate, $Cr(OH)_3$. The filtrate may be tested for oxalic acid as above, or with $CaCl_2$; a white precipitate being CaC_2O_4.

Acids of Group IV.

The remaining acids of importance not included in either of the three preceding groups are nitric, HNO_3, chloric, $HClO_3$, and acetic, $HC_2H_3O_2$.

Nitrates. — Saturate 5 c.c. of a very dilute nitrate solution with $FeSO_4$. Filter and carefully underlay the clear filtrate with concentrated sulphuric acid; a dark ring (pale red-brown to nearly black) at point of contact of the two liquids shows presence of a nitrate.

Chlorates. — A solution free from chlorids or hypochlorites treated with Zn and dilute H_2SO_4 will give a test for HCl if chlorates were originally present, the chlorate having been reduced by the nascent H:

$$2\,KClO_3 + 6\,Zn + 7\,H_2SO_4 = 6\,ZnSO_4 + K_2SO_4 + 2\,HCl + 6\,H_2O.$$

Boiling with sulphurous acid also reduces $HClO_3$ (and HClO) to HCl.

If the substance is in solid form, a *very small particle* may be warmed with concentrated H_2SO_4. Chlorates detonate and give off yellow fumes of ClO_2:

$$3\,KClO_3 + 2\,H_2SO_4 = 2\,KHSO_4 + KClO_4 + 2\,ClO_2 + H_2O.$$

Acetates give with ferric chlorid a red color which is not discharged by $HgCl_2$ (difference from sulphocyanate), but may be discharged by HCl (difference from sulphocyanate and meconate).

A more positive test is the formation of the ethyl ester

or acetic ether. A blank test for comparison should always be made, the method of procedure being as follows:

Take two test-tubes of practically equal diameter, mix in each equal volumes of alcohol and strong H_2SO_4; warm the tubes together; then into one introduce a few centimeters of the unknown solution, and into the other an equal volume of H_2O. Heat again to a boiling-point and compare the odors from the two tubes. The acetate is easily detected if present.

Laboratory Exercises XXIV and XXV.

Unknown Solutions Containing Acids and Bases of Group VI.

CHAPTER X.

ANALYSIS IN THE DRY WAY.

In the examination of solid substances much may be learned by a few simple tests directly applied to the substance, which has been reduced (if necessary) to the form of a powder.

Some of these are usually used as preliminary to the solution of the substance and regular analysis in the wet way. These tests may be made quickly, and, with a little elaboration, will often give all the information required regarding an unknown substance.

The practical questions of actual experience are usually simple ones. It is not an analysis of an unknown solution possibly containing all the metals of one or more groups that interests an active practitioner, but a specific inquiry as to whether or not this or that preparation contains or does not contain the necessary or the undesirable ingredient, whether the thing is of the composition or of the strength represented, and a few minutes' work in the laboratory, especially if aided by the microscopical tests given in a subsequent chapter, will frequently be found sufficient to answer questions of this character.

The tests made in the dry way are not as delicate, nor are the results obtained (especially negative ones) as conclusive, as those of a systematic analysis of the substance in solution, and in occasional cases it may be necessary to resort to the more tedious process.

Before undertaking the analysis of a substance, note carefully its physical properties of odor, color, and solubility; also whether it is magnetic, metallic, or crystalline.

The volatile acids, certain ammonium compounds, bromin, and iodin may be detected frequently by their odor.

Colors of Salts and Solutions.

The following colored salts are *soluble* in water:

Black	Silver albuminate (argyrol, etc.).
Violet or purple	Chromic salts and permanganates.
Red	CrO_3 and acid chromates, K_3FeCy_6, sodium-nitro-prusside, H_2PtCl_6.
Reddish brown or purple-red	Manganic salts.
Reddish yellow	Ferric salts and $AuCl_3$.
Yellow	Neutral chromates of the alkalies, salts of uranium.
Pale yellow	K_4FeCy_6 (Potassium ferrocyanide).
Pink	Salts of cobalt.
Pale pink	Manganous salts.
Green	Ferrous salts, nickel salts, certain copper salts.
Dark green	Some chromic salts.
Blue-green	Chromates.
Blue	Cupric salts.

The following colored substances are *insoluble* in water:

Black	Carbon and carbids, metals, many metallic sulphids, oxids of Cu, Fe, Mn, and Pb. Iodin is bluish black.
Red	HgO, HgS, HgI_2, Pb_3O_4, As_2S_2.
Brick-red	Amorphous phosphorus, Fe_2O_3.
Light brown	PbO (litharge).
Yellow	S, HgO, CdS, As_2S_3, PbI_2, Ag_3PO_4, ammonium phospho-molybdate, and chromates of the heavy metals, $PbCrO_4$, $BaCrO_4$.
Green	Some copper compounds, Cu_2I_2, Paris green, etc., Cr_2O_3.
Blue	Some copper compounds, Prussian blue, ultramarine; anhydrous salts of cobalt.

METHODS OF EXAMINATION.

Powder the substance and apply tests described in this chapter, which will be considered in the following order:

A. Ignition with free access of air.
B. Closed-tube test.
C. Flame test on platinum wire.
D. Examination with the blow-pipe on plaster slab.
E. Bead tests on platinum wire.
F. Special tests, distinguishing or confirmatory.

A. Ignition in Air.

This test may be made on a crucible cover or on platinum foil. If there is any probability of I, Br, Cl, P or easily reduced metallic compounds in the unknown substance, the platinum foil is likely to be destroyed; hence, the porcelain is recommended.

The heat employed should be very low at first; then it should be gradually increased and the test carefully watched.

The majority of phenomena occurring under A are more easily observed in the test made with the closed tube, B, and will be given under that head.

Observed Phenomena.	Indications.
The substance *melts* and steam is given off.	Water of crystallization, NH_4NO_3 or $H_2C_2O_4$, which entirely disappear.
The substance *burns* (*a*) at comparatively low temperature with blue flame and odor of SO_2 or burning matches.	Sulphur.
(*b*) With yellow flame and much smoke.	Fat, waxes, resins, etc.
(*c*) Blackens and then burns at fairly high temperature, leaving white or gray ash.	Carbonaceous matter other than fats, etc.
(*d*) Blackens without burning.	Formation of oxids of Fe, Co, Ni, or Cu.
Vapors are given off:	
(*a*) Of a violet color.	Iodin.
(*b*) Of a red-brown color.	Br or nitrogen oxids.
(*c*) Of a greenish-yellow color.	Chlorin or ClO_2.
(*d*) White, practically odorless.	Some ammonium salts, NH_4Cl, $(NH_4)_2SO_4$, etc.

Observed Phenomena.	Indications.
(*e*) White with odor of NH_3.	Ammonium carbonate.
(*f*) White with odor of garlic.	Arsenic.
(*g*) White and yellow with ammoniacal or empyreumatic odor.	Organic matter.
The substance decrepitates.	Water held mechanically by crystals, as NaCl, etc.
Examine residue on foil (porcelain); add a drop or two of water and test with litmus-paper.	
If found to be acid.	Acid salts.
If alkaline without blackening.	Fixed alkali hydrates or carbonates.
If alkaline with blackening.	Carbonate formed by combustion of organic compounds.
Add a drop of dilute HCl, effervescence.	Carbonates.

B. Closed-tube Test.

Select a tube of soft glass about 5 or 6 inches in length. Seal one end and enlarge slightly. Into the bulb thus formed introduce a few grains of the unknown powdered substance. Heat carefully, making the following tests at various stages of the process. Note the odor of escaping gases.

Test for oxygen by inserting a glowing splinter into the tube.

Test for combustible gases by occasionally applying flame to the open end of the tube.

Bring to the mouth of the tube a clear drop of $Ba(OH)_2$ solution. If the drop becomes turbid, CO_2 is indicated.

Observed Phenomena.	Indications.
Steam condenses in cold part of tube.	See under A.
Oxygen is evolved.	A peroxid, chlorate, some oxids (as HgO), alkali nitrates.
Carbon Dioxid is evolved.	Carbonates, oxalates (at high temperature), organic matter.
A Combustible Gas is formed:	
(*a*) Burning with a luminous flame, black residue remains in tube.	Hydrocarbons from organic matter.
(*b*) Burning with a blue flame.	CO from oxalates.
(*c*) Burning as in (*b*) and with odor of SO_2.	H_2S from moist sulphids.
A Sublimate forms in the cooler part of the tube. Examine under microscope.	

Observed Phenomena.	Indications.
Colorless with partial decomposition.	Oxalic acid. Plate 1, Fig. 1.
Color is *white* with production of garlic odor, crystalline.	As_2O_3. Plate 1, Fig. 2.
Color is *white* when cold. Yellow when hot, crystalline.	$HgCl_2$. Plate 1, Fig. 3.
Color is white — it sublimes directly without melting and blackens with NH_4OH.	HgCl.
A white sublimate which by treatment with slaked lime yields NH_3.	Ammonium salts. Plate 1, Fig. 4.
A white sublimate of As_2O_3 with black residue in tube and odor of acetic acid.	Paris green.
Sublimate is gray, consisting of small globules which can be made to unite by rubbing.	Hg from HgO, amalgam, etc. Plate 1, Fig. 5.
Sublimate consists of reddish yellow to red globules, yellow when cold.	Sulphur.
Sublimate darker than above and reddish yellow when cold.	Native sulphid of arsenic.
Sublimate is brown to black " metallic mirror," soluble in NaClO.	Metallic arsenic.
Ditto; dead black, insoluble in NaClO.	Metallic antimony.
Sublimate is black accompanied by violet vapor.	Iodin. Plate 1, Fig. 6.
Sublimate black, turning red when rubbed.	HgS, cinnabar.
No sublimate is formed, but the COLOR CHANGES to	
Yellow when hot, white when cold.	ZnO.
Reddish brown when hot, yellow when cold.	PbO or Bi_2O_3. (See D.)
Black when hot, red when cold.	HgO (Hg sublimes).
Black when hot, brick-red when cold.	Fe_2O_3.
Dark orange when hot, yellow when cold.	Chromates of Pb, etc.
BLACK RESIDUE without other visible manifestation.	Oxids of Cu, Co, etc. (See A.)
SUBSTANCE MELTS without a sublimate being formed.	Salts of the alkaline metals.

C. Flame Test with Platinum Wire.

Introduce the substance on platinum wire into the edge of the flame. More satisfactory results are sometimes obtained if the solid is first moistened with HCl (page 71, note). The flame is colored as follows: by Na, yellow; K, violet; Li, carmine; Sr, crimson; Ca, orange-red; Ba, yellowish green; Cu, usually bright green; $CuCl_2$, an intense blue; H_3BO_3, pale green; Sb, greenish blue; Pb, As, Bi, livid blue.

PLATE I.—SUBLIMATES.

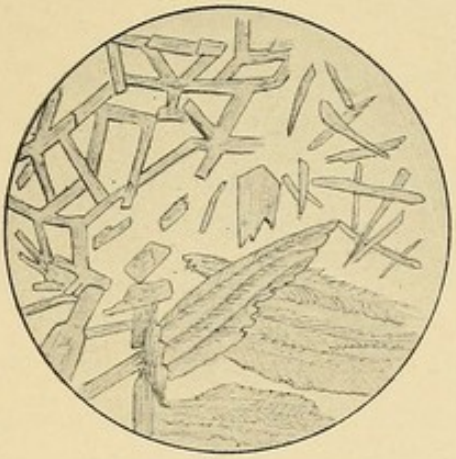


FIG. 1.
Oxalic Acid (Sublimed).

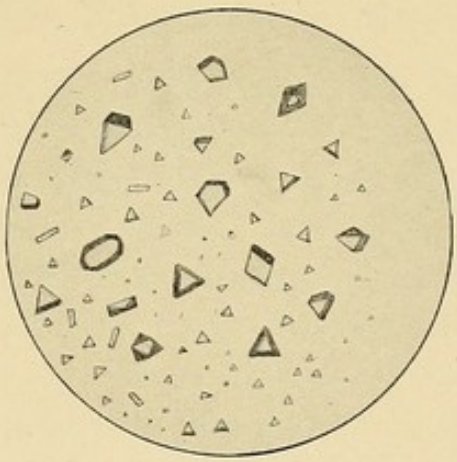


FIG. 2.
Arsenic Trioxid.

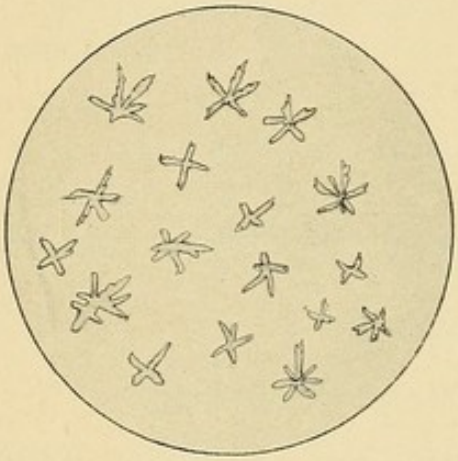


FIG. 3.
Mercuric Chlorid (Sublimed).

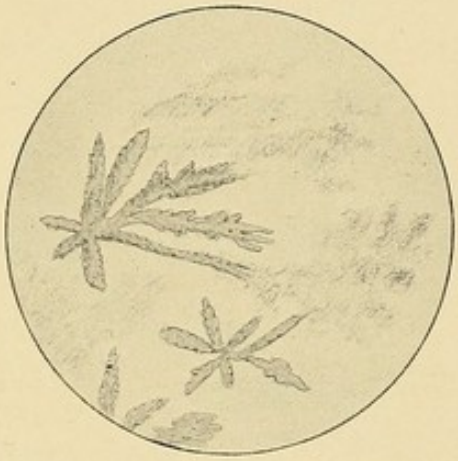


FIG. 4.
Ammonium Sulphate (Sublimed).

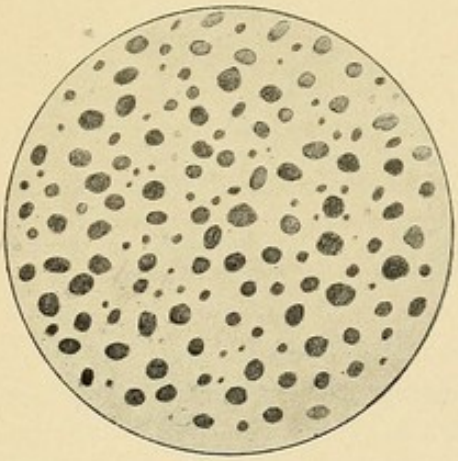


FIG. 5.
Mercury from HgO.

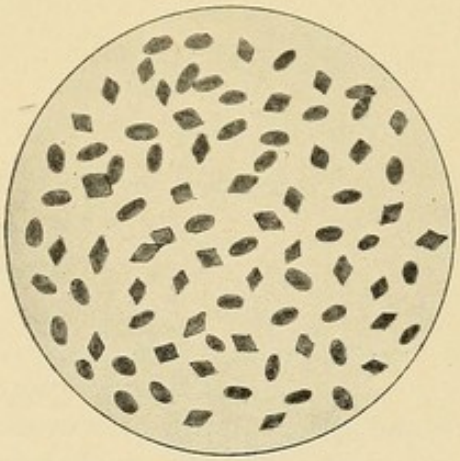


FIG. 6.
Iodin.

D. Blowpipe Test on Plaster.*

Smooth plaster slabs about 1 inch wide and 4 inches long are well suited for these tests. These may be prepared by making a magma of calcined plaster and pouring upon a glass plate. Before it hardens mark deeply with a spatula into slabs of desired shape and, after it is thoroughly dried, break as marked.

Make a little depression near one end of the slab and in it place a small amount of the substance to be tested; then if a fine oxidizing flame is made to play over the *surface* of the assay, characteristic coatings of oxid or sublimate may be obtained.

In many cases the character of the substance may be determined more easily by first moistening the assay with various reagents. Tetrachlorid of tin, cobalt nitrate, and "sulphur iodid" are the most valuable of the reagents so used. The "sulphur iodid" is not of definite composition, but a mixture of about equal weights of sulphur and potassium iodid.

D. I. *Examination without Reagents.*

Observed Phenomena.	Indications.
Substance melts to bright metallic globules with brownish-yellow deposit near assay. Requires high heat. Assay revolves.	Silver.
Substance melts to bright globule with coating on plaster, deep orange when hot, light yellow when cold.	Lead or bismuth (See D. II.)
Substance remains or becomes black without melting. No coating on plaster.	Copper or iron. (See A; also F.)
Substance volatilizes with white fumes, but leaves dark stain; gray to black.	Antimony or arsenic. See F.)
Substance melts with white or gray oxid on assay.	Tin. (See D. III.)
Forms a white or gray oxid *without* fusion. Coating on plaster is yellow over brownish black.	Cadmium.

* Substances sufficiently identified by previous tests have been omitted. This method will be found useful mainly in the identification of metals.

The Author was greatly aided in the preparation of this list by Mr. Geo. F. S. Pearce of the Harvard Dental School, who carefully verified each test.

Observed Phenomena.	Indications.
Forms bulky white oxid with active combustion of assay.	Magnesium.
Forms gray coating easily volatilized.	Mercury from amalgams. (See D. II.)
Cherry-red — crimson to black according to amount of substance deposited. Odor of rotten horse-radish; coating not permanent.	Selenium.
White coating or white fumes at very high heat. Assay burns with bluish-white light.	Zinc. (See D. III.)
Silver-white. Assay remains unchanged.	Platinum, metallic.

D. II. *Cover Substance with KI and S. Use Oxidizing Flame.*

Observed Phenomena.	Indications.
Dirty-white and light-gray coating. Treated with fumes of strong NH_3 and again placed in oxidizing flame gives bright-red color. Metallic globule is dull and brittle.	Bismuth.
Dirty white half an inch from assay. Brown directly under assay. No change when treated as above with strong ammonia fumes. Metallic globule is bright and malleable.	Lead.
No coating near assay. Lead-colored, one to one and a half inches, shading to yellow.	Mercury.
Coating bright red when hot, fading to yellow when cold.	Cadmium.
Fine brown coating, very volatile.	Antimony.

D. III. *Examination with Solution of Cobalt Nitrate.*

Heat substance on plaster in the oxidizing flame, moisten well with cobalt nitrate, and again apply oxidizing flame.

Observed Phenomena.	Indications.
Color is deep blue.	Aluminium.
Substance is infusible.	Infusible silicates. (See F.)
Color is fine blue. Substance fusible.	Alkaline silicate, borate, or phosphate.
Color is yellowish green.	Zinc.
Drab to bluish green.	Tin.

D. IV. *Examination with Tetrachlorid of Tin.*

Observed Phenomena.	Indications.
Coating pale blue to lavender.	Bismuth.
Coating fine blue, in places almost black.	Antimony.
Delicate pink to red produced only by oxidizing flame.	Neutral and acid chromates.

E. Bead Tests.

The bead tests are made with borax, as described on page 51, or in a similar manner with microscosmic salt, $NaNH_4HPO_4$, which by action of the heat gives up NH_3 and H_2O, becoming sodium metaphosphate, $NaPO_3$. These substances fused on a loop of platinum wire unite with many of the metallic oxids, forming "beads" of various characteristic colors, some of the more important being given below.

With Borax.

Co in the oxidizing flame gives an intense blue bead.
Ni gives a red-brown, yellow when cold.
Cu gives a green, blue, or bluish green when cold.
Cr gives green.
Fe gives a red, yellowish when cold.
Mn gives an amethyst.

With Microcosmic Salt.

Cobalt, copper, nickel, and iron give colors similar to those obtained with borax. Manganese gives a violet bead when heated in the oxidizing flame, but a colorless one in the reducing flame.

F. Special Tests Distinctive or Confirmatory.

The oxids of copper and iron may be distinguished by adding a drop of HNO_3, warming gently to drive off excess

of acid (high heat will decompose the nitrate, giving the oxid again), and then adding a drop of solution of K_4FeCy_6. Fe will give a dark-blue coloration; Cu will give a brown.

To distinguish between As and Sb stains, add a drop of hypochlorite solution (NaClO). The arsenic stain will dissolve; the antimony stain will remain unaffected (see page 33).

Antimony gives a very characteristic coating on plaster if treated with tetrachlorid of tin. The coating is bluish black near assay, fading away to a very delicate color at greater distance. It appears almost immediately and is permanent.

In case of suspected silicates make the "silica skeleton" with a bead of microcosmic salt (page 92).

Laboratory Exercise XXVI.

Preliminary tests with metals and solids other than salts.

Laboratory Exercises XXVII and XXVIII.

Identification of unknown metals and analysis of solid substances.

PART II.

DENTAL METALLURGY.

INCLUDING THE CHEMISTRY OF ALLOYS, AMALGAMS, SOLDERS, AND CEMENTS.

CHAPTER XI.

THE METALS.

Properties of the Metals.

Metals are *malleable* in order as follows from gold, the most malleable, to nickel, the least: Au, Ag, Al, Sn, Cu, Pt, Pb, Cd, Zn, Fe, Ni.

Metals are *ductile* from most to least as follows: Au, Ag, Pt, Fe, Ni, Cu, Cd, Al, Zn, Sn, Pb.

Metals conduct heat and electricity in the same order until Sn is reached. From Sn the order given is correct for heat but not for electricity: Ag, Cu, Au, Al, Zn, Cd, Sn, Fe, Pb, Pt, Bi.

The melting-point of the various metals is of considerable importance in the preparation of alloys. The following table has been compiled from the latest available results. The degrees given are according to the centigrade scale:

Pt	2000°	Cu	1054°	Zn	420° (burns)
Ni	1450°	Ag	954°	Pb	326°
Cast steel	1375°	Al	700°	Cd	320°
Cast iron	1275°	Mg	500° (burns)	Bi	268°
Au	1075°	Sb	432°	Sn	238°

The expansion of the various metals under the influence of heat is fairly constant and there have been determined *coefficients of expansion.* These represent the amount of linear expansion of the metals due to a rise in temperature of 1° C., usually from 0° to 1°. The coefficients are not *absolutely* constant, and the amount of expansion observed between 0° and 1° may differ somewhat from that between 50° and 51°. The coefficients vary widely for the different metals; for instance, in passing from 0° to 100° mercury expands 1/16 of its linear measure, copper 1/598, and platinum 1/1123.

Hall's Dental Chemistry gives the following table of expansion from cadmium to platinum:

Cd	1/326	Ag	1/518	Ni	1/787
Pb	1/342	Cu	1/598	Fe (cast)	1/934
Zn	1/343	Bi	1/617	Sb	1/952
Al	1/432	Au	1/689	Pt	1/1123
Sn	1/448				

The only other general property of the metals directly affecting their use in dental practice is the electric or galvanic, that is, the electropositive or negative relations they sustain to one another.

The metals are electropositive to each other in the following order from zinc, the most positive, to platinum, the least: Zn, Cd, Sn, Pb, Fe, Ni, Bi, Sb, Cu, Ag, Au, Pt; and C is negative to all.

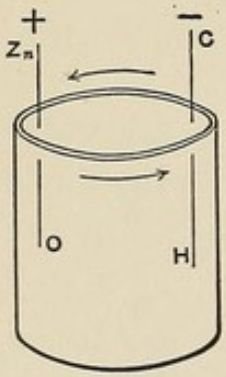


FIG. 5.

Thus if a battery is constructed with Zn as represented in the cut (Fig. 5), and iron in place of the carbon, then the iron will be electronegative to the zinc, and hydrogen will be evolved from its surface; if, on the other hand, Fe is used in place of the zinc, and the carbon remains as in the cut, the Fe will be electropositive to the carbon, and oxygen will be evolved from its surface. This property of metals has a direct bearing upon

dental science, because human saliva may be an exciting fluid for the generation of galvanic currents, its activity being increased by an abnormal reaction either acid or strongly alkaline, and it is only necessary to place in the mouth properly related metals, as amalgam fillings or otherwise, to produce the elements of a galvanic battery.

The currents thus generated are, of course, infinitesimal, but they are constant and may aid in the disintegration of fillings and in the solution of the constituent metals. Regarding the extent to which electric currents may exist in the mouth, see Miller's Micro-organisms of the Human Mouth.

CHAPTER XII.

ALLOYS.

An intimate union of two or more metals, usually produced by fusion, forms an *alloy*. Such a union of one or more metals with mercury is an *amalgam*.

An alloy designed to be used in the preparation of dental amalgams is known as an *amalgam alloy*.

Some metals can be fused together in all proportions, as Pb and Ag. Others can be made to unite only in limited proportions, as Pb and Zn. Lead will carry only 1.6% of zinc, while zinc will unite with only 1.2% of Pb. Excess in either case separates out.

The *properties* of an alloy are, as a rule, the modified properties of its constituent metals. An exception to this rule might be made of the sonorous quality of bell-metal and like alloys, this being hardly a property of the constituent metals at all.

Following are some of the more common alloys. The proportions given are general formulæ and may, as a rule, be varied considerably:

Aluminium bronze, yellow, resembles gold, Cu 92, Al 8.
Bell-metal, Cu 80, Sn 20.
Brass, Zn 1, Cu 2.
Britanniametal, Cu 2, Sn 82, Sb 16.
Bronze, Cu 65 to 84, Zn from 31.5 to 11, Sn from 2.5 to 4.
Coin silver, Ag 90, Cu 10.
Dental alloys, see page 117.
Dental gold, Cu 85, Zn 15.
German silver, Cu 50, Ni 30, Zn 20.

Composition of different samples of German silver may differ widely; some contain about 2.5% of iron and the amount of Cu may vary from 40 to 60%.

Gun metal, Sn 11, Cu 100.

Solder, see page 127.

Sterling silver must contain 92.5% Ag.

Type metal, Pb 78, Sb 15, Bi 7.

All alloys (excluding amalgams) are solid at ordinary temperatures with one exception; this one is an alloy of one part potassium with three parts sodium.

The *melting-point* of an alloy is often lower than that of the metals entering into its composition and usually lower than the mean melting-point of its constituents.

In *making alloys* the tendency to separation of the several metals is greater if the alloy is allowed to cool slowly; hence three essentials in the process are: *Complete fusion*, which makes possible *thorough mixing*, and after this has been attained *rapid cooling*. As the fused mass is to be cooled as quickly as possible after fusion is complete, it is desirable to use the least amount of heat practicable in effecting the desired result. To this end fuse first the metal with the lowest melting-point, then add other metals in the order of their melting-points. The more difficultly fusible metal will in a sense dissolve in the more easily fusible metal; an alloy is formed and its temperature has been kept far below the melting-point of the high fusing constituent. This general rule, however, may be modified by the proportion of metal used; thus, in making a silver-tin amalgam-alloy containing 60% of silver it is better first to melt the silver under a flux of carbonate of sodium or borax to prevent superficial oxidation, then add the tin, and lastly any other metal to be used. The *mixing* is attained by stirring with a *wooden* stick and the *cooling* by turning quickly into a cold clean mold. For class work or in making small amounts (20 grams) of alloy, the Fletcher melting arrangement shown in Fig. 6 is

very convenient. The metals are melted in the graphite crucible and then by tipping up the whole contrivance the melted metals flow back into the ingot mold. If the alloy is to be used in the preparation of dental amalgams it must be reduced to fine turnings or filings suitable for ready amalgamation. This is best accomplished in the laboratory by means of a coarse file, the ingot being held by a vise. The fine particles of iron must next be carefully removed with a magnet, and then the filings may be annealed if desired.



FIG. 6.

The *annealing* of the amalgam-alloys may be accomplished by placing the freshly cut sample in a dry test-tube and keeping the test-tube in boiling water for ten or twelve minutes. It has been claimed that this process is one of superficial oxidation and the changes produced seem to be consistent with this theory. Again, it is claimed that the change is a molecular one of some sort due to change of temperature, and Prof. G. V. Black has shown that an alloy will anneal as rapidly in an atmosphere of nitrogen as of oxygen. The modification of properties produced by annealing varies somewhat with the composition of the alloy; for instance, the liability to discoloration is less in the annealed than in the unannealed sample, if the alloy contains Ag and Sn, or Ag, Sn, and Zn, but if Cu is a constituent the reverse condition has been found to exist.

According to Professor Hall of Northwestern University, "annealed alloys take up less mercury than unannealed and yield upon mixing a greater quantity of dirt, which consists of a lower oxid of tin." The amalgam made from an annealed alloy works more easily than from an unannealed.

The process of annealing up to a certain point seems to be, in general, beneficial; but beyond this point it may be detrimental, the amalgam being less strong and more liable to shrink.

Professor Black has shown that while it may be possible to stop the process of annealing at such a point that a given alloy

will neither shrink nor expand, it is easy to carry the process too far and the farther it is allowed to go the greater the shrinkage. It is probably true that the exact effect of annealing will vary with the composition of the alloy, and with different proportions of metals in alloys of the same general composition.

Annealing of Gold.

When gold-foil is heated to redness it recovers the cohesive property which has been lost largely by hammering. It is recommended that the heating be done in an electric furnace or on plates of mica or platinum, thus insuring uniformity of effect throughout the mass which it is practically impossible to obtain by holding the metal in the flame. See Dental Cosmos, Vol. XLVII, page 233.

Non-cohesive gold, or gold in which the cohesive property cannot be developed by heating, may be prepared by alloying or treatment with carbon. **Corrugated gold** is of this variety and is prepared, according to Essig, by carbonization of unsized paper in intimate contact with the metal. See Essig, Dental Metallurgy, page 173.

In annealing *platinum* a high degree of heat is required, but the heat should be raised gradually, and in this case also the electric furnace furnishes an ideal method.

Laboratory Exercise XXIX.

Analysis of an Unknown Alloy.

CHAPTER XIII.

AMALGAMS.

In general, amalgams may be made in three different ways: First, by direct union of the constituents, as in the manufacture of sodium amalgam (page 113); second, by electrolysis of strong solutions of metallic salts in presence of mercury, as in copper amalgam (page 114), and third, by double decomposition as illustrated in the preparation of ammonium amalgam (page 114).

Amalgams possess the peculiar property of "setting" or hardening within a short time after mixing. This in some cases seems to be a process of crystallization, and in all cases is probably due to molecular rearrangement of some sort.

After an amalgam has "set" to a sufficient extent to make it hard to work it may be softened by application of gentle heat. Continued reheating is detrimental to the quality of the amalgam, and should be avoided; this is particularly true of copper amalgam. It is also possible to sometimes restore the plastic quality of an amalgam by adding a further slight amount of mercury, but the union of the second lot of Hg after the first has partly hardened is very unsatisfactory and results in a weakened product.

Flow of Amalgams. — This property may be defined as the tendency to flatten or change shape under stress or pressure. It is common to most amalgams (copper amalgam being an exception, according to Dr. Black), and is possessed by many alloys other than amalgams.

Tests for "flow" may be made with the "dynamometer" on cubes of alloy or amalgam measuring one-tenth of an inch each way and the results expressed in percentage of increase or de-

crease of one dimension. The dynamometer used for this purpose is pictured in Fig. 7 and is a modification of the apparatus devised by Dr. Black and described on pages 408 and 409 of the Dental Cosmos, Vol. 37, *A-A* being the molds in which the cubes of amalgams are set and *B* the point in the apparatus where the cube after setting is introduced with a pair of fine forceps. The dial is supplied with two hands, one which flies back the instant the cube breaks, the other remaining to indicate the number of pounds applied necessary to crush the cube. The cubes of 1/10 inch are best suited for students' practice,

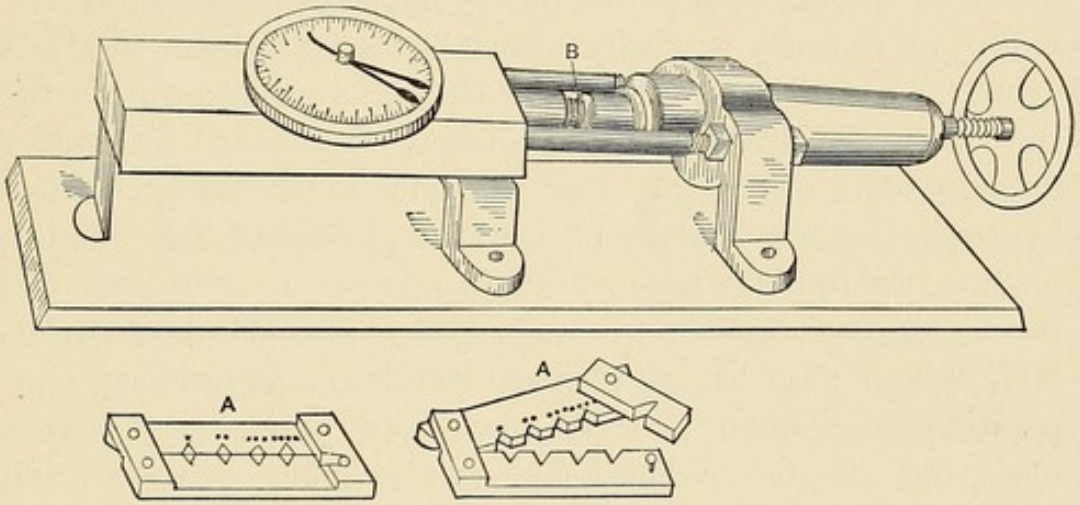


FIG. 7.

with a dial constructed to record 250 pounds pressure. For accurate comparisons of thoroughly made amalgams the cubes must be made smaller.

Binary amalgams, as they are sometimes called, are those consisting of only one metal besides mercury. These are rarely used in dental practice, but from them the properties of the amalgamated metal are most easily observed.

Sodium amalgam may be made by direct union of the constituent elements. The mercury should be placed in an open dish under a hood, and the sodium added in *small* well-cleaned pieces.

The union is accompanied by a slight hissing noise, an elevation of temperature and evolution of vapor carrying more or less mercury, hence dangerous to breathe. An amalgam containing 1% sodium is a viscid liquid; if it contains 5% sodium it is a hard solid and intermediate percentages give varying degrees of firmness. Sodium amalgam, if made with arsenic-free Hg, is a very convenient reagent to use in making Fleitmann's Test (page 29).

Ammonium amalgam has no use in dentistry, but it is of interest in that it is the nearest approach to which we may attain to the isolation of the purely hypothetical metal ammonium. It is easily made by adding sodium amalgam to a *cold* saturated solution of ammonium chlorid, thus illustrating the third general method of preparation of amalgams. It rapidly decomposes at ordinary temperature with the liberation of free hydrogen, ammonia-gas, and metallic mercury. The H thus liberated exhibits the properties of nascent H, indicating that in the amalgam it existed in true chemical combination, that is NH_4, rather than in any physical solution. At ordinary temperature ammonium amalgam is a soft, pasty, very porous mass, but at much reduced temperature it becomes solid and crystalline, although at -39° (the freezing-point of Hg) H and NH_3 are still given off.

Copper amalgam is by far the most valuable of this class of amalgams. It may be made by amalgamating precipitated copper after moistening it with nitrate of mercury (Essig). The precipitated Cu may be prepared by action of metallic Zn in a slightly acid copper sulphate solution, but must be thoroughly washed with hot water to free it from zinc chlorid. The amalgamation may be effected by use of mortar and pestle. Rollins' method* by electrolysis of strong copper sulphate solu-

* Details of this method may be found in the Boston Medical and Surgical Journal, February, 1886; also in Mitchell's Dental Chemistry.

tion is rather unwieldly, but illustrates very well the second general process for the manufacture of amalgams.

Copper amalgam, according to Black, is absolutely rigid after it has once set and does not flow even to a slight extent. It is fine-grained and very hard. It is reduced in strength by reheating and does not expand or contract. In the mouth copper amalgam dissolves with comparative rapidity owing to the ready formation first of copper sulphid, then, by the oxidation of this compound, of the sulphate. It blackens rapidly and in consequence of the tendency to dissolve just mentioned, it may penetrate the dentine and thus discolor the tooth itself.

Gold amalgam is readily made, but does not, by itself, harden well. An amalgam containing one part of gold to six of mercury will crystallize in four-sided prisms (Litch).

Platinum amalgam is very smooth, is formed with difficulty unless the Pt is *very* finely divided, and, like gold, does not harden well.

Silver amalgam, easily made but tends to expand.

Tin amalgam, alone shrinks badly.

Zinc amalgam, readily made, is white, but too *brittle* to be of service.

Cadmium amalgam may be easily made at ordinary temperature, "sets quickly, and resists sufficiently, but fillings containing it gradually soften and disintegrate and may stain the dentine bright yellow by formation of cadmium sulphid." (Mitchell.)

Effect of Various Metals in Amalgam Alloys.

With the properties of these simpler combinations before us it becomes easy to understand the effect the addition of the various metals will have upon the properties of a silver-tin alloy; for practically *all* amalgam alloys are silver-tin alloys, either simple or combined with one or more other metals.

Silver and tin are the most valuable constituents of amalgam

alloys. Silver is essential to the proper setting and hardening of the amalgam. It tends to increase expansion and to hasten setting, while tin possesses the opposite characteristics. Combined with tin in the proportion of 65% silver to 35% tin, it forms an amalgam alloy perhaps more largely used than any other. It was this combination that Dr. Black succeeded in "annealing to zero," that is, so that upon testing it showed neither expansion nor contraction.

Pure silver-tin alloys will flow from 2.5 to 10%.

Authorities seem to agree that if a Ag-Sn alloy contains 75% or more of silver it will expand only; while an alloy containing from 50 to 61 or 62% of silver will shrink only; and one containing less than 50% of silver will first shrink and then expand.

The larger the proportion of tin the easier will the alloy cut, but the coarser will be the filings.

Zinc added to a silver-tin alloy tends to whiten the amalgam, hastens setting, increases the flow, and, according to Essig, "causes a great but slow expansion."

Cadmium, see above.

Antimony gives a fine grain alloy and when the Ag is less than 50% is supposed to control shrinkage.

Bismuth will increase the flow of the amalgam; it is sometimes used in low-grade Ag-Sn alloys to control shrinkage.

Copper tends to diminish flow and gives a strength under pressure, sets quickly, gives better margins, and by some is believed to have preservative influence on the tooth substance, but the more copper in an alloy the more rapidly does it discolor.

Gold. — From three to seven per cent of Au in a silver-tin alloy diminishes shrinkage, helps the color and adds to crushing strength. The filing from such an alloy will be very fine.

Dr. Black says 5% of gold gives a softer working property but retards setting of the amalgam, and makes it otherwise

difficult to give a good finish to the filling (Dental Cosmos, Vol. 38, page 988).

Platinum, according to Black, is not a desirable addition to a silver-tin alloy. It gives an alloy furnishing *very* fine filing, which produces a dirty working, slow-setting amalgam.

Excess of Mercury. — In the preparation of an amalgam from a dental alloy it is usual to add more mercury than the finished product requires and then squeeze out the excess between the fingers or otherwise. In filling a cavity, still more mercury is forced out, so that the composition of the deeper portions of a filling varies from the outer portions and probably accounts for the inequalities in expansion or contraction. The excess of Hg from the surface of a filling may be absorbed by a little hot gold or pure tin or by finely divided silver.

Following is a short list of dental alloys, most of which may be easily prepared:

	Sn.	Ag.	Au.	Cu.	Zn.	Sb.
Arington's (S. S. White's)	57.5	42.5				
*(C. A. S.) alloy, C. Ash Sons Co.	27.16	66.54		5.02	0.90	
Chase copper-amalgam alloy	50	50		10		5
Chase's incisor alloy	40	50				10
*Fellowship alloy	26.80	67.45		5.73	0.55	
Flagg's submarine alloy	35	60		5		
Fletcher's gold alloy (old)	56	40	4			
High-grade alloy (7½% gold)	41.5	49	7.5		2	
Harris's amalgam alloy	48.1	40		4.9	7	
King's occidental alloy	54.75	42.75			2.5	
*Odontographic alloy	26.48	66.87	0.28	6.21	trace	
*Standard alloy	35.03	53.55	8.82	2.76		
Standard dental alloy (Eckfeldt)	40.6	52	4.4	3		
60% silver alloy	40	60				
Temporary alloy	88	10			2	
*True dentalloy	27.13	65.91		5.21	1.52	
*Twentieth century	27.13	67.03		4.87	1.10	

* Analyses by Dr. P. J. Burns of the Mass. Inst. Technology, reported in the Journal of the Allied Societies, June, 1908.

The excess of mercury which has to be squeezed out of an amalgam carries with it more or less of the constituent metals.

Hall found that whatever the amount of mercury expressed, it carried just about 1% of tin. In the author's experience this amount has reached nearly $1\frac{1}{3}$% of tin. Silver is carried out to a much less extent than tin, so it is not impossible to carelessly make an amalgam and squeeze out enough mercury to change the proportion of Ag and Sn in the alloy. This change will, of course, be very slight, but we have seen that the contraction and expansion of amalgams may be affected by slight changes in composition.

These formulæ have been selected from various sources with a view to giving the student opportunity to study effects obtained by varying percentages of Sn and Ag, and by introduction of other metals, Cu, Zn, etc.

Tests for Amalgams.

Color Test. — This is made upon a freshly amalgamated alloy, rolled into about the shape and size of a small pea, with a view to determine the amount of discoloration the amalgam is liable to undergo in the mouth.

A ball of amalgam carefully smoothed on at least one side is placed for forty-eight hours in a saturated solution of hydrogen sulphid, and after that time its color is compared with other amalgams similarly treated, or with amalgam of a similar composition which has not been treated.

Test for Expansion or Contraction.

Black has shown that tests of this nature to be of any value must be made in such a way that the *amount* of change in the volume can be measured, and that the simple method of packing glass tubes and using colored ink is wholly unreliable.

The author uses for this purpose an apparatus similar to one described by Prof. Vernon J. Hall. The amalgam is packed closely into a "well" in a steel block, then the block is placed

in the apparatus so that a counterpoised steel plunger rests on the column of amalgam. This plunger is operated by a very long needle and attached at a point so near the pivotal support of the needle that a rise or fall of the plunger of 1/2500 of an inch moves the tip of the needle, at the scale, 1/16 of an inch, or one degree. If the needle rises half a degree, which may easily be read, it would indicate an expansion of the amalgam of 1/5000 of an inch.

There are two wells in each block and both of exactly the same depth. The figure given below will make this explanation easily understood, *A* being the steel block carrying the amalgam.

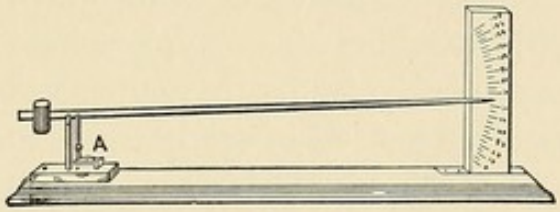


FIG. 8.

Test for Crushing Strength and Flow. — The test is made with Dr. Black's dynamometer (page 113) upon cubical blocks of amalgam which have been allowed to "set" for at least two days, and which measure 1/10 of an inch each way.

Specific gravity may be obtained by weighing the sample first in water, then in air, and dividing the weight in air by the difference between the two weights obtained.

It is instructive to make these tests on amalgam from alloys of varying composition, also on annealed and unannealed alloys of the same composition.

CHAPTER XIV.

DENTAL CEMENTS.

DENTAL cements, largely used as temporary fillings and linings of cavities, contain oxid of zinc, oxid of copper, or rarely sulphate of zinc, combined, at the time the cement is used, with phosphoric acid or with a solution of zinc chlorid.

There are six forms of dental cements which might be mentioned: the oxyphosphate of zinc, oxyphosphate of copper, artificial enamel, oxychlorid of zinc, oxysulphate of zinc, and tin cement. Of these the last three are but little used.

Oxyphosphate of Zinc. — This is the most serviceable of the preparations of this class unless exception is made of the new artificial enamels, which have not been in use long enough to warrant positive assertions as to their comparative value.

The oxyphosphate cement is usually made by adding a powder, consisting largely of pure oxid of zinc, colored by a slight amount of other metallic oxids, to a liquid consisting of deliquesced phosphoric acid (or a solution of phosphoric acid in which zinc phosphate, and possibly slight amounts of other phosphates, have been dissolved), till a putty-like mass results, which rapidly hardens and becomes capable of receiving a considerable polish. When the phosphoric acid used is the glacial acid, the cement may be spoken of as a metaphosphate, because the glacial acid, before the addition of water, and to a certain extent afterwards, is actually metaphosphoric acid, HPO_3. The metaphosphoric acid by boiling with water or gradually by addition of water without boiling becomes the orthophosphoric acid (H_3PO_4).

Hall's Dental Chemistry takes the following tests from

Flagg's Plastics and Plastic Filling, as characterizing a good oxyphosphate cement.

General Tests. 1. When first mixed it should yield a tough mass which when removed from the spatula does not adhere to the fingers and can be rolled into a pliable pellet.

2. It should have a glassy surface; and, at the end of two or three minutes, it should rebound when dropped upon wood, glass, or porcelain.

3. At the end of five minutes it should be quite hard and should sound like porcelain when tapped.

4. After ten or fifteen minutes it should be dented with difficulty, and when broken should show a clean, sharp fracture.

5. After twenty minutes it should be very hard, and should be capable of taking a good burnish.

6. In thirty minutes it should have little or no acid taste.

Arsenic is a frequent impurity in both zinc oxid and phosphoric acid, and if present is very liable to produce an irritating cement, sometimes causing considerable trouble; hence, the material entering into the composition of any dental cement should be free from arsenic (see pages 28 to 31 for arsenic tests).

The purer the zinc oxid and the phosphoric acid, from which the cement is made, the more durable it is found to be; so, aside from any question of irritation, it is quite necessary for the sake of the cement itself that the ingredients be pure.

It is not intended to give the impression that the liquid should consist *only* of glacial phosphoric acid or the powder *only* of oxid of zinc. A cement thus made would set so rapidly that it would be of no practical value. The resulting mass would also probably be crumbly. The powder or the liquid, one or the other, is usually mixed with phosphates of the heavy metals which would be insoluble in water, but which would dissolve in the strong phosphoric acid.

A pure ZnO may be made by calcining the precipitated carbonate of zinc, $Zn_5(OH)_6(CO_3)_2$ + heat = 5 ZnO + 2 CO_2 +

3 H_2O. The heat should be below 500° F., because, if too strongly heated, the color suffers, becoming yellowish.

Another method of making pure oxid of zinc is given as follows: Dissolve pure zinc in nitric acid, evaporate to dryness, and heat till fumes cease to be given off. The mechanical effect of the escaping oxids of nitrogen is said to leave the ZnO in the form of a *very* fine powder.

A pure phosphoric acid can be made from the ortho-acid by heating till the white fumes begin to come off, then heating to redness, cooling and dissolving in H_2O to a thick syrup. In mixing cements, the powder should be worked into the liquid till the desired consistency is obtained.

Oxyphosphate cement and all cements having zinc oxid for a base tend to dissolve in the fluids of the mouth, lactic acid and ammonium salts being particularly good solvents for this class of compounds. The addition of ferric oxid to oxyphosphate cement increases resistance to disintegration. One part of ferric oxid to 6 to 10 of zinc oxid is recommended by Rollins in the International Dental Journal.

Oxychlorid of zinc is more easily soluble than oxyphosphate. It shrinks more, but is credited with a preservative action on dentine and hence is used to some extent as a lining.

The powder of the oxychlorid cement is ZnO with sometimes a little borax, or silica, or both, added. A good oxychlorid cement will set in fifteen or twenty minutes, but keeps on growing harder for several hours. The following formula is recommended.

FORMULA FOR OXYCHLORID CEMENT.

Oxid of zinc 10 grams, borax 0.1 gram, and powdered silica 0.2 gram.

Transfer to clay crucible and calcine for one-half hour in furnace at bright-red heat. Pulverize, sift, and bottle. The liquid to be used with this powder consists of 10 c.c. of pure HCl *saturated* with pure zinc and filtered through glass wool.

Oxysulphate of Zinc. — This is used still less than the oxychlorid. It is non-irritating, dissolves easily, and is comparatively soft. The following formula is taken from Hall's Dental Chemistry.

FORMULA FOR OXYSULPHATE CEMENT.

Ten grams oxid of zinc, 4 grams sulphate of zinc. Dry, mix, calcine for one-half hour, and sift.

Liquid to be used with the powder may be made by dissolving 2 grams of zinc chlorid in 10 c.c. of water. This gives a turbid solution and should be shaken when used.

Oxyphosphate of copper cement (Ames's) consists of the usual powder and liquid. The powder contains oxids of copper, iron (slight amount), cobalt, and zinc, and, of course, is black in color. The liquid is phosphoric acid holding in solution a certain amount of phosphate of zinc.

The cement resulting from this combination was found to be hard, showing practically no change of volume and resisting the solvent action of the saliva.

TIN CEMENT.

Dr. Arthur Scheuer, of Teplitz, Bohemia, recommends a preparation composed of a finely pulverized tin sponge and zinc oxid mixed with glacial phosphoric acid. "The powder is of a light-gray color, becoming slightly darker when mixed with the acid, but regains its original color after setting. A tin-cement filling can be easily inserted and when polished it has a metallic appearance." (Dental Cosmos, May, 1904.)

Artificial Enamel. — Several preparations have been put on the market under this name, in each case with the claim that it makes a much harder cement and one which resists disintegration to a much greater extent than the ordinary zinc preparations.

The specifications of a German patent, under which one of these preparations is manufactured, claim that the powder con-

sists of a mixture of the oxids of beryllium and silicon, together with alumina and lime. The liquid consists of a 50% solution of orthophosphoric acid in which aluminium phosphate and zinc phosphate have been dissolved.

When mixed in the usual manner these produce a cement which is much harder and less soluble than any of the preparations previously considered.

An advertisement of one of these preparations claims that its success is due to the use of a very valuable compound, without which it would be worthless, and, so far as the author has had opportunity to investigate this subject, this statement seems to be true. A qualitative analysis confirms the claim of the patent specifications both in regard to the composition of the liquid and the presence of oxid of beryllium in the powder, and it is probable that the value of these preparations depends largely upon the proportion of beryllium entering into their composition.

Beryllium is a rare metal which occurs naturally with aluminium as a silicate. It forms basic compounds of such character as makes it suitable for use in dental cement.

The cement powders may be tested for beryllium as follows: Fuse a little of the powder with sodium carbonate (or the double sodium potassium carbonate); dissolve the fused mass in dilute hydrochloric acid; evaporate to dryness and heat to 120° C. to dehydrate the silica; take up in water with a little HCl and filter; to the filtrate (probably containing Al, Be, Zn, and Ca) add a little ammonium chlorid, and an excess of ammonium carbonate, $Al(OH)_3$, $Be(OH)_2$, and $CaCO_3$, will be precipitated. The beryllium, however, is easily soluble in the excess of $(NH_4)_2CO_3$. Warm (not boil) and allow to stand for some time to insure complete separation of Al. (Note. — $Al(OH)_3$ is much less soluble in solution of $(NH_4)_2CO_3$ than in either NH_4OH or even NH_4OH and NH_4Cl.) Filter. Boil the filtrate for a long time, when the beryllium and some zinc will

be precipitated. Filter and dissolve precipitate off paper in dilute HCl. To the filtrate containing $BeCl_2$ and $ZnCl_2$ add NH_4Cl in excess and NH_4OH, which will give a precipitate of $Be(OH)_2$. If Be and Zn only are present, the separation by boiling may be unnecessary.

The liquid may be tested for dissolved phosphates by diluting with water and adding ammonia till alkaline; if the mixture remains clear, phosphates of alumina, calcium, or zinc are absent. Care should be used, however, in the addition of the ammonia, as an excess of this reagent will redissolve phosphate of zinc.

If the ammonia is too strong, a precipitate of ammonium phosphate may be obtained, but this may be easily re-dissolved by the simple addition of water.

CHAPTER XV.

FUSIBLE METALS AND SOLDERS.

Fusible Metals.

Under the head of fusible alloys properly come many of the alloys considered on page 128 as solders. The fusible alloy usually contains lead or bismuth together with tin and occasionally cadmium. This may be mixed in such proportions that the melting-point may be anything desired down to 63° C. These alloys are largely used in the dental laboratory. Mellot's metal, composed of bismuth 8 parts, tin 5 parts and lead 3 parts, is perhaps the most serviceable. This melts at about the temperature of boiling water. Wood's metal, melting at about 65° C., is composed of bismuth 4 parts, tin 1, lead 2, and cadmium 1. Rose's metal is bismuth 2 parts, tin 1, and lead 1. This melts at about 95° C.

Babbitt Metal, much used in the manufacture of dies, is composed of copper 1 part, antimony 2, and tin 8. The formula of common Babbitt metal on the market will be found to differ somewhat from the above and is not so well suited for dental purposes.

According to Essig's Dental Metallurgy, Dr. C. M. Richmond used a fusible alloy in crown and bridge work which he states is as hard as zinc and can be melted at 150° F. and poured into a plaster impression without generating steam. The formula of this alloy is as follows: Tin 20 parts, lead 19, cadmium 13, and bismuth 48. The following fusible-metal alloys are also suitable for the purpose.

Tin.	Lead.	Bismuth.	Melting-point of Alloy.
1	2	2	236° F. or 113° C.
5	3	3	202° F. or 94° C.
3	5	8	197° F. or 92° C.

The fusing-point of an alloy may be determined by melting under a liquid of sufficiently high boiling-point and then carefully noting the temperature at which the melted alloy solidifies. Care must be taken that the temperature of the alloy is exactly the same as recorded by the thermometer. To insure this, in the case of an alloy with low melting-point, it is usually sufficient to place the alloy in water or brine in a test-tube which is immersed in a beaker of similar fluid, then, by raising the heat gradually with constant stirring and by taking the mean of two or three determinations, fairly accurate results are obtained.

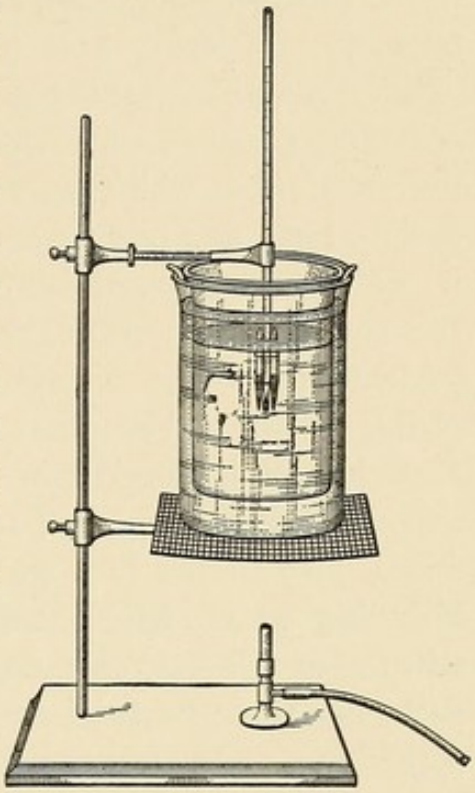


FIG. 9. — Apparatus for Taking Melting-Point.

SOLDERS.

Solders are alloys used in joining pieces of metal of the same or of different kinds. One of the constituent metals of the alloy forming the solder is usually the same as the surface upon which it is to be used, hence the various metals require solders of special composition; for instance, common solder is entirely unsuited for soldering aluminium or gold.

Common Solder is composed of tin and lead in different proportions. The larger the proportion of tin the finer is the solder, and the following three grades may usually be obtained: "Fine" or "hard" (tin two parts and lead one), "Common" or "medium" (tin and lead equal parts), "Coarse" or "soft" (tin one part and lead two parts).

In soldering metals, it is absolutely essential that the surfaces be kept clean and free from superficial coating of oxids which may form easily with the elevated temperature employed in the process. Soldering acid and the various fluxes serve this purpose. Soldering acid is an acid solution of zinc chlorid usually made by taking a few ounces of strong hydrochloric acid and adding zinc as long as the metal dissolves. Among the substances which may be used as a flux to prevent oxidation, rosin and borax are the most common.

Soft Solders are those fusing below a red heat and include the common solders above mentioned, also the most fusible solders containing bismuth. These last are more properly fusible metals and are discussed under that head.

Solders for Aluminium. — Aluminium solders with considerable difficulty owing in part to the low melting-point of the metal, also to the fact that aluminium is attacked by alkalis, including borax, which makes it necessary to find some substitute for this convenient flux. Essig recommends a flux consisting of three parts of copaiba balsam, one part of Venetian turpentine, and a few drops of lemon-juice. The mixture is to be used in the same manner as soldering acid with a solder consisting of zinc from 80 to 92 parts, aluminium from 8 to 20 parts. Fused and finely powdered silver chlorid may also be used as a flux, the salt being reduced and the silver forming a superficial alloy. Richards recommends a solder for aluminium consisting of tin 29 parts, zinc 11 parts, aluminium 1 part, phosphor-tin 1 part.

Hall says that a solder which he has found very satisfactory may be prepared from aluminium 45 parts, tin 45, mercury 10; further, that the following formulæ suggested by Schlosser are particularly adapted to soldering dental work since they resist the reaction of corrosive substances.

Platinum-Aluminium Solder.	
Gold	3 parts
Platinum	0.1 part
Silver	2 parts
Aluminium	10 "

Gold-Aluminium Solder.	
Gold	5 parts
Copper	1 part
Silver	1 "
Aluminium	2 parts

For soldering articles of aluminium the following solder is given in the Pharmaceutical Era, January 10, 1895: Silver 2, nickel 5, aluminium 9, tin 34, and zinc 50 parts, to be used without flux. See also Dental Cosmos for 1906 (page 115).

Solder for brass requires a high heat for fusion and on this account is known as hard solder.

Edwinson gives the following formulæ: (1) copper 13 parts, silver 11; (2) copper 1 part, brass 1, silver 19; (3) brass 5 parts, zinc 5, silver 5. The flux for brass soldering is powdered borax, which may be mixed with water to a paste and applied with a feather or a small brush.

Solder for Gold. — Gold soldering is the most particular work of this class which the dentist has to do. There are a few requirements for a good gold solder which might be noted and which are also applicable to the other solders mentioned: (1) The color should be as nearly as possible that of the metals upon which it is to be used. (2) The solder should have a fusing-point but very slightly below that of the metal to be soldered. (3) The solder should flow freely.

Litch gives the following instructions for making a zinc-gold solder which will have the above-mentioned properties:

"To make the zinc-gold solder take 1 pennyweight of the same gold upon which it is to be used and add $1\frac{1}{2}$ grains of zinc. If this is done in a crucible in the furnace, first fuse the gold (which should either be clean scraps or be cut from the plate; never use filings for this purpose), using but little borax; when thoroughly fused take the crucible in the tongs, drop the zinc into it, give the crucible a rather vigorous yet skilful shake to assist in mixing its contents, but without causing any to be

thrown out, and immediately pour into the previously prepared ingot mold. This must be done very quickly or the solder will require too high a heat for the fusion on account of a large proportion of the zinc being volatilized or oxidized and thus be lost as alloys "

Essig gives the following formulæ for alloys of gold employed in dentistry as solders:

No. 1. 14 Carats Fine.

American gold coin	$10.00
Pure silver	4 dwts.
Pure copper	2 "

No. 2. 14 Carats Fine.

American gold coin	16 dwts
Pure copper	3 " 18 grs.
Pure silver	5 "

No. 3. 14 Carats Fine.

Pure silver	2½ dwts.
Pure copper	20 grs.
Pure zinc	35 "
18-carat gold plate (formula No. 11)	20 dwts.

No. 4. 15 Carats Fine.

Gold coin	6 dwts.
Pure silver	30 grs
Pure copper	20 "
Brass	10 "

No. 5. 16 Carats Fine.

Pure gold	11 dwts.
Pure silver	3 " 6 grs.
Pure copper	2 " 6 "

No. 6. 16 Carats Fine.

Pure gold	11 dwts. 12 grs
Pure copper	1 dwt. 12 "
Pure silver	3 dwts.
Pure zinc	12 grs.

No. 7. 18 Carats Fine.

Gold coin	30 parts
Pure silver	4 "
Pure copper	1 part
Brass	1 "

No. 8. 20 Carats Fine, for Crown and Bridge Work.

American gold coin (21.6 carats fine) $10 piece	258 grs.
Spelter solder	20.64 "

No. 9. 20 Carats Fine, Same Use as No. 8.

Pure gold	5 dwts.
Pure copper	6 grs.
Pure silver	12 "
Spelter solder	6 "

No. 10. 20 Carats Fine, for Crown and Bridge Work.

Zinc	1½ grs.
Pure gold	20 "
Silver solder	3 "

No. 11. Dr. C. M. Richmond's Solder for Bridge Work.

Gold coin	5 dwts.
Fine brass wire	1 dwt.

No. 12. Dr. Low's Formula for Solder for Crown and Bridge Work, 19 Carats Fine.

Coin gold	1 dwt.
Copper	2 grs.
Silver	4 "

Solder for Platinum. — Platinum utensils may be soldered with any good gold solder, and a flux may be used if desired. When, however, the solder is used in connection with porcelain work, it must be pure gold or a gold and platinum alloy. A 25% platinum alloy has been found to give excellent results. The following in regard to gold and platinum alloy is from the Dental Review, August, 1905:

"The colleges and text-books tell us the proper proportions of gold and platinum alloys, but they usually fail to tell us *how to do it.* In most cases the platinum appears in white spots on the plate without producing a proper alloy. Take a small piece of 22-carat gold and fuse it under the blowpipe. Then work in all the platinum you can in small pieces until it has taken up all that is required. It will produce a small button of a white alloy which is very brittle. Add this alloy in required proportions to the gold in the crucible and it will produce a real platinum alloy. By this method you can make clasp gold that is pretty nearly as stiff as a steel spring and yet will roll and work without fracture. (Mark G. McElhinney, Ottawa, Canada.)"

Solder for Silver. — Solder for silver usually consists of alloys of silver and copper with sometimes zinc and sometimes tin. Litch recommends a silver solder made by alloying pure

silver with one-third its weight of brass. "Brannt's Metallic Alloys" give alloys of silver and copper simply. Hall recommends silver 8 parts, copper 1, and zinc 2. In the preparation of solder containing copper, zinc, or tin, the use of a flux is necessary to prevent the formation of metallic oxid. For this purpose borax is usually employed. The silver, constituting, as it does, the greater proportion of the alloy, should be melted first and be covered with considerable borax. When this has been thoroughly fused, the other metals may be added and mixed by agitation or by stirring with wood. Finally, the solder may be cast in the usual ingot mold.

CHAPTER XVI.

RECOVERY OF RESIDUE.

Gold. — The gold scrap may be recovered in two ways: first, by fusion with suitable flux; second, by dissolving in aqua regia and precipitation of the metal. In the first method it is necessary to remove mechanically the impurities as far as possible, then mix the fairly clean gold waste with potassium nitrate and a little borax, and fuse in a clay crucible. The gold will separate as a button at the bottom of the thoroughly fused slag.

In the second method the scrap gold is dissolved in aqua regia and the resulting solution of $AuCl_3$ is precipitated with ferrous sulphate or oxalic acid. The later precipitant, although working more slowly than the iron, does not precipitate platinum, hence in case platinum is present it is the better reagent to use. The precipitated gold is next filtered, thoroughly washed, and fused in clay crucible under borax and potassium nitrate.

Silver. — The recovery of silver is best accomplished by dissolving the scrap or waste in nitric acid and precipitating as chlorid, then reducing the chlorid to metallic silver either by treatment with pure zinc or by fusion with sodium carbonate. If tin is present in the scrap, the nitric acid will form metastannic acid, a white insoluble powder rather difficult to filter. Hence, it is better to wash this by decantation several times with distilled water, which will remove practically all the silver. From the nitric-acid solution the Ag may be precipitated by salt or hydrochloric acid. This precipitate must be washed till the wash-water is practically free from chlorin, then dried and fused with sodium carbonate, when a button of pure silver will be obtained.

If preferred, the precipitated chlorid of silver may be washed once by decantation, then agitated with pure zinc, when the following reaction takes place:

$$2\,AgCl + Zn = ZnCl_2 + 2\,Ag.$$

The finely divided Ag (in the form of nearly black powder) must be washed free from chlorin, carefully dried and fused under carbonate of sodium, or, after drying, it may be weighed and dissolved at once if a solution is desired. If the silver residue contains mercury this may be driven off by heat before solution is attempted.

Mercury. — Mercury which has been used in making amalgams is best purified by distillation. Mercury which needs simply to be freed from dirt, dust, or slight traces of other metals may be purified as follows: If a piece of filter-paper is fitted closely in a glass funnel, a pin-hole made in the joint and the paper thoroughly wetted with water and the mercury to be purified placed on the paper, the heavy metal will run through the pin-hole, leaving practically all the dirt clinging to the wet filter-paper. Such mercury may also be cleansed by filtering through chamois-skin.

In case the mercury contains slight amounts of other metals, if it is digested with a very dilute nitric acid, the acid will generally first dissolve the impurities and afterwards a little of the mercury itself. Then thorough washing with water will remove all excess of acid and all soluble salts which may have been formed. Pure mercury should have no coating of any sort on its surface, and if a few globules are allowed to run down a smooth inclined plane, they should leave no "tail" behind.

Laboratory Exercises XXX to XXXIV.

During the study of alloys and volumetric analysis the student will be required to make qualitative analyses of several commercial alloys, dental cements, etc. He will also have to

prepare and test carefully six alloys, the formulæ for which will be given on a mimeograph sheet similar to that represented below.

The properties of the various alloys are to be carefully compared and it is often desirable for two or more students to vary a given formula in some one particular and note the result of such a variation upon the properties of the amalgam obtained.

ALLOYS.

Date.....

DESK NO..... NAME.....

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Gold.....						
Silver.....			18	60	55	
Tin.....	3	1	65	40	37	
Copper.....					4	
Zinc.....					4	
Lead.....	5	2				
Antimony.....			17			
Bismuth.....	8	4				
Cadmium.....		1				

Nos. 1 and 2 contain lead and must not under any circumstances be made in the graphite crucible which you intend to use for silver-tin alloys. These are solders or fusible metals. Make 8 to 10 grams and determine melting-point of each.

No. 3 is a very low grade dental alloy. Make 10 grams and test for expansion, discoloration, and crushing strength.

Nos. 4 and 5 are better-grade alloys. Make 10 or 12 grams of each. Hand one in as sample of work; test the other, annealed and unannealed, as No. 3 was tested.

No. 6, your own formula. Make 15 to 20 grams. Make complete tests and also return sample. Return all remaining portions of alloys with desk number and composition of the alloy plainly written on envelopes furnished, in order to obtain proper credit for the work.

PART III.

VOLUMETRIC ANALYSIS.

CHAPTER XVII.

STANDARD SOLUTIONS.

VOLUMETRIC analysis is the determination of the quantity of a particular substance contained in a given sample by means of volumetric or standard solutions. By means of standard solutions, it is possible to determine easily and quickly the strength of a peroxid of hydrogen solution, the percentage of silver in an amalgam alloy, or the amount of gold in a plate or solder, and it is volumetric analysis thus specialized and adapted to dental purposes that we shall consider.

The standard solution may be so prepared that it has an arbitrary or special value, such, for instance, as the silver-nitrate solution usually used in determining the amount of chlorin in urine, 1 c.c. of this solution being equal to 10 milligrams of salt (NaCl); or its standardization may be made with reference to the molecular weights of the reagents employed, so that solutions of a similar nature will be of equivalent values. That is, a solution containing the hydrogen equivalent of the reagent, weighed in grams, per liter, is known as a *normal solution* and 10 c.c. of any normal acid will be of the same value in neutralizing an alkali as 10 c.c. of any other normal acid. On the other hand, 10 c.c. of a normal acid is equal to 10 c.c. of any normal alkali solution whatever the alkali may be.

The *normal factor* is the weight of reagent contained in *one cubic centimeter* of the normal solution.

The volumetric process and the use of the normal factor will be most clearly understood by the explanation of a specific example.

We will suppose that we have prepared a normal solution of NaOH and wish to ascertain the strength of a sample of dilute HCl. The normal solution will contain the molecular weight in grams of NaOH per liter or 40 grams absolute NaOH.

The molecular weight of HCl being 36.4 (36.37), a normal solution of HCl will contain 36.4 grams absolute HCl; and, if a liter of normal NaOH were added to a liter of normal HCl, *exact* neutralization would result:

$$\underset{40}{NaOH} + \underset{36.4}{HCl} = \underset{58.4}{NaCl} + \underset{18}{H_2O}.$$

The 1 liter of normal alkali (containing 40 grams NaOH) is exactly neutralized by 36.4 grams of HCl, or 1 c.c. of normal alkali by 0.0364 gram of HCl. 0.0364 is normal factor of HCl.

Now, if by our process of analysis we find that it takes just 21 c.c. of the NaOH solution to exactly neutralize 10 c.c. of HCl solution, 1 c.c. of NaOH being equal to 0.0364 gram HCl, 21 c.c. of NaOH will be equal to 0.0364×21, or 0.7644 gram HCl, or 10 c.c. of the HCl solution contains 0.7644 gram of absolute HCl, equivalent, approximately, to 7.64%.

It has become apparent that in carrying out this process three things are absolutely necessary:

1. Methods for the preparation of standard solutions.

2. Apparatus for *accurate* measurements of both the standard solution and the unknown.

3. Means for determining just when the point of exact neutralization is reached. This point is known as the "*end point*" and is shown by "*indicators*" of various kinds.

Preparation of Standard Solutions. — Experience has shown that normal solutions are in many cases less convenient to work with than those much more dilute, both on account of the keep-

ing qualities of the standard solution and the accuracy of manipulation; and, for the purposes of dental chemistry, a *decinormal* or one-tenth normal solution represented by N/10 will generally be used.

In working with an N/10 solution, the factor used in calculations of results will be one-tenth of the normal factor and is termed an *N/10 factor.* Other fractional proportions of the normal solution may be used as the centinormal, N/100, or seminormal, N/2. While the decinormal solution contains one-tenth of the hydrogen equivalent of reagent in grams per liter, and this amount is very easy to calculate, it is often very difficult to *weigh out* the exact amount required. For instance, we want an N/10 solution of HCl. HCl is a gas soluble in water and the strengths of the solutions vary greatly, so we cannot weigh out 3.637 grams of absolute HCl to put in 1000 c.c. of water though we know this is just the amount necessary to produce our N/10 solution. Thus, one of the first practical difficulties in making up standard solutions is to find some substance which can be weighed accurately and the exact chemical composition of which may be relied upon.

Crystallized oxalic acid is such a compound, although care must be taken that the crystals are dry and yet contain all their water of crystallization; in other words, are actually represented by the formula $H_2C_2O_4, 2\,H_2O$. Fused carbonate of sodium is another such compound. If the purest obtainable bicarbonate of soda is fused till no further change takes place, cooled, and powdered, the product is pure enough for the preparation of a standard solution for ordinary use.

For the preparation of volumetric solutions it is necessary to have a balance which will weigh accurately to at least two decimal points. It will be much better to have a balance sensitive to one milligram. Balances of this sort inclosed in a glass case can be obtained at a very reasonable price. Fig. 10 on page 141 represents such a balance.

It is also essential to have flasks capable of holding 100, 250, 500, and 1000 c.c. carefully graduated on the neck, represented in Fig. 11, page 141.

Graduated cylinders (Fig. 12) are not so well suited for the preparation of standard solutions, as the greater breadth of the column of liquid makes accurate reading much more difficult.

Small cylinders of 100 c.c. or less are useful in making up odd amounts of solution.

In the process of analysis it will be necessary to have pipettes (Fig. 13) measuring 5 and 10 c.c., also a burette (Fig. 14), from which the standard solution may be used. The burettes may be had in a variety of styles and sizes, a very serviceable one being of 25 c.c. capacity and graduated in tenths of a cubic centimeter. It may have a glass stop-cock or it may be furnished with a glass tip with rubber connector and pinch-cock.

A set of measuring-instruments which have been carefully compared with one another should be kept; that is, the 1000-c.c. flask should be exactly filled by taking the 100-c.c. flask full to the mark just 10 times, thus enabling one accurately to take aliquot parts of any given solution.

Indicators.

The third requisite for carrying out a volumetric process is a method for determining the end point of the reaction; that is, we must know when there has been a sufficient quantity of a standard solution added to an unknown solution. *Phenolphthalein* gives a red color with alkalis, which is discharged by the addition of acid till the solution becomes colorless as it becomes neutral or acid. *Litmus* gives a blue color with alkalis and a red with acids; *Methyl orange* can be used with carbonates and mineral acids; it does not work so well with organic acids. The color is pink in acid and yellow in alkaline solution. *Lacmoid* is useful in cases where the acid properties of such salts as alum or zinc chlorid might interfere with

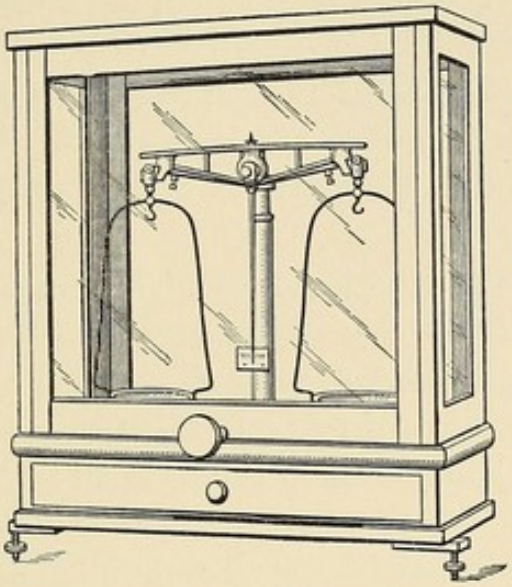


FIG. 10.

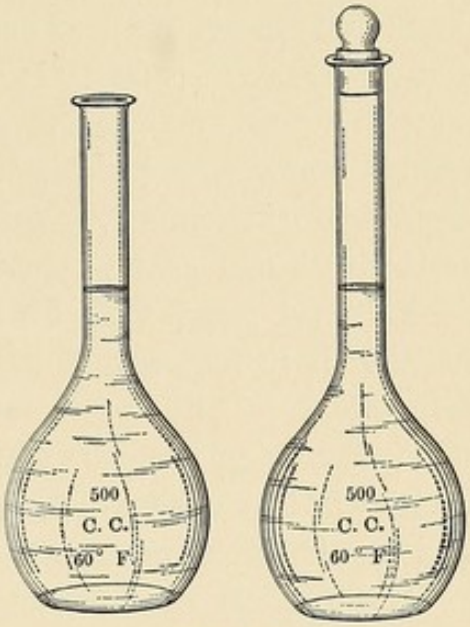


FIG. 11.

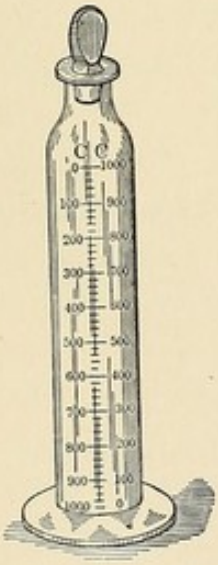


FIG. 12.

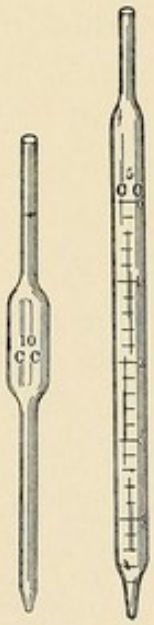


FIG. 13.

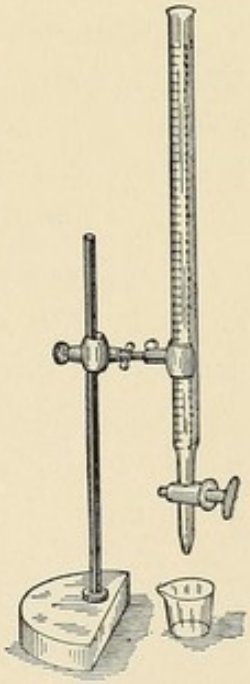


FIG. 14

the use of litmus or phenolphthalein. The different indicators do not all change color at exactly the same point in the process of neutralization, and it is possible for a solution to be alkaline to litmus and acid to phenolphthalein at the same time. Hence uniformity in the use of indicators is desirable. In physiological chemistry, Congo red, tropæolin oo, and dimethylaminoazobenzol are also used.

The end point may be indicated by excess of a standard solution if it happens to be highly colored, as potassium permanganate. Thin starch paste is used as an indicator in operations involving the use or liberation of free iodin. Other indicators will be considered as we have occasion to use them in the various analytical processes.

The process of volumetric analysis may be divided into three classes: First, *acidimetry* and *alkalimetry*. Second, *oxidation* and *reduction*. Third, *precipitation*.

Acidimetry and Alkalimetry.

Acidimetry and alkalimetry includes all standardized solutions, either acid or alkaline, which may be used in neutralizing solutions of unknown strength of an opposite character. For instance, the strength of vinegar is determined by neutralizing a known volume with standard alkali.

For present purposes two standard acids and one standard alkaline solution will be sufficient. The first of these may be decinormal oxalic solution prepared from recently recrystallized and carefully dried acid. The composition of these crystals should be $H_2C_2O_4\,2\,H_2O$, having molecular weight of 126. This being a dibasic acid it will be necessary to divide the molecular weight by 2 for a decinormal solution and then again by 10 to obtain the number of grams which must be dissolved in 1 liter of water. For class use, each student may prepare 500 c.c. of this solution by dissolving 3.15 grams of pure crystallized oxalic acid in water and dilute to a half-liter. The graduated

flasks are usually constructed to be used at a temperature of 60° F. or 15° C. and for accurate work solutions must be brought to this temperature. After the oxalic acid solution has been prepared the decinormal alkali may be made as follows:

Weigh out carefully $2\frac{1}{2}$ grams of caustic soda or 3 grams of caustic potash and dissolve in less than 500 c.c. of distilled water. After the solution has thoroughly cooled, fill a burette with it. Place 10 c.c. of standard acid previously prepared in a white porcelain dish of about 250 c.c. capacity, add 50 c.c. distilled water and 2 or 3 drops of phenolphthalein (2% phenolphthalein in alcohol and water, equal parts); then carefully run in from the burette, with constant stirring, the alkali solution until a permanent pink tint is produced.

The work will be more satisfactory if the titration is made for the appearance of color rather than the disappearance of color, as would have been the case had the standard acid run *into* the measured alkali solution. This process is known as "titration," and will hereafter be so designated.

The Calculation.—Supposing it has taken 8.2 c.c. of the alkali to exactly neutralize the 10 c.c. of N/10 acid, it follows that in the 8.2 c.c there is sufficient alkali to equal or to make 10 c.c. of an N/10 alkali solution; hence we may add 1.8 c.c. of distilled water to every 8.2 c.c. of alkali solution, thereby reducing it to decinormal strength. Practically we should take 410 c.c. of alkali solution and in a graduated flask make it up to 500 c.c. with distilled water. It will be necessary to make several titrations and average the results before making the calculation.

From the standard alkali N/10 solutions of HCl or H_2SO_4 may be prepared in a similar manner, it being impossible to accurately weigh either of these two acids. In titrating a carbonate, if an indicator, such as phenolphthalein, which is sensitive to carbonic acid, is used, it is necessary to keep the solution at a boiling temperature or at least bring it to a boil after every addition from the burette.

EXAMPLE OF ACIDIMETRY AND ALKALIMETRY.

Determine the strength of a sample of vinegar as follows:

Measure accurately into a white porcelain dish of 150–250 c.c. capacity 1 c.c. of the sample. This may be measured either with a carefully graduated 1-c.c. pipette or more accurately by diluting 10 c.c. of the sample to 100 c.c. in a graduated flask, then using 10 c.c. of the dilution for the titration, the titration to be performed with N/10 NaOH, using phenolphthalein as an indicator.

The molecular weight of acetic acid is, in round numbers, 60; hence the N/10 factor of acetic acid will be 0.006 (acetic acid being monobasic, $HC_2H_3O_2$). To ascertain the strength of the sample of vinegar it is necessary to multiply the number of cubic centimeters used by this factor, 0.006, which will give the amount of absolute acid calculated as acetic in 1 c.c. (practically 1 gram) of the sample. Thus, if 8 c.c. of N/10 alkali were required to neutralize 1 c.c of vinegar, multiplying the factor 0.006 by 8 would give 0.048 gram of absolute acetic acid in 1 c.c. of vinegar, which is equivalent to 4.8%.

Carbonate Titration.

While perhaps phenolphthalein is the most serviceable of all indicators in common use, it is so sensitive to carbon dioxid that any titration which results in the liberation of CO_2 must be modified by boiling the solution thoroughly after each addition of acid. This makes the operation somewhat tedious, but it is to be preferred to the use of other and less sensitive indicators which may not be affected by the carbon dioxid.

Analysis by Oxidation and Reduction.

If to a hot solution of oxalic acid containing sulphuric acid, permanganate of potash be added, the following reaction takes place:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

This reaction represents a very valuable method of volumetric analysis; but, inasmuch as it is not a process of neutralization, it cannot properly come under the head of acidimetry and alkalimetry, but rather under a distinct classification, the determination involving *oxidation* and *reduction*.

Standard Permanganate Solution. — In the reaction given above we may consider that, as the molecule of $K_2Mn_2O_8$ breaks up, three of the eight atoms of oxygen are required to form the basic oxids K_2O and 2 MnO (soluble in the acid as K_2SO_4 and 2 $MnSO_4$), while the remaining five atoms are liberated and constitute the active chemical agent whereby the oxalic acid is oxidized to CO_2 and H_2O. Hence, to reduce this double molecular weight (316) to the hydrogen equivalent necessary for a normal solution, it is divided by 10 (five atoms of oxygen having a valence of 10).

The Decinormal Solution may be made by dissolving 3.16 grams of pure recrystallized and thoroughly dried crystals, if they can be obtained, in distilled water, and making the solution up to 1000 c.c., or it may be standardized by titration with the N/10 oxalic acid previously prepared; in this case one would proceed as follows:

Make a solution slightly stronger than the standard required, say about 3.5 grams of the ordinary pure crystals in a liter of water; with this fill a burette, place 10 c.c. of N/10 oxalic acid measured from a pipette in an evaporating-dish or casserole, dilute with about 50 c.c. of water, add about 10 c.c. of dilute sulphuric acid, and heat the mixture nearly to the boiling-point. Then titrate with the permanganate from the burette. The permanganate will at first be rapidly decolorized, but as the operation progresses the color fades more slowly till at last a faint *permanent* pink color indicates that the "end point" has been reached.

The temperature must be kept above 60° C. throughout the titration or the oxidation will take place too slowly and an apparent end point will be obtained before the reaction is completed.

If the solution turns muddy during the operation, it is due to an insufficient amount of sulphuric acid and more should be added. The calculation is made as in the case of the N/10 NaOH described on page 143. The standard permanganate should be preserved in full, well-stoppered bottles and kept in a dark place.

It is better to have the $KMnO_4$ solution made up a day or two before it is standardized, thereby oxidizing traces of ammonia, etc., which the water may contain.

DETERMINATION OF PEROXID OF HYDROGEN.

In determining the strength of peroxid use 1 c.c. of the sample measured as in the case of vinegar (which see), dilute with 50 c.c. of distilled water, add 10 c.c. of dilute sulphuric acid, and titrate with the permanganate in exactly the same manner as detailed in the preceding paragraph, the reaction in this case being as follows:

$$2\,KMnO_4 + 5\,H_2O_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,O_2 + 8\,H_2O.$$

The aqueous solutions of peroxid on the market used as antiseptics contain about 3% absolute H_2O_2 and yield approximately ten volumes of available oxygen; that is, 10 c.c. of solution will yield 100 c.c. of oxygen. The calculation may be made to express strength of the peroxid in terms of percentage of absolute H_2O_2 by multiplying the number of cubic centimeters of N/10 $KMnO_4$ decolorized by 1 c.c. of solution by 0.17, or to express the strength in volumes of available oxygen by multiplying the number of cubic centimeters of solution by 0.56 (more accurately 0.5594).

DECINORMAL IODIN.

A decinormal solution of iodin may be prepared by dissolving 12.68 grams of pure iodin crystals in one liter of water by the aid of about 18 grams of pure potassium iodid.

Iodin of sufficient purity may be obtained by carefully resubliming selected and carefully dried crystals of so-called "chemically-pure" iodin.

DECINORMAL SODIUM THIOSULPHATE.

$Na_2S_2O_3.5\,H_2O$ = molecular weight, 248.24. This solution may be made by weighing directly 24.824 grams of the pure crystallized salt, dissolving in water and diluting to 1000 c.c., or it may be standardized by titration with a decinormal iodin solution, the reaction being as follows:

$$2\,Na_2S_2O_3 + 2\,I = 2\,NaI + Na_2S_4O_6.$$

The indicator used is a very dilute starch paste, which gives the characteristic blue color as soon as free iodin is in excess.

By means of these two standard solutions (iodin and sodium thiosulphate) a variety of determinations may be made with great accuracy. Any substance which will liberate iodin from potassium iodid may be quantitated by adding an excess of the potassium salt and titrating the free iodin with thiosulphate solution, using starch paste as usual for an indicator.

Peroxid of hydrogen may be thus determined as easily as by the permanganate method previously given. The process, being that of Kingzett, is given as follows by Sutton:

Mix 10 c.c. of peroxid solution to be examined with about 31 c.c. of dilute sulphuric acid (1–2) in a beaker, adding crystals of potassium iodid in sufficient quantity, and after standing five minutes titrating the liberated iodin with N/10 thiosulphate and starch. The peroxid solution should not exceed the strength of two volumes; if stronger, it must be diluted proportionately before the analysis.

In the case of a very weak solution it will be advisable to titrate with N/100 thiosulphate.

1 c.c. N/10 thiosulphate = 0.0017 gram H_2O_2 or 0.0016 gram.

VOLUMETRIC DETERMINATION OF ARSENIC.

Mohr's method of oxidation with iodin is a practical one. The titration is made with N/10 iodin and starch as usual, except that the solution should be at first neutral and then about 20 c.c. of saturated solution of sodium bicarbonate should be added to every 0.1 gram of As_2O_3 supposed to be in the unknown, thus giving a certain definite alkalinity. If the solution is acid, neutralize with sodium bicarbonate, then make alkaline with more bicarbonate as above.

VOLUMETRIC DETERMINATION OF GOLD.

(See also p. 154.)

While gold is usually determined quantitatively by assay in a dry way (page 157) it may be determined very accurately by titration with thiosulphate solution. Fatka (Chem. Zeit.) recommends the following process based upon the facts that a neutral solution of gold salt with potassium iodid will give a greenish precipitate. When an excess of potassium iodid is used no precipitate is formed, but a solution of AuI_3 as $AuKI_4$ results. This is of a brown color and may be titrated with N/10 thiosulphate solution, when the following reaction takes place:

$$AuKI_4 + 2\,Na_2S_2O_3 = AuKI_2 + 2\,NaI + Na_2S_4O_6.$$

Process: 10 c.c. of gold solution containing approximately 2% of gold is treated with 4 grams of potassium iodid diluted to 100 c.c. with water and titrated with N/10 $Na_2S_2O_3$ solution, using starch as an indicator.

ANALYSIS BY PRECIPITATION.

Because certain elements possess a selective affinity for other elements it is possible to determine many substances

quantitatively by precipitation. That is, if silver nitrate is added to a mixture of a soluble chlorid and a chromate, the chlorin will combine first with the silver, forming AgCl, to the exclusion of the chromate. After the last trace of chlorin has been so combined, then the silver chromate will be formed, which is a salt with an intense red color; hence it is possible to determine the strength of solutions of soluble chlorids by titration with standard $AgNO_3$, using potassium chromate as an indicator. This process is used in analysis of drinking-water, of saliva, and of urine, but for each of these it is desirable to have solutions of special strength.

A DECINORMAL SILVER SOLUTION

may be made by dissolving 17 grams of pure crystallized $AgNO_3$ in a liter of distilled water, and with this a

DECINORMAL SODIUM CHLORID SOLUTION

may be prepared as follows:

Weigh out 6 grams of the purest salt obtainable and dissolve in approximately 1 liter of distilled water. With a pipette measure 10 c.c. of this solution into a white porcelain dish, dilute to about 20 c.c. with H_2O, add two to five drops of neutral potassium chromate (K_2CrO_4) and add $AgNO_3$ from a burette till a faint pink color *persists*.

The calculation and dilution is made exactly as described on page 143 in the preparation of a standard NaOH solution. The silver nitrate solution used to determine chlorin in urine is usually prepared of such a strength that 1 c.c. precipitates just 10 milligrams of sodium chlorid. This is equivalent to 0.006065 gram of chlorin. A solution of this strength is produced when 29.075 grams of pure, fused silver nitrate are dissolved in sufficient distilled water to measure 1 liter of solution. If chlorin is to be determined in drinking-water, it is usually necessary to concentrate the water at least 1/5 its bulk

and then use not more than one or two drops of neutral chromate as indicator. The standard silver nitrate for this titration should be very dilute. A convenient solution may be prepared by diluting the standard $AgNO_3$ for urine 1 to 10. In saliva the sample may be diluted with an equal volume of water and titrated the same as in the case of drinking-water. In all quantitative processes where silver chromate is used to determine the end point the solution must be practically neutral, as the formation of this salt is prevented by either acids or alkalis.

Volumetric Determination of Silver by Standard Potassium Sulphocyanate Solution.

Silver may be determined volumetrically in nitric acid solution by titration with standard KCyS solution, using ferric alum as an indicator. The sulphocyanate solution must be standardized against decinormal $AgNO_3$ as follows: Prepare a solution containing not less than 10 grams of chemically pure KCyS per liter. Place this solution in the burette and put in the porcelain dish 10 c.c. of decinormal $AgNO_3$ which has been strongly acidified with nitric acid and 15 or 20 drops of a solution of ferric alum, added as an indicator. The end point is indicated by the faint red color of ferric sulphocyanate, produced by the first excess of KCyS. The calculation will be the same as previously described in the preparation of N/10 NaOH (page 143).

Now, to determine the silver in solution of an alloy, take a measured volume of the filtrate, about 30 c.c., and put in a porcelain dish and add the indicator as above.

Then place the standard KCyS in the burette and titrate till the faint red color is produced.

Suppose 8 c.c of KCyS is used. The weight of silver in 1 c.c. of a decinormal solution is 0.0108 gram. Multiplying 8 by 0.0108 = 0.0864. Divide by number of c.c. of solution taken, 0.0864 ÷ 30 = 0.00288 gram Ag in 1 c.c. of solution.

Multiply by whole number of cubic centimeters and divide by weight of alloy taken and result will be percentage of silver.

VOLUMETRIC DETERMINATION OF COPPER.

Into a solution of copper, free from other metals of Group I or II, pass H_2S gas. Wash the resulting copper sulphid thoroughly with H_2S water, and dissolve in dilute nitric acid; then wash the paper in warm water, add to the filtrate (wash water) sodium carbonate until precipitate formed is nearly dissolved; then add 1 c.c. of dilute NH_4OH. Titrate, to complete disappearance of blue color, with KCN solution previously standardized after this same method against pure copper wire. A little practice is required in determining the end point to give the process any degree of accuracy. An excess of ammonia should be avoided, as it interferes with the accuracy of the end point.

VOLUMETRIC DETERMINATION OF ZINC.

The solution from which silver and copper have been removed, together with all wash-water, may be concentrated; if acid in reaction it should be evaporated to dryness, and the residue dissolved in water; then add a fairly strong solution of oxalic acid and an equal volume of strong alcohol. Allow to stand 15 to 30 minutes, filter, and wash with 70% alcohol till oxalic acid is removed, dry until the alcohol has disappeared, dissolve in dilute sulphuric acid, and titrate the solution with N/10 permanganate and calculate the zinc from the amount of oxalic acid found.

This method is usually fully as satisfactory as the gravimetric determination given on page 156.

VOLUMETRIC METHODS APPLICABLE TO ANALYSES OF SALIVA OR URINE.

DETERMINATION OF CHLORIN.

Chlorids may be determined, without separating other constituents, by titration with silver nitrate, using neutral potassium

chromate as an indicator, according to the method indicated on page 149, or a more accurate determination may be made by a double titration as follows: To 5 or 10 c.c. of solution add an excess (10 or 15 c.c.) of standardized silver nitrate; then adding a little nitric acid to prevent precipitation of the phosphates, etc., and a solution of ferric alum as an indicator, titrate the mixture with a solution of potassium sulphocyanate KCyS.

If the sulphocyanate solution has been standardized, so that it is the same relative strength as the silver nitrate used, the number of cubic centimeters of the KCyS required may be subtracted directly from the number of cubic centimeters of $AgNO_3$ added, and the difference will represent the amount of silver nitrate required to precipitate chlorin in the quantity of fluid taken.

VOLUMETRIC DETERMINATION OF CALCIUM.

This method is based upon that recommended by Dr. Percy R. Howe, Dental Cosmos, April, 1912. To 5 c.c. of saliva, add as much more distilled water and a slight excess of oxalic acid or ammonium oxalate (5 c.c. of normal solution will be sufficient). Add ammonium water to alkaline reaction, heat nearly to the boiling point, and allow to stand for 20 to 30 minutes. Filter through a hardened filter paper into a small beaker which is allowed to stand on a piece of black glazed paper. Under these circumstances, a slight rotary motion of the beaker will show if any of the white precipitate of calcium oxalate is passing through the paper.

After filtration is complete, wash five times in hot distilled water; then place the precipitate, together with the paper, into a small beaker, add about 30 c.c. of dilute sulphuric acid, and heat nearly to the boiling point; then titrate with N/20 permanganate solution.

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID.

The determination of total phosphoric acid, calculated as P_2O_5, requires the following solutions:

A standard uranium solution, containing 35.5 grams of pure uranium nitrate or acetate in distilled water sufficient to make 1000 c.c.; next an acid solution of sodium acetate, containing 10% of sodium acetate and 3% of acetic acid, and lastly a saturated solution of potassium ferrocyanide, to be used as an indicator.

Process (as given by Ogden's Clinical Examination of Urine): Take 30 c.c. of the urine in a porcelain evaporator, add 5 c.c. of the sodium acetate solution, and heat the mixture to 80° C. over a water-bath. Titrate the hot mixture slowly with standard uranium solution until a drop from the evaporating dish placed on a porcelain tile with a drop of the potassium ferrocyanide gives a distinct brown color. When this point is reached the number of cubic centimeters of uranium solution used is noted and multiplied by 0.005 which will give the quantity of phosphoric acid in 30 c.c. of urine, and from this one can calculate the percentage of total phosphoric acid.

This same process may be used for saliva by diluting the reagent 1 part to 5, and preparing the sample for titration as follows: Take from 2 to 5 c.c. saliva, add sufficient alcohol to make 10 c.c of mixture, warm and filter. This serves to separate the protein substance. Take 5 c.c. of the filtered solution and titrate with the diluted uranium solution as by the process given above for urine. In this case, of course, 1 c.c. of the standard uranium will represent 1 milligram of P_2O_5 rather than 5.

GRAVIMETRIC DETERMINATIONS.

Gravimetric determinations are, as a rule, more accurate than volumetric; but they require greater care and attention to details, making them less satisfactory in the hands of the

beginner. Some determinations, however, on account of difficulties in obtaining accurate end points and absolute separations, are really easier when made by gravimetric processes. A few of these will be given.

GRAVIMETRIC DETERMINATION OF TIN AS SnO_2.

Tin may be separated from dental alloys in the absence of gold or platinum by simply dissolving the alloy in nitric acid. Tin will remain as a white insoluble metastannic acid. As stated on page 33 metastannic acid, upon long standing, will change to somewhat soluble compounds, hence this operation should be completed with reasonable rapidity. After complete disintegration of the alloy, the insoluble tin compound may be separated by filtration through asbestos fiber, contained in a Gooch crucible. The method of procedure is as follows:

A little fine asbestos fiber, washed in acid and held in suspension in water, is placed on the bottom of the crucible. The crucible is then placed in the top of a filtering flask from which the air is exhausted by the suction pump. This packs the asbestos down firmly on the bottom of the crucible in a thin layer, and care should be taken that the quantity of asbestos used is such that water will pass through it easily. The crucible with asbestos is next dried, ignited, and weighed. Now transfer the precipitate of tin oxid (metastannic acid) to the crucible, taking care that none is lost, and wash thoroughly six or eight times, then dry, ignite strongly, and weigh again.

If the ignited residue, weighed as tin oxid, does not contain gold or platinum, the weight of tin may be obtained by multiplying the weight of the ash by 0.788.

VOLUMETRIC DETERMINATION OF GOLD.

If the residue of tin oxid *does* contain gold, it should be separated and its weight deducted before the calculation for Sn is made as above. This separation may be made by the

fire assay as given on page 157, or by solution in aqua regia and subsequent precipitation with oxalic acid, according to the following method as given by Schimpf in his Manual of Volumetric Analysis.

The gold must be in the form of chlorid ($AuCl_3$).

To the solution of gold chlorid a measured excess of N/1 oxalic acid solution is added and the mixture set aside for twenty-four hours.

The solution is then made up to a definite volume (say 300 c.c.). Then, by means of a pipette, 100 c.c. are removed, and the excess of oxalic found by titrating with N/10 permanganate in the presence of sulphuric acid. The reaction is

$$2\,AuCl_3 + 3\,H_2C_2O_4 = 2\,Au + 6\,HCl + 6\,CO_2.$$

Each cubic centimeter of N/1 oxalic acid solution = 0.06523 gram of Au, or 0.1004 gram of $AuCl_3$.

GRAVIMETRIC DETERMINATION OF SILVER.

The gravimetric determination of silver is not difficult, and is rather more accurate than the volumetric method. The silver is obtained in the form of AgCl. This is separated by filtration through an ashless paper, and dried. Then the dried precipitate is removed as completely as possible onto a square of black glazed paper and preserved under a funnel or bell glass. The filter paper, containing traces of AgCl which could not be removed, is next incinerated in a previously weighed porcelain crucible.

As slight reduction of AgCl to Ag may take place during the ignition of the paper, it is necessary to add, after the paper is completely burned, a drop or two of nitric acid, and after the excess has been driven off by gentle heat, a drop or two of HCl. This treatment dissolves any reduced silver and reprecipitates AgCl. After carefully heating to dry the precipitate in the crucible, the reserved portion of silver chlorid is carefully brushed

into the crucible and the whole ignited until the silver chlorid begins to fuse. It is then cooled and weighed as AgCl.

GRAVIMETRIC DETERMINATION OF COPPER.

Copper may be determined quite easily by electrolysis of the faintly acid (H_2SO_4) solution. The copper solution must be freed from other metals and preferably be obtained as a solution of copper sulphate of approximately 0.1 of 1% of copper. 50 c.c. of such a solution are put into a platinum dish which is placed upon a copper plate connected with the negative pole of a battery. A strip of platinum suspended from the positive pole is immersed in the solution and the current allowed to pass for from three to twelve hours, according to the strength of the copper solution. The ordinary 110-volt (direct) current employed for electric lighting may be used by introducing a resistance of from three to six 16-c.p. lamps. After the copper has been entirely deposited the residual solution is drained out of the platinum dish, a little alcohol added, which is also drained out, and by setting fire to the last traces of alcohol the precipitated copper is dried and in condition to weigh. Care must be taken to avoid oxidation of the finely divided Cu; if it turns black too much heat has been used and partial oxidation has taken place, which has of course resulted in an increase of weight.

GRAVIMETRIC DETERMINATION OF ZINC.

Zinc may be determined gravimetrically by precipitation as zinc sulphide as follows: To a measured portion of the solution, free from all metals (except zinc) of Groups I, II, III, and IV, add ammonium chlorid, ammonium hydroxid, and ammonium sulphid, as in qualitative analysis. Filter the precipitated ZnS on to counterpoised filters, wash thoroughly with water containing a little ammonium sulphid, dry in an atmosphere free from oxygen, (hydrogen or hydrogen sulphid), and weigh as ZnS.

Gravimetric Assay of Gold and Silver in the Dry Way.

It is often more convenient to determine gold and silver by the fire assay than by the volumetric methods previously given. This is accomplished usually by fusion with an excess of lead and a borax flux. The mixture is kept at a high heat for upwards of thirty minutes, with a current of air passing over the surface of the molten metals. This serves to oxidize and carry away the baser metals, leaving the gold and silver with but a slight amount of lead, possibly a trace of copper and tin. The purification is completed by cupellation. When the traces of lead and other metals are absorbed by the cupel or are driven off as volatile oxids, the button of gold and silver is next cooled *very slowly* and carefully weighed. From this the silver may be dissolved by nitric acid unless the gold is in considerable excess, which would rarely be the case. If it happens that the gold is present in sufficient quantity to prevent the solution of the silver in nitric acid a known weight of pure silver may be added in amount sufficient to increase the percentage of silver to 75 or over, fused, and then all the silver dissolved out with HNO_3, leaving the gold.

The gold which has resisted solution may be found as small black particles or grains in the bottom of the crucible. This should be carefully washed with distilled water by decantation, very carefully dried and brought to a red heat, which will give a button of pure gold. This may be weighed and the weight subtracted from the weight of gold and silver button previously obtained.

QUANTITATIVE ANALYSIS OF DENTAL ALLOYS CONTAINING Au, Sn, Ag, Cu, Zn.

Weigh accurately 0.5 of a gram of alloy which has been reduced to fine filings and from which all particles of iron have been carefully removed by a magnet, transfer to a beaker and

dissolve in 15 c.c. of strong HNO_3 and 10 c.c. of H_2O by aid of gentle heat. If the sample contains tin or gold, complete solution will not be effected, but, by watching the character of the sediment through the bottom of the beaker, it is possible easily to determine when the alloy has been completely disintegrated.

If silver is to be determined by titration with NaCl and K_2CrO_4, evaporate on a water-bath till all nitric acid has been expelled.

If silver is to be determined by the sulphocyanid solution, evaporation at this point is not necessary. In either case, make the whole solution up to 250 c.c. with distilled water; then filter out tin and gold, following the method given under gravimetric determination of tin (page 154), reserving the filtrate before any wash-water has been added. For convenience this filtrate may be marked "A". Titrate 25 or 50 c.c. of this filtrate ("A") for silver (page 150.)

Take 100 c.c. of filtrate "A" and precipitate silver by slight excess of HCl. Filter and wash precipitate thoroughly with warm water. Concentrate filtrate and wash-water, which may be designated as filtrate "B." Pass H_2S gas into "B" till copper is entirely separated as CuS. Filter and wash CuS seven or eight times with dilute H_2S water. Reserve filtrate and wash-water as filtrate "C". Dissolve CuS in dilute HNO_3, wash paper carefully, concentrate and determine amount of copper by deposition upon platinum (page 156). Concentrate filtrate "C" and determine Zn by volumetric method given on page 151.

During the study of volumetric analysis, taking probably about two weeks' time, consequently covering twelve Laboratory exercises (Nos. 35 to 46 inclusive), the student will be required to make the various standard solutions, to use them more or less on solutions of unknown strength, and to make a complete quantitative analysis of at least one dental alloy.

PART IV.

MICROCHEMICAL ANALYSIS.

CHAPTER XVIII.

METHODS.

The advantages of microchemistry are many, as claimed by its enthusiastic advocates, and there are two particulars in which these methods strongly recommend themselves to the dental practitioner: (1) Microchemical analysis deals with exceedingly minute portions of matter, making the examination of very small particles of substance easily possible. (2) Three or four one-ounce "drop-bottles" and a few two-drachm vials will contain all necessary reagents, and in consequence three feet of bench-room will furnish ample laboratory space.

The principles of microchemical analysis are, of course, the same as for any analysis, but the processes employed are quite different and need some explanation. In microchemical analysis the production of crystals of characteristic form furnishes perhaps the most rapid method of detection of an unknown substance, and in this we are greatly aided by the use of polarized light, which not only helps in the differentiation of crystals but often makes it possible to see and distinguish small or transparent crystals which might otherwise escape notice altogether.

Use of Microscope. — For the examination of the crystals mentioned in this chapter, also for the work required on saliva or urine, lenses of comparatively low power are sufficient. For most of the microchemical tests, a No. 3 Leitz or a 16 mm. Bausch & Lomb objective will be found satisfactory. For a few micro-

chemical tests and for urine, a ¼-inch Bausch & Lomb or a No. 5 Leitz objective will give better results in the hands of a beginner than one of higher power.

In using the microscope for microchemistry, the preparation should *always* be covered with a cover glass and the examination be made with the low-power lens if possible. The object in covering is to prevent any action by reagent upon the objective. As a further precaution, it is well to form the habit of first lowering the objective and then focusing by upward movement of the draw-tube.

Formation of crystals may be brought about in two ways: *first*, by precipitating insoluble crystalline salts by use of reagents, as in ordinary qualitative analysis; *second*, by allowing salts to crystallize by spontaneous evaporation of the solvent.

If the first method is to be employed it is essential to have the dilution fairly constant in order to obtain crystals which shall be comparable with those obtained at other times or by other individuals. The tendency of strong solution is to give amorphous precipitates. Sometimes the precipitate will be amorphous when first thrown down, but upon standing will assume crystalline form. To secure the uniformity of results necessary to correct deductions, the following method of procedure should be *exactly* followed *every* time.

The reagent should be of uniform strength, usually 1 or 2 per cent. Place on a clean microscope-slide a small drop of the solution to be tested, and as close as possible without touching it, one of about equal size of the reagent to be used. Now bring the drops together by tapping the slide or with a small glass rod. If a precipitate forms immediately, *cover with a cover-glass* (this must *always* be done) and examine with the microscope. If the precipitate is crystalline, note the form, and in any case, whether crystalline or not, repeat the test after diluting the unknown solution one-half. If the second test gives an amorphous precipitate, or crystals of different shape from the first, *continue*

the *dilution* of the *unknown* till a point is reached when admixture with the drop of reagent gives *no immediate* precipitate, but one appearing in a few seconds' time (five to thirty). In this way we have produced the precipitate under standard conditions or as nearly such as is possible with unknown solutions.

Until thoroughly familiar with the forms obtained by drying the various reagents, it is well to evaporate a small drop of the reagent alone, on the same slide on which a test is made, for the sake of subsequent comparisons.

Filtration in microchemical examinations, when perhaps only a few drops of solution are to be had, may be effected in a very satisfactory manner and without appreciable loss by absorption as follows:

Cut a filter-paper about 1 cm. wide and 6 cm. long, double it and crease the middle so that it assumes the shape of an inverted V. Put the solution to be filtered in a small watch-glass placed at a slight elevation above a microscope slide; now place one "leg" of the strip of filter-paper in the watch-glass, allowing the end of the other to touch the slide. By capillary attraction the clear solution will follow over the bend in the strip of paper and a drop or two of perfectly clear filtrate suitable for the test will be found upon the slide.

Evaporation of a *solution* is best effected on a small watch-glass *held in the fingers* and moved back and forth over a low Bunsen flame, or else placed over a water-bath.

The purpose of the microchemical tests here outlined is not so much a method of general qualitative analysis, to which they are not suited, as it is a specific application of well-known reactions to concrete examination of substances, the uses and probable composition of which are known. The details of the various tests will be given under classification furnished by the substances investigated.

Our study may include alloys and amalgams, teeth, tartar, dental anæsthetics, cement, mouth-washes, antiseptics, disin-

fectants, and sediments obtained from the saliva and from the urine.

The following crystals are selected as among those most frequently met with in the analysis of the above substances or best suited for the study of microchemical processes, and the student should make each test here indicated and carefully draw the crystals produced:

1. Calcium oxalate from 2% $H_2C_2O_4$ and $CaCl_2$ solutions (Plate II, Fig. 1).

2. Cadmium oxalate from 2% $H_2C_2O_4$ and $CdSO_4$ solutions (Plate II, Fig. 2).

3. Strontium oxalate from 2% $H_2C_2O_4$ and $Sr(NO_3)_2$ solutions (Plate II, Fig. 3).

4. Sodium oxalate by evaporation of aqueous solution, also by evaporation of urine containing $Na_2C_2O_4$ (polarized light) (Plate II, Fig. 4).

5. Urea oxalate from 2% $H_2C_2O_4$ and urea solution (Plate II, Fig. 5).

6. Ammonium-magnesium-phosphate from magnesium mixture * and sodium phosphate (Plate IV, Fig. 2).

7. Ammonium platinic chlorid (Plate III, Fig. 1).

8. Ammonium phosphomolybdate from ammonium molybdate and phosphate of sodium (Plate III, Fig. 2).

9. Sodium urate by evaporation (polarized light) (Plate X, Fig. 3, opp. page 368.)

10. Crystals formed from cocain and potassium permanganate (Plate III, Fig. 4).

11. Crystals formed from carbolic acid and dilute bromin water (tribromphenol) (Plate III, Fig. 5).

12. Crystals formed from morphin solutions and ammonia (morphia) (Plate III, Fig. 6).

* Magnesium mixture as used in urine analysis to precipitate phosphates contains $MgCl_2$ (or $MgSO_4$), NH_4Cl and NH_4OH.

PLATE II.—MICROCHEMICAL ANALYSIS.

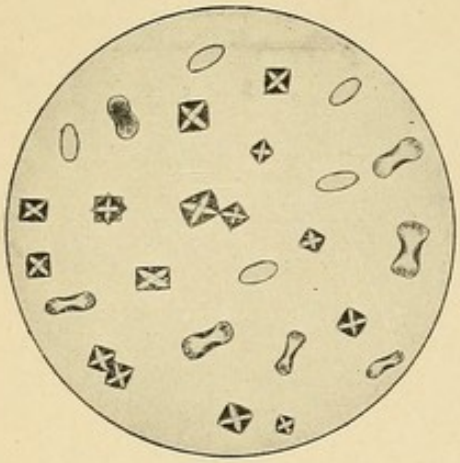


FIG. 1.
Calcium Oxalate.

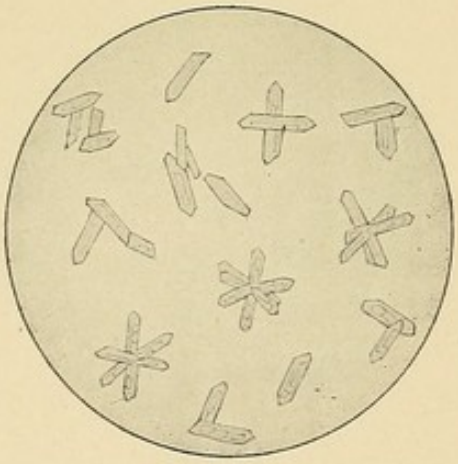


FIG. 2.
Cadmium Oxalate.

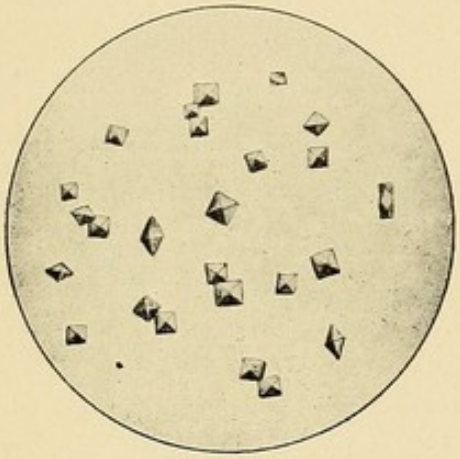


FIG. 3.
Strontium Oxalate.

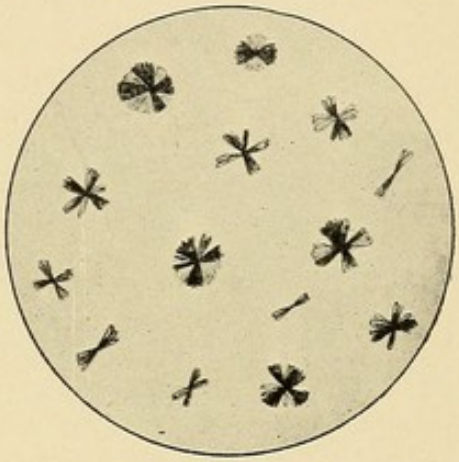


FIG. 4.
Sodium Oxalate (P.L.).

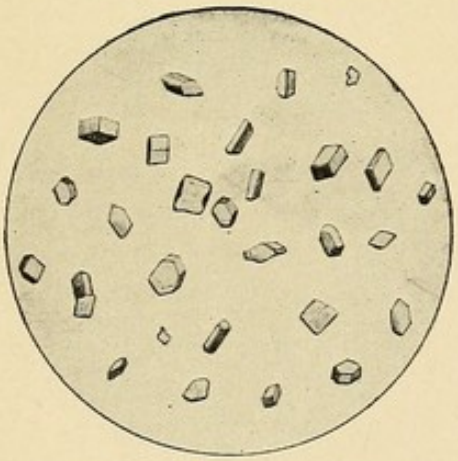


FIG. 5.
Oxalate of Urea.

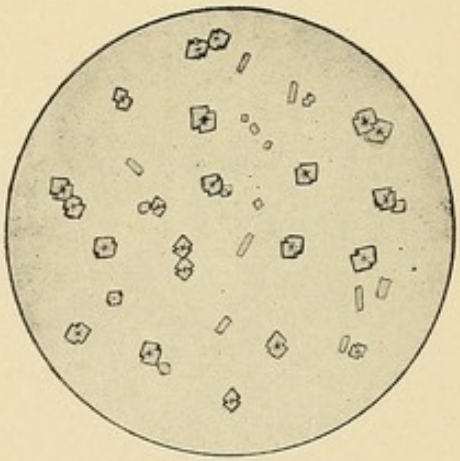


FIG. 6.
Zinc Oxalate.

PLATE III. — MICROCHEMICAL ANALYSIS.

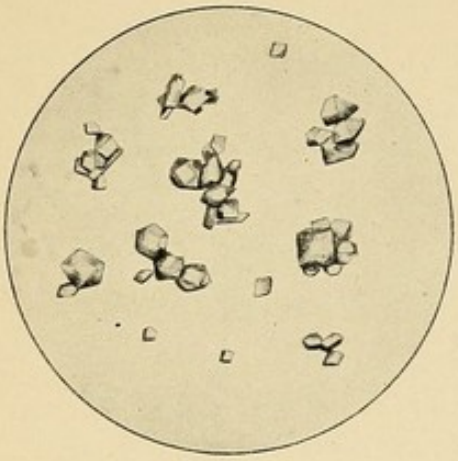


FIG. 1.
Ammonium Platinic Chlorid.

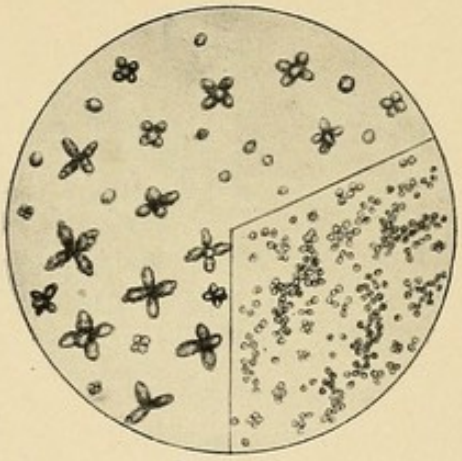


FIG. 2.
Ammonium Phosphomolybdate.
No. 3 and No. 7 Leitz Objective.

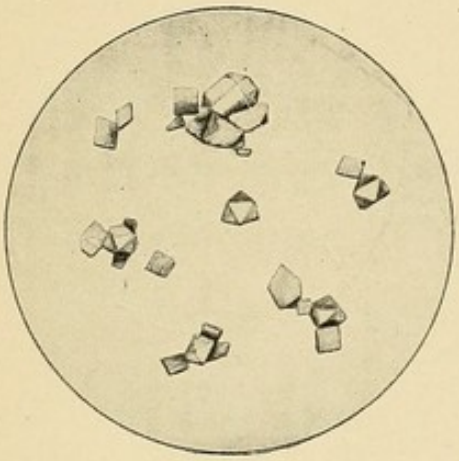


FIG. 3.
Potassium Platinic Chlorid.

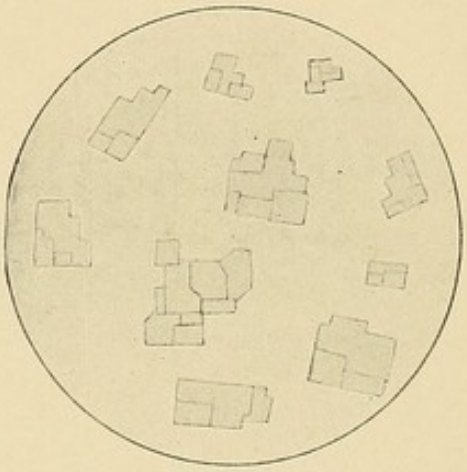


FIG. 4.
Cocain and Potassium Permanganate.

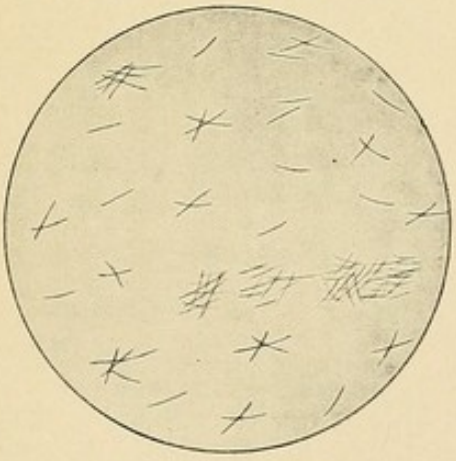


FIG. 5.
Tri-brom-phenol.

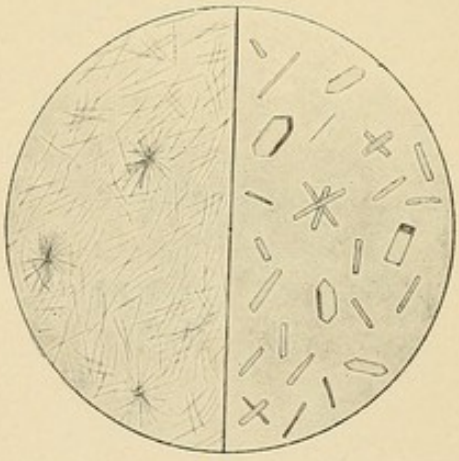


FIG. 6.
Morphin.

PLATE IV.—MICROCHEMICAL ANALYSIS.

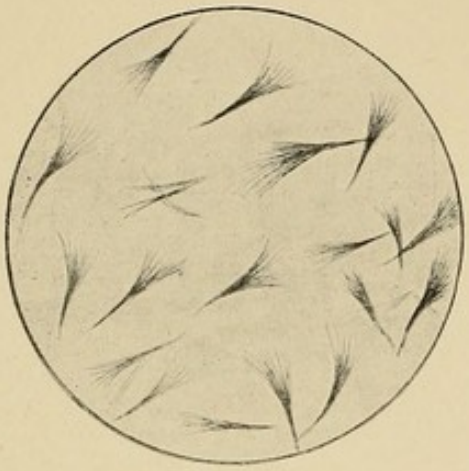


FIG. 1.
Morphin and Marme's Reagent.

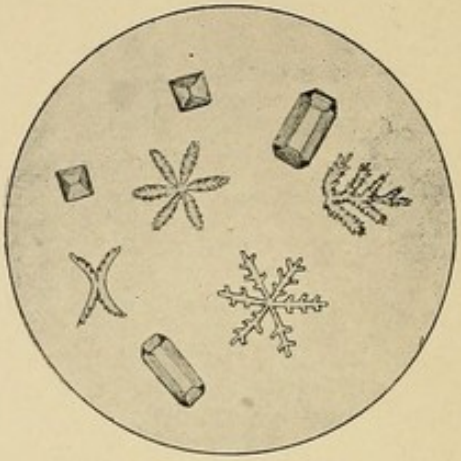


FIG. 2.
Magnesium Ammonium Phosphate.

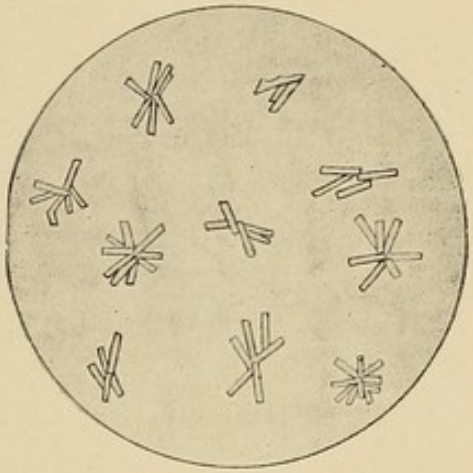


FIG. 3.
Cocain with Tin Chlorid.

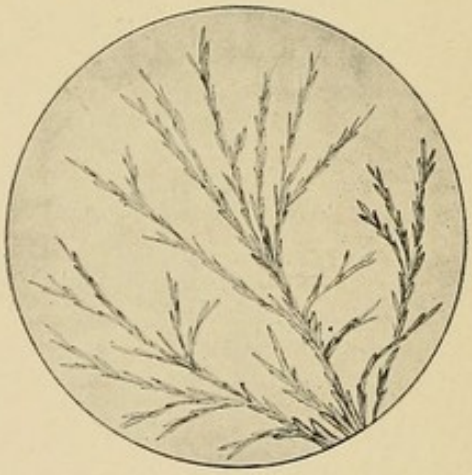


FIG. 4.
Chloretone and Sodium Hypochlorite.

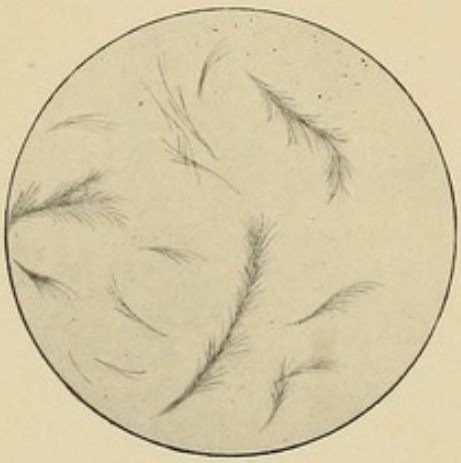


FIG. 5.
Palmitic Acid.

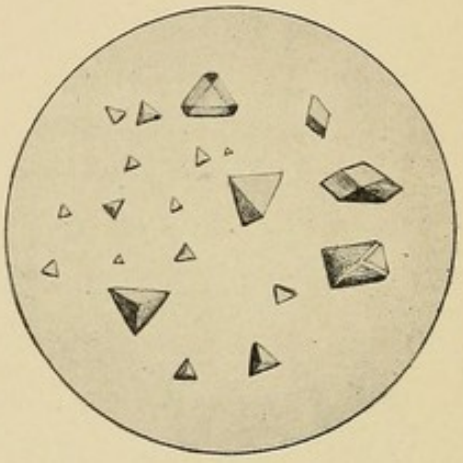


FIG. 6.
Uranyl Sodium Acetate.

13. Crystals formed from morphin and Marme's reagent (Plate IV, Fig. 1).

14. Crystals formed from chloretone and sodium hypochlorite (Plate IV, Fig. 4.)

The list may be extended to include the crystals produced by various alkaloidal salts with the common reagents, also substances usually employed in the manufacture of the various dental preparations.

CHAPTER XIX.

LOCAL ANÆSTHETICS.

In considering the chemistry of local anæsthetics we may divide them into two classes as follows:

First. Those of definite or well-known composition, and

Second. Preparations of a proprietary nature, the composition of which is always problematical.

In the first class will be found cocain, eucain, tropacocain, acoin, ethyl chlorid, etc., which will be later alphabetically considered. The second class contains a large number of preparations of all degrees of value, among them some of exceeding merit and largely used, others of doubtful worth, some worthless if not dangerous. Many of the preparations of this class contain cocain as the anæsthetic, and frequently a little nitroglycerin as a cardiac stimulant to counteract the depressant effect of the alkaloid. Carbolic acid and oil of cloves are also frequently used.

Many of the constituents of this class of anæsthetics may readily be identified by the processes of microchemical analysis to which previous reference has been made; others may be detected by special tests, some of which are given under the various substances in the following list. This list has been extended to include a considerable number of preparations of common occurrence.

Acoin, a synthetic compound (chemically diparanisyl-monophenetyl-guanidine hydrochlorid, $C\begin{cases}(NC_6H_4OCH_3)_2 \\ (NC_6H_4OC_2H_5)\end{cases}HCl$) soluble in both alcohol and water. Strongly antiseptic and a valuable anæsthetic, especially in conjunction with cocain.

Acoin should be used only in solution and this should be kept in a dark place.

Adrenalin, a valuable hæmostatic and frequently used in conjunction with dental anæsthetics, is the active principle of the suprarenal gland or capsule. It occurs as very small white crystals which are not very stable and only slightly soluble in water, hence the article is usually sold in solution with sodium chlorid, according to the following formula taken from a commercial sample:

Adrenalin chlorid, 1 part; normal sodium chlorid solution (with 0.5% chloretone,) 1000 parts. This solution is usually diluted with the normal (0.6%) salt solution. According to the Druggists' Circular, preparations similar to the above are also marketed under the names of adrenol, adnephrin, hemostatin, supraredalin, etc.

Alypin. — Benzoyl - dimethylamino - methyl - dimethylamino-butane hydrochlorid, white crystalline, hygroscopic, melts at 169° C. Soluble in water and alcohol.

Alypin can be sterilized without decomposition, is not half so poisonous as cocain and is cheaper. Is used in 2% solution. Solution should be freshly made and prolonged boiling avoided. Sometimes used with adrenalin. (Cosmos, 1908, p. 889).

Alypin nitrate occurs as a white, crystalline powder melting at 159° C., readily soluble in ether. Mfrs.: Farbenfabriken of Elberfeld, Elberfeld (Germany) and New York. (Mod. Mat. Med., page 21).

Ammonium bifluorid is strongly recommended as a solvent for tartar by Dr. Joseph Head of Philadelphia. In Items of Interest, Vol. 31, page 174, Dr. Head gives the following method for its preparation. Hydrofluoric acid is neutralized with ammonium carbonate, the solution filtered and evaporated to half its bulk, the original volume restored by adding more hydrofluoric acid and then the resulting mixture is again concentrated to half its volume by evaporation.

Anesthol, or Anæsthol, is a mixture of ethyl chlorid and methyl chlorid, used as a local dental anæsthetic. The name is also applied to a general anæsthetic given by inhalation and consisting of a mixture of ethyl chlorid 17 parts, chloroform 35.89 parts, and ether 47.1 parts.

Anæstheaine, a local anæsthetic, contains 5 grains of stovain to the fluid ounce.

Argyrol, a protein compound of silver, occurs as dark brown crystals containing 30% of Ag. It is easily soluble in water. It does not precipitate chlorin nor coagulate albumin, and is recommended for use in place of ordinary silver nitrate.

Aristol is given by the U. S. D. as a synonym for dithymol-diiodid which contains 45% of iodin and is used as an antiseptic similarly to iodoform.

Atropin, an alkaloid obtained from belladonna, usually used combined with sulphuric acid, $(C_{17}H_{23}NO_3)_2H_2SO_4$; the alkaloid is only sparingly soluble in water but the sulphate is easily soluble, dissolving in about one half part of water at ordinary temperature. A 1% solution is said to produce complete insensibility of the nerves in cases in which an artificial tooth is inserted in a living root. (U. S. D., page 249.)

Tests. — Atropin may be separated from a local anæsthetic by first rendering the mixture alkaline with ammonia and shaking with chloroform. Upon evaporation of the chloroform solution on a watch-glass the resulting residue may be tested by adding a drop or two of sulphuric acid and a trace of potassium bichromate and a little water. The odor of bitter almonds is produced. A more conclusive test is to convert the alkaloid, which has been dissolved by the chloroform, into a salt by the addition of a few drops of acetic acid, evaporating to *complete* dryness, taking up in a few drops of distilled water and placing one or two drops of this solution in the eye of a cat, when, if atropin is present, a dilation of the pupil occurs

in from fifteen minutes to an hour and a half, according to amount present.

Borax. — Sodium tetraborate, $Na_2B_4O_7$, is used in antiseptic solutions and may be detected as follows: evaporate a little of the solution to dryness, add a little HCl, evaporate to dryness a second time, then add a very dilute HCl solution containing tincture turmeric. Upon drying this mixture a beautiful pink color appears. If much organic matter is present it may be burned off in the Bunsen flame *before* the addition of any acid.

Carbolic Acid. — See Phenol.

Chloral Hydrate, $CCl_3CHO.H_2O$, a crystalline solid composed of trichloraldehyd or chloral with one molecule of water, (U. S. P.) easily soluble in water, may become with alcohol a chloral alcoholate comparatively insoluble in water.

Tests. — Chloral may be detected by adding to the suspected mixture a few cubic centimeters of fairly strong alcoholic solution of KOH or NaOH with one drop of aniline oil and heating, when isobenzonitril is produced, which has a peculiarly disagreeable and characteristic odor. This test is also given by chloroform, which is produced by heating chloral hydrate with caustic alkali. If more than traces of chloral are present this latter reaction may be a sufficient test.

Chloretone, $CCl_3COH(CH_3)_2$, is the commercial name of acetone-chloroform or tertiary trichlorbutyl alcohol. Made from chloroform, acetone, and an alkali, and occurs as small white crystals, with taste and odor like camphor. It is dissolved by alcohol and glycerin and to a slight extent by water.

Tests. — A convenient microchemical test for chloretone devised by Dr. Niles, Harvard Dental School, '06, consists simply of treatment with a solution of hypochlorite of sodium. A precipitate is at once formed of a coarsely branching character which thus far seems to be characteristic of chloretone solutions (Plate IV, Fig. 4).

Chloroform, trichlormethane, $CHCl_3$, prepared by action of chlorinated lime on acetone. Chloroform is a heavy colorless liquid with a specific gravity of 1.490 at 15° C. Is very volatile and used as a solvent for gutta-percha, caoutchouc, many vegetable balsams, camphor, iodin, bromin, and chlorin; it also dissolves sulphur and phosphorus to a limited extent.

Tests. — It may be detected by its odor, when heated, or by the isobenzonitril test to which reference has been made under chloral hydrate.

Cocain is the alkaloid obtained from erythroxylon coca. The hydrochlorate, $C_{17}H_{21}NO_4HCl$, is the salt most usually employed. This is easily soluble in water and very largely used as a dental anæsthetic in a 1 or 2 per cent solution.

Tests. — Cocain solutions respond to the usual alkaloidal reagents. With 1% solution potassium permanganate gives pink plates in form resembling cholesterin (Plate III, Fig. 4) in form but not in color.

Dilute cocain solution with picric acid gives a yellow precipitate which becomes crystalline on standing. Quite characteristic crystals also may be obtained from dilute cocain solutions and stannous chlorid in the presence of free HCl (Plate IV, Fig. 3).

Creosote. — A mixture of phenols derived from the destructive distillation of wood tar. It is a heavy oily liquid acting when pure as an escharotic. It is analogous in many respects to carbolic acid and may be used for similar purposes. To distinguish between creosote and carbolic acid, boil with nitric acid until red fumes are no longer given off. Carbolic acid will give yellow crystalline deposit; creosote will not. An alcoholic solution of creosote is colored emerald green by an alcoholic solution of ferric chlorid. Phenol is colored blue.

Cresol is the next higher homologue to phenol, having a formula $C_6H_4CH_3OH$, boiling at 198° C. It is largely used,

usually together with allied compounds from coal-tar, as antiseptic and disinfectant solutions.

Ektogan. — Peroxid of zinc, ZnO_2, designed for external use (London, July 9, 1904).

Ethyl Chlorid monochlorethane, C_2H_5Cl. This is a gaseous substance at ordinary temperature, but when used as a dental anæsthetic it is compressed to a colorless liquid which has a specific gravity of 0.918 at 8° C., is highly inflammable and usually sold in sealed glass tubes of from 10 to 30 grams each.

β-Eucain is the hydrochlorate of benzoylvinyldiacetonealkamine, and occurs as a white, neutral powder, soluble in about 30 parts of cold water. It is used like cocain as a local anæsthetic, and is claimed to be less toxic, and sterilizable by boiling without danger of decomposition. It is usually applied in from 1 to 5 per cent solutions, which are conveniently prepared in a test-tube with boiling water. It is also marketed in the form of $1\frac{1}{2}$- and 5-grain tablets. (Druggists' Circular.)

Eucain Lactate. — " Eucain lactate is used in 2 to 5 per cent solution as a local anæsthetic in ophthalmic and dental practice and in 10 to 15 per cent solution when used in the nose or ear." (Review of American Chemical Research, page 97, 1905).

Eudrenin is a local anæsthetic marketed in capsules of 0.5 c.c. containing 1/12 grain of eucaine and 1/4000 grain of adrenalin hydrochlorid. It is used as a local anæsthetic, chiefly in dentistry. The contents of one or two capsules, according to the number of teeth to be extracted, are injected into the gums ten minutes before extraction. Mfrs.: Parke, Davis & Co., Detroit, Mich. (Mod. Mat. Med., page 147.)

Eugenol, $C_{10}H_{12}O_2$, synthetical oil of cloves. Eugenol is miscible with alcohol in all proportions. Exposure to air thickens and darkens it. Should be kept in well-stoppered amber-colored bottles (U. S. D.).

Europhen — recommended by Dr. J. P. Buckley as a substitute for iodoform (Dental Review, Vol. 21, page 1284).

Di-iso-butyl-cresol is described as a bulky yellow powder of faint saffron odor and containing 28% of iodin. (Mod. Mat. Med., page 152.)

Formalin, Formol, Formin, etc., are commercial names for a 40% aqueous solution of formaldehyd, HCHO, prepared by the partial oxidation of methyl alcohol. Formalin is a powerful disinfectant very generally used. (For test see page 201, Exp. 62.)

Glycerol is a triatomic alcohol, $C_3H_5(OH)_3$, a colorless liquid of syrupy consistence and sweetish taste, specific gravity 1.250 at 15° C. It is easily soluble in either water or alcohol.

Tests. — Upon heating strongly it is decomposed, giving off odor of acrolein, which is usually sufficient for its identification. A further test may be made by moistening a borax bead on a platinum wire with the suspected solution (after concentration) and holding in a non-luminous flame, to which it will give a deep-green color which does not persist. Glycerol when present is apt to interfere with characteristic crystallization of many precipitates.

Gram's Solution, Kuhne's modification, contains 2 grams of iodin, and 4 grams potassium iodid in 100 c.c. of water.

Gutta-percha. The name signifies scraps of gum. It is obtained as a milky exudate from a number of tropical trees. It is soluble in ether, chloroform, carbon disulphid, toluene and, petroleum ether. It may be freed from impurities by shaking the solution with calcium sulphate, which will mechanically carry coloring matter and other impurities with it as it slowly settles out from the mixture. It is not soluble in alcohol or in water.

Heroin is a diacetic ester of morphin. It is usually obtained as the hydrochlorid and occurs as a white powder, soluble in two parts of water. Its action is similar to that of morphin; it answers to the usual tests for morphin, but may be distinguished from it by the fact that it will yield acetic ether upon heating with alcohol and sulphuric acid.

Hopogan (also known as biogen) is a peroxid of magnesium, MgO_2, recommended as a non-poisonous and non-astringent intestinal germicide.

Hydrogen Peroxid, or dioxid, H_2O_2, is, when pure, a syrupy liquid without odor or color. It is sold under various trade names in aqueous solution containing about 3% and yielding upon decomposition about 10 volumes of oxygen gas. It is used also as an escharotic in etherial solutions containing 25 to 50 per cent H_2O_2. Peroxid solutions may be concentrated by heat without decomposition if kept *perfectly* free from dirt or traces of organic matter. It is readily prepared by treatment of metallic peroxids, as BaO_2 with dilute acids.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

or

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

This latter reaction has the advantage of producing an insoluble barium compound and at the same time introducing no objectionable acid. The peroxids of sodium, calcium, magnesium, and zinc may also be used; ZnO_2, however, is comparatively expensive and used in powder form as an antiseptic dressing rather than as a source of H_2O_2. Na_2O_2 is valuable as a bleaching agent, because for this purpose an alkaline solution is required and the solution of Na_2O_2 in water produces both alkali and H_2O_2 according to the following reaction:

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2.$$

Sodium perborate (page 175), also sold as euzone, is a powder advertised to produce H_2O_2 in water. Commercial H_2O_2 solutions are usually acid in reaction, as such solutions are more stable than if neutral or alkaline.

Lugol's Caustic Iodin is made of iodin and potassium iodid, 1 part of each dissolved in 2 parts of water.

Lugol's Iodin Solution contains 5 grams of odin and 10 grams of potassium iodid dissolved in sufficient water to make 100 grams.

Menthol is the stearopten obtained from the oil of peppermint. It is a volatile crystalline substance having a formula $C_6H_9OHCH_3C_3H_7$. Menthol is but slightly soluble in water but freely soluble in alcohol, ether, chloroform, or glacial acetic acid. The presence of menthol may usually be detected by its odor. If the odor should be suggestive but not distinctive it is well to place a little of the substance on a filter-paper, rub it between the thumb and finger, thereby obtaining a "fractional evaporation," when the more easily volatile substance will pass off first, thus producing a partial separation of substances.

Mercuric Chlorid, corrosive sublimate, $HgCl_2$, is soluble in about 16 parts of water and 3 parts of alcohol. It is a powerful antiseptic, in aqueous solution 1/1000 to 1/5000, but should never be used in mouth-washes.

Tests. — A drop of the suspected solution with a trace of potassium iodid will give a red precipitate of mercuric iodid soluble in excess of either reagent. With lime-water or fixed alkaline hydroxids a black precipitate is produced. A drop of mercurial solution placed on a bright copper plate will leave a tarnished spot due to the reduction of the mercuric salt and subsequent amalgamation of the metal.

Methethyl. — Ethyl chlorid mixed with a little methyl chlorid and chloroform is said to be the composition of a local anæsthetic sold under the name of methethyl (U. S. D.).

Methyl Chlorid, CH_3Cl, is a colorless gas which condenses to a liquid at 23° C. Methyl chlorid is easily soluble in alcohol, somewhat in water, and is used in a similar manner to ethyl chlorid.

Morphin, $C_{17}H_{19}NO_3$, alkaloid from opium. Solutions for use are made from the sulphate, hydrochlorate, or acetate. The alkaloid itself is insoluble in water; its salts are easily soluble.

Morphin may be separated from solutions containing it by making the solution alkalin with ammonia, and shaking out the precipitated alkaloid with warm amyl alcohol. Upon

evaporation of the alcohol the residue may be tested with Fröhde's reagent (sodium molybdate, 1%, in strong sulphuric acid). The color obtained should be a *violet*, changing usually to brown; a pure blue color is not distinctive for morphin. If the morphin solution is of sufficient strength the addition of ammonia will produce minute crystals of the alkaloid as shown on Plate III, Fig. 6. Dental anæsthetics containing morphin will give precipitates with the usual alkaloidal reagents. Marme's reagent (CdI_2) gives crystals represented on Plate IV, Fig. 1.

Nirvanin, hydrochlorid of diethyl-glycocoll-*p*-amino-*o*-oxybenzoic-methylester, of the formula

$$\begin{array}{l}(CH_2N) = (C_2H_5)_2HCl \\ \quad | \\ (CO.NH.C_6H_4(OH)COOCH_3.\end{array}$$

White prisms soluble in water and in alcohol, melt at 185° C., violet reaction with ferric chlorid.

Nitroglycerin, $C_3H_5(NO_3)_3$, is used as a cardiac stimulant in alcoholic solution, the U. S. P. Spiritus Glonoini, containing 1% by weight of the substance.

Novocain, discovered by Uhlfelder and Einhorn, is a hydrochlorid *p*-aminobenzoyl-diethylamino-ethanol. It occurs as thin colorless needles; melts at 156° C., soluble in 1 part H_2O and 30 parts alcohol. It is seven times less toxic than cocain, and three times less toxic than stovain. It can be sterilized by boiling, and is used in 1/2 to 2% solution often with adrenalin 1/1000. (Mod. Mat. Med., page 275).

Novocain, if intended to represent a solution which is isotonic with the blood corpuscles, must be dissolved in a 0.92 per cent sodium chlorid solution. (Dental Cosmos, 1910, page 605.)

Oil of Cloves, oil of Gaultheria, and other essential oils may be detected by the same process of fractional evaporation as suggested for menthol. In testing for the presence of any sub-

stance by its odor, it is usually necessary to make a comparative test on known samples using the same methods.

Orthoform, $C_6H_3OH(NH_2)COOCH_3$, methylparaamino-metaoxybenzoate, used as an anæsthetic and antiseptic, is without odor, color, or taste, is slightly soluble in water and easily soluble in alcohol or ether.

Phenol. — Carbolic Acid. C_6H_5OH, obtained from the destructive distillation of coal-tar. A light oily liquid of specific gravity of 0.94–0.99. Carbolic acid is usually obtained as a white crystalline mass soluble in 20 parts of water. The pure acid turns pink with age, but does not suffer deterioration on account of this change of color. The addition of from 5 to 8 per cent of water will cause liquefaction of the crystals and the preparation becomes permanently liquid. It is easily soluble in glycerol and strong solutions may thus be prepared. Carbolic acid is sometimes added to local anæsthetics with the intent of rendering the solution sterile, but as shown by Dr. Endelman (Dental Cosmos Vol. 45, page 44) it would be necessary, in order to prevent the development of micro-organisms, to add the acid in proportion that would render the solution unfit for hypodermic purposes.

Tests. — Phenol may be detected in the majority of preparations by the addition of bromin-water, which gives white crystals of tribromphenol (see Plate III, Fig. 5).

Phenol Compound — Dr. Buckley's formula for treatment of root canals — menthol 1.3 grams, thymol 2.6 grams and phenol 12 c.c.

Potassium Hydroxid, KOH, gives an alkaline reaction to litmus paper and may be detected by the ordinary methods of inorganic analysis.

Rhigolene is a light inflammable liquid obtained from petroleum, boiling at about 18° C., used as a spray for the production of low temperature, similarly to methyl or ethyl chlorid. It is readily inflammable, and the vapor, mixed with

certain proportions of air is explosive. It should be kept in a cool place.

Saccharin — the commercial name of benzosulphinid, a derivative of toluene — is a white crystalline powder 300 times sweeter than cane sugar and is used in mouth-washes, tooth-paste, etc., as a flavor and an antiseptic.

Silver Nitrate, $AgNO_3$, crystallizes in colorless plates without water of crystallization; used as an antiseptic, disinfectant, or escharotic. It is freely soluble in water and may be detected by the ordinary methods of qualitative analysis (page 19).

Sodium Chlorid, NaCl, is a constituent of many preparations designed to be used hypodermically. Experience has proved the value of such addition; perhaps the reason for its desirability is given by Dr. G. Mahe, of Paris, in the Dental Cosmos for September, 1903, in the statement that sodium chlorid added in excess to a toxic substance diminishes its toxicity by one half, and this has been demonstrated particularly with cocain.

Sodium Perborate, a powder said to have the composition $NaBO_3.4\,H_2O$, which will furnish 10% of available oxygen and produce H_2O_2 with water; very stable and recommended as a bleach-powder.

Sodium perborate may be made * by thoroughly mixing 78 grams Na_2O and 248 grams of crystallized H_3BO_3 and stirring the mixture gradually into 2 liters of cold H_2O. The sodium perborate, $Na_2B_4O_8 + 10\,H_2O$, is formed spontaneously and settles out from the solution as a white crystalline powder. Its solubility is increased by addition of weak organic acids, citric or tartaric.

Sodium Peroxid, Na_2O_2. — A white powder easily soluble in water, usually with evolution of more or less oxygen and formation of hydrogen dioxid.

* Dental Cosmos, Nov., 1905, page 1381.

Somnoform. — A general anæsthetic administered in manner similar to chloroform; introduced by Dr. Rolland, of Bordeaux; consists of 60% ethyl chlorid, 35% ethyl bromid, and 5% methyl bromid. (Dental Cosmos, Vol. XLVII, page 236.)

Stovain. — Benzoylethyldimethyl-aminopropanol hydrochlorid, $C_{14}H_{21}O_2N.HCl$, closely related to alypin, small shining scales freely soluble in alcohol or water. Incompatible with alkalies and all alkaloidal reagents. Can be sterilized by boiling. (Mod. Mat. Med., 2nd edition.)

It melts at 175° C., is very soluble in H_2O, and gives reaction similar to cocain, which is also a benzoyl derivative. (U. S. D., page 1661.)

It is less powerful than cocain and physiologically incompatible with adrenalin. (Dental Cosmos, 1905, page 146.)

Tannic Acid, or tannin, sometimes called gallotannic acid, is an astringent organic acid obtained from nutgalls. It may be obtained as crystals carrying 2 molecules of water, $HC_{14}H_9O_9$ 2 H_2O. Tannic acid is a white or slightly yellowish powder soluble in about one part of water or 0.6 part alcohol. It is used as an alkaloidal precipitate, also in astringent washes. It may be detected by the addition of ferric solutions which form with it a black tannate of iron of the nature of ink.

Thymol, $C_6H_3(CH_3)(OH)(C_3H_7)$ 1:3:4: a phenol, occurring in volatile oils of thymus vulgaris (Linne). Melts at 44° C.; sparingly soluble in water, easily in alcohol and ether.

Tests. — It may usually be detected by its odor or by dissolving a small crystal in 1 c.c. of glacial acetic acid, when if 6 drops of sulphuric acid and 1 drop of nitric acid be added, the liquid will assume a deep bluish-green color. (U.S.D.)

Thymophen, a mixture of equal parts of thymol and phenol.

Trichloracetic Acid occurs as deliquescent crystals, readily soluble in water. Distils at 195° C. and is a powerful caustic. Dilute solutions are recommended for treatment of pyorrhœa.

Tropa-cocain is an alkaloid originally isolated by Giesel from the leaves of the small-leaved coca-plant of Java and introduced by Arthur P. Chadbourne, Harvard Medical School. Used hypodermically in normal salt solution. It is probably superior to cocain, but rather more expensive. It is obtained as an oil which, when quite dry, solidifies in radiating crystals, melting at 49° C. It is easily soluble in alcohol.

Laboratory Exercises XLVII to XLIX.

A number of commercial mouth-washes and local anæsthetics will be given to the class for identification, the object being to familiarize the student with the more easily made tests for the principal ingredients of these preparations. Complete analysis will rarely be attempted. The following table, taken from the Druggist's Circular of June, 1910, may be helpful.

DIFFERENTIATION OF COCAIN AND ITS SUBSTITUTES.

	Iodin potassium iodid.	Bromin water.	Sodium hydroxid.	Potassium permanganate.
Eucain — *a*.	Yellow-maroon precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, blackening quickly.
Eucain — *b*.	Deep-red precipitate, soluble on boiling.	Yellow precipitate, slightly soluble on heating, reprecipitated white on boiling.	White precipitate, insoluble in excess and on boiling.	No precipitate immediately; color persists for a day.
Cocain.....	Yellow-maroon precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, color persists for one hour, then deposits MnO_2.
Novocain.....	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, blackening quickly.
Stovain.....	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess; aromatic odor on boiling.	Violet precipitate, blackening almost immediately.
Nirvanin.....	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating, but the liquid becomes red and gives an agreeable fruity odor.	Precipitate very soluble in excess of the reagent.	Precipitate, first maroon, then brown.
Alypin.....	Yellow-maroon precipitate, insoluble on boiling; orange red deposit.	Yellow precipitate, soluble on gentle heating.	White precipitate, insoluble in excess and on boiling.	Bluish-violet precipitate, slowly blackening.

CHAPTER XX.

TEETH AND TARTAR.

THE chemical examination of teeth and tartar, while coming more properly under the head of physiological chemistry, will be considered in part in this place, as the tests made, especially on tartar, are practically all microchemical. The composition of the cement is practically that of true bone, the dentine and enamel differing principally in the proportion of organic matter which they contain. In all of these the presence of lime, phosphoric acid, carbonic acid, and traces of magnesium and calcium fluorid may be demonstrated. The tartar contains a greater proportion of carbonic acid, less calcium phosphate, and much less organic matter than the teeth, taken as a whole, or than dentine, but about the same as enamel. According to Berzelius, sodium chlorid and sodium carbonate may also be found.

The composition of the different parts of the tooth substance has been given as follows:

	Organic Matter.	Ash.	$Ca_3(PO_4)_2$.	$MgHPO_4$.	$CaCO_3$.
Dentine	23.2	76.8	70.3	4.3	2.2
Cement	32.9	67.1	60.7	1.2	2.9
Enamel	3.1	96.9	90.5	traces	2.2

Also traces of magnesium carbonate, calcium sulphate, fluorids, and chlorids. An increase in the percentage of calcium phosphate of fluorid increases the hardness of the tooth, while an increase of calcium carbonate decreases the hardness.

Potassium sulphocyanate, ferric phosphate, sulphites, and uric acid have been found in tartar, as additional chemical constituents, while after the solution of the mineral matter

the presence of epithelium cells, mucus, and the leptothrix may be demonstrated by the microscope.

According to Vergness, *Du tartre dentaire*, quoted by Gamgee, the tartar from incisor teeth and that from molars show decided difference in their content of iron and calcium phosphates, the analysis being as follows:

	Tartar of Incisors.	Tartar of Molars.
Calcium phosphate	63.88–62.56	55.11–62.12
Calcium carbonate	8.48– 8.12	7.36– 8.01
Phosphate of iron	2.72– 0.82	12.74– 4.01
Silica	0.21– 0.21	0.37– 0.38
Alkaline salts	0.21– 0.14	0.37– 0.31
Organic matter	24.99–27.98	24.40–24.01

Tartar from patients with pyorrhœa has been found to contain oxalates and urates, not necessasily together, but often one or the other. The deficient oxidation and high acidity usually occurring in such cases is conducive to the production of large amounts of oxalic or uric acids (most generally the latter) whether these substances have etiological relations to pyorrhœa or not.

Lactic and other organic acids have been found in minute quantities in tartar, but these as well as the qualitative tests for urates will be considered more in detail under the Chemistry of Saliva.

Analysis of Teeth and Tartar.

The substance for analysis should be reduced to a moderately fine powder by crushing in a mortar and a fair sample of the whole taken for each test.

Moisture may be detected by the closed-tube test (page 99) and may be determined by accurately weighing out 1 gram of the substance in a counterpoised platinum dish or crucible and drying at 100° C. to constant weight.

Inorganic Matter may be determined by careful ignition of dried substance; raise the temperature slowly till full red heat is reached; cool in a desiccator and weigh.

Organic Matter may be ascertained by difference.

Lactates and other organic acids may be detected by careful crystallization and examination with the micropolariscope.

The several inorganic constituents may be demonstrated as follows:

Phosphoric Acid. — Dissolve a little of the powdered substance in dilute HNO_3; then to a few drops of the clear solution add an excess of ammonium molybdate in nitric acid. A yellow crystalline precipitate of ammonium phosphomolybdate will separate. Avoid heating above 60° C., as the ammonium molybdate may decompose and precipitate a yellow oxid of molybdenum.

Carbonic Acid may be detected by liberation of CO_2 and passing the gas into lime-water as described on page 87 or with closed tube and drop of baryta-water, page 99.

Chlorin may be detected in the dilute nitric acid solution by the usual silver nitrate test.

Calcium and Magnesium may be separated and identified by the usual methods of analysis in the presence of phosphates.

Test for calcium and magnesium as follows: Add to the HCl solution an excess of ammonia; calcium phosphate and magnesium phosphate are precipitated, white. Filter, and to the filtrate add ammonium oxalate; a white precipitate shows lime, not as phosphate. Wash the precipitate produced by NH_4OH, dissolve in dilute HCl, and add Fe_2Cl_6 carefully till a drop of the solution gives, when mixed with a drop of NH_4OH, a yellowish precipitate. Nearly neutralize with Na_2CO_3 and add $BaCO_3$, which precipitates ferric phosphate. Filter, heat the filtrate, precipitate the barium with dilute sulphuric acid, and filter again. From the filtrate calcium is precipitated as white calcium oxalate by making it alkaline with NH_4OH and adding $(NH_4)_2C_2O_4$ as long as a precipitate is formed. Filter and add to the filtrate sodium phosphate, which precipitates magnesium as ammonio-magnesium phosphate, white.

LABORATORY EXERCISES No. L will consist of the examination by microchemical methods of one or more samples of tartar.

PART V.

ORGANIC CHEMISTRY.

CHAPTER XXI.

THE HYDROCARBONS AND SUBSTITUTION PRODUCTS.

Our work up to this point has been confined to inorganic chemistry excepting a few microchemical tests for organic substances.

We are now to consider briefly the organic compounds which will serve as a basis for the intelligent study of physiological chemistry, and also some which are of peculiar interest in dentistry.

We shall touch but lightly on some of the subdivisions of the subject and take up a little organic chemistry proper, a little physiological chemistry, a little pathological chemistry, and from it all pick out such facts as may help us to a better understanding of the problems of dentistry.

As in many other departments of science, absolute rules for classification are impracticable; yet we may consider in a general way that the organic compounds are those containing carbon as a molecular constituent. The old conception that the organic compound must have been produced by a vital process of some sort (animal or vegetable) is of little value unless we confine our thought to substances found in nature only.

The compounds of carbon are practically innumerable and very widely distributed, constituting the great bulk (aside from water) of all vegetable or animal substances.

The carbon compounds contain the elements of C and H, and when these two only are present they are *hydrocarbons*. They more frequently contain C, H, and O, and when the H and O are present in the proportions in which they occur in water, the compound is a *carbohydrate* (with exceptions).

In the chemistry of the animal body the majority of substances which we meet contain C, H, O, and N and often in addition S or P. Many other elements, notably the halogens, and often the metals, may be found in organic compounds.

The question of its composition is then the first one presenting itself in the consideration of an organic substance.

The analysis of organic bodies may be made from two distinct standpoints: first, to determine the various substances which may be separated from a given organized body, as from some part of a plant; secondly, to determine the constituent elements of one of the substances so separated.

As an example of the first sort of analysis, we may find in a potato a certain basic principle (alkaloid), more or less water, and considerable starch. These may be called proximate principles, and the separation of them would be proximate analysis, while the second sort of analysis determines the composition of the starch molecule and is known as ultimate analysis.

Qualitative Tests.

Carbon. — The presence of this element may be shown by the "carbonization" obtained in the preliminary test, as given on page 98.

Hydrogen shows itself by the production of moisture in these same tests.

Nitrogen may or may not be indicated by the preliminary test. It may be detected with certainty by either of the following methods:

(*a*) Conversion into a cyanogen compound;

A small piece of thoroughly dried albumen together with

a little metallic potassium, is placed in a matrass, such as is described on page 28, and heated to redness for a few minutes. (Metallic sodium will work as well in most cases.) An alkali cyanide, which may be dissolved in water after breaking the tube, is formed, and by addition of a little yellow ammonium sulphid and evaporation to dryness on a water-bath will be changed to sulphocyanate, NH_4CNS. If the dry residue is taken up with dilute HCl, filtered, and tested with a drop of ferric chlorid solution, the presence of the sulphocyanate is at once shown by the red color produced.

(*b*) Conversion into free ammonia.

Almost any nitrogenous substance may be made to evolve ammonia-gas by simply heating in a test-tube with several times its bulk of soda-lime. Test for NH_3 by moistened red litmus paper or by odor. (This test is known as that of Wöhler, also of Will and Varrentrap.)

The Kjeldahl or moist combustion process is much employed as a quantitative method but may be used qualitatively as follows: The substance is heated in an ignition-tube with concentrated sulphuric acid till a clear (not necessarily colorless) solution is obtained. The mixture is cooled, diluted with water, an excess of caustic soda added, and heat applied when NH_3 is evolved, which may be detected by litmus paper or by odor.

Sulphur and Phosphorus are first completely oxidized either by fusion of the substance with alkali nitrate and carbonate, or by treatment in the wet way with fuming HNO_3 or mixture of $KClO_3$ and HCl. The resulting sulphate or phosphate is detected by the usual qualitative methods (page 92).

A sulphur test may also be made by heating the substance with a little concentrated NaOH in the test-tube. A little sodium *sulphid*, which may be detected by dropping onto a bright silver coin or by testing with lead acetate solution, will thus be formed.

Halogens. — Cl, Br, and I cannot be detected in organic combinations by the ordinary qualitative test with $AgNO_3$ and dilute NHO_3, but must first be converted into corresponding inorganic haloid salts. This may be done by heating the organic substance strongly with pure lime, when calcium chlorid, bromid, etc., which may be dissolved in water and tested in the usual way, will be formed. (See pages 90 and 91.)

A test for chlorin or iodin may also be made by heating with copper oxid on a platinum wire in the Bunsen flame, chlorin giving first a blue then a green color to the flame. Iodin gives a green only (Beilstein).

Test for presence of C, H, and S in dried albumen.

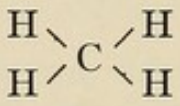
Test for S by the caustic soda test.

Test for P in casein precipitated from milk.

Test a few drops of chloroform for the presence of chlorin.

The Hydrocarbons.

The hydrocarbons are organic compounds of carbon and hydrogen only. The simplest of these is marsh-gas or methane (CH_4). The molecule of this substance consists of a single carbon atom with each of its four points of atomic attraction (valence) satisfied by an atom of hydrogen.



If one of these four atoms of H is replaced by a chlorin atom, for instance, we have a *substitution product.* Its formula will be CH_3Cl, its name monochlormethane or *methyl* chlorid. If two molecules of methyl chlorid are brought together and the Cl removed by metallic sodium the residual molecules (methyl radicals) will unite, forming a new hydrocarbon, as follows:

$$2\,CH_3Cl + Na_2 = 2\,NaCl + C_2H_6 \text{ (ethane).}$$

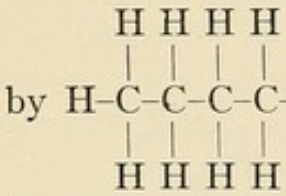
By a similar reaction we may form the third member of the series, C_3H_8 (propane), from ethyl chlorid (C_2H_5Cl) and sodium; the fourth member, butane, C_4H_{10}, from propyl chlorid, etc. A tabulated list of the first five compounds of this series will plainly show their chemical relationship:

CH_4, methane or methyl hydrid (CH_3H).
C_2H_6, ethane or ethyl hydrid (C_2H_5H).
C_3H_8, propane or propyl hydrid (C_3H_7H).
C_4H_{10}, butane or butyl hydrid (C_4H_9H).
C_5H_{12}, pentane or amyl hydrid ($C_5H_{11}H$).

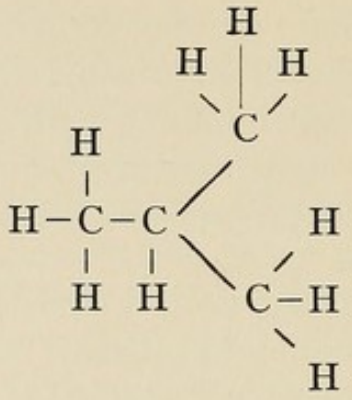
Note that the various members of this series differ from one another by CH_2; that is, each higher compound contains one carbon atom and two hydrogen atoms more than its predecessor. This holds true through the series, and the compounds of this or any such series are termed homologues and the series homologous series. Note further that any member of this series (which is known as the paraffin series) may be represented by the general formula C_nH_{2n+2}. This likewise holds true throughout the series, and a compound having sixty carbon atoms will have a formula of $C_{60}H_{122}$. The first four hydrocarbons of this series are gaseous at ordinary temperatures; from C_5H_{12} to about $C_{16}H_{34}$ the hydrocarbons are liquid; from $C_{16}H_{34}$ (melting at about 18°) up they are solids.

Isomers. — When two or more compounds are of exactly the same molecular composition in regard to numbers and kind of atoms, they are isomeric substances or isomers.

Thus we may have a normal butane represented graphically



by H–C–C–C–C–H (C_4H_{10}), then we may have an isomeric or isobutane represented by



also C_4H_{10}, but having different physical and chemical properties from the normal compound. The greater the number of carbon atoms in the molecule, the more numerous the possible isomers.

Polymers. — When one compound has a formula which may be regarded as a multiple of another, it is said to be a polymer of it; thus, paraform, a white crystalline solid, $(CH_2O)_3$, is a polymeric form of the gaseous formaldehyd, CH_2O.

The hydrocarbons of the paraffin series are known as *straight chain* or *aliphatic hydrocarbons*, their graphic formulæ consisting of "chains" of carbon atoms, as butane, $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$, in distinction from the closed-chain or cyclic compounds as represented by the "benzole-ring" (page 240) carbon nucleus with the C atoms united in a continuous *closed* chain or "cycle."

The paraffins are called saturated hydrocarbons because they are incapable of forming *addition* products by absorption of Cl, for instance, without first giving off an equivalent number of atoms of H. This is because of the complete "saturation" or union of every carbon "bond" with some other atom.* Paraffin wax and mineral oil are mixtures of saturated hydrocarbons and resist chemical action even of strong nitric acid or sulphuric acid.

The natural sources of hydrocarbons of the paraffin series

* Notice that while addition products of saturated hydrocarbon cannot be formed, substitution products are easily possible. See page 184.

are natural gas and crude petroleum, or rock oil. Many of these hydrocarbons exist as such in the petroleum, and some undoubtedly are produced by the heat used to effect a separation of the various compounds. This separation is effected by distilling the oil in an apparatus similar to that pictured in Fig. 15, and is known as fractional distillation, the different hydrocarbons passing over at different temperatures. Separation by this method, however, is by no means complete, and the resulting products are themselves mixtures of hydrocarbons, and are distinguished by physical depravities rather than by chemical composition.

When crude petroleum is thus distilled, the following products are obtained: first, rhigoline, which comes over at a temperature of 20° to 22° C.; then petroleum ether or benzine at from 50° to 60° C.; then gasolene or naphtha at about 75° C.; then 1 or 2 unimportant commercial products, and kerosene or burning oil is obtained at 150° to 250° C. Above this, we may obtain paraffin oil or light lubricating oils; then the heavy lubricating or cylinder oils, and from the residue we obtain the solid substances known as vaseline or petrolatum and paraffin of various degrees of hardness.

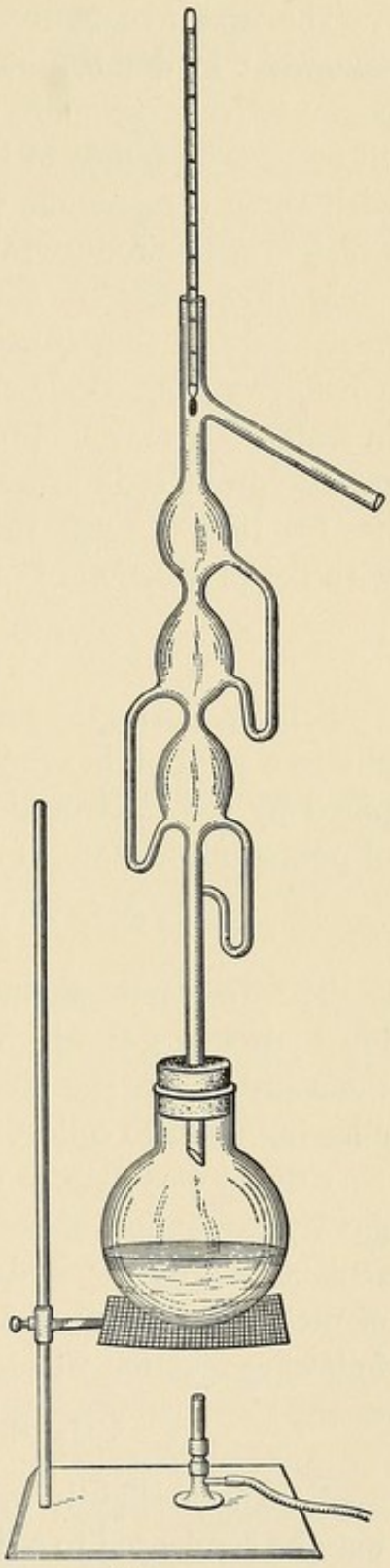


FIG. 15.

The first five hydrocarbons of this series we will consider somewhat in detail, not only because they are important and comparatively common, but also because they serve as types of all other compounds of the series and reactions which we study with these compounds, or, as a rule, general typical reactions which may be produced with other members of the series.

Methane, CH_4, occurs as marsh gas in stagnant ponds or pools and is a constituent of "fire damp" in coal mines. It is a colorless gas, odorless when pure, and very slightly soluble in water. It may be prepared artificially by the decomposition of anhydrous sodium acetate, with sodium hydroxid and lime. See reaction on page 191, Exp. 50. Methane burns in the air with the production of carbon dioxid and water

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$

Ethane, C_2H_6, the second member of the series, occurs naturally in a solution in crude petroleum, and can be artificially prepared by the electrolytic decomposition of a saturated solution of potassium acetate as follows:

$$2\,CH_3COOK = C_2H_6 + 2\,CO_2 + K_2.$$

The free potassium, of course, decomposes H_2O, liberating hydrogen gas which collects at the negative pole, and, if the solution contains sufficient KOH, the CO_2 will be dissolved, allowing C_2H_6 to collect at the positive pole.

Ethane may also be made from a haloid derivative of marsh gas by the action of metallic sodium; that is, in CH_4 we may replace one of the hydrogen atoms with iodin, forming CH_3I of methyl iodid; then by treatment with metallic sodium, the following reaction will take place:

$$2\,CH_3I + 2\,Na = C_2H_6 + 2\,NaI.$$

Ethane is slightly more soluble in water than methane. It may be condensed to a liquid at a pressure of 46 atmospheres.

Propane, C_3H_8, also occurs in petroleum, and can be made by treating a mixture of ethyl iodid and methyl iodid with metallic sodium:

$$C_2H_5I + CH_3I + 2\,Na = C_3H_8 + 2\,NaI.$$

This is a general method for building up hydrocarbon compounds. Propane at ordinary atmospheric pressure is condensed to liquid at 17° below zero.

Butane, C_4H_{10}, is the first of the series capable of existing in two forms, isomers. The structural formulæ of these two compounds are shown in the illustration of the term isomer on page 185. This compound, as well as the next higher homologue pentane, C_5H_{12}, are of importance only in their relation to some of their derivatives which will be subsequently studied.

DOUBLE-BONDED HYDROCARBONS.

If two carbon atoms are united by a double bond, as in $\begin{matrix} H & & H \\ \diagdown & & \diagup \\ & C=C & \\ \diagup & & \diagdown \\ H & & H \end{matrix}$ (C_2H_4), chlorin may be added directly by the breaking of the double bond, forming ethylene chlorid, $C_2H_4Cl_2$.

Note that the formula of ethylene does not conform to the general formula of the paraffins (C_nH_{2n+2}), but is the first member of the new series of "unsaturated" hydrocarbons; the olefin or ethylene series with a general formula of C_nH_{2n}.

The hydrocarbons of this series take their names from corresponding members of the paraffin series, with "ene" as a distinguishing termination — ethylene, C_2H_4, propylene, C_2H_6, butylene, C_5H_{10}, etc. They are unimportant in dental or physiological chemistry. Some of the higher oxygenated compounds of this class are, however, of great importance, as olein, which is a constituent of vegetable and animal fats and oils.

TRIPLE-BONDED HYDROCARBONS.

A third series of the straight chain hydrocarbons is the acetylene series; these are triple bonded, and of course unsaturated, with a general formula of C_nH_{2n-2}.

The only members of this series of special interest are, first, *acetylene*, $H - C \equiv C - H$, (C_2H_2), made from calcium carbid and water. It is poisonous, combining directly with the hæmoglobin of the blood, has a disagreeable odor, and is inflammable; second, *allylene*, C_3H_4, derivatives of which occur in onions, garlic, mustard-oil, etc.

Laboratory Exercise LI.

Experiments with Carbon and Hydrocarbons.

Exp. 45. Carbon as a decolorizing agent. To 25 or 30 c.c. of a dilute solution of aniline color, contained in a small beaker, add a teaspoonful of bone charcoal. Heat to the boiling-point, rotate or stir thoroughly for a few minutes, and filter.

Exp. 46. Absorption of metallic salts. To 25 c.c. of solution of lead acetate of such strength that H_2S water gives marked color but no precipitate, add a teaspoonful of bone charcoal and treat as in preceding experiment. Test the filtrate with H_2S water and note whether lead has been removed.

Exp. 47. Perform an experiment with a view to determining whether bone charcoal will absorb H_2S from H_2S water.

Exp. 48. Repeat either of the three immediately preceding experiments, using wood charcoal in place of bone charcoal. Does the wood charcoal work as well as the bone charcoal in the absorption of color or other substances? How does bone charcoal differ in composition from wood charcoal?

Exp. 49. 25 c.c. of crude petroleum in a boiling flask is connected with a long piece of tubing which serves as an air condenser. The flask is fitted to the thermometer and the contents heated slowly until at least three fractional products

are obtained with boiling points differing by at least 15°. Note any other physical differences between the distillates thus obtained.

Exp. 50. Charge an ignition-tube with dry "marsh-gas mixture," found on side shelf (consisting of $NaC_2H_3O_2$, NaOH, and CaO_2H_2). Fit with a delivery-tube and collect two small bottles of the gas over water.

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

Test the inflammability of this gas. Notice the odor.

Exp. 51. Mix carefully in a test-tube 2 c.c. of alcohol and 8 c.c of strong sulphuric acid. Heat gently and notice odor of gas. Fit a bent glass tube to the test-tube and collect over water a test-tube full of the gas. To this apply a flame. Note the color of the burning gas.

$$C_2H_5OH - H_2O = C_2H_4.$$

Haloid Derivatives of the Paraffins.

Methane furnishes three chlorin substitution products which are more or less in common use: first, the monochlor-methane, or methyl chlorid; second, the trichlor-methane CHCl or chloroform, and third, the tetrachlorid of carbon CCl_4.

Methyl Chlorid, CH_3Cl, may be made from methyl alcohol, zinc chlorid, and hydrochloric acid. It is a colorless gas, condensing to a liquid at 23° C.; used as a spray in producing local anæsthesia (page 172); also as a constituent of anæsthetics, such as anesthol, somnoform, etc.

Dichlor-methane, CH_2Cl_2, also known as methylene chlorid, has been used as a general anæsthetic usually mixed in more or less chloroform and alcohol. Its use in this way is open to criticism because of its poisonous action, affecting the heart.

Chloroform, $CHCl_3$, trichlormethane, is a general anæsthetic prepared by distilling a mixture of chlorinated lime and acetone. Alcohol and water were formerly used in place of acetone (see

Exp. 56, page 193). While it is not regarded as inflammable, its heated vapor can be made to burn with a greenish flame.

Methyl Chloroform, CH_3CCl_3, formed by replacing the H atom of chloroform by a methyl group, CH_3, has been used as an anæsthetic.

Tetrachlorid of carbon is a colorless liquid used quite largely as a solvent. It also has anæsthetic properties, but like dichlor-methane, is dangerous because of its action on the heart.

Methyl bromid, or monobrom-methane, is used to some extent as a constituent of anæsthetics.

Bromoform, $CHBr_3$, tribrom-methane, is prepared from bromin and a solution of alcoholic potash. Its properties are similar to those of chloroform, but it is more poisonous.

Methyl Iodid, CH_3I, is a heavy liquid, with pleasant odor, boiling-point 43° C.; has been used somewhat as a vesicant.

Iodoform, HCl_3, tri-iodomethane, is a much-used and very valuable antiseptic. It is a light-yellow crystalline powder with characteristic persistent odor (Plate V, Fig. 1, page 222).

Iodoform may be made by heating in a retort two parts of potassium carbonate, two of iodin, one of strong alcohol, and five of water, till the mixture is colorless.

Iodoform is also produced from action of the above reagents with acetone in place of alcohol. This test is a very delicate one and advantage is taken of it in testing for acetone in saliva, which see.

Ethyl Chlorid, C_2H_5Cl, chlorethyl, may be made by distillation of a mixture of alcohol and hydrochloric acid and purification of the distillate. It is extremely inflammable, boils at 12° C., and is used as a local anæsthetic in similar manner to methyl chlorid. Its higher boiling-point makes it the more convenient of the two preparations (see page 169).

Ethyl Bromid, C_2H_5Br, prepared from alcohol, sulphuric acid, and potassium bromid. It is a heavy colorless liquid,

does not burn, and has been used to considerable extent as a general anæsthetic.

Laboratory Exercise LII.

Experiments with Hydrocarbons (continued) and their Halogen Derivatives.

Exp. No. 52. Shake together, in separate test-tubes, small quantities of petroleum and sulphuric acid in one tube, and petroleum and nitric acid in the other. If no action results, mix contents of the two tubes and shake again. Explain any change or absence of change which may be apparent.

Exp. 53. In a small generator (see model) place a few small pieces of calcium carbid (CaC_2), add strong alcohol through the funnel tube till the lower end of the tube is "sealed." Now add very slowly a little water till a brisk evolution of gas is obtained. Collect over water two or three test-tubes full of the gas. (Acetylene.)

Test with a lighted splinter. Note odor of gas cautiously, as it is poisonous when inhaled in quantity.

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$

Exp. 54. Conduct a little of the acetylene gas into an ammoniacal cuprous chlorid solution. What is the red precipitate?

Exp. 55. If the evolution of gas has not been interrupted the delivery-tube may be replaced by a short tube drawn out to a fine point and the gas ignited. Note color of flame. If it smokes badly, explain the reason for it.

Exp. 56. Place in a test-tube a little bleaching-powder, cover with strong alcohol and heat the mixture to boiling. Notice carefully the odor of the vapor produced and compare with a little chloroform ($CHCl_3$) from side shelf.

$$4\,C_2H_5OH + 8\,Ca(ClO)_2 = 2\,CHCl_3 + 3\,\underset{\text{(Formate of Ca)}}{Ca(CHO_2)_2} + 5\,CaCl_2 + 8\,H_2O.$$

Exp. 57. Place in a test-tube about 1 gram of crystallized carbonate of sodium, about half as much iodin and 1 or 2 c.c. of alcohol. Now add 10 or 15 c.c. of H_2O and keep the mixture at moderate heat (not boiling) till the color of the iodin is discharged. Allow to cool; collect on a small filter-paper some of the yellow crystals which have been formed and examine under the microscope. What are the crystals? Explain their relation to marsh-gas.

CHAPTER XXII.

ALCOHOLS.

If we substitute for one of the hydrogen atoms of methane, a hydroxyl group (OH), we shall produce the first of a series of alcohols, several of which will claim our attention.

The alcohols may be considered as hydroxids of alkyl * radicals, CH_3OH being methyl alcohol; C_2H_5OH, being ethyl or ordinary alcohol; C_3H_7OH being propyl alcohol; and $C_5H_{11}OH$, amyl alcohol or fusel oil.

The alcohols as a class may be prepared by the action of moist silver oxid on the corresponding halogen compounds; e.g.,

$$CH_3Br + AgOH = CH_3OH + AgBr.$$

In many instances, the alkaline hydroxids will act in the same way.

$$CH_3Br + KOH = CH_3OH + KBr.$$

Alcohols treated with metallic sodium or potassium liberate hydrogen gas, forming compounds known as alcoholates; e.g.,

$$CH_3OH + K = CH_3OK + H;$$

or

$$C_2H_5OH + K = C_2H_5OK + H.$$

While these compounds are, as just stated, called alcoholates, they may be distinguished, one from another, by using the name of the alkyl radical involved, and CH_3OK will be potassium methylate, while C_2H_5OK will be potassium ethylate.

Alcohols may contain more than one hydroxyl group, and,

* Alkyl—a term used to denote any hydrocarbon radical as CH_3-, C_2H_5-, C_3H_7-, etc.

according to number of the OH groups, are termed mono-, di-, tri-atomic, etc. Thus, ordinary alcohol, C_2H_5OH, is monoatomic; glycerol, $C_3H_5(OH)_3$ is triatomic, while mannite $C_6H_8(OH)_6$ is a hexatomic alcohol.

Alcohols may also be classified according to the relative position of the hydroxyl group. By this classification, we may have primary alcohols with OH replacing a hydrogen of the $-CH_3$ group; secondary alcohols with OH replacing the hydrogen of a $-CH_2$ group; and tertiary alcohol with OH replacing the hydrogen of a $-CH$ group. This may be illustrated by the formula of an alcohol of each class. $CH_3-CH_2-CH_3$, being the hydrocarbon, a primary alcohol will have the formula $CH_3.CH_2.CH_2OH$, and $-CH_2OH$ may be considered distinctive grouping of the primary alcohols. Again from the same hydrocarbon, if OH is substituted for an H of CH_2 then the secondary alcohol will be $CH_3-CHOH-CH_3$ and $-CHOH$ may be regarded as a distinctive group of this class.

The tertiary alcohols, however, must be produced from compounds having at least four carbon atoms, as a CH group is only possible when there are sufficient carbon atoms to produce a forked chain; that is, in a compound with three carbon atoms, one must of necessity be placed between the other two, while with four carbon atoms, the carbons may be attached in a straight chain, such as C–C–C–C, or they may be arranged as a forked chain $C-C\begin{matrix}\diagup C\\ \diagdown C\end{matrix}$, and by supplying the hydrogen atoms necessary to satisfy the valence of each carbon, in this latter chain we find a CH group. OH introduced in place of the hydrogen of this group gives us the tertiary alcohol,

$$CH_3-COH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}.$$

Notice that the forked chain gives us possible isomeric compounds.

The hydroxyl derivatives (alcohols) of isopentane are well suited to illustrate the three (primary, secondary, and tertiary) characteristic alcohol groupings.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH\text{–}CH_2\text{–}CH_3 \text{ is isopentane}$$

and by introducing the OH group (hydroxyl) into the CH_3 group there is formed a *primary* amyl alcohol,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH\text{–}CH_2CH_2OH, \text{ or isobutyl carbinol,}$$

and the *primary* alcohol grouping is $-CH_2OH$. By introducing hydroxyl (OH) into the CH_2 group we should have $-CHOH-$ as a characteristic combination in *secondary* alcohols,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH\text{–}CHOH\text{–}CH_3, \text{ methylisopropyl carbinol;}$$

and lastly, by putting the OH in place of the H of the CH group of the hydrocarbon, we should have $(CH_3)_2 = COH\text{–}CH_2\text{–}CH_3$, a tertiary alcohol with the group $\equiv COH$ as its characteristic.

Methyl Alcohol, CH_3OH, $(H\text{–}CH_2OH)$,* wood spirit, carbinol, is a product of the destructive distillation of wood or can be made synthetically from methane. It is a colorless, inflammable liquid, with a gravity of 0.802 at 15° C., with solvent properties similar to ordinary alcohol, and boils at 66°.

Ethyl Alcohol, C_2H_5OH, $(CH_3\text{–}CH_2OH)$, methyl carbinol, grain alcohol, or ordinary alcohol is made by fermentation of solutions of various carbohydrates and purified by distillation. Carbon dioxid is evolved as follows:

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2.$$

95% alcohol has a specific gravity 0.8164, boils at about 78° C., dissolves many inorganic salts, vegetables, waxes, resins

* Note that CH_2OH is the "alcohol group" peculiar to this class of alcohols.

(not gums), oils, etc., and is miscible with water, ether, or chloroform.

Amyl Alcohol, $C_5H_{11}OH$, (C_4H_9–CH_2OH), isobutyl carbinol, is a colorless, oily liquid with a specific gravity of 0.818. It boils at about 130° C., and burns with a bluish flame.

Fusel-oil, or potato spirit, consists of amyl alcohol carrying traces of various other alcohols as impurities.

Amyl alcohol is a valuable solvent and is largely used in the manufacture of artificial fruit flavors, banana essence, and the like.

Oxidation of the Alcohols.

Aldehyds.

The first step in the oxidation of an alcohol consists not in the addition of oxygen but in the withdrawal of hydrogen; thus the oxidation of methyl alcohol produces formaldehyd (CH_2O) and water.

$$CH_3OH + O = CH_2O + H_2O.$$

Aldehyds may be considered compounds containing an alkyl radical and a distinctive group, $-\overset{H}{\underset{\|O}{C}}$; thus $\overset{H}{\underset{CHO}{CH_3}}$ is formaldehyd, $\overset{H}{\underset{CHO}{CH_3}}$, is acetaldehyd, etc. (compare Alcohol, page 197).

Formaldehyd coagulates albumen and hardens gelatin; when used as a preservative it renders the proteins tougher and less digestible.

Formaldehyd polymerizes, producing the paraform or paraformaldehyd of trade, trioxymethylene, with a probable formula of $(CH_2O)_3$. It also forms one lower polymer $(CH_2O)_2$ and at least one higher, formose, a substance allied to glucose.

Acetaldehyd, aldehyd, CH_3–CHO or C_2H_4O, the aldehyd from ethyl alcohol, may be made by addition of H_2SO_4 to a

mixture of alcohol and bichromate of potassium. It is a colorless, inflammable liquid with pungent etherial odor and boils at 22° C.

Paraldehyd, $(C_2H_4O)_3$ a polymer of acetaldehyd, is a "colorless liquid with a strong pungent odor, soluble in 8.5 parts of water at 15° C., miscible in all proportions with alcohol, ether, and fixed or volatile oils." (U. S. P.) It is a valuable hypnotic.

Chloral, CCl_3CHO, trichloraldehyd, is an oily liquid formed by action of dry Cl gas on pure alcohol; soluble in ether and chloroform, boiling at from 94° C. to 98° C., and forming, with a molecule of H_2O *chloral hydrate*, $CCl_3CHO.H_2O$, a crystalline solid, and this is the "chloral" of the pharmacopœia (see page 167).

Chloral hydrate is decomposed by sodium or potassium hydrate with liberation of chloroform (see Exp. 72, page 211): CCl_3–CHO + KOH = $CHCl_3$ + KCOOH (potassium formate).

Upon warming a drop or two of aniline oil in an excess of alcoholic potash, chloral hydrate forms, first, chloroform, then phenylisocyanid, C_6H_5NC, the persistent disagreeable odor of which furnishes a delicate test for chloroform or chloral (see Exp. 73, page 211). By using $CHCl_3$ as the reagent in place of the aniline, the same reaction becomes a test for aniline or organic compounds, from which aniline may be produced by heating with alcoholic potash as acetanilid. Other aldehyds from hexatomic alcohols are dextrose (glucose) and galactose. They are represented by the formula CH_2OH–$(CHOH)_4$–CHO, and will be considered more fully in a subsequent lecture.

Laboratory Exercise LIII.

Alcohols and Aldehyds.

Exp. 58. The detection of water in alcohol. Prepare a little anhydrous copper sulphate by heating a few crystals of $CuSO_4$ on a crucible cover until the water is driven off and a

nearly white powder results. If this white powder, after boiling, is added to a half a test-tube full of alcohol, the absorption of water, if present, will result in reforming the crystallized salt and a consequent production of blue color.

Exp. 59. Water may be separated from alcohol by saturating with potassium carbonate. To demonstrate this, take a mixture of alcohol and water, containing 15 or 20 per cent of alcohol, and add solid potassium carbonate until the salt will no longer dissolve. Agitate and allow to stand. Two layers will form, one consisting of alcohol the other of the water solution of K_2CO_3.

Exp. 60. To about 75 c.c. of a 10% glucose solution add a little yeast and allow to stand for twenty-four hours at a temperature of about 37° C.; then distil by means of gentle heat 10 or 15 c.c., and test distillate for alcohol by iodoform test, as given on page 194, Exp. 57. The production of CO_2 may also be demonstrated if the gases evolved during the fermentation are passed into clear lime-water:

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2.$$

Exp. 61. A test for methyl alcohol. This test is applicable only to slight traces of methyl alcohol and may be made with a 1 to 2 per cent solution or with the first cubic centimeter of distillate from the substance suspected of containing methyl alcohol. Place 2 or 3 c.c. of very dilute methyl alcohol in a test-tube, heat a spiral of copper wire to white heat in a Bunsen flame and plunge immediately into the solution to be tested. Cool the contents of the tube by immersion in freezing mixture or ice water, and repeat the treatment with the hot copper wire. Cool again, and a third time introduce the hot copper wire. The copper spiral can be made by winding copper wire around a lead pencil, and should be of such a length that it is not wholly covered by the liquid in the tube.

This process serves to oxidize a portion of the alcohol to

aldehyd. Now add to the solution which is being tested a few drops of a 1/2% water solution of resorcin and underlay the mixture with strong sulphuric acid. A violet ring will indicate the presence of methyl alcohol. The higher alcohols will give red or brown rings when similarly treated.

Exp. 62. Mix about 1 c.c. of a very dilute solution of formaldehyd with four or five times its volume of milk in a test-tube. Carefully underlay the mixture with commercial sulphuric acid of a specific gravity of 1.80. At the point of contact of the two layers of liquid a violet-colored ring indicates the presence of formaldehyd. It is necessary that the sulphuric acid should contain a trace of iron: this the *commercial* acid usually does. It is also undesirable that the acid should be stronger than of 1.80 specific gravity; for, if it is, a *reddish-brown* ring may be formed, due to partial carbonization of the casein.

Exp. 63. To about 5 c.c. of a *strong* aqueous solution of potassium dichromate add a little sulphuric acid, then a few cubic centimeters of alcohol, and notice the odor of acetaldehyd produced by oxidation of the alcohol. Note also the reduction of the dichromate to $Cr_2(SO_4)_3$, as follows:

$$K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,C_2H_5OH = K_2SO_4 + Cr_2(SO_4)_3 + 3\,C_2H_4O + 7\,H_2O.$$

Exp. 64. Test a dilute solution of both formic and acetic aldehyd by Tollen's test for aldehyd as follows: Into a clean test-tube which has been rinsed with NaOH solution, place 5 c.c. of Tollen's reagent, add 10 c.c. of solution to be tested, shake; the silver is reduced, forming a metallic mirror on the inner surface of the tube.

To make Tollen's reagent, dissolve 3 grams of silver nitrate in 30 c.c. ammonia water and add 3 c.c. of solution of sodium hydroxid.

Ketones.

The oxidation of *secondary* alcohols (page 196) will not yield aldehyds, but a class of substances known as *ketones:*

$$\underset{\substack{\text{A secondary alcohol.}\\ \text{Methyl isopropyl carbinol.}}}{(CH_3)_2\text{–CH–CHOH–}CH_3} + O = \underset{\text{Methyl isopropyl ketone.}}{(CH_3)_2\text{–CH–C : O–}CH_3} + H_2O,$$

or $$\underset{\text{Isopropyl alcohol.}}{CH_3\text{–CHOH–}CH_3} + O = \underset{\text{Dimethyl ketone.}}{CH_3\text{–CO–}CH_3} + H_2O.$$

The converse of each of these reactions is possible, and, by reduction of a ketone with nascent H (sodium amalgam), the secondary alcohol will be formed:

$$\underset{\text{Acetone.}}{CH_3\text{–CO–}CH_3} + H = \underset{\text{Isopropyl alcohol.}}{CH_3\text{–CHOH–}CH_3}.$$

Likewise primary alcohols may be produced by the reduction of aldehyds:

$$\underset{\text{Acetaldehyd.}}{CH_3\text{–CHO}} + H_2 = \underset{\text{Ethyl alcohol.}}{CH_3\text{–}CH_2OH}.$$

Note that the grouping peculiar to ketone is =CO or –CO–.

Acetone, or dimethylketone, CH_3–CO–CH_3, a colorless liquid of peculiar odor, boils at 56° C. and is made commercially by the dry distillation of acetate of lime.

It occurs in the blood and urine of patients suffering from advanced diabetes. According to von Noorden, the acetone found in the blood is formed by an intracellular process and indicates an acid auto-intoxication and an insufficient *utilization* of carbohydrates. In the experience of the author, acetone may sometimes be found in the saliva when it cannot be found in the urine (for test, see Acetone under Saliva and Urine).

Another ketone of interest is lævulose, fruit-sugar, CH_2OH–CHOH.CHOH.CHOH.CO.CH_2OH, which, with glucose, will be studied later.

While the oxidation of a primary alcohol will produce an aldehyd and the oxidation of a secondary alcohol will produce a ketone, the tertiary alcohol, by action of an oxidizing agent, is split into two new carbon compounds, that is, the chain is broken and simpler ketones and acids are formed.

CHAPTER XXIII.

ETHERS.

ETHERS may be regarded as oxids of the hydrocarbon radicals, as $\begin{matrix} C_2H_5 \\ \\ C_2H_5 \end{matrix}\!\!\diagdown\!\!\diagup O$, or as anhydrids of the monatomic alcohols, H_2O having been removed from two molecules of the alcohol:

$$2\,C_2H_5OH - H_2O = (C_2H_5)_2O.$$

Ethers may be simple, mixed, or compound. The simple ether is illustrated above by the formula for ordinary or ethyl ether, where two radicals of the *same* kind are united by an atom of oxygen.

In a mixed ether, these radicals will be of different kinds; as, for example, CH_3–O–C_2H_5, methyl-ethyl ether.

The compound ethers are compounds of alcohol radicals with acid radicals, that is, the salts of alcohol radicals. The acid may be either organic or inorganic; thus, we have nitric ether, ethyl nitrate, $C_2H_5NO_3$, and we have acetic ether, ethyl acetate, $C_2H_5C_2H_3O_2$. The compound ethers are often called esters and form a large and important class of organic compounds.

A general method for the preparation of simple and mixed ethers is that of distillation of the corresponding alcohols with sulphuric acid, as illustrated by experiment No. 69, page 210. They may also be produced by the action of silver oxid on the corresponding alkyl iodids:

$$2\,C_2H_5I + Ag_2O = (C_2H_5)_2O + 2\,AgI,$$

also, by treating the sodium alcoholate with an alkyl iodid,

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI$$

or
$$CH_3ONa + C_2H_5I = \begin{matrix} CH_3 \\ \\ C_2H_5 \end{matrix} \!\!\diagdown\!\!\diagup O + NaI.$$

Methyl Ether. — Methyl oxid, $(CH_3)_2O$, also known as formic ether, is isomeric with ordinary alcohol, and may be made in a manner similar to that used in the production of ethyl ether (*q. v.*). At ordinary temperature it is a gas, but liquefies at $-20°$ C. (Bernthsen). It has been used as a general anæsthetic, and the anæsthesia is said to be profound and quickly produced (U. S. D. from A. J. P., Sept., 1870).

Methyl-ethyl Ether. — This name, besides indicating a definite compound as referred to in the preceding paragraph, has been applied to a mixture of methyl ether and ethyl ether, used for purposes of general anæsthesia.

Methylene Ether. — A name applied to a mixture of methylene dichlorid and ethyl ether, used as an anæsthetic, but it has been found unsafe (U. S. D.).

Ethyl Ether. — Ethyl oxid, $(C_2H_5)_2O$, consisting of 96% by weight of the "æther" of the pharmacopœia (the other 4% being alcohol and a little water). Ether is a general anæsthetic, widely used. It is made by the action of sulphuric acid on ethyl alcohol, and from this fact has been known as sulphuric ether, but this name is, of course, incorrectly used, sulphuric ether being properly an ethyl sulphate $(C_2H_5)_2SO_4$.

In the preparation of ether, sulphuric acid may be mixed with rather more than its own bulk of alcohol, the mixture heated to a temperature of from 130° to 138° C. in a suitable retort or still, the distillate (ether) being collected in a *cold* receiver.

The reaction takes place in two steps, as follows: One molecule of acid and one of alcohol react to form ethyl sulphuric acid (ethyl acid sulphate) and H_2O, $H_2SO_4 + C_2H_5OH = C_2H_5HSO_4 + H_2O$. Then the ethyl sulphuric acid reacts with

a second molecule of alcohol to form ether and sulphuric acid, $C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$. Thus the sulphuric acid, from two molecules of alcohol, has produced one molecule of ether and is in condition to repeat the process, having suffered itself only to the extent of adulteration with one molecule of water. In accordance with this theoretic formation of ether by simple dehydration of alcohol by H_2SO_4, provision is made for a continuous process, by the introduction of a constant supply of fresh alcohol into the retort during the distillation, and so regulated that the total bulk of liquid is neither increased nor diminished. The product is then purified, and freed from water and traces of acid by redistillation over a mixture of lime and calcium chlorid.

Ether, according to the U. S. P. requirements, is "a transparent, colorless, mobile liquid with characteristic odor and a burning and sweetish taste"; specific gravity of 0.725 to 0.728 at 15° C. and boiling at about 37° C. It is readily inflammable, and this fact, together with its easy volatility, makes it necessary to use considerable care when handling it. Absolute ether boils between 34° and 35° C.

The action of sulphuric acid upon alcohol needs careful regulation; because there may be produced three other products in addition to the ethyl oxid already considered. These are, first, ethyl sulphuric acid, $C_2H_5HSO_4$; second, ethyl sulphate $(C_2H_5)_2SO_4$, these being respectively the acid and neutral ethyl esters of H_2SO_4; third, the hydrocarbon *ethylene*, C_2H_4. This latter compound is the first of the ethylene series of hydrocarbons with the general formula C_nH_{2n}, and containing "double-bonded" carbon atoms, $\begin{matrix} H \\ H \end{matrix}\!\!\diagdown\!\!\diagup\!\!C = C\!\!\diagup\!\!\diagdown\!\!\begin{matrix} H \\ H \end{matrix}$ or $CH_2 = CH.CH_3$. These are unsaturated hydrocarbons (see page 189). Ethylene is produced by the action of an excess of concentrated H_2SO_4, which abstracts H_2O from each molecule of alcohol

($C_2H_5OH - H_2O = C_2H_4$), whereas in the preparation of ether the more dilute acid abstracts H_2O from *two* C_2H_5OH.

Compound Ethers or Esters.

One of the most important of this class of compounds, from a dental standpoint, is the benzoyl-ecgonine methyl ester or cocain, $CH_3N\begin{cases} C_5H_7 \\ | \\ CH.C_7H_5O_2.CH_2.CO_2CH_3 \end{cases}$ While of considerable interest, the elucidation of the exact chemical relationship of this compound to tropa-cocain, etc., is beyond the scope of this work.

Another methyl ester of much simpler chemical composition is methyl salicylate, CH_4–CH–$COOCH_3$.

Salicylic acid is CH_4–OH–$COOH$ (oxybenzoic acid), and its methyl ester constitutes the methyl salicylate of the U. S. P. It is identical with the volatile oil of betula and with 90% of the oil of gaultheria (wintergreen). This latter oil is much used as a flavor in dental preparations, tooth-washes, powders, etc.

Ethyl Acetate, CH_3–$COO.C_2H_5$, is formed by heating ethyl alcohol, sulphuric acid, and acetate of sodium. This reaction constitutes a qualitative test for acetic acid or acetates, the odor of the ester being sufficiently characteristic to furnish a delicate test (page 94).

The acetic ether of the U. S. P. is "a liquid composed of about 98.5% of ethyl acetate and 1.5% alcohol."

Ethyl Butyrate, CH_3–CH_2–CH_2–$COOC_2H_5$. This ester dissolved in 10 parts of alcohol forms pineapple essence. It may be made in a manner similar to the preparation of ethyl acetate, i.e., by heating together alcohol, butyric acid, and concentrated sulphuric acid. The production of the ester is likewise used as a qualitative test for the presence of the acid, and employed in the examination of gastric contents as follows:

"Heat 10 c.c. of contents with 5 c.c. of strong sulphuric acid and 4 c.c of 95% alcohol: odor of pineapple indicates butyric acid." (Hewes.)

Ethyl Nitrite, $C_2H_5NO_2$, may be made by heating sodium nitrite with concentrated sulphuric acid and alcohol, also by the reduction of nitric acid by copper in presence of alcohol and sulphuric acid. The ethyl nitrite is distilled, and must be collected in a receiver surrounded by a freezing mixture of ice and salt. Pure ethyl nitrite boils at 18° C., and has a gravity of 0.900. An alcoholic solution constitutes sweet spirits of nitre, the spiritus ætheris nitrosi of the U. S. P.

This preparation should, according to Dr. E. R. Squibb, contain 4.5% ethyl nitrite.

Amyl Acetate and Amyl Butyrate may be obtained by heating the respective acids with amyl alcohol ($C_5H_{11}OH$) and strong sulphuric acid. These esters may also be used in detecting the presence of the acid, amyl alcohol being used in place of ordinary alcohol. Amyl acetate gives the odor of pears, amyl butyrate that of bananas.

Amyl nitrite, $C_5H_{11}NO_2$, is a compound used in medicine to a considerable extent, usually administered by inhalation. The U. S. P. preparation contains about 80% of amyl nitrite. It is very soluble and inflammable.

The **Fats** are esters of glyceryl, C_3H_5, also called tritenyl, propenyl, etc. This radical forms with hydroxyl (OH) the propenyl alcohol, $C_3H_5(OH)_3$, which is ordinary glycerin or glycerol.

Glyceryl butyrate or butyrin, $CH_3–(CH_2)_2–COOC_3H_5$, constitutes (together with smaller quantities of the glyceryl esters of capric, caproic, and caprylic acids) about 7% of butterfat. These esters are readily saponified by treatment with alcoholic potash; then, by decomposition of the potassium salts with H_2SO_4, the acids, being volatile, may be separated by distillation. The amount of volatile fat acids thus obtained is a valuable test for the genuineness of the butter.

Glyceryl Palmitate, $C_3H_5(C_{16}H_{31}O_2)_3$, tripalmitin; **glyceryl stearate,** $C_3H_5(C_{18}H_{35}O_2)_3$, tristearin, and **glyceryl oleate,** $C_3H_5(C_{18}H_{33}O_2)_3$, triolein; these in varying proportions make up the greater part of animal and vegetable fats and oils.

The prefix "tri" is used because the "mono" and "di" compounds, as monopalmitin, $C_3H_5(OH)_2$–$C_{16}H_{31}O_2$, etc., are possible and may be prepared by synthesis. Triolein is liquid at ordinary temperature, solidifies at −6° C., is a "double-bonded" compound, hence forms addition-products with the halogens as stearin and palmitin cannot do, they being "saturated hydrocarbons."

The amount of chlorin or bromin which a fat or oil can thus absorb is an index of the proportion of unsaturated fatty acids contained in it, and hence becomes a valuable method of identification. Olive-oil and lard-oil contain large amounts of olein.

Tripalmitin melts at 66° C., is usually obtained from palm-oil. Tristearin melts at 72° C., occurs with palmitin and olein in beef-fat, mutton-tallow, etc., the consistence of the fat being dependent upon the proportions of the constituent esters.

The fats, stearin for example, may be split into glycerol and fatty acid by steam under pressure as follows:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\,H_2O = C_3H_5(OH)_3 + 3\,HC_{18}H_{35}O_2.$$

A partial result of this sort is brought about by the fat-splitting enzyme (lipase) of the pancreatic juice (see Steapsin).

Saponification of the fats by caustic alkali takes place as follows:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\,KOH = C_3H_5(OH)_3 + 3\,KC_{18}H_{35}O_2.$$

The potassium salts of the fatty acids constitute the soft soaps, while the sodium salts are in general the hard soaps. The "salting-out" process in soap manufacture brings about a double decomposition resulting in the production of ordinary soap.

Laboratory Exercise LIV.

Experiments with Acetone and Ethers.

Exp. 65. Preparation of Acetone: Heat a few grams of dried calcium acetate in an ignition tube, collect the distillate, which consists of an impure acetone. If this is mixed with a little water and filtered, part of the impurities may be removed, and the filtrate tested for acetone by the following experiment.

Exp. 66. Dilute the filtrate from the last experiment with distilled water; add a crystal of potassium nitroprussid. After the crystal is dissolved, add a few drops of acetic acid, and then an excess of ammonia water. A violet or purple color indicates the presence of acetone. Using a dilute solution of acetone in place of the alcohol in experiment 57, on page 194, produce iodoform crystals by similar reaction with iodin and sodium or potassium carbonate.

Exp. 67. Acetone may be dissolved or mixed with water in all proportions; but, upon saturating the water with KOH, the acetone will form a separate layer which may be drawn off as in the separation of alcohol in experiment 59, page 200.

Exp. 68. To a dilute aqueous solution of acetone add potassium permanganate slowly until the mixture is permanently colored pink; filter, add dilute sulphuric acid and distil until 1 or 2 c.c. of distillate are obtained. This may be tested for acetic acid by litmus paper or ferric chlorid.

Exp. 69. Into a large test-tube put a little alcohol and about half its volume of strong H_2SO_4. Warm gently and notice the odor.

Ether is formed by two reactions. First, $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$. Then the ethyl-hydrogen sulphate ($C_2H_5HSO_4$) is acted upon by a second molecule of H_2SO_4, as follows: $C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$.

Exp. 70. The production of compound ethers may be demonstrated by the test for acetic acid forming ethyl acetate,

page 94, or by the following experiment used to detect butyric acid in gastric contents:

Exp. 71. Mix in a test-tube 5 c.c. of a dilute (1/2%) solution of butyric acid with an equal volume of strong H_2SO_4 and as much strong alcohol. Heat gently and note the odor of ethylbutyrate (pineapples).

Exp. 72. To about 5 c.c. of an aqueous solution of chloral hydrate add a few cubic centimeters of strong NaOH solution and boil. Note odor of chloroform.

Exp. 73. Isobenzonitril test for chloral or chloroform: Place a few drops of a dilute chloral hydrate solution (or a small drop of chloroform) in a test-tube, add 5 c.c. of an alcoholic solution of alkali hydrate* (NaOH or KOH) and one drop only of fresh aniline oil. Heat till the mixture just begins to boil and note the odor of the nitril.

* If alcoholic potash or soda is not at hand, the test may be performed with 5 c.c. of alcohol and 1 or 2 c.c. of a 40% aqueous solution of NaOH.

CHAPTER XXIV.

ORGANIC ACIDS.

If the oxidation of an alcohol is carried beyond the formation of aldehyd or ketone, i.e., if the aldehyd or ketone be oxidized, an organic acid results. The first atom of oxygen involved in this process does not become a constituent part of the new molecule, but simply withdraws hydrogen from the old (the alcohol), as shown in the formation of aldehyds on page 198. The second atom of oxygen, however, attaches itself to the molecule and does become a part of the new substance (the acid):

$$\underset{\text{Alcohol.}}{CH_2OH} + O = \underset{\text{Aldehyd.}}{CHO} + H_2O \qquad \underset{\text{Aldehyd.}}{CHO} + O = \underset{\text{Acid.}}{COOH}$$

The group –COOH is known as carboxyl and is the characteristic grouping of the acids. The H of the carboxyl differs from the other atoms of H in the molecule in that it is united to oxygen rather than to carbon, and constitutes the basic or replaceable H of the acid; hence acetic acid is monobasic, and the only possible salt, of potassium, for instance, is CH_3–COOK.

The basicity of the acid depends on the number of *carboxyl* groups it contains.

Among the monobasic acids of the fatty or paraffin series which we will study are the following:

Representative Fatty Acids.

$H.COOH$ = formic acid or hydrogen formate;
$CH_3.COOH$ = acetic acid or hydrogen acetate;
$C_2H_5.COOH$ = propionic acid or hydrogen propionate;

C_3H_7COOH = butyric acid or hydrogen butyrate;
C_4H_9COOH = valeric acid or hydrogen valerate;
$C_{15}H_{31}COOH$ = palmitic acid or hydrogen palmitate;
$C_{17}H_{35}COOH$ = Stearic acid or hydrogen stearate.

The acids of these series are represented by the general formula $C_nH_{2n}O_2$. They are all monobasic; i.e., they contain only one atom of replaceable hydrogen.

Formic Acid, (H.COOH), originally distilled from the bodies of ants (formica, from which the name is derived), is a colorless, easily volatile liquid. It may be prepared in the laboratory by heating oxalic acid with glycerol, when the oxalic acid breaks up into formic acid and CO_2,

$$C_2H_2O_4 = CO_2 + HCOOH.$$

Carbon monoxid, passed over hot KOH, results in the formation of potassium formate,

$$CO + KOH = HCOOK.$$

Also by treatment of ammonium carbonate with nascent hydrogen (sodium amalgam),

$$CO_3(NH_4)_2 + 2\,H = HCOO(NH_4) + H_2O + NH_3),$$

and

$$HCOO(NH_4) + NaOH = HCOONa + NH_3 + H_2O.$$

Formic acid, according to the above reaction, is apparently carbonic acid less one atom of oxygen, and the fact that formic acid acts easily as a reducing agent, taking away oxygen from other bodies and becoming H_2CO_3, is further proof of this relationship.

Acetic Acid, CH_3COOH, is obtained commercially by the oxidation of ethyl alcohol. It is the acid of vinegar, which, according to Massachusetts law, should contain $4\frac{1}{2}\%$ of acid. Glacial acetic acid is a commercial name of the acid containing 1% or less of water: it is a colorless solid at a temperature below 15° C. The U. S. P. acetic acid contains only 36% (by weight) of the pure acid.

Either one, two, or all three of the hydrogen atoms of the CH_3 group may be replaced by chlorin, forming respectively the mono-, di-, and tri-chloracetic acids, the trichloracetic acid being used to a considerable extent in dentistry (page 176).

Acetic acid, by the abstraction of water, forms an anhydrid, $C_4H_6O_3$:

$$2\,HC_2H_3O_2 = (C_2H_3O)_2O + H_2O.$$

This substance is of considerable inportance in organic reactions. It is a colorless liquid with a boiling-point of 138° C., and, with the halogens, forms compounds such as acetyl chlorid, C_2H_3OCl, the radical C_2H_3O being known as the acetyl radical.

Propionic acid, $CH_3.CH_2.COOH$, is a colorless liquid, boiling at 140° C. According to Witthaus, it is best prepared by heating ethyl cyanid with caustic potash until the odor of the ester has disappeared:

$$C_2H_5CN + KOH + H_2O = C_2H_5COOK + NH_3.$$

Then, by treatment with H_2SO_4, the propionic acid is liberated, and may be separated by distillation.

Butyric Acid, C_3H_7COOH, occurs as a product of fermentation of butter, or other animal fat containing butyrin; also from the decomposition of lactic acid, two molecules of lactic acid furnishing one of butyric acid, 2 CO_2 and 2 H_2. It is an occasional constituent of the gastric contents, and may be detected by formation of the ethyl ester (page 207). The pure acid is a heavy, colorless liquid with characteristic odor, soluble in H_2O in any proportion. See page 208 for the glyceryl ester of butyric acid (butyrin); also for stearic and palmitic acids.

Valeric Acid, C_4H_9COOH, may be made by the oxidation of amyl alcohol ($C_5H_{11}OH$). It is an oily liquid boiling at 174° C. It occurs as a constituent of valerian, and in consequence has been called valeric acid. Its salts are used in medicine as sedatives.

The valeriate of amyl has an odor resembling that of apples, and is used in alcoholic solutions as apple essence.

Palmitic Acid, $C_{15}H_{31}COOH$, a solid "fat acid," occurs as a glyceryl ester in butter (to a very slight extent), in olive oil, palm oil, and bayberry wax. Combined with certain alcohols it occurs in white and yellow wax; also in spermaceti.

Palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, occurs in all animal fat and in large quantities in human fat.

Stearic Acid, $C_{18}H_{35}COOH[CH_3–(CH_2)_{16}–COOH]$, as glyceryl stearate or stearin occurs in vegetable and animal fats, particularly in tallow. Stearic acid is only slightly soluble in alcohol or in ether. Its melting-point is 69.3° C.

Laboratory Exercise LV.

Experiments with organic acids. $(C_nH_{2n}O_2)$.

Exp. 74 and 75. Experiments 70 and 71 may be used as illustrating the laboratory test for acetic and butyric acids. In addition a test for lactic acid may be made with the ferric chlorid test, which is also applicable to gastric contents. Exp. 91, page 225.

Exp. 76. Introduce into a small flask (250 c.c. capacity) about 30 c.c. of anhydrous glycerin and an equal weight of oxalic acid crystals. Boil for several minutes; CO_2 is given off and a compound formed between the acid and glycerin; then, upon addition of more acid and continued heating, formic acid may be distilled. Collect about 10 c.c. of distillate; test reaction with litmus-paper. Make silver-mirror test, described on page 201, Exp. 64. The silver solution will be reduced, but difficulty will be experienced in obtaining the mirror.

Exp. 77. To 5 c.c. of formic acid solution add 2 or 3 c.c. of dilute H_2SO_4 (1–5) and a little potassium permanganate solution; heat the mixture and conduct the gas evolved into a tube containing lime water.

Exp. 78. From a mixture of formic acid, alcohol, and sul-

phuric acid, ethyl formate may be evolved in a manner similar to that in the production of ethyl acetate (page 95). Compare the odors of these two ethers.

Exp. 79. To a dilute solution of ferric chlorid add a little acetic acid; divide the solution into two parts; to one add mercuric chlorid and to the other HCl, and note results.

Exp. 80. Repeat Exp. 79, using diacetic acid in place of acetic.

Exp. 81. Repeat Exp. 79 using meconic acid * in place of acetic.

Compare results of these three experiments and save record for future use in the study of saliva.

Exp. 82. In a small flask saponify a little butter by heating with alcoholic potash over a steam bath till mixture is dry. Dissolve in water, add dilute H_2SO_4, and distil off a portion of the butyric acid. Record whatever can be learned from this experiment regarding the physical properties of the butyric acid.

Exp. 83. Take about 5 c.c. each of alcoholic solution of stearic and oleic acids and treat separately with about 1 c.c. of 1% iodin solution (alcoholic); allow to stand for some time, and explain *fully* the difference in action exhibited by the two fatty acids.

Acrylic Acid Series.

Acrylic acid, CH_2: CH.COOH, is a type of the double-bonded acids. It is a liquid with boiling-point at 140° C. Nascent hydrogen breaks the double bond, forming propionic acid, $CH_3.CH_2.COOH$. HI will also break the double bond by direct union of its constituents, forming CH_2I–CH_2–COOH, (β-iodo propionic acid).

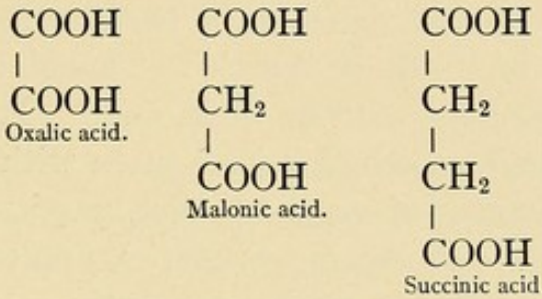
Acrylic aldehyd, or acrolein, is a colorless liquid boiling at 52° C. Its vapor has an irritating, pungent odor, sufficiently

* Laudanum diluted with water till color is light brown may be used.

characteristic to be used as a qualitative test for glycerol, from which it is obtained by heating with $KHSO_4$.

The only other acid of particular importance in this series is oleic acid, $C_{17}H_{33}COOH$. It is an important constituent of oils, both animal and vegetable, and consists, to a great extent, of such substances as lard oil, cotton seed oil, etc.

Dibasic Acids.



Dibasic acids contain two carboxyl groups. These are referable to, and in many cases may be formed from, the diatomic alcohols. Thus glycol, $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$, upon oxidation yields glycollic acid, $\begin{matrix}CH_2OH\\|\\COOH\end{matrix}$, and oxalic acid, $\begin{matrix}COOH\\|\\COOH\end{matrix}$.

Carbonic acid, $O = C\begin{matrix}\diagup OH\\\\\diagdown OH\end{matrix}$, is dibasic in that it contains two atoms of replaceable hydrogen, though not two carboxyl groups. It is claimed that a molecule of this sort cannot exist because a single carbon atom cannot hold more than one hydroxyl group in combination. This acid has never been isolated, all attempts to separate it in the pure form resulting in the formation of carbonic acid gas and water. Its compounds (carbonates) are very common and very important, both in organic and inorganic chemistry. Organic salts of carbonic acid may be made by treating silver carbonate with alkyl iodid.

$$CO\begin{matrix}\diagup OAg \\ \diagdown OAg\end{matrix} + 2\,C_2H_5I = CO\begin{matrix}\diagup OC_2H_5 \\ \diagdown OC_2H_5\end{matrix} + 2\,AgI.$$

Oxalic Acid, which may be considered as a type of the dibasic acids, occurs as small, colorless crystals (four- or six-sided prisms), containing two molecules of water of crystallization ($H_2C_2O_4.2\,H_2O$); it is but slightly efflorescent, and, if carefully crystallized, is suitable for the preparation of standard acid solution. Salts of oxalic acid occur in many plants; the acid potassium oxalate, "salt of sorrel," is found in common red sorrel (Rumex acetora) and in wood sorrel (Oxalis acetocella). Oxalic acid in various combinations, often with lime, is widely distributed in articles of vegetable diet, particularly tomatoes, rhubarb, spinach, and asparagus; grapes, apples, and cabbages also carry oxalates, but in smaller amounts.

The source of oxalates in the system is twofold, — the ingested oxalates and those produced by oxidation, incident to metabolism, the exact nature of which has not been clearly demonstrated (see Calcium and Sodium Oxalates, under Urine and Saliva).

Oxalic acid was previously made commercially by the action of strong nitric acid on starch or sugar; it is now prepared by heating cellulose (in form of sawdust) with a mixture of KOH and NaOH, precipitating the acid as CaC_2O_4, and decomposing the salt by H_2SO_4. The acid is then purified by repeated crystallization.

Malonic Acid, $COOH–CH_2–COOH$, is an oxidation product of malic acid (from apples), and is comparatively unimportant.

Succinic Acid, $COOH(CH_2)_2–COOH$, occurs in amber, from which it takes its name (Amber-Succinum). It has been detected in the urine after asparagus and some fruits have been eaten. It occurs as colorless crystals, soluble in water, and only slightly soluble in ether. Succinic acid may be obtained by the saponification of ethylene cyanid, $C_2H_4(CN)_2$, and is a dibasic

acid containing four carbon atoms. It is a constituent of some transudates and cyst fluids. It occurs in the spleen and thyroid gland, and has been found in sweat and in the urine (Hammarsten).

Pyro-tartaric Acid, formed by the distillation of ordinary tartaric acid, is one of four isomers of formula $C_5H_8O_4$, and is of interest only in its relation to some of the amino acids which result from protein digestion. Formula for pyro-tartaric acid is $CH_3–CHCOOH–CH_2–COOH$.

Oxyacids.

Hydroxy acids, or alcohol acids, contain hydroxyl in place of one or more hydrogen atoms of the fatty acids. Thus we may consider

Carbonic acid as hydroxyformic acid, HO–COOH;

Glycolic acid as hydroxyacetic acid, $\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$;

Lactic acid as hydroxypropionic acid, $\begin{matrix} C_2H_4OH \\ | \\ COOH \end{matrix}$;

Malic acid (from apples) as hydroxysuccinic acid, $\begin{matrix} CHOH–COOH \\ | \\ CH_2–COOH \end{matrix}$.

Tartaric acid is dihydroxysuccinic acid, $\begin{matrix} CHOH–COOH \\ | \\ CHOH–COOH \end{matrix}$.

Citric Acid, from lemons, limes, etc., is in a class by itself. It is a tribasic acid (has three carboxyl groups and one hydroxyl); the formula is $C_3H_4OH–(COOH)_3$.

Glycollic Acid occurs in nature in unripe grapes, and possibly as antecedent to oxalates in the system (Dakin, Journal of Biol. Chem., 3.57). Glycollic acid is formed from glycol by oxidation, and from glycocoll, by action of nitrous acid.

Nitric acid will oxidize glycollic acid to oxalic acid.

Lactic Acid. — Oxypropionic acid, or i* -ethylidene lactic acid, CH_3–CHOH–COOH, is ordinary lactic acid produced by fermentation of milk-sugar, etc. It occurs in the gastric juice and in contents of the intestine, "particularly during a diet rich in carbohydrates," possibly in muscle and brain tissue (Foster). It is not volatilized at temperature below 160° C.

Sarcolactic or paralactic acid, d†-ethylidene lactic acid, occurs in meat extract. The presence of this acid causes the acid reaction of dead muscle, possibly of contracted muscle. It occurs in the blood and at times in the urine, and it is probable that it is this modification that may be found as lactates and acid lactates in the saliva and urine, the crystalline forms of which have been identified by Dr. E. C. Kirk of Philadelphia, by the use of the micropolariscopic method of Dr. Joseph P. Michaels of Paris. This statement as yet lacks confirmatory demonstration.

Both of these acids form characteristic crystalline salts of zinc and of calcium. In cold water the zinc sarcolactate is more soluble than zinc lactate; on the other hand, the calcium sarcolactate is rather less soluble than calcium lactate.

β-Oxybutyric Acid, CH_3–CHOH–CH_2–COOH. If there is introduced into butyric acid, CH_3–CH_2–CH_2–COOH, an OH group, an oxybutyric results. If this alcohol group (OH) occupies the secondary or β position (i.e., attached to the carbon atom twice removed from the carboxyl), the acid is the β-oxybutyric as above.

By oxidation of the compound, the alcohol group is broken up and H withdrawn to form water, leaving a keto acid, CH_3–CO–CH_2–COOH, known as diacetic acid. This in turn may give off carbon dioxid and become dimethyl ketone, or acetone, CH_3–CO–CH_3. These three substances, β-oxybutyric acid, diacetic acid, and acetone, are classed in von Noorden's

* Optically inactive. † Dextrorotary.

"Autointoxication," and in the works of other recent writers, as "the acetone bodies," and by this convenient term we may refer to them collectively. They occur in diabetic urine and, according to von Noorden, in other cases of perverted oxidation (not insufficient oxidation).

Tartaric Acid is a dihydroxysuccinic acid, $COOH-(CHOH)_2-COOH$, obtained from grape-juice. The double tartrate of sodium and potassium (Rochelle salt), $KNaC_4H_4O_6$, is much used in medicine.

Tartaric acid combines with potassium and antimony to form tartar emetic, $(KSbOC_4H_4O_6)_2H_2O$.

The "*scale salts of iron*," "ferri et ammonii tartras" and "ferri et potassii tartras," are prepared by dissolving freshly precipitated ferric hydroxid in the acid tartrate of ammonia or potash, and, after evaporation to thick syrup, solidifying in thin layers on glass plates.

Potassium Bitartrate, or acid tartrate, $KHC_4H_4O_6$, is cream of tartar, and one of the few salts of potassium, only sparingly soluble in water. Its commercial source is the wine-vat.

Monobasic Amino Acids.

Amino acids, formerly called amido acids, are characterized by an NH_2 group in place of $H-$; for example, acetic acid is $\begin{matrix} CH_3 \\ | \\ COOH \end{matrix}$. Amino acetic acid is $\begin{matrix} CH_2NH_2 \\ | \\ COOH \end{matrix}$. These acids are of particular interest because of their close relationship to protein, many of them being among the cleavage products of protein hydrolysis.

That many of the amino acids are formed as intermediate steps in the reduction of the complex protein molecules to urea is certain.

A faulty metabolism, which stops short of normal oxidations,

results in throwing these amino acids off in the urine or fæces and their presence indicates abnormal conditions of one sort or another.

Amino formic or carbamic acid, $\begin{matrix}NH_2\\|\\COOH\end{matrix}$, is a hypothetical acid which would consist simply of an amino group, NH_2, united to a carboxyl group, COOH. By the union of ammonia and carbon dioxid the ammonium salt of this acid is formed,

$$2\,NH_3 + CO_2 = \begin{matrix}NH_2\\|\\COONH_4\end{matrix}.$$

Ammonium carbamate, is a constituent of commercial ammonium carbonate and an antecedent of ammonium carbonate in the hydrolysis of urea.

Amino-acetic Acid, also called glycocoll and glycin, is obtained with other amino acids by boiling glue with either acids or alkalis.* It is also obtained, by the hydrolysis of glycocholic acid, from bile.

Hippuric Acid (Plate V, Fig. 4) consists of benzoic acid united chemically to glycocoll, and may be produced synthetically by the union of these two substances.

Amino-valeric Acid, $CH_2(NH_2)–(CH_2)_3–COOH$, may be obtained with glycocoll from elastin, the protein of the elastic fibres, of tendons, etc.† Isomeric with amino-caproic acid is *leucin*, an amino-isobutyl-acetic acid,‡

$$\begin{matrix}CH_3\\\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH–CH_2–CH(NH_2)–COOH.$$

Leucin is a cleavage product in the decomposition of proteins, including keratin and collagen. It results from the tryptic

* Bernthsen, Organic Chemistry.

† Foster, Chemical Basis of the Animal Body.

‡ Novy, Physiological Chemistry.

PLATE V.—ORGANIC CHEMISTRY.

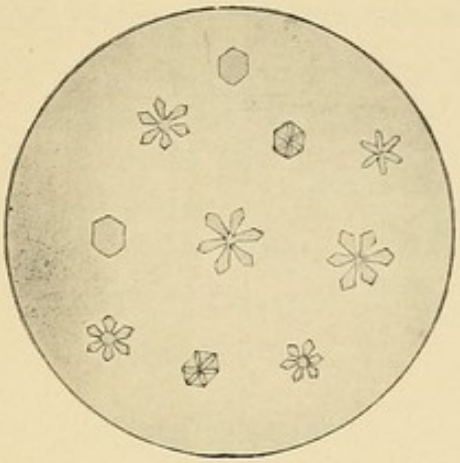


FIG. 1.
Iodoform.

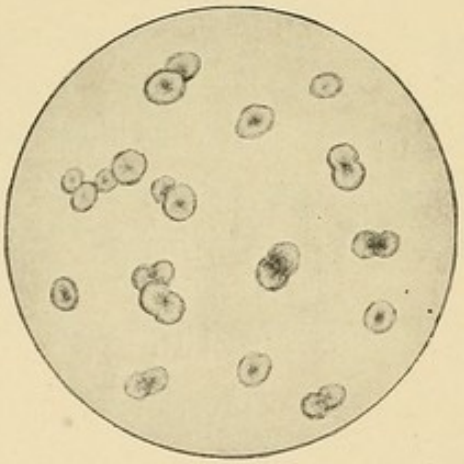


FIG. 2.
Leucin.

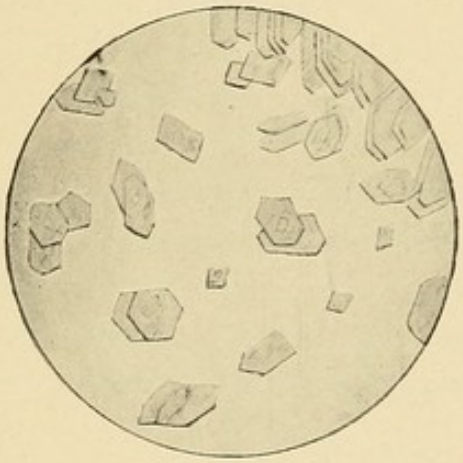


FIG. 3.
Urea Nitrate.

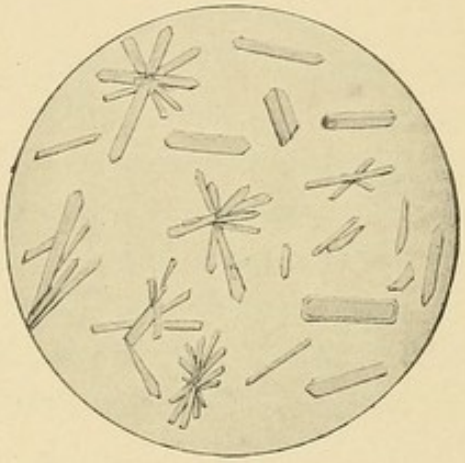


FIG. 4.
Hippuric Acid.

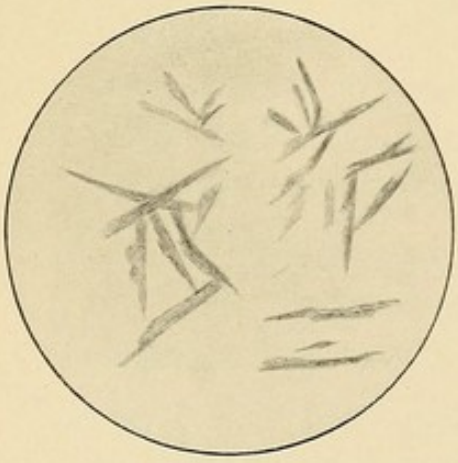


FIG. 5.
Benzoic Acid (sublimed).

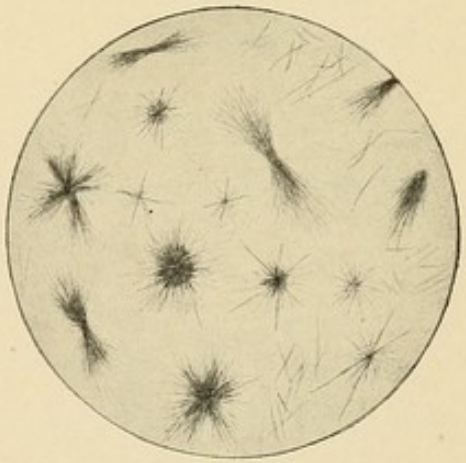


FIG. 6.
Tyrosin.

digestion of the hemipeptones and is regarded, as are other amino acids, as antecedent of urea (Plate V, Fig. 2).

Cystin, $C_6H_{12}N_2S_2O_4$, is an amino acid occasionally found in the urine in diseases where the sulphur compounds fail to be properly oxidized. It occurs under these circumstances as regular colorless hexagonal plates (Plate X, Fig. 6).

By the oxidation of crystin and subsequent splitting off of CO_2 taurine is produced.

Taurine, (Amino-ethyl-sulphonic acid) $\begin{matrix} CH_2NH_2 \\ | \\ CH_2(SO_2OH) \end{matrix}$, results from the cleavage of protein, also from the decomposition of taurocholic acid from bile.

Leucin, $(CH_3)_2.CH.CH_2.CHNH_2.COOH$), is an α amino isobutyl acetic acid and occurs usually with tyrosin as a decomposition product of protein (casein). It is occasionally found in the urine as "leucin spheres" (represented in Plate V, Fig. 2).

Tyrosin is a complex amino acid obtained from the decomposition of protein substances, particularly old cheese. It is occasionally found in urinary sediments as colorless needle-shaped crystals usually grouped as tufts or "sheaves." (Plate V, Fig. 6).

Dibasic Amino Acids.

Of this class of compounds two may be mentioned: amino-succinic, aspartic or asparaginic acid, $COOH–CH_2–CH(NH_2)–COOH$, may be obtained from animal and vegetable proteins and in the pancreatic digestion of fibrin.

Glutamic Acid is an amino-glutaric (pyrotartaric) acid, and occurs similarly to aspartic acid, except that it is not formed by pancreatic digestion.

Laboratory Exercise LVI.

Experiments with Organic Acids not of the $C_nH_{2\,n}O_2$ Series.

Exp. 84. To a dilute solution of permanganate of potassium add a few drops of sulphuric acid and heat nearly to boiling.

Note if any change takes place. Now add a few crystals of oxalic acid and watch carefully. Explain the use of sulphuric acid.

Exp. 85. In separate test-tubes, insoluble oxalates may be produced by adding a solution of ammonium oxalate to a solution of (*a*) calcium chlorid, (*b*) silver nitrate, (*c*) zinc sulphate, (*d*) copper sulphate, (*e*) lead nitrate.

Exp. 86. Place in an ignition-tube, fitted with delivery-tube to collect evolved gas in test-tube, about 3 grams of dry calcium oxalate. Heat strongly and test gas evolved with lighted match or splinter. After ignition-tube has become *cold* add dilute H_2SO_4 and pass gas evolved into lime water.

Exp. 87. Dissolve about 3 grams of dry oxalic acid (100° C.) in a test-tube half full of methyl alcohol. It will probably be necessary to boil the mixture before solution is complete and great care must be used to avoid burning of the alcohol. The use of a water-bath is recommended. As the hot mixture cools, dimethyloxalate will crystallize out.

Separate sufficient of the crystals to obtain melting-point, which should be about 54° C.

Exp. 88. The ester prepared in above experiment may be dissolved in alcohol and upon addition of NH_4OH will give a precipitate of oxamid.

Exp. 89. Take a test-tube half full of calcium chlorid (10%), make strongly alkaline with NH_4OH and pass CO_2 into the mixture for several minutes. A solution of calcium carbonate will result.

Write reaction, $CaCl_2 + 2\ CO_2 + 4\ NH_4OH = ?$. Heat the solution of calcium carbonate just produced till a precipitate of $CaCO_3$ is produced.

Write reaction with one molecule of water on left-hand side of equation.

Exp. 90. To 1/3 test-tube of cider vinegar add a few cubic centimeters of basic acetate of lead solution; a bulky precipitate of lead malate separates out.

Exp. 91. Dilute a few drops of neutral ferric chlorid solution until no color is discernible, then to 10 c.c. of this dilution add 4 to 5 drops of 1/2% solution of lactic acid. A greenish-yellow color constitutes the test.

In practical application of this test, it needs further confirmation by boiling the unknown solution with a drop or two of HCl and then extracting with ether. Evaporate the ether, take up the residue in 2 or 3 c.c. of water and repeat the test as given above. If the yellow color persists, it is due to lactic acid.

CHAPTER XXV.

AMINS OR SUBSTITUTED AMMONIAS.

If one or more of the H atoms of ammonia, NH_3, be replaced by a hydrocarbon group, the resulting compound is an amin; thus $CH_3–NH_2$ is methylamin, and $(CH_3)_2NH$ is dimethylamin. Trimethylamin, $(CH_3)_3N$, has been found among the decomposition products of fresh brain, human liver, and spleen.* It is poisonous and possesses a strong, fishy odor. At ordinary temperature it is a gas, but, like ammonia, is freely soluble in H_2O and forms a variety of salts.

Diamins are derived from two molecules of ammonia, as ethylene diamin, $C_2H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$.

To this class of compounds belong many of the "ptomains," produced by the putrefaction of organic matter, as putrescin, (butylene diamin), $CH_2NH_2–(CH_2)_2–CH_2NH_2$, and cadaverin, (penta-methylene diamin), $CH_2NH_2–(CH_2)_3–CH_2NH_2$. A large number of the ptomains are aromatic compounds and as such will be referred to later.

Amids.

If the hydrogen of NH_3 be replaced by an oxygenated or acid radical, an amid results; thus $NH_2(C_2H_3O)$ is acetamid, or this compound may be regarded as acetic acid, $CH_3–COOH$, in which the OH has been replaced by NH_2.

Formamid, $CHO.NH_2$, is a liquid miscible with both alcohol and water. It boils with partial decomposition at about 200° C.

* Vaughn and Novy, Cellular Toxins.

Upon heating quickly, it splits into CO and NH_3. (Bernthsen.)

Phenyl-formamid, $CHO.NHC_6H_5$, known as formanilid, occurs as yellow crystals soluble in water and in alcohol.

Hydrazines.

From diamid, $NH_2–NH_2$, or hydrazine, may be derived such substitution products as methyl-hydrazine, $CH_3–NH–NH_2$; ethyl-hydrazine, $C_2H_5–NH–NH_2$; and phenyl-hydrazine, $C_6H_5NH–NH_2$.

This latter compound forms, with the monosaccharids and with many of the disaccharids, yellow crystalline compounds, known as osazones, which are precipitated in characteristic crystalline forms, recognizable upon microscopical examination and by their melting-points (see under Carbohydrates, page 260).

CHAPTER XXVI.

CYANOGEN COMPOUNDS.

CYANOGEN, C_2N_2, is an intensely poisonous gas, colorless, heavy (specific gravity 1.81), and inflammable. It is very easily soluble in water or alcohol, forming unstable solutions, which, upon decomposition, give rise to various nitrogen compounds, among them ammonia, hydrocyanic acid, and urea.

Hydrocyanic Acid, HCN, may be produced by the fermentation of the glucoside amygdalin from bitter almonds; also from the kernel of peach-stones, cherry-laurel leaves, etc. HCN may be formed by direct synthesis of C_2H_2 (acetylene) and nitrogen. The synthesis is induced by passing electric sparks through the mixed gases. It is conveniently prepared in the laboratory by distilling a mixture of dilute sulphuric acid with potassium ferrocyanide, $K_4Fe(CN)_6 + 5\,H_2SO_4 = 6\,HCN + FeSO_4 + 4\,KHSO_4$. Hydrocyanic acid is a colorless, poisonous liquid, boiling at 26.5° C., with a characteristic odor often designated as a peach-stone odor. It is soluble in H_2O, and a 2% aqueous solution constitutes the acidum hydrocyanicum dilutum of the pharmacopœia, also known as prussic acid.

Potassium Cyanide (KCN or KCy) occurs in trade as a white solid, sometimes granular, more often as a powder. It is intensely poisonous owing to the dissociation of the salt and activity of the free cyanogen.

KCN is decomposed by carbonic acid of the air with liberation of HCN. The aqueous solution of KCN hydrolyzes in two distinct ways: the most easily apparent at ordinary temperature is with the formation of HCN and KOH giving the solution an alkaline reaction:

$$KCN + H_2O = HCN + KOH.$$

Upon boiling a solution, the second hydrolysis may be demonstrated whereby NH_3 and potassium formate are produced:

$$KCN + 2\,H_2O = HCOOK + NH_3$$ (Exp. 96, page 230).

The organic cyanids are known as *nitrils* or *isonitrils*, according as the hydrocarbon radical is attached directly to the C or to the N of the cyanogen group. That is, methyl cyanid would be represented by CH_3–CN, while the isocyanid would be CH_3–NC (methyl carbamin); the nitrogen atom being in the first place trivalent, in the second quinquivalent.

Of these two classes of compounds, the isocyanids are of much greater interest to the student of dental medicine owing to their relation to the isocyanates and to urea.

Phenyl-isocyanid, C_5H_6NC, also known as isobenzonitril, is produced by warming aniline ($C_6H_5NH_2$) with alcoholic potash and chloroform, the intensely disagreeable odor of which is utilized as a test for chloroform or chloral hydrate (page 167); or, with chloroform and potassium hydrate, the production of isocyanid may become a test for aniline, acetanilid (antifebrin), etc.

Isocyanic Acid, O = C = N–H (carbimid), is supposed to be the acid of ordinary potassium and ammonium cyanates.

Fulminic acid (C ≡ N–O–H), isomeric with cyanic acid N ≡ C–O–H and isocyanic acid (O = C = N–H), is important only because of its relation to the fulminates, which are explosive compounds of the acid, with some of the heavy metals, such as Ag and Hg.

Thiocyanic Acid or Sulphocyanic Acid. — In this acid and its salts, the atom of S replaces the oxygen of the cyanate in the empirical symbol (HCNS); but, graphically, the S is attached to the basic element (metal or H) rather than to C: thus, K–S–C ≡ N, that is, the sulphocyanate is not an isocompound. For occurrence and relations of HCNS in the human body, see chapter on Saliva.

Laboratory Exercise LVII.

Experiments with Cyanogen Compounds.

Exp. 92. In a test-tube dissolve 1/2 gram or *less* of potassium ferrocyanid in about 4 c.c. of H_2O. Add a little H_2SO_4 and boil, conducting the gas evolved into another test-tube by means of a bent glass tube. Note the odor of this dilute solution. (Do not smell of the contents of generating-tube, as the strong acid is intensely poisonous.)

$$2\,K_4FeCy_6 + 6\,H_2SO_4 = K_2Fe(FeCy_6) + 6\,KHSO_4 + 6\,HCy.$$

Exp. 93. To one half of the dilute hydrocyanic acid prepared in the previous experiment add a drop or two of $AgNO_3$ solution with a little HNO_3. After the precipitate has settled, decant the fluid, then add an excess of ammonia-water.

Exp. 94. To the other half of the HCy from Exp. 92 add a little solution of ferrous sulphate; also a few drops of ferric chlorid solution; then a little KOH solution; mix thoroughly and acidify with HCl. A blue precipitate, $Fe_4(FeCy_6)_3$, is a test for HCy or any soluble cyanid.

Exp. 95. To a few drops of KCN solution add a little yellow ammonium sulphid, $(NH_4)_2S$, and evaporate to dryness. Dissolve in water; acidify with HCl and add Fe_2Cl_6 solution.

Exp. 96. In a small flask boil a solution of KCN. While boiling, test the vapors for ammonia gas. Solution of potassium formate remains in the flask.

Complete reaction, $KCN + 2\,H_2O = ?$.

Exp. 97. To a little dilute (2%) solution of K_4FeCy_6 add a little bromin water and boil. Prove the formation of K_3FeCy_6 by use of $FeCl_3$.

From this experiment what is the relative valence of iron in the two compounds? Why?

Exp. 98. To a fresh solution of K_3FeCy_6 add a little 10% KOH solution and some PbO, shake and filter. To the clear filtrate add $FeCl_3$.

Give reason for the statement that the PbO has acted as a reducing agent.

CHAPTER XXVII.

UREA.

THIS substance forms about 50% of the total solids and about 85% of the nitrogenous matter contained in the urine. When we consider that only 5% of the nitrogenous waste passes off in the feces and 95% in the urine, the importance of urea as an index of the nitrogen excreted and of protein metabolism becomes apparent.

Urea was the first organic substance synthesized from inorganic compounds. This was accomplished by producing a molecular rearrangement of ammonium isocyanate. The reaction is conveniently brought about by the double decomposition of potassium cyanate and ammonium sulphate and subsequent evaporation of the solution to dryness:

$$2\,CNOK + (NH_4)_2SO = OCN.NH_4 + K_2SO_4.$$

Then $O = C = N - NH_4$ (ammonium isocyanate) + heat =

$$O = C\begin{<}{NH_2}{NH_2}\quad\text{(urea)}.$$

Urea is the amid of carbonic acid, $O = C\begin{<}{OH}{OH}$, and from this type may be explained the rapid transformation of urea into ammonium carbonate in stale urine. $O = C\begin{<}{NH_2}{NH_2}$ with one molecule of H_2O becomes $O = C\begin{<}{ONH_4}{NH_2}$ or ammonium carbamate, and this, by addition of a second molecule of water, be-

comes $O = C\begin{<}ONH_4\\ONH_4\end{>}$ or ammonium carbonate, $(NH_4)_2CO_3$. The last part of the reaction takes place whenever commercial "ammonium carbonate" [really a mixture of carbamate (NH_4–NH_2–CO_2) and acid carbonate (NH_4HCO_3)] is dissolved in water.

Urea crystallizes in long needle-shaped crystals of the rhombic system. It is insoluble in water, somewhat soluble in alcohol, and nearly insoluble in ether. It fuses at 132°, and at a somewhat higher temperature it gives off ammonia and ammonium carbonate, and at 160° leaves a residue of ammelid, cyanuric acid, and biuret. Urea is decomposed by solutions of the alkaline hypochlorites or hypobromites being broken up into N, CO_2, and H_2O, as follows:

$$CO(NH_2)_2 + 3\,NaOBr = CO_2 + N_2 + 2\,H_2O + 3\,NaBr.$$

Cyanuric Acid, ($N_3C_3O_3H_3$), is a polymer of cyanic acid (NCOH), which is, at first, formed in the above decomposition.

Biuret, $H-N\begin{<}CO-NH_2\\CO-NH_2\end{>}$, may be obtained by heating urea. When pure, it occurs as white, needle-shaped crystals. With NaOH and 1% $CuSO_4$ it gives the characteristic violet and rose-red shades obtained in the biuret reaction (Piotrowski's proteid test). Exp. 157, page 277.

Urea Nitrate may be precipitated from fairly concentrated urine by addition of HNO_3. It separates in hexagonal crystals or plates, easily recognizable under the microscope (Plate V, Fig. 3, opposite page 222).

Urea Oxalate. — Upon addition of a solution of oxalic acid to concentrated urine, crystals of oxalate of urea are precipitated. They are rather more easily obtained in characteristic forms (Plate II, Fig. 5, opposite page 162) than are the crystals of nitrate, and, in consequence, treatment with oxalic acid constitutes a better method for the qualitative detection of urea in

the body fluids than the nitric acid test formerly used. These crystals polarize light, and the use of the micropolariscope facilitates their detection.

Substituted Ureas. — The hydrogen of the amino group may be replaced by alcohol radicals forming what are known as alkylated ureas; thus, $O=C\begin{smallmatrix}/\,HN_2\\ \backslash\,NHCH_3\end{smallmatrix}$ is methyl urea, $O=C\begin{smallmatrix}/\,NH_2\\ \backslash\,NHC_2H_5\end{smallmatrix}$, ethyl urea, and one, two, three, or all four of the H atoms may be so replaced.

When, in place of an alcohol radical, the *acid* radical is introduced, a class of compounds known as "ureids" results; thus,

$$O=C\begin{smallmatrix}/\,NH_2\\ \backslash\,NH(C_2H_3O)\end{smallmatrix}\text{(acetyl urea).}$$

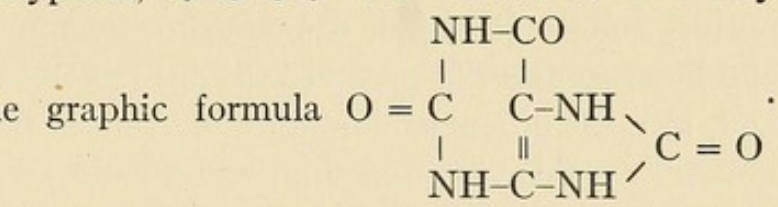
In case of a dibasic acid, such as oxalic, $\begin{smallmatrix}COOH\\ |\\ COOH\end{smallmatrix}$, entering into the reaction, one or both (OH) groups may be split off, forming in the first instance a ureid acid, as $O=C\begin{smallmatrix}/\,NH_2\\ \backslash\,NH.CO,\ COOH\end{smallmatrix}$, oxaluric acid,

$$\begin{smallmatrix}COOH\\ |\\ COOH\end{smallmatrix} + O=C\begin{smallmatrix}/\,NH_2\\ \backslash\,NH_2\end{smallmatrix} = O=C\begin{smallmatrix}/\,NH_2\\ \backslash\,NH\text{–}CO\\ \qquad\ |\\ \qquad COOH\end{smallmatrix} + H_2O,$$

or, in the second case, a ureid, as $O=C\begin{smallmatrix}/\,NH\text{–}C=O\\ \backslash\,NH\text{–}C=O\end{smallmatrix}$ parabanic acid.

If the residue of *two* molecules of urea enter into the composition of the new molecule, the compound is a diureid. Of this class one of the most important is:

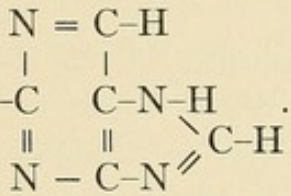
Uric Acid, trioxypurin, $C_5H_4N_4O_3$. Its relation to urea may be shown by the graphic formula



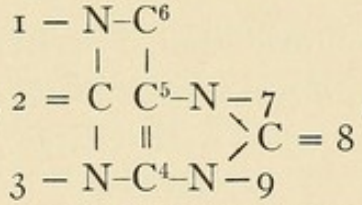
Uric acid is also referable to a purely hypothetical base, "purin," by the use of which the relationship of xanthin, hypoxanthin, and other "purin" or nuclein bases is easily demonstrated.

These bases are of great physiological interest, in that they form an unquestioned link between the decomposition products of the proteins, nuclein, etc., on the one hand, and uric acid and the urates on the other.

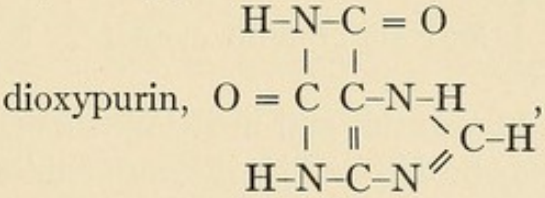
Purin is represented by the formula $C_5H_4N_4$, or graphically as



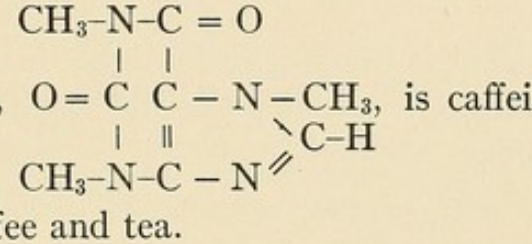
. If we now break all double bonds except those linking two carbon atoms (4 and 5), we obtain a graphic nucleus,



, by numbering the atoms of which we may easily designate any structural formula of the group; thus, 2–6–8, trioxypurin, is uric acid as above, while xanthin is 2–6, dioxypurin,



, and 1–3–7, trimethyl-xanthin,



, is caffein and thein, alkaloids from coffee and tea.

Traces of xanthin (2.6 dioxypurin), hypoxanthin (6 oxypurin), guanin (2 imino, 6 oxypurin), adenin (6 amino purin), and heteroxanthin (7 methyl xanthin) have been found in urine, and, in cases of leukæmia, many of them in increased amounts, notably xanthin, hypoxanthin, and adenin (Witthaus).

Uric acid occurs in the urine; there are traces of it in the blood; and it is occasionally found, in the form of urates, in saliva. It is a dibasic crystalline acid, colorless when pure; but, in urinary sediment, it occurs generally as crystals, yellow to red, "whetstone"-shaped, and in various other forms (Plate X, Figs. 1 and 2). The "brickdust" deposit occasionally found in urine consists of uric acid. It is insoluble in alcohol and nearly insoluble in water; but its solubility in water is increased by the presence of urea.

Upon heating uric acid, urea and cyanuric acid may be obtained; NH_3 and CO_2 are given off. We are not to infer from this decomposition that the uric acid is an antecedent of urea in the animal body; for such is not the case, except possibly to a limited extent.

Uric acid produces, upon oxidation, a variety of compounds, according to the temperature and the oxidizing agent employed.

Cl, hot, yields cyanuric acid, $C_3H_3(OH)_3$. Cl or Br, cold, forms oxalic acid, alloxan, $(CO\langle^{NHCO}_{NHCO}\rangle CO)$, parabanic acid, $\left(CO\langle^{NH-CO}_{NH-CO}\rangle\right)$, and ammonium cyanate. HNO_3 in the cold, forms alloxan, alloxantin, and urea (Witthaus).

Uric acid may be detected by the murexid test. See Exp. 104, page 239.

While uric acid is practically insoluble in H_2O and the acid urates only sparingly soluble, the uric acid in the system is

Note. — Murexid is a definite chemical compound ($C_8H_5N_5O_6$) and may be produced from alloxantin, an oxidation product noted above.

apparently held in solution as an acid urate ($NaH\overline{U}$) by the presence of the sodium phosphates, NaH_2PO_4 and Na_2HPO_4, possibly also aided by the presence of some unknown organic combination.

$NaH\overline{U} + NaH_2PO_4$ forms, at 38° C., a solution with an acid reaction; if, however, the mixture is cooled to room temperature, the reaction becomes alkaline from Na_2HPO_4, and uric acid is precipitated (Bunge):

$$NaH\overline{U} + NaH_2PO_4 = Na_2HPO_4 + H_2\overline{U}.$$

Na_2HPO_4 is a normal constituent of the blood, and a tendency to precipitate uric acid may be met by the following reaction: $Na_2HPO_4 + H_2\overline{U} = NaH_2PO_4 + NaH\overline{U}$. Because the acid urate of lithium is much more soluble in water than any of the other monometallic urates, lithium salts have long been used as uric acid solvents. But the fact that lithium solutions will precipitate from solutions of Na_2HPO_4 crystals of Li_2HPO_4, has been made the basis for a claim that such use of lithium salts is without effect other than to decompose and render insoluble the alkaline phosphate, which has been acknowledged a valuable factor in keeping uric acid in solution. While the disodic phosphate is regarded by many as superior to lithium salts as a uric acid solvent, the fact of comparative insolubility of Li_2HPO_4 can hardly be regarded as conclusive evidence that lithium compounds are not effective.

The following in regard to our need for "sarsaparilla" in the spring is given by Dr. E. C. Hill, of the University of Denver, in his text-book of chemistry, page 370: "Reduced alkalinity of the blood, as in winter from eating meats freely, throws uric acid out of solution to collect in the more acid tissues (spleen, liver, and joints). With the vernal tide of alkalinity (due to freer sweating, with excretion of fatty acids) these deposits are swept out in the blood-current, irritating the nerves and giving rise to 'that tired feeling.'"

Laboratory Exercise LVIII.

Urea and Uric Acid.

Exp. 99. Make separate solutions of 10 grams of potassium cyanate * and 8.25 grams of ammonium sulphate. Mix and evaporate on a water-bath in a shallow dish. Separate the potassium sulphate as the evaporation proceeds; finally, evaporate to dryness and extract with absolute alcohol. Evaporate alcohol and reserve the urea for subsequent experiments. (See Urea, page 232.)

Exp. 100. Heat a few crystals of urea in a test-tube until they fuse and no more gas is given off; cool, and dissolve the fused mass in water; add one or two c.c. of strong NaOH solution, then not more than one or two drops of a 1% $CuSO_4$ solution. Note the pink to violet color produced. This constitutes the biuret reaction used in physiological chemistry as a test for albumoses and peptones. Biuret is formed from urea as follows:

$$2\,O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} = \begin{matrix}O=C\diagup NH_2\\ \qquad\diagdown NH\\ O=C\diagup NH_2\\ \qquad\diagdown NH_2\end{matrix} + NH_3.$$

Exp. 101. Produce crystals of urea nitrate and oxalate (page 233) and examine under the microscope. *Repeat with* urea obtained from urine.

This experiment may be performed by concentrating to about 1/5 its bulk a little urine and using the concentrated solution as a solution of urea.

Exp. 102. Treat 5 c.c. of urea solution (urine may be used) with a little sodium hypochlorite or hypobromite; note results and study reaction given on page 233.

* For method of making potassium cyanate, see Preparation of Reagents and Organic Compounds, in the Appendix.

Exp. 103. Heat one-third of a test-tube of urine with barium hydroxid (baryta-water); test vapor with red litmus for NH_3.

Exp. 104. *Murexid test* for uric acid: Place a very small quantity of uric acid on a porcelain crucible cover, or in a small evaporating-dish. Add two or three drops of strong nitric acid and evaporate to dryness over a water-bath. A yellowish-red residue remains, which changes to a purplish red upon addition of a drop of strong NH_4OH, and purple-violet upon further addition of a drop of KOH solution, the color disappearing upon standing or upon the application of heat. (Difference from xanthin, which also gives a deeper red color.)

Exp. 105. Repeat No. 104, using caffein in place of uric acid.

Exp. 106. Heat a little sodium acid urate in a dilute solution of NaH_2PO_4. Allow to cool, and examine any deposit for uric acid crystals. Test reaction of solution both hot and cold (page 237).

Exp. 107. Mix, and allow to stand for some time at reduced temperature, 30 c.c. of urine (a 2% urea solution), 2 or 3 c.c. of strong Na_2CO_3 solution, and 5 c.c. of saturated NH_4Cl solution.

A precipitate consists of ammonium urate.

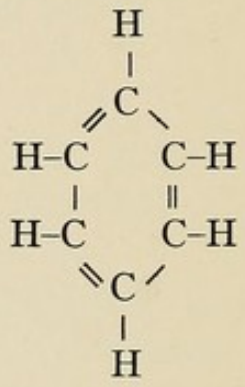
Examine under the microscope and make murexid test.

CHAPTER XXVIII.

CLOSED-CHAIN HYDROCARBONS.

In illustrating the simpler relationship of organic compounds we have, as far as possible, carefully avoided reference to the closed-chain or aromatic compounds, as the characteristic groupings are more easily seen by the use of simple formulæ. The distinguishing feature of the aromatic (also called cyclic) compounds is a nucleus consisting of a closed chain of atoms; this chain may contain three, four, five, six, or seven members, but the six-carbon ring is by far the most important, and the only one which we are to consider.

The hydrocarbons of the aromatic series have, for a general formula, C_nH_{2n-6}, the simplest being *benzene* or benzol, C_6H_6; and we may consider that the aromatic compounds are derived from this. The structure of the benzene molecule is represented by "Kekulé's" benzene ring. Note that there are three double bonds, which of course permit of addition products, as $C_6H_6Cl_2$, benzene di-chlorid, etc. The substitution products are, however, of far greater importance.



Benzene, C_6H_6 (benzol), is a colorless liquid from the "light-oil" obtained by distillation of coal-tar. It boils at 80°, has a gravity of 0.899, is soluble in ether, alcohol, and chloroform, but insoluble in H_2O. It may be made pure by distilling an intimate mixture of benzoic acid and quicklime, and at a temperature of about 5° C. may be obtained as a crystalline solid, $C_6H_5COOH + CaO = CaCO_3 + C_6H_6$. (See Exp. 108, page 250.)

Toluene, C_7H_8 (toluol). — The next higher homologue of the series will be C_7H_8; this is methyl benzene, ($C_6H_5CH_3$), or toluene.

The hydrocarbons of this series may be prepared in a manner similar to that used in the preparation of the hydrocarbons of the paraffin series.

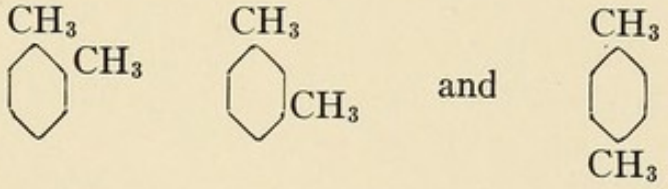
Toluene may be made by the action of metallic sodium upon a mixture of brombenzene and methyl iodid.

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5CH_3 + NaBr + NaI.$$

Toluene is a colorless liquid boiling at 110° C., and yielding upon oxidation a benzene derivative; i.e., the CH_3, or so-called side chain, is the part of the compound changed by oxidizing agents rather than the benzene ring,

$$C_6H_5CH_3 + 3\,O = C_6H_5CO_2H + H_2O.$$

Xylene, C_8H_{10} (xylol) or dimethylbenzene, the next hydrocarbon of this series, exists in coal tar as a mixture of three isomeric compounds which may be graphically represented as follows:



These three possible positions of the *second* substitution are known as ortho-, meta-, and para-; thus, the first representation at the left will be ortho-xylene, or ortho-dimethylbenzene. The other two will be meta-xylene and para-xylene respectively.

A trisubstituted benzene may be "adjacent," if the substituted element or group is attached to the carbon atoms 1–2–3 or "unsymmetrical" (1–2–4) or "symmetrical" (1–3–5).

A fourth isomer of dimethylbenzene would be an ethyl benzene, $C_6H_5C_2H_5$. This, upon oxidation, yields benzoic acid, a benzene derivative in a manner similar to toluene.

Mesitylene, C_9H_{12}, is a trimethylbenzene. Only two isomers are possible. It can be prepared by dehydrating acetone by the use of sulphuric acid:

$$3\,C_3H_6O - 3\,H_2O = C_9H_{12}.$$

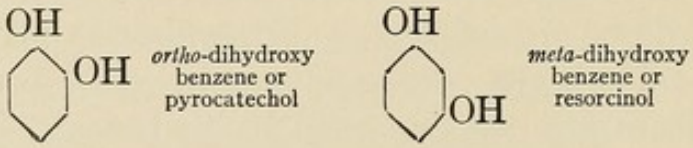
Derivatives of the Hydrocarbons of the Aromatic Series.

The derivatives of the closed-chain hydrocarbons are very numerous, and many of them have very complex formulæ. We shall confine our study to a few of the most simple and at the same time most common.

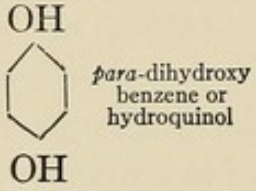
The halogen derivatives are numerous and easily made, but are not of particular importance from a dental standpoint. The hydroxyl derivatives, on the other hand, are of great importance. The first is phenol.

Phenol, carbolic acid, or oxybenzene, C_6H_5OH, obtained from the distillation of coal-tar, and used as an antiseptic and disinfectant. For properties and test, see page 174. Phenol acts like an acid, in that it forms salts with the metallic bases, C_6H_5OK, potassium phenolate, but it does not have an acid reaction on litmus paper or other indicators, i.e., it does not have free hydrogen ions when in solution, but belongs to the alcohols rather than the acids.

The three di-hydroxybenzenes are all of interest and are graphically represented as follows:



and



The ortho compound is **pyrocatechol.** Its ethereal sulphate (acid sulphate) is given by Hoppe-Seyler as a constituent of normal urine, and its monomethyl ether, **guaiacol,** $C_6H_4OH–O–CH_3$, is obtained from beech-wood creosote, of which it constitutes the greater part (60 to 90 per cent U. S. D.). Guaiacol and various compounds produced from it have been widely recommended for tubercular diseases.

Pyrocatechol has been found to be the most practical reagent for the detection of oxydizing enzymes* in the saliva.

Resorcinol is a white crystalline solid, becoming more or less colored upon exposure to the light. It melts at 118° C., and, in solution, gives a purple color with ferric chlorid. Heated with sodium nitrate, it produces a substance known as "Lacmoid" which is used to a considerable extent as an indicator.

The **hydroquinol** or hydrochinon, is a white powder melting at 169° C., and is largely used as a photographic developer.

Trihydroxybenzene, or pyrogalol, $C_6H_3(OH)_3$ (1–2–3), may be made by heating gallic acid, and because of this fact is usually called pyrogallic acid. It is a white silky crystal which, like hydroquinol, is used as a photographic developer. Dissolved in a solution of caustic potash it absorbs oxygen to a marked degree, and may be used as a reagent for the quantitative determination of oxygen in gas analysis.

Phloroglucinol is another trihydroxybenzene, isomeric with pyrogalol but with the hydroxyl groups occupying positions 1–3–5 in the ring. The formula is $C_6H_3(OH)_3$ (1–3–5).

It crystallizes in rhombic prisms, soluble in water, alcohol and ether. This is used in physiological chemistry as a reagent with vanillin as a test for free hydrochloric acid.

Thymol (3methyl-6 isopropyl-phenol), $C_6H_3OH_{(1)}CH_{3(3)}C_3H_{7(6)}$, is a solid of the nature of camphor, melting at 44° C., and is obtained from various volatile oils, particularly from the oil obtained from Thymus Vulgaris. It is very sparingly soluble in

* Journal of the Allied Societies, Vol. 4, page 346. Dec., 1909.

water. The addition of a little alcohol increases the solubility. It is largely used in the preparation of antiseptic dental preparations, mouth washes, etc.

Phenol-sulphonic Acid. — When phenol is treated with several times its volume of cold, strong H_2SO_4, phenol sulphonic acid,  or  results. If the mixture is heated for some time over a water-bath, the disulphonic acid results. This acid, warmed with a nitrate and the mixture treated with excess of ammonia, yields ammonium picrate, and constitutes a delicate test for nitrates present in drinking-water.

Phenol-sulphonic acid has been used in dentistry as a therapeutic agent (as antiseptic and otherwise). Such use is discussed in detail by Herman Prinz, M.D., D.D.S., in the *Dental Cosmos* for April, 1912, with the conclusion that the ortho compound is several times more active than either the meta or para compounds: that a 1 per cent solution is about equal in antiseptic strength to a 1 per cent phenol solution, but in this strength it decalcifies the tooth structure, discolors the teeth, and should not be used in the mouth on account of its pronounced acid character.

Sulphonic Acids as a class may be obtained by the oxidation of an organic sulphydrate (mercaptan). This oxidation may be produced by the action of HNO_3 or $KMnO_4$, and may be written as follows:

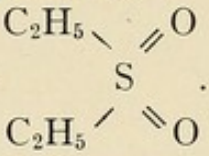
$$C_2H_5SH + 3\,O = C_2H_5.SO_2.HO.$$

Compounds of this class are not confined to the hydrocarbons of the aromatic series as the above typical reaction shows.

Aromatic sulphonic acids may be made by a similar process:

$$C_6H_5SH + 3\,O = C_6H_5SO_2HO,$$

and also by the action of sulphuric acid or the hydrocarbons.

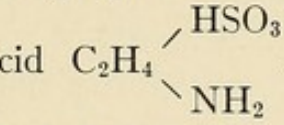
Sulphons are oxidation products of organic sulphids: as, or example, ethyl sulphone  .

Mercaptan, an organic sulphydrate. Representatives of this class of compounds are found as derivatives of both the open and the closed-chain hydrocarbons.

Ethyl mercaptan, also called thioalcohol, C_2H_5SH, is a type of this class. It is a colorless liquid used in the preparation of sulphonal.

The mercaptans may be prepared by action of KHS on the alkyl haloids:

$$C_2H_5Cl + KHS = C_2H_5SH + KCl.$$

Taurine is an important sulphonic acid of the paraffin series. Its graphic formula shows it to be an amino ethyl sulphonic acid  . Taurine is derived from taurocholic acid by hydrolysis. This acid is representative of one of the two principal acid groups occuring in the bile, the salts of which may be found in pathologic conditions in the urine, or, according to Dr. J. P. Michaels and others, in the saliva.

Nitro-benzene, $C_6H_5NO_2$, may be produced by treating benzene with a mixture of nitric and sulphuric acid at reduced temperature. (Exp. 110, page 251.) It is a yellow, oily liquid, with the odor of bitter almonds, commercially known as oil of mirbane, and used in the manufacture of aniline.

Phenyl Sulphuric Acid, $C_6H_5HSO_4$, occurs only in combination, the acid being unstable if attempt is made to isolate it. Its potassium salt is present in the urine as a product of intestinal putrefaction.

Aniline or Amino-benzene, $C_6H_5NH_2$. By reaction of nitrobenzene with nascent hydrogen, the NO_2 group becomes an NH_2 group and aminobenzene or aniline is produced. Aniline, a colorless liquid, also called aniline oil, is important from a commercial rather than from a medical standpoint, as it forms the basis of the aniline dyes. When pure it is a colorless liquid, but changes quite rapidly when exposed to the light. It is used in testing for chloral and chloroform. It is slightly soluble in water, and easily soluble in alcohol and ether. At 8° C. it becomes a crystalline solid.

Cresol, $C_3H_4CH_3OH$, is a hydroxy-toluene. Three isomeric compounds of this formula are obtained from the distillation of coal tar between 200° and 210° C. The ortho and para cresols are solid at ordinary temperatures, the ortho compound melting at 31° C., the para at 36° C. Meta cresol is a liquid which does not solidify unless under extreme conditions of cold and pressure.

The cresols are similar to phenol not only in composition but also in physical and therapeutic properties; hence, cresol has been called cresylic acid, just as phenol has been called carbolic acid.

A mixture of the cresols, said to be composed of meta cresol 40%, ortho 35%, and para cresol 25%, constitutes the tricresol very largely used in dentistry as a germicide and antiseptic similar to carbolic acid.

An emulsion of cresol, obtained by the solution of resin soap as an emulsifying agent, is known as creolin. Cresol is also a constituent of the disinfectant lysol.

Tricresol is miscible with formalin in all proportions, and the mixture is recommended in the treatment of root canals.

Picric Acid is trinitrophenol, $C_6H_2.OH.(NO_2)_3$. It may be formed by action of strong HNO_3, or mixture of H_2SO_4 and HNO_3 on phenol. It occurs as yellow plates slightly soluble in H_2O, easily soluble in alcohol and ether, and is used in Esbach's reagent for the estimation of albumin in urine and as an alkaloidal precipitant.

Benzoic Acid, C_6H_5COOH, was originally produced from gum benzoin, but may be made from hippuric acid (q. v.), which (from urine of horses) formerly constituted a commercial source. It is chiefly prepared, however, from toluene; it crystallizes in colorless plates or long prismatic crystals (from solution). It is sparingly soluble in cold water, more soluble in hot water, easily soluble in alcohol. It sublimes and is inflammable, burning without residue.

Benzoates of sodium, ammonium, lithium, and lime are all used in medicine. Benzoated lard is prepared by digesting gum benzoin in hot lard. This is much used as a base for ointments and keeps well.

Benzaldehyd, $C_6H_5–CHO$, is a colorless liquid, soluble in alcohol and ether, and sparingly soluble in water. The U. S. P. oil of bitter almonds is practically benzaldehyd; it is a volatile oil, very poisonous, and upon standing deposits benzoic acid from partial oxidation.

Salicylic Acid, orthohydroxybenzoic acid, $C_6H_4–OH.COOH$, is a white crystalline powder, odorless, irritating to mucous surfaces, soluble in alcohol and ether, and in about 450 parts of water at 15° C. (U. S. D.). Salicylic acid may be made by action of CO_2 on sodium phenate and subsequent decomposition of the sodium salicylate. By heating rapidly the acid may be changed into phenol and CO_2.

Salicylates have been used to considerable extent in various uric-acid diseases. Methyl salicylate constitutes 90% of natural oil of wintergreen (page 207). The alcoholic solution is essence of checkerberry.

Salol is phenylsalicylate, $C_6H_4OH.COO(C_6H_5)$, a white crystalline powder, practically insoluble in water and not decomposed by the dilute acids of the stomach juices; but in the intestine it becomes salicylic acid and phenol, as follows:

$$C_6H_4.OH.COOC_6H_5 + H_2O = C_6H_4OH.COOH + C_6H_5OH.$$

Sulphanilic acid, $C_6H_4\begin{cases}HSO_3\\NH_2\end{cases}$, is isomeric with taurine, but is obtained, however, from an entirely different source. It is made by treating aniline with concentrated sulphuric acid. It is a strong acid, occurring as white crystals, is soluble in water, and is used in the manufacture of aniline dyes and also with naphthylamin as a reagent for the detection of nitrites.

Phthalic acid, $C_6H_4\begin{cases}COOH\\COOH\end{cases}$, occurs in the form of rhombic crystals. By heating phthalic acid, phthalic anhydrid may be obtained.

Phthalic anhydrid, $C_6H_4\begin{cases}CO\\CO\end{cases}O$, heated with phenol and H_2SO_4 will give phenolphthalein, a valuable and familiar indicator in volumetric analysis.

Hippuric Acid, benzoyl glycocoll, $C_6H_5.CO.NH.CH_2–COOH$, occurs in traces in human urine, to a considerable extent in the urine of the herbivora, but not at all in that of the carnivora. It crystallizes in prismatic needles (Plate V, Fig. 4), often resembling crystals of ammonium magnesium phosphate; but as these latter only occur in neutral or alkaline urine and hippuric acid, usually in acid urine, there is little danger of confounding the two substances. Hippuric acid is hydrolyzed by the urease of fermenting urine, forming benzoic acid and glycocoll (amino-acetic acid):

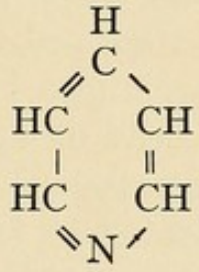
$$C_6H_5CO–NH–CH_2–COOH+H_2O = C_6H_5COOH+CH_2NH_2COOH.$$

Tryosin, $C_6H_4.OH.–CH_2CH(NH_2)–COOH$, may be crystallized as fine silky needles. It is formed from protein substances, particularly casein and fibrin, both by the action of proteolytic enzymes and by putrefactive processes. It rarely

occurs in urinary sediment; when found it is in bundles or sheaves (Plate V, Fig. 6, page 222), and is usually indicative of acute liver disease, phosphorus poisoning, etc.

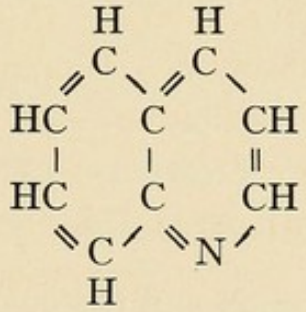
Heterocyclic Compounds. — The closed-chain or cyclic compounds are known as isocyclic or homocyclic when the atoms constituting the "ring" or nucleus of the molecule are all of the same sort (carbocyclic, if all of carbon), as has been the case in all the aromatic compounds which we have thus far taken up, i.e., the structure of compounds has been based upon the six-carbon or benzene ring. If the ring is made up of atoms of different sorts the compound is heterocyclic, and one or two of these are of importance.

First, pyridin, C_5H_5N, which may be regarded as benzene, in which one CH group has been replaced by an atom of nitrogen:



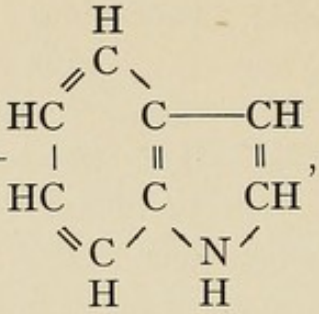
It is a liquid miscible with water, boiling-point 115° C.

Second, quinalin, C_9H_7N, a colorless liquid.



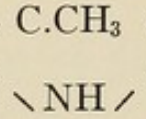
Upon one or the other of these two bases may be constructed the graphic formula of many of the vegetable alkaloids.

A certain number of alkaloids, such as caffein and thein (trimethylxanthin), are referable to the purin nucleus (page 235).

Indol, C_8H_7N,  is produced from pro-

tein by the putrefaction occurring in the small intestine, also by action of the proteolytic enzyme of the pancreatic juice (trypsin). The indol, by oxidation (after absorption from the intestines), becomes indoxyl, C_8H_6NO, which, with K_2SO_4, forms indoxyl-potassium sulphate, $C_8H_6NKSO_4$, and, as such, is eliminated (in part) by the kidneys. This substance is a type of the so-called ethereal or conjugate sulphates, skatoxyl-potassium sulphate (skatol) and phenol-potassium sulphate being other compounds of this class. The ethereal sulphates are not precipitated by $BaCl_2$ in alkaline solutions, but may be decomposed by prolonged boiling with HCl and then precipitated as usual.

The oxidation of indoxyl produces indigo blue, and this fact is utilized in the qualitative test for indoxyl in urine (q. v.).

Skatol, methylindol, C_6H_4  , occurs in similar

manner to indoxyl, and likewise passes into the urine as an ethereal sulphate (skatoxyl-potassium sulphate). Skatol is a constituent of the feces and possesses a strong fecal odor.

Laboratory Exercises LIX and LX.

Experiments with Aromatic Hydrocarbons.

Exp. 108. Into a small and thoroughly dry flask (250 c.c.) introduce about 50 grams of a mixture consisting of 1 part of benzoic acid and 2 parts of quicklime; connect with a condenser and heat. Benzene (benzol) distils over:

$$CaO + C_6H_5COOH = CaCO_3 + C_6H_6.$$

Exp. 109. Turn a little of the benzene prepared in the last experiment onto some water contained in a porcelain capsule. Set fire to it and note that it burns with a *smoky* flame. Cool a few cubic centimeters of pure benzene contained in a narrow test-tube by immersion in a freezing mixture of ice and salt.

Exp. 110. In a wide test-tube mix 5 c.c. of concentrated H_2SO_4 with about half its volume of *strong* HNO_3; cool in ice-water or cold running water, and add *very slowly* about 2 c.c. of benzene. Nitrobenzene is formed and may be separated as a heavy oily liquid by pouring the mixture into an excess of water. Notice the odor of oil of bitter almonds.

Exp. 111. Observing the same precaution against overheating as given in Exp. 110 reduce nitrobenzene to amino benzene as follows: In a large test-tube or small flask place 1 or 2 c.c. of nitrobenzene with three times its weight of tin powder. To this add 10 or 15 c.c. of strong HCl in successive small portions, keeping cool as indicated. The odor of nitrobenzene should be replaced by that of aniline.

Exp. 112. Shake together in a test-tube 1 part of aniline oil and 5 parts of water. Is the oil soluble in water?

Agitate with HCl added in small portions till liquid becomes clear. Explain.

Exp. 113. To a few cubic centimeters of a 3% phenol solution add dilute bromin water. A yellowish-white crystalline precipitate of tribromphenol is produced (see page 174).

Exp. 114. To an aqueous solution of phenol add a few drops of solution of ferric chlorid.

Exp. 115. Produce a tribromaniline according to method given for tribromphenol in Exp. 113.

Exp. 116. Repeat Exps. 113 and 114, using an aqueous solution of cresol in place of phenol.

Exp. 117. To a test-tube 1/3 full of nitric acid, (50% absolute HNO_3), add, 1 drop at a time, about 1 c.c. of phenol with constant agitation. When the phenol has all been added heat

carefully to boiling. Allow to cool slowly when trinitrophenol will be precipitated.

Exp. 118. Evaporate a few drops of a 1% solution of potassium nitrate to dryness in a small porcelain capsule. Add 2 c.c. of phenoldisulphonic acid;* stir thoroughly, and keep hot for three to five minutes; dilute with water, make strongly alkaline with ammonia, and note the intense yellow color of ammonium picrate. The reaction is used as a test for nitrates in drinking water.

Exp. 119. Determine melting-point of benzoic acid.

Exp. 120. Arrange two watch glasses of equal size with the concave surfaces together and a piece of filter paper stretched between them. The glasses may be held together with a small brass clamp.

A little benzoic acid placed in the lower glass may be sublimed by means of a gentle heat through the paper and collected upon the upper glass. Examine the sublimate by polarized light. See Plate V, Fig. 5, opposite page 222.

Exp. 121. With an aqueous solution of benzaldehyd determine whether Tollen's test for aldehyds (Exp. 64, page 201) is applicable to aromatic compounds.

Exp. 122. Boil 10 c.c. of oil of wintergreen with a little of 20% NaOH; keep the volume constant by frequent addition of water. When the oil has entirely disappeared, cool and add HCl to acid reaction. Salicylic acid will separate, white and crystalline.

Exp. 123. To a dilute solution of sodium salicylate, or saturated aqueous solution of salicylic acid, add a few drops of Fe_2Cl_6. A slight amount of salicylates in the urine will produce this color when a test is being made for diacetic acid (q. v.)

Exp. 124. Mix in a test-tube a little dry slaked lime and salicylic acid, heat and collect a few drops of distillate in a second tube. Test distillate for phenol. Write reaction.

Note. — After the first heating, the tube containing the lime and acid may be inclined so that any moisture distillate will run into collecting tube rather than back onto the mixture.

* For method of preparation of phenoldisulphonic acid, see Appendix.

PART VI.

PHYSIOLOGICAL CHEMISTRY.

CHAPTER XXIX.

FERMENTS OR ENZYMES.

PHYSIOLOGICAL chemistry treats of the substances which go to make up the animal body, the changes which these substances undergo in the process of digestion and assimilation, and the final products of metabolism.

This subject, like others, will receive our attention in outline, with a view simply to enable the student to understand the conditions which at present seem to have the most direct bearing on dental science. The changes produced by the class of bodies known as ferments are of great importance and the first to be considered.

If yeast is allowed to grow in a sugar solution of moderate strength, the sugar molecule is split into carbonic-acid gas and alcohol. The process is one of fermentation; the yeast is the ferment. There are various substances which cause similar splitting of complex molecules into simpler compounds.*

The distinction between the organized and the unorganized ferments is no longer recognized, as it has been proved that the activity of an organized ferment is due to the presence of the unorganized ferment or enzyme, and we shall, by preference, refer to these substances as enzymes.

The enzymes, as a class, possess certain general properties which should be remembered.

* Occasionally fermentation may produce a synthesis (putting together) rather than an analysis (pulling apart).

First. Their action is limited to a very few substances; i.e., the enzyme from yeast, referred to above, will convert a few sugars only as indicated. They will not act in any other way nor upon other substances.

Second. The enzymes act only at ordinary temperatures, usually showing the greatest activity at about the temperature of the animal body, 37° to 40° C.

Third. Enzymes act only within very narrow limits as regards the chemical reaction (acid or alkaline) of the media.

Fourth. Enzymes are destroyed (killed) by the heat of boiling water.

Fifth. In regard to the nature of their composition, many of the enzymes are closely allied to the proteins.

An enzyme may be classified according to the sort of work it does. Many of the chemical changes involved in the utilization of food consist of breaking up a complex molecule and by the use of a molecule of water forming new and simpler compounds. This sort of change is called "Hydrolysis" and an enzyme which will produce it is a hydrolytic enzyme. By hydrolysis or hydrolytic cleavage, the molecule of cane-sugar, $C_{12}H_{22}O_{11}$, becomes two molecules of a simpler sugar, such as glucose, $C_6H_{12}O_6$. $C_{12}H_{22}O_{11} + H_2O = 2\ C_6H_{12}O_6$.

Hydrolysis is not dependent upon enzyme action, as the same change is produced by prolonged boiling with very dilute mineral acids.

Besides the classification of enzymes by the character of the work they do, the name of the substance acted upon may also be used to designate an enzyme; thus, a proteolytic enzyme produces a cleavage of protein substances. A lipolytic enzyme (lipase) splits the fat molecule, etc.

Several of the digestive enzymes, notably the proteolytic or flesh-digesting enzymes, such as pepsin, trypsin, etc., exist in the animal cell, not as active agents, but as inactive parent enzymes which are called pro-enzymes or zymogens. Enzymes

of this class are set to work (liberated from the parent substance) by a class of substances known as "activators" (illustrated by the enterokinase of the intestine, p. 337).

Neither the zymogen nor the activator has of itself any digestive action whatever. A provision which results in the prevention of autodigestion (autolysis) of the cells containing them.

Another large and very important class of enzymes are those which produce oxidative changes. They may be divided into the oxidases, which produce direct oxidation, and the peroxidases, which produce oxidation only in the presence or by the aid of peroxide.

Catalase is a term which has been applied to enzymes, similar in action to the peroxides; i.e., they destroy a peroxide with the formation of molecular oxygen, although, according to Hammarsten, they differ from both the oxidases and peroxidases in giving no reaction whatever with Guaiac.

Oxidases have been found to exist in saliva, in milk, blood, nasal mucus, tears, and semen, in many of the organs, and also in the muscular tissue. They exist moreover in the vegetable kingdom from which the subject of oxidizing enzymes was first studied by Bertrand and Bourquelot.* The urine, bile and intestinal secretions are said not to contain a ferment of this kind.

The name of a specific enzyme usually ends in "-ase" as zymase, the enzyme contained in yeast; lipase, a fat-splitting enzyme; urease, the urine ferment.

Laboratory Exercise LXI.

Preparation of Oxidase.

Exp. 125. Clean thoroughly a small potato and grate the skin into a small beaker; cover with water and allow to stand in a cool place for an hour. Filter through coarse paper. Turn

* "Enzymes and their Applications," Effrant: Prescott's translation. This work is also authority for statement immediately preceding regarding the source of oxydizing enzymes.

about 5 c.c. of the filtrate slowly into 25 c.c. of strong alcohol. The enzyme will be precipitated. Filter and test as follows:

Exp. 126. Transfer the moist precipitate from the above experiment into a half a test tube of distilled water. Shake frequently for about 10 minutes and filter. The filtrate will contain oxidizing enzymes in solution. Divide the solution into two parts; to one add a few drops of tincture of guaiacum, and to the other a little of a 1% solution of pyrocatechol. The guaiacum gives a blue color, and the pyrocatechol a red-brown color in the presence of oxidizing enzymes.

Experiments with Enzymes.

Hydrolytic enzymes produce cleavage of the molecule.

Exp. 127. Take five test tubes, "a–b–c–d–e." Make a thin paste by rubbing one-sixth of a yeast cake with water, and place a little in each of the five tubes; then fill "a" with a dilute glucose solution; "b" with a dilute solution of milk sugar; "c" with dilute solution of cane sugar; to "d" add a little invertase (an enzyme from the mucosa of the small intestine of a pig) (see Appendix); then fill with the same solution used for "c". Prepare "e" exactly the same as "d" except that before adding the sugar solution the enzymes are boiled for at least one minute. Fit each tube with short delivery tube and allow to stand overnight.

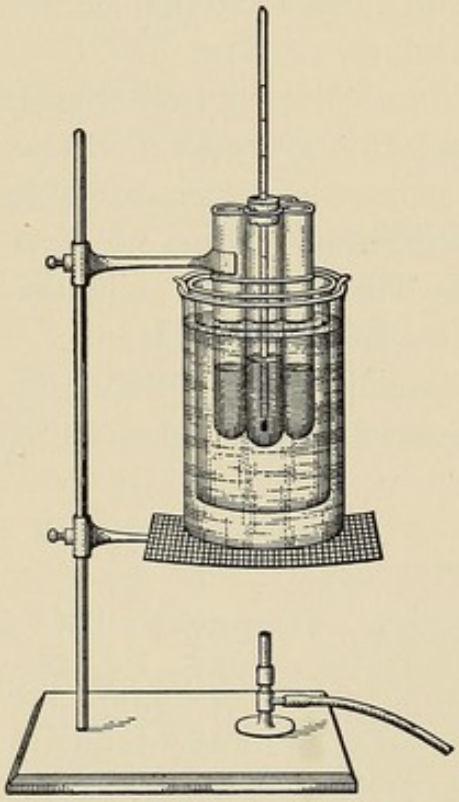


FIG. 16.

Arrange as indicated in Fig. 16. Explain result in each case.

Exp. 128. Take four test-tubes, "a–b–c–d," and half fill

each with some thin starch paste (see page 383 of Appendix). Into "a" put a little of the yeast from last experiment; into "b" a little pepsin solution; into "c" a little saliva (the enzyme of the saliva in ptyalin); into "d" a little invertase as used in preceding experiment. Warm all the tubes to about 37 or 38° C., and allow to stand overnight; then test contents of each tube for a reducing sugar which may have been produced from the starch. (Use Exp. 136, page 262).

Exp. 129. If time and sufficient material are available, the student may prepare a fat-splitting enzyme (lipase) from an animal source, pigs, pancreas,* or from a vegetable source, castor beans.*

Exp. 130. To one-third of a test-tube of milk, colored slightly blue with nearly neutral litmus solution, add half as much solution of lipase (fresh pancreatic extract) and keep at about 40° C. for twenty to thirty minutes. Sufficient fat acid should be separated to change the blue litmus to red. Write reaction.

* For preparation of lipase see Appendix, pages 380 and 381.

CHAPTER XXX.

CARBOHYDRATES.

Classification:

Sugars	Arabinose, Xylose	Pentoses.
	Dextrose, Lævulose, Galactose	Monosaccharids or monoses.
	Saccharose, Maltose, Lactose	Disaccharids or dioses.
Starch	Starch, Glycogen	Polysaccharids or polyoses.
Gum, Cellulose	Dextrin	

Characteristics. — The monosaccharids are reducing bodies of either the aldehyd or the ketone type. The termination "ose" is applied to all sugars, and may also be used in designating the type; thus dextrose is an "aldose," while lævulose is a "ketose;" i.e., dextrose is an aldehyd, containing the characteristic –CHO group, while Lævulose is a ketone containing the –C=O group.

The pentoses ($C_5H_{10}O_5$) are represented by two important compounds, arabinose and xylose. The first of these occurs occasionally in the urine (pentosuria), and can be prepared by boiling gum arabic with dilute mineral acids. The second, xylose, has been obtained from the pancreas, but may be prepared more easily from bran or straw by boiling with dilute HCl (Exp. 131, page 261).

The pentoses, as a class, boiled with dilute mineral acid (HCl or H_2SO_4), yield furfuraldehyd by splitting off the elements of three molecules of water:

$$C_5H_{10}O_5 - 3\,H_2O = C_5H_4O_2.$$

The formation of furfuraldehyd can be easily demonstrated by various color reactions as given in experiment 131, page 261.

The hexoses, $C_6H_{12}O_6$, also called monoses, occur quite generally in nature (not true of the pentoses). They constitute the various fruit sugars, and may be obtained by hydrolysis of the dioses and polyoses.

They all reduce Fehling's copper solution (galactose less easily than the others), and they are all fermented by yeast (galactose more slowly than the others).

Dextrose or **Glucose,** $C_6H_{12}O_6$, also known as grape-sugar and as diabetic sugar, occurs in grapes, honey, etc. It is formed by the action of diastatic ferments on the disaccharids; also from many of the polysaccharids. Glucose thus occurs in the processes of digestion and constitutes the sugar of diabetic urine. It may be obtained commercially as a white solid, and also as a thick, heavy syrup, known as confectioners' glucose. The commercial glucose is prepared by the action of dilute acids on starch, when hydrolysis takes place, as follows:

$$C_6H_{10}C_5 + H_2O = C_6H_{12}O_6.$$

Dextrose can be oxidized first to gluconic acid ($CH_2OH.(CHOH)_4.COOH$), and by further oxidation to dibasic saccharic acid:

$$COOH.(CHOH)_4.COOH.$$

This oxidation can be effected by the use of nitric acid. Saccharic acid forms a definite soluble salt with calcium. Whether the fact has any bearing whatever on the relation of poor teeth and excessive use of candy has not been demonstrated.

Tests. — Glucose boiled with Fehling's solution precipitates the red suboxid of copper (Cu_2O).

Glucose responds to Molisch's test for carbohydrates, which is made with an alcoholic solution of α-naphthol and concentrated sulphuric acid. (Exp. 133.) It may be distinguished not only from other carbohydrates but from other sugars by heating with Barfoed's solution (copper acetate in dilute acetic acid), which is reduced with precipitation of Cu_2O.

Heated with phenylhydrazine solution nearly to the boiling-point of water, glucose forms phenylglucosazone, which crystallizes, as the mixture cools, in characteristic yellow needles usually arranged in bundles or sheaves. (Plate VI, Fig. 1.)

Osazones are the various compounds formed by the different sugars and phenylhydrazine when treated as above. They crystallize in fairly distinctive forms and furnish valuable tests for the sugars. The phenylhydrazine test is considered at least ten times more delicate than Fehling's test. Glucose readily undergoes alcoholic fermentation, yielding C_2H_5OH and CO_2. (See Exp. 140, page 262.)

Lævulose, $C_6H_{12}O_6$, or fruit-sugar, turns the ray of polarized light to the left, and to a greater degree than glucose turns it to the right. It occurs in honey and in many fruits, and is produced with glucose by hydrolysis of cane-sugar. Lævulose forms an osazone not to be distinguished from glucosazone. It reduces copper solutions in a manner similar to glucose, and, like it, is easily fermented by yeast.

Galactose is the product of the hydrolysis of lactose, or milk-sugar, and some other carbohydrates. It is a crystalline substance which reduces Fehling's solution and ferments slowly with yeast.

Disaccharids or Dioses.

Disaccharids have the general formula $C_{12}H_{22}O_{11}$. They are converted into the monosaccharids by hydrolysis brought about either by action of enzymes or by boiling with mineral acid.

PLATE VI. — PHYSIOLOGICAL CHEMISTRY

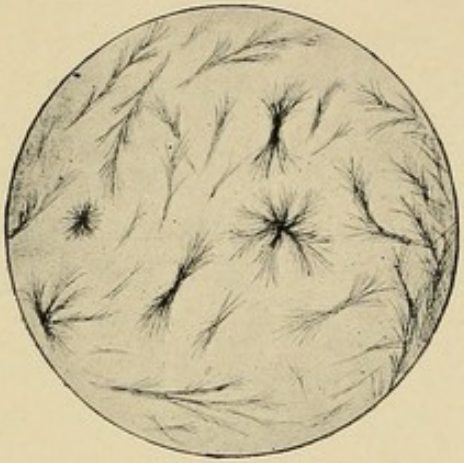


FIG. 1.
Glucosazone.

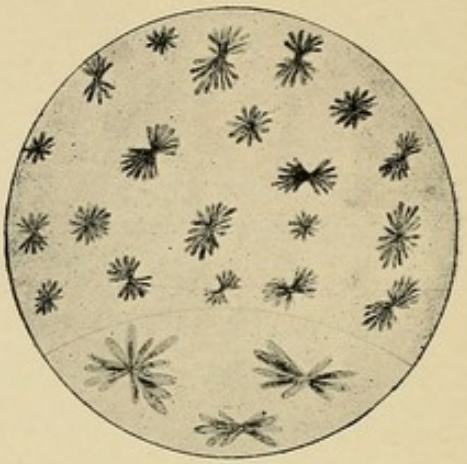


FIG. 2.
Maltosazone.

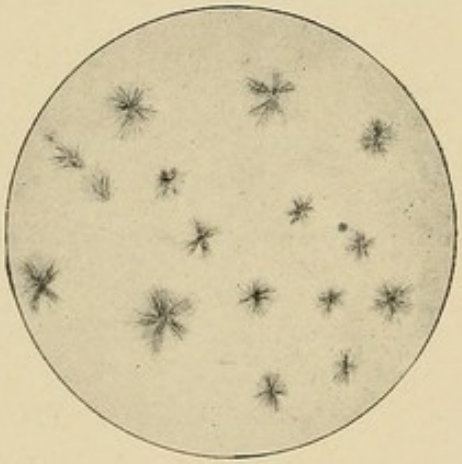


FIG. 3.
Lactosazone.

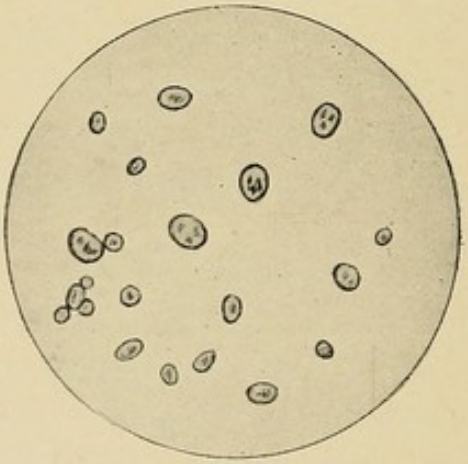


FIG. 4.
Wheat Starch.

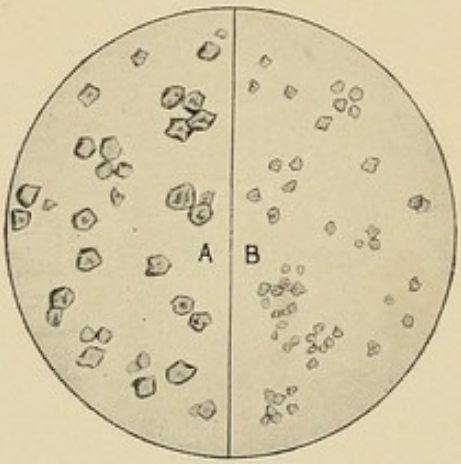


FIG. 5.
A, Corn starch; *B*, Rice starch.

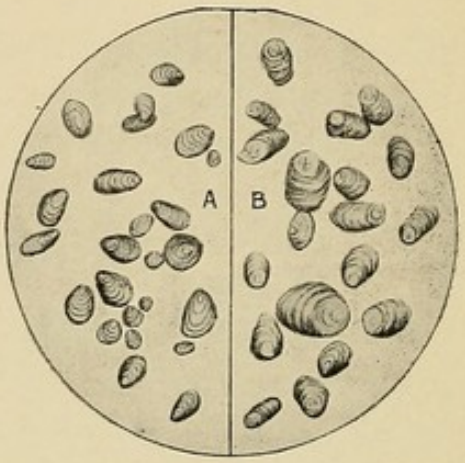


FIG. 6.
A, Potato starch; *B*, Arrowroot starch.

Cane-sugar, $C_{12}H_{22}O_{11}$, sucrose or saccharose, obtained from the sugar-cane (various varieties of sorghum), also from the sugar-beet (*Beta vulgaris*) and the sugar-maple (*Acer saccharinum*). Cane-sugar is a white crystalline solid soluble in about 1/2 part of water and in 175 parts of alcohol (U. S. P.). It does not reduce copper solutions, nor does it form an osazone with phenylhydrazine; but it is easily hydrolyzed with the formation of dextrose and lævulose, and then, of course, the reactions peculiar to these substances may be obtained. It does not ferment directly, but, by the action of invertin contained in yeast, it takes up water, becoming glucose and lævulose as above, these latter sugars being easily fermentable.

Maltose, $C_{12}H_{22}O_{11}$, or malt-sugar, is an intermediate product in the hydrolysis of starch, and by further hydration becomes two molecules of dextrose: $C_{12}H_{22}O_{11} + H_2O = 2\ C_6H_{12}O_6$. It is formed in the fermentation of barley by diastase (the ferment of malt), and with phenylhydrazine it produces an osazone distinguished from glucosazone and lactosazone by its microscopical appearance (Plate VI, Fig. 2) and its melting-point.

Lactose, $C_{12}H_{22}O_{11}$, obtained from milk, is a disaccharid with far less sweetening power than sucrose. It forms an osazone which crystallizes in small burr-shaped forms (Plate VI, Fig. 3). It reduces Fehling's solution, but does not reduce Barfoed's solution. It resists fermentation in a marked degree. Upon hydration it is converted into dextrose and galactose.

Laboratory Exercise LXII.

Experiments with Sugars.

Exp. 131. Fill a test-tube about one-third full of dry straw. Cover with 10% hydrochloric acid; boil, collecting the distillate in a dry tube. Divide the distillate into two parts, and make the following tests for furfuraldehyd which has been produced from the pentose contained in the straw. Treat the contents

of one tube with a little aniline and HCl. Red coloration indicates the presence of furfuraldehyd. To the contents of the other tube add a little solution of casein (skimmed milk) and underlay with strong sulphuric acid. Furfurol will give a blue or purple line at the point of contact of the two liquids.

Monosaccharids. — Exp. 132. Test for C and H, using cane-sugar. Make closed-tube test for H, which is given off as H_2O, and for C, which remains as such in tube. (See page 182.) Write reactions.

Exp. 133. *Molisch's Test for Carbohydrates.* — To a few cubic centimeters of a 3% glucose solution add a few drops of an alcoholic solution of α-naphthol, and carefully underlay the mixture with strong H_2SO_4.

Exp. 134. To a few cubic centimeters of $CuSO_4$ solution in a test-tube add a little NaOH. Boil and write reaction.

Exp. 135. Repeat Exp. 134 with the addition of Rochelle salt; if solution remains clear on boiling, add a few drops of a glucose solution.

Exp. 136. *Fehling's Test for Sugars.* — Take about 5 c.c. of Fehling's solution* made by mixing equal parts of the $CuSO_4$ solution and the alkaline tartrate on side shelf. Boil and add immediately a few drops of glucose solution. Set aside for a few minutes, watching the results.

Exp. 137. Repeat Exp. 136, using diabetic urine instead of glucose.

Exp. 138. Repeat Exp. 136 without heat and allow to stand for twenty-four hours.

Exp. 139. *Barfoed's Test.* — To about 5 c.c. of Barfoed's reagent add a few drops of glucose solution; boil and set aside for a few minutes, watching results.

Exp. 140. *Fermentation Test.* — Fill the "fermentation-tube" (Fig. 17, page 263) found in the desk with glucose solution; add a little yeast; insert stopper, with long arm of tube

* For preparation, see Appendix.

extending into glucose mixture nearly to bottom of tube, and allow it to stand upright, in a *warm* place, overnight. On the next day, test the gas, with which the tube is filled, with lime-water.

Exp. 141. *Phenylhydrazine Test.* — Place about 5 c.c of glucose solution in a test-tube; add an equal volume of phenylhydrazine solution; keep the tube in boiling water for thirty minutes. Allow to cool gradually. Examine the precipitate microscopically and sketch the crystals.

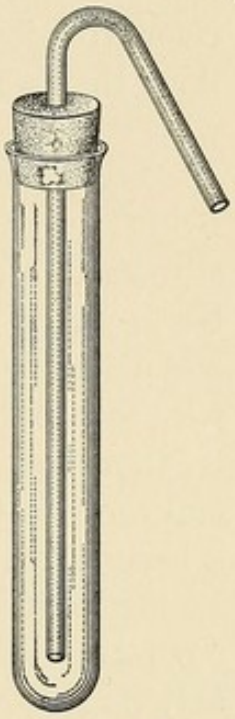


Fig. 17.

Disaccharids. — Exp. 142. Use dilute solutions of cane-sugar, milk-sugar, and maltose, and make on each Fehling's test (Exp. 136), Barfoed's test (Exp. 139), and the phenylhydrazine test (Exp. 141). Sketch the different osazone crystals obtained.

Exp. 143. To a dilute solution of cane-sugar add a few drops of dilute H_2SO_4 and boil for five minutes. Cool the mixture and make slightly alkaline with NaOH. With this solution perform Exps. 136–139 and 141. Explain results. Compare with Exp. 142.

Polyoses — Polysaccharids.

Starch. — This well-known and widely distributed plant-constituent is a carbohydrate represented by $C_6H_{10}O_5$, the actual molecule, however, being many times this simple formula. The microscopical appearance of the starch granule is quite characteristic, and recognition of the more common starches by this method is not at all difficult (see Plate VI, page 261).

Starch is not soluble in cold water, but in hot water, or in solutions containing "amylolytic" enzymes, or in solutions containing certain chemical substances, as chlorid of zinc or of magnesium, dilute HCl or H_2SO_4, capable of forming hydrolytic products, the starch granules swell up, and ultimately dissolve,

being converted into dextrose. The conversion, however, takes place in several well-defined steps, as follows: Soluble starch is first formed, answering the same chemical test with iodin (Exp. 214, p. 328); next, *erythrodextrin*, which gives a red color with iodin solution; then *achroo-* and *maltodextrin*, which give no color with iodin, but react slightly with Fehling's copper solution; then *maltose*, also negative with iodin, but reacting strongly with Fehling's solution; and finally *dextrose*.

Dextrin ($C_6H_{10}O_5$) is a yellowish powder, also known as British gum; is formed from starch, as indicated above; constitutes to a considerable extent the "crust" of bread; is soluble in water, the solution giving a red color with iodin, and is also distinguished from starch by its failure to give a precipitate with solution of tannic acid.

Glycogen, or animal starch, is a carbohydrate, with the general formula $C_6H_{10}O_5$, occurring *principally* in the liver, and to a lesser extent in nearly all parts of the animal body. Freshly opened oysters are a convenient source of the substance for laboratory demonstration. It occurs in horse-flesh in considerably larger proportions than in human flesh.

Properties. — Glycogen is a white powder without odor or taste. It dissolves in water, producing an opalescent solution. It is closely allied to the starches of vegetable origin in that the products of its hydrolysis are dextrin* and ultimately dextrose. It differs in its ready solubility in water, and in the fact that it is precipitated by 66% alcohol, also in its power of rotation, which is much stronger than that of starch.

Physiology. — Glycogen is formed by the liver, and stored by this same organ for future use. It is derived principally from carbohydrates, but may also be derived from proteins. It disappears during starvation. In dead liver or muscle it rapidly undergoes hydrolytic change with the production of a reducing sugar.

* Foster's Text-book of Physiology.

Cellulose, $C_6H_{10}O_5$, is a carbohydrate which occurs as a principal constituent of woody fiber, and which may be found in the laboratory in nearly a pure state, as absorbent cotton or Swedish filter-paper. It is insoluble in water, alcohol, or dilute acids; it may be dissolved, however, by an ammoniacal copper solution. It is converted into monosaccharids by acids, only after first treating with concentrated H_2SO_4, which partially dissolves it. Cellulose aids digestion in a purely mechanical way; treated with a mixture of nitric and sulphuric acids, it is converted into nitro-substitution products which are known as guncotton. The soluble cotton from which collodion is prepared is a mixture of tetra- and pentanitrates, while the more explosive but insoluble guncotton is a hexanitrate, formerly known as trinitrocellulose.

Experiments with Starches and Cellulose.

Polysaccharids. — Exp. No. 144. Examine potato, corn, and wheat starch under the microscope, use a drop of water and a cover glass. Sketch the granules of each in note-book, and, while still on the slide, treat with a dilute iodin solution. Note changes in appearance of granules.

Exp. 145. Preparation of starch. Grate a little raw potato. Mix thoroughly with water and strain through "bolting" cloth or stout coarse muslin. After the liquid has run through, compress the cloth by twisting till no more liquid can be squeezed out. The starch has passed through the cloth and may be washed by decantation, dried on filter paper, examined, and used for the following experiments:

Exp. 146. Make some starch paste by rubbing 1 gram of starch to a smooth, *thin* paste with water; then slowly pour it into 100 c.c. of boiling water, stirring constantly. With this solution compare a 1% solution of dextrin and a solution of glycogen * as follows:

* For the isolation of glycogen, see Appendix.

(*a*) Treat each by boiling with Fehling's solution.

(*b*) Add to 5 c.c. of each a few drops of tannic-acid solution.

(*c*) To each solution add a drop of iodin solution. Note color of mixture while cold. Heat nearly to boiling and allow to cool again, watching the color during process.

(*d*) To 5 c.c. of each solution add twice its volume of 66% alcohol.

(*e*) Tabulate results of the tests and formulate method of distinguishing these three substances from one another.

CHAPTER XXXI.

FATS AND OILS.

NATURAL fats and oils of animal or vegetable origin are mixtures of several compound glyceryl ethers or esters (see page 209), and by subjecting them to cold and pressure they may be separated into two portions, one solid with comparatively high melting-point, and the other liquid at ordinary temperatures. The solid portion is known as the stearopten, and the liquid as the eleopten, of the fat. Thus from beef-fat we may express a fluid eleopten consisting largely of olein and obtain as a residue a stearopten, stearin. The stearopten of the volatile or essential oils are classed as camphors, on account of their resemblance to ordinary camphor. Menthol, from oil of peppermint, and thymol, from oil of thyme, are examples of this class of compounds, both of which are largely used in dental practice.

Properties. — Fats are insoluble in water, easily dissolved by ether, chloroform, and carbon disulphid, less easily by alcohol, crystallizing on evaporation of the solvent. (Plate VII, Fig. 3, page 296.) They are emulsified by mechanical subdivision of the fat globules, in the presence of some agent which prevents their reuniting. The vegetable mucilages, soap, jelly, etc., are such emulsifying agents. On exposure to the air, fats and oils are more or less easily oxidized, which causes a separation of the fat acid. This produces an unpleasant odor or taste, and the fat is said to become rancid. (For saponification of fats see page 209 and Exp. 150, page 268.)

Physiology. — Fats are not digested to any appreciable extent until they reach the intestine; here they are broken up by a fat-splitting enzyme, emulsified, and to a slight extent

saponified, after which they may be absorbed by the system (see Pancreatic Digestion).

Experiments with Fats and Oils.

Exp. 147. Test solubility of olive-oil in water, ether, chloroform, and alcohol, carefully avoiding the vicinity of a flame.

Exp. 148. Let one or two drops of an ether solution of the oil drop on a plain white paper, also an ether solution of a volatile oil found on side shelf. Watch behavior of the two oils, and report differences, if any.

Exp. 149. Dissolve a little butter in warm alcohol, examine with the microscope, and micropolariscope the crystals, which separate on cooling.

Note.— If possible perform the next experiment in triplicate, i.e. carry three experiments along at the same time using for "fat" the Glyceryl ester of the three most common fat acids: Olein (lard oil or olive oil), Stearin (beef fat or tallow), Palmatin (bayberry wax or tallow, which contains a large amount of free palmitic acid).

Exp. 150. *Saponification.* — To about 2 grams of solid fat placed in a narrow beaker, or 150 c.c. Erlenmeyer flask, add 10 or 15 c.c of alcoholic solution of potassium hydroxid. Allow the beaker to stand on the water-bath till the alcohol is entirely evaporated, then dissolve the resulting soap in water; filter, if necessary, to obtain a clear solution and make the following tests:

(*a*) Add to a portion of solution a saturated solution of sodium chlorid. What takes place?

(*b*) To another portion add a few cubic centimeters of a solution of calcium or magnesium chlorid. Explain the results.

(*c*) Pour the remainder slowly, and with constant stirring, into warm dilute H_2SO_4, and heat on the water-bath. What is the result? Write the equation. Transfer the mixture to a filter-paper which has been moistened with hot water, and wash with hot water till all H_2SO_4 is removed. Reserve the filtrates.

Exp. 151. *Fatty acids.*

(*a*) Dissolve a portion of the above precipitates (150 *c*) by warming with strong alcohol. Test the reaction of the solution.

Examine the crystals, which separate upon standing, with microscope and micropolariscope. (Plate VII, Fig. 3, page 296.)

(*b*) Add to a portion a few cubic centimeters of a strong Na_2CO_3 solution, and heat till the fatty acids dissolve. Cool. What takes place? Explain the reaction. Reserve the jelly.

Exp. 152. Neutralize the filtrates of 146 *c* and evaporate almost to dryness on the water-bath. Extract with alcohol and evaporate. Note the taste. Heat another portion of the residue with a little powdered dry $KHSO_4$ in a dry test-tube, and note the odor, which is due to acrolein, $CH_2=CH-CHO$. Fuse some borax and glycerin on a platinum loop: green color.

Exp. 153. *Emulsification.* — (*a*) Put 1 to 2 c.c. of a solution of sodium carbonate (0.25%) on a watch-glass, and place in the center a drop of rancid oil. The oil-drop soon shows a white rim, and a white milky opacity extends over the solution. Note with the microscope the active movements in the vicinity of the fat-drop, due to the separation of minute particles of oil (Gad's experiment).

(*b*) Take six test-tubes and arrange as follows:

1. 10 c.c. of a 0.2% Na_2CO_3 solution + 2 drops of neutral oil.
2. 10 c.c. of a 0.2% Na_2CO_3 solution + 2 drops of rancid oil.
3. 10 c.c. of soap-jelly (see 151 *b*), warm, + 2 drops of neutral oil.
4. 10 c.c. of albumin solution + 2 drops of neutral oil.
5. 10 c.c. of gum-arabic solution + 2 drops of neutral oil.
6. 10 c.c. of water + 2 drops of neutral oil.

Shake all the mixtures thoroughly and note the results. What conclusions do you form relative to the influence of conditions upon emulsification?

(*c*) Examine a drop of an emulsion under the microscope.

CHAPTER XXXII.

PROTEINS.

PROTEIN * is a general term used to designate the nitrogenized bodies which constitute the greater proportion of animal tissue.

While meat and "protein" are usually associated, it must not be forgotten that meat is not the exclusive source of protein, for we usually find protein in vegetable substances and often to a considerable extent.

Unlike the two other great divisions of food substances (carbohydrates and fats), the structure of the protein molecule is so complex that with a few exceptions of the simplest kind its representation has not been attempted.

The protein molecule contains nitrogen (often as the amino group NH_2) in addition to the C, H, and O of the carbohydrates and fats. It frequently contains sulphur, often phosphorus, and occasionally the metallic elements, particularly iron.

As examples of the complexity of protein molecules, the following proposed formulæ are given in Hawk's Physiological Chemistry.

Serum albumin, $C_{450}H_{720}N_{116}S_6O_{140}$.

Oxyhæmoglobin, $C_{658}H_{1181}N_{207}S_2FeO_{210}$.

While a classification of proteins according to their chemical composition is at present practically impossible, the following may be of interest.

After Hofmeister, Ergebnisse der Physiologie, Jahrg. I.

* The term Proteid was formerly used instead of Protein, but in accordance with the recommendations of the Committees of the American Physiological and Biochemical Societies, it has been abandoned. The classification and definitions herewith given are taken from their recommendation as printed in Science, Vol. 27, No. 692, page 554.

I. Groups of the Aliphatic Series.

A. Group containing C, N, H.

The only representative known is the guanidin radical $(CNH).NH_2$.

B. Groups containing C, N, H, O.

1. Amino-acids.

(*a*) Monamino-acids.

1. Monobasic monamino-acids, $C_nH_{2n+1}NO_2$.

C_2 is glycocoll.

C_3 is alanin.

C_5 is aminovalerianic acid.

C_6 is leucin, which occurs universally.

2. Dibasic monamino-acids, $C_nH_{2n-1}NO_4$.

C_4 is asparaginic acid.

C_5 is glutaminic acid.

(*b*) Diamino-acids (all monobasic acids).

C_2 is diaminoacetic acid (rare).

Argynin (guanidin-α-aminovalerianic acid). Here the diamino-acid is combined with the guanidin radical,

$$NH_2.NH.C.NH.CH_2.(CH_2)_2.CH.NH_2COOH.$$

Lysin (α-ϵ-diaminocapronic acid),

$$NH_2.CH_2.(CH_2)_3.CH.NH_2.COOH.$$

2. Amino-alcohols.

Glucosamin, $C_6H_{11}O_5(NH_2)$, a hexose into which NH_2 has entered the carbohydrate group of the protein molecule.

C. Groups containing C, N, H, O, S.

Cystein, aminothiolactic acid, $CH_2.SH.CH(NH_2).COOH$.

Cystin, the sulphid of cystein, $C_6H_{12}S_2N_2O_4$.

α-thiolactic acid.

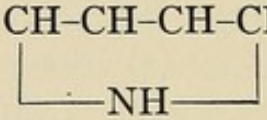
II. Groups of the Aromatic Series.

A. Phenylalanin, $C_6H_5.CH_2.CH(NH_2).COOH$.

B. Tyrosin, $C_6H_4.OH.CH_2.CH(NH_2).COOH$.

III.

A. Pyrrol group.

1. α-pyrrolidin carbonic acid, 

B. Indol group.

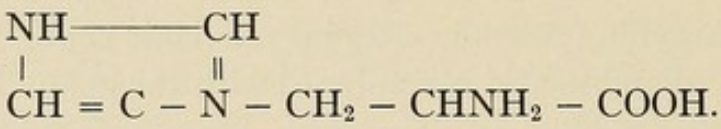
1. Indol, see page 250.
2. Skatol (methyl indol), see page 250.
3. Tryptophan (indolaminopropionic acid), $C_{11}H_{12}N_2O_2$.
4. Skatosin, $C_{10}H_{16}N_2O_2$.

C. Pyridin group.

Pyridin, see structural formula on page 249.

D. Pyrimidin group.

Histidin: structural formula probably



Excepting the carbohydrate group, and perhaps the pyridin and pyrimidin groups, which are absent in a few special instances, all typical proteins contain at least one representative from each group.

A much more practical classification, based in part upon the *properties* of the substance, is that suggested by the Joint Committees on Protein Nomenclature (footnote, page 270).

"Since a chemical basis for the nomenclature of the proteins is at present not possible, it seems important to recommend a few changes in the names and definitions of generally accepted groups, even though, in many cases, these are not wholly satisfactory." The recommendations are as follows:

First. The word proteid should be abandoned.

Second. The word protein should designate that group of substances which consists, so far as is known at present, essentially of combinations of α-amino acids and their derivatives, e.g., α-aminoacetic acid or glycocoll; α-amino propionic acid or alanin; phenyl-α-amino propionic acid or phenylalanin; guanidin-amino valerianic acid or arginin, etc., and are therefore essentially polypeptids.

Third. That the following terms be used to designate the various groups of proteins:

I. Simple Proteins.

Protein substances which yield only α-amino acids or their derivatives on hydrolysis.

Although no means are at present available whereby the chemical individuality of any protein can be established, a number of simple proteins have been isolated from animal and vegetable tissues which have been so well characterized by constancy of ultimate composition and uniformity of physical properties that they may be treated as chemical individuals until further knowledge makes it possible to characterize them more definitely.

The various groups of simple proteins may be designated as follows:

(*a*) *Albumins.* — Simple proteins soluble in pure water and coagulable by heat; e.g., ovalbumin, serum albumin, lactalbumin, vegetable albumins.

(*b*) *Globulins.* — Simple proteins insoluble in pure water, but soluble in neutral solutions of salts of strong bases with strong acids;* e.g.,† serum globulin, ovoglobulin, edestin, amandin, and other vegetable globulins.

* The precipitation limits with ammonium sulphate should not be made a basis for distinguishing the albumins from the globulins.

† The examples of the various proteins are those given by Prof. P. B. Hawk.

(*c*) *Glutelins.* — Simple proteins insoluble in all neutral solvents but readily soluble in very dilute acids and alkalies;* e.g., glutenin.

(*d*) *Alcohol-soluble Proteins* (*Prolamins*). — Simple proteins soluble in relatively strong alcohol (70 to 80 per cent), but insoluble in water, absolute alcohol, and other neutral solvents;† e.g., zein, gliadin, hordein, and bynin.

(*e*) *Albuminoids.* — Simple proteins which possess essentially the same chemical structure as the other proteins, but are characterized by great insolubility in all neutral solvents;‡ e.g., elastin, collagen, keratin.

(*f*) *Histones.* — Soluble in water and insoluble in very dilute ammonia and, in the absence of ammonium salts, insoluble even in an excess of ammonia; yield precipitates with solutions of other proteins and a coagulum on heating which is easily soluble in very dilute acids. On hydrolysis they yield a large number of amino acids, among which the basic ones predominate; e.g., globin, thymus histone, scombrone.

(*g*) *Protamins.* — Simpler polypeptids than the proteins included in the preceding groups. They are soluble in water, uncoagulable by heat, have the property of precipitating aqueous solutions of other proteins, possess strong basic properties and form stable salts with strong mineral acids. They yield comparatively few amino acids, among which the basic amino acids greatly predominate; e.g., salmine, sturine, clupeine, scombrine.

* Such substances occur in abundance in the seeds of cereals and doubtless represent a well-defined natural group of simple proteins.

† The sub-classes defined (*a*, *b*, *c*, *d*) are exemplified by proteins obtained from both plants and animals. The use of appropriate prefixes will suffice to indicate the origin of the compounds, e.g., ovoglobulin, myoalbumin, etc.

‡ These form the principal organic constituents of the skeletal structure of animals and also their external covering and its appendages. This definition does not provide for gelatin, which is, however, an artificial derivative of collagen.

II. Conjugated Proteins.

Substances which contain the protein molecule united to some other molecule or molecules otherwise than as a salt.

(*a*) *Nucleoproteins.* — Compounds of one or more protein molecules with nucleic acid; e.g., cystoglobulin, nucleohistone.

(*b*) *Glycoproteins.* — Compounds of the protein molecule with a substance or substances containing a carbohydrate group other than a nucleic acid; e.g., mucins and mucoids (osseomucoid, tendomucoid, ichthulin, helicoprotein).

(*c*) *Phosphoproteins.* — Compounds of the protein molecule with some, as yet undefined, phosphorus-containing substance other than a nucleic acid or lecithins;* e.g., caseinogen, vitellin.

(*d*) *Hæmoglobins.* — Compounds of the protein molecule with hematin or some similar substance; e.g., hæmoglobin, hæmocyanin.

(*e*) *Lecithoproteins.* — Compounds of the protein molecule with lecithins (lecithans, phosphatids); e.g., lecithans, phosphatids.

III. Derived Proteins.

1. *Primary Protein Derivatives.* — Derivatives of the protein molecule apparently formed through hydrolytic changes which involve only slight alterations of the protein molecule.

(*a*) *Proteans.* — Insoluble products which apparently result from the incipient action of water, very dilute acids or enzymes; e.g., myosan, edestan.

(*b*) *Metaproteins.* — Products of the further action of acids and alkalies whereby the molecule is so far altered as to form products soluble in very weak acids and alkalies, but insoluble in neutral fluids.

* The accumulated chemical evidence distinctly points to the propriety of classifying the phosphoproteins as conjugated compounds; i.e., they are possibly esters of some phosphoric acid or acids and protein.

This group will thus include the familiar "acid proteins" and "alkali proteins," not the salts of proteins with acids; e.g., acid metaproteins (acid albuminate), alkali metaprotein (alkali albuminate).

(*c*) *Coagulated Proteins.* — Insoluble products which result from (1) the action of heat on their solutions, or (2) the action of alcohols on the protein.

2. *Secondary Protein Derivatives.** — Products of the further hydrolytic cleavage of the protein molecule.

(*a*) *Proteoses.* — Soluble in water, uncoagulated by heat, and precipitated by saturating their solutions with ammonium sulphate or zinc sulphate; † e.g., protoproteose, deuteroproteose.

(*b*) *Peptones.* — Soluble in water, uncoagulated by heat, but not precipitated by saturating their solutions with ammonium sulphate; ‡ e.g., antipeptone, amphopeptone.

(*c*) *Peptids.* — Definitely characterized combinations of two or more amino acids, the carboxyl group of one being united with the amino group of the other, with the elimination of a molecule of water; § e.g., dipeptids, tripeptids, tetrapeptids, pentapeptids.

Laboratory Exercise LXIII.

General Protein Reactions.

Exp. 154. Test dried egg-albumin for C, H, S, and N, according to the methods described on pages 182 and 183. Test casein for phosphorus, and dried blood for iron.

* The term *secondary hydrolytic derivatives* is used because the formation of the primary derivatives usually precedes the formation of these secondary derivatives.

† As thus defined, this term does not strictly cover all the protein derivatives commonly called proteoses; e.g., heteroproteose and dysproteose.

‡ In this group the kyrins may be included. For the present we believe that it will be helpful to retain this term as defined, reserving the expression peptid for the simpler compounds of definite structure, such as dipeptids, etc.

§ The peptones are undoubtedly peptids or mixtures of peptids, the latter term being at present used to designate those of definite structure.

There are several reactions which are common to nearly all proteins. For the following tests use a solution of egg-albumin (1/50) in water, as a general type of a protein.

1. *Color Reactions.*

Exp. 155. *Xanthoproteic Test.* — To 10 c.c. of the albumin solution add one third as much concentrated HNO_3; there may or may not be a white precipitate produced (according to the nature of the protein and the concentration). Boil; the precipitate or liquid turns yellow. When the solution becomes cool add an excess of NH_4OH, which gives an orange color. (This color constitutes the essential part of the test.)

Exp. 156. *Millon's Test.* — Add a few drops of Millon's reagent * to a part of the albumin solution. A precipitate, which becomes brick-red upon heating, forms. The liquid is colored red in the presence of non-coagulable protein or minute traces of albumin.

Exp. 157. *Piotrowski's Test.* — To a third portion add 2 drops of a *very* dilute solution of $CuSO_4$, and then 5 to 10 c.c. of a 40% solution of NaOH. The solution becomes blue or violet. Proteoses and peptones give a rose-red color (biuret reaction) if only a trace of copper sulphate is used; an excess of $CuSO_4$ gives a reddish-violet color, somewhat similar to that obtained in the presence of other proteins. This test responds with all proteins.

2. *General Precipitants.*

Proteins are precipitated from solution by the following reagents (peptones are exceptions in some cases):

Exp. 158. *Acetic Acid and Potassic Ferrocyanid.* — Make part of the solution to be tested strongly acid with acetic acid,

* Mercuric nitrate in nitric acid. For the preparation of this and other reagents, see Appendix.

and add a few drops of potassic ferrocyanid solution. A white flocculent precipitate is formed (not with peptones).

Exp. 159. *Alcohol.* — To another part add one or two volumes of alcohol.

Exp. 160. — *Tannic Acid.* — Make the solution acid with acetic acid, and add a few drops of tannic-acid solution.

Exp. 161. *Potassio-mercuric Iodid.* — Make acid another portion with HCl, and add a few drops of the reagent.

Exp. 162. *Neutral Salts.* — Certain neutral salts precipitate most proteins. $(NH_4)_2SO_4$ added to complete saturation to protein solutions, faintly acid with acetic acid, precipitates all proteins, with the exception of peptones.

Simple Proteins.

Albumins.

The albumins are conveniently represented by egg-albumin and serum-albumin. They are soluble in water, respond to the general protein reactions (Exp. 155, page 277, etc.), and may be completely precipitated by saturation of the solution by ammonium sulphate. Albumin is coagulated by heat (75° to 80° C.).

Egg-albumin differs from serum-albumin in that it is not absorbed when injected into the circulation, but appears unchanged in the urine. Egg-albumin is readily precipitated from aqueous solution by alcohol, while serum-albumin is precipitated only with difficulty. Albumins in general form, with acids or with alkalies, *derived albumins* known as acid or alkali albumins or albuminates (acid or alkali metaproteins). An acid albumin derived from myosin is known as syntonin. It differs but slightly from other acid albumins. The acid and alkali albumins are both precipitated by neutralization, but neither of them are coagulated by heat.

If the hydrolysis of albumin is brought about by HCl at the body temperature, it causes the molecule to split into two

proteins, one known as antialbuminate and the other as hemialbumose, these in turn becoming respectively antialbumid and hemipeptone. Sulphuric acid at a boiling temperature produces a similar change, except that the hemipeptone is further changed to leucin and tyrosin. Digestive ferments, pepsin, and trypsin produce antialbumose, hemiantipeptone, and hemialbumose, but trypsin alone converts the hemipeptone into leucin and tyrosin.

Albumin normally occurs in all the body fluids except in the urine. The amount in milk is extremely slight; the amount in saliva seems to vary in inverse proportion to mucin. Albumin occurring in urine in appreciable quantity is always abnormal, although in many cases it has no serious significance unless persistently present in more than the slightest possible trace.

Globulin occurs in both plants and animals, and crushed hemp seed may be used as a convenient source for laboratory experiment. It is also associated with albumin in blood-plasma, and may be separated from it by half saturation with ammonium sulphate, which precipitates the globulin only, but it is not to be distinguished by the ordinary protein tests and reactions. The albumin of albuminous urine always consists of a mixture of these two proteins, globulin and albumin, not, however, always in the same proportion. The globulins are not soluble in distilled water as the albumins are, but a very small quantity of neutral salt, such as sodium chlorid, will serve to effect the solution. Globulin is thrown out of solution by action of carbon dioxid as a white flocculent precipitate. By dialysis the inorganic salts necessary for its solution will be removed and the protein will be precipitated. It is also thrown out by saturation of sodium chlorid or magnesium sulphate. Globulin is coagulated by heat at practically the same temperature as serum-albumin; i.e., 75° C.

Laboratory Exercise LXIV.

Experiments with Albumin and Globulin.

The albumins and globulins respond to all the general reactions of Laboratory Exercise No. 63.

Exp. 163. A specimen of solid egg-albumin, prepared by evaporating a solution to dryness at 40° C., is provided. Test its solubility in water, alcohol, acetic acid, KOH solution, and concentrated HCl. Report results.

Perform the following additional experiments, using a dilute (1/50) solution of egg-albumin.

Exp. 164. *Nitric-acid Test.* — Take 15 c.c. of the solution in a wine-glass, incline the glass, and allow 5 c.c. of concentrated HNO_3 to run slowly down the side to form an under layer. What other proteins respond to this test?

Exp. 165. *Picric-acid Test.* — Take a portion of the albumin solution and add a few drops of a solution of picric acid acidified with citric acid (Esbach's reagent). What other proteins respond to this test?

Exp. 166. *Action of* $(NH_4)_2SO_4$. — To 10 c.c. of the albumin solution in a test-tube add some solid $(NH_4)_2SO_4$, shaking until solution is thoroughly saturated. Allow to stand a little while, shaking occasionally, then filter, saving the filtrate to test for albumin by the heat test. Report result. Test the solubility of the precipitate on the filter-paper.

Exp. 167. *Action of* $MgSO_4$. — Perform an experiment similar to Exp. 166 using solid $MgSO_4$ instead of $(NH_4)_2SO_4$. With what results?

Exp. 168. *Salts of the Heavy Metals.* — Note the action of the following: $AgNO_3$, $HgCl_2$, $CuSO_4$, $Pb(C_2H_3O_2)_2$. Use solutions of the salts and of albumin.

Why is white of egg an antidote in cases of metallic poisoning?

Globulins.

The following tests serve to distinguish the globulins from other proteins.

The tests may be made upon blood serum, or upon a globulin (edestin) which may be separated from hemp seed according to the following experiment:

Extract about 1 ounce of crushed hemp seed with water containing about 5% sodium chlorid. This extraction should take from one-half hour to one hour at a temperature of about 60° C. Filter while hot. Upon cooling, a portion of the globulin (edestin) will probably separate out. Use the clear separated fluid for the general protein reactions and precipitates. Boil the cloudy portion until the precipitated globulin has dissolved. Then set aside for 24 hours that the edestin may crystallize slowly, when hexagonal plates should be obtained. Examine by the microscope. (See Plate VII, Fig. 1, page 296.)

Exp. 169. *Action of* CO_2. — To 5 c.c. of blood serum add 45 c.c. of ice-cold water. Place the mixture in a large test-tube or cylinder, surround it with ice-water, and pass through it a stream of CO_2. A flocculent precipitate (paraglobulin) * will be formed.

Exp. 170. *Precipitation by Dialysis.* — Into a parchment dialyzing-tube, previously soaked in distilled water, pour 20 c.c. of serum, swing the tube, with its contents, into a large vessel of distilled water, which is to be changed at intervals. Let stand twenty-four hours, then examine the serum in the dialyzing-tube; it will contain a flocculent precipitate of paraglobulin. Give explanation of cause of precipitation.

Exp. 171. Pour a solution of globulin, drop by drop, into a large volume of distilled water (in a beaker). What takes place? Explain.

* Paraglobulin is a name applied to the globulin separated from blood serum.

Exp. 172. *Precipitation by Magnesium Sulphate.* — Saturate about 5 c.c. of globulin solution with solid magnesium sulphate. A heavy precipitate will be formed. Compare this with the action of the same salt on the egg-albumin solution. Paraglobulin is so completely precipitated by this salt that the method is used for its quantitative estimation.

THE GLUTELINS AND PROLAMINS thus far studied have been mostly obtained from vegetable sources.

Glutenin constitutes about one-half of wheat gluten, and the prolamins mentioned on page 274; Zein is obtained from maize — Hordein from barley, Gliadin from wheat or rye and Bynin from malt.

ALBUMINOIDS.

Albuminoids are the simple protiens characterized by pronounced insolubility in all neutral salivas, and the common examples are Keratin, from nails and hoofs, etc.; Collagen, from bone and connective tissue; and Elastin, from tendons and ligaments.

The differences in these substances are slight, the keratin being less soluble and less easily acted upon by digestive ferments than either of the other two. Keratin also contains more sulphur. It is the principal constituent of horn, nails, hair, feathers, egg membrane, and some shells, such as turtle and tortoise. The sulphur content of these various sources differs considerably, ranging from about 5% in hair, about 3% in nail and horn, to 1.4% in egg membrane.

The *keratins* are characterized by the fact that the sulphur which they contain is loosely combined; i.e., easily separated by the formation of hydrogen sulphide and other sulphur compounds as proved by experiment No. 174. The keratins are insoluble in dilute acids and unaffected by any of the digestive ferments; they do, however, dissolve in the caustic alkali solutions, and may be used as the source of leucin, tyrosin, cystin, and other well-known products of protein digestion.

Collagen, upon hydrolization with boiling water, produces gelatin, which is a characteristic property of this class of proteins. It may be dissolved by both the gastric and pancreatic juices, especially if previously treated with warm acidulated water.

Elastin contains the least sulphur of either of the three substances which we have considered. It may be obtained from the ligamentum nuchæ of an ox by chopping the ligament finely and extracting for two or three days with *half* saturated solution of calcium hydroxid. Like collagen it is dissolved upon prolonged treatment with proteolytic ferments.

Bone.

If all organic matter is burned off from bone, there remains the bone-earth, so called, made up of the phosphates and carbonates of lime and magnesia, with slight amounts of chlorin, fluorin, and of sulphates, the proportion being practically the same as given for dentine, under Teeth, on page 178. Because in some diseases, in which the bones are softened or decalcified (as osteomalacia), the relation of the CaO and P_2O_5 remains unchanged, it has been claimed that these substances exist in the bone in the form of a definite phosphate-carbonate containing three molecules of the tribasic phosphate to one of carbonate: $3\ Ca_3(PO_4)_2.CaCO_3$.

If, by treatment with dilute hydrochloric acid, the mineral constituents are entirely dissolved out of bone, there remains a substance from which glue (gelatin) is derived, of similar composition to collagen, from connective tissue, and known as *ossein*. Neither of these (ossein or collagen) is soluble in water or in dilute acids.

Gelatin is made by hydrolysis of ossein or collagen brought about by *prolonged* boiling with dilute mineral acids. Gelatin, if first treated with cold water till soft, may be dissolved in hot

water. The solution is precipitated by mercuric chlorid, alcohol, tannic, and picric acids. It responds but feebly to the general protein reactions, but, by digestion with either pepsin or trypsin, compounds are obtained analogous to those resulting from similar protein digestion.

Laboratory Exercise LXV.

Experiments with Keratin and Gelatin.

Keratins are characterized by their insolubility, and by their high content of loosely combined sulphur.

Exp. 173. Test solubility of keratin (nail or horn) in water, acids, alkalies, gastric and pancreatic juices.

Exp. 174. Warm a bit of keratin with 5 c.c. strong NaOH solution for a few minutes, and add a few drops of a lead acetate solution. What is the result?

Exp. 175. *Gelatin.* — Take about 10 grams of bone, preferably small pieces of the shaft of a long bone, clean carefully, and allow to stand for a few days in 60 c.c. of dilute HCl (1/20). The dilute acid dissolves the inorganic portion of the bone, leaving the collagen. Note the effervescence due to the presence of carbonates. The acid solution is poured off and kept for further investigation. The remains of the bone are allowed to stand over night in a dilute solution (1/10) of Na_2CO_3, and then boiled in 100 c.c. of water for an hour or two. The collagen undergoes hydration and is converted into gelatin, which dissolves. A core of bone untouched by the acid usually remains. Evaporate the solution to 25 c.c. bulk and allow to cool. A firm jelly is formed if the solution is sufficiently concentrated. If the solution gelatinizes, add an equal bulk of water and heat anew. With the solution perform the following experiments. (If too little gelatin is obtained for all the tests, a solution will be provided.)

Gelatin may also be prepared from tendons which consist

almost wholly of white fibers. Collagen is the substance of which white fibers are made up.

Exp. 176. With a solution of gelatin make the usual tests for protein.

Exp. 177. Precipitate gelatin from dilute solution with the following reagents:

(*a*) Tannic acid.
(*b*) Alcohol.
(*c*) Acetic acid and potassium ferrocyanid.
(*d*) Mercuric chlorid.
(*e*) Picric acid.

Conjugated Proteins.

These are substances which contain the protein molecule united to some other molecule or molecules otherwise than as a salt. The conjugated proteins which we shall study are mucin, a type of glyco-protein, yielding upon decomposition a substance containing a carbohydrate group; caseinogen (from milk), a phosphorus containing substance; and hemoglobin (from blood).

The glyco-protein. Mucin, a selected type of this class of protein substance, occurs in various forms in saliva, in urine, bile, and other body fluids. The mucin substances are differentiated from the true mucins, according to Hammarsten, by the fact that the latter form mucilaginous or ropy solutions by the aid of a trace of alkali, from which they are precipitated by acetic acid. The precipitate is insoluble in excess of acid, or soluble only with great difficulty.

True mucins have been separated and examined from the secretion of the submaxillary glands, from snails, from mucous membranes of the air passages, from synovial fluid, and from the navel cord.

Mucin is quite readily converted to metaprotein by boiling with dilute acid, and, by action of strong acid, will yield a

number of the simpler amino acids. Mucin itself is acid in reaction, but there is no evidence that it has power to form salts.

The mucins are insoluble in pure water, but dissolve upon the addition of traces of alkali. The solution thus obtained will give the usual color reactions for the proteins.

The action of mucin as a factor in dental caries, formation of gelatinous plaques, etc., will be discussed under Saliva.

Caseinogen, the second conjugated protein which we shall consider, is the principal nitrogenous constituent of milk and will be studied as such.

Milk.

Milk is the characteristic secretion of mammals and contains the three great classes of food material, viz.: the proteins, carbohydrates and fats. The fat is held as a permanent emulsion in so-called milk plasma.

The plasma consists of water holding in solution caseinogen, albumin with a trace of globulin, milk sugar (lactose) and mineral salts.

Specific Gravity. — Milk contains two different sorts of substances influencing the gravity; first, the fat being lighter than the water tends to decrease the gravity; second, the solids not fat which are heavier than water tend to increase the gravity of the milk. Consequently, it may happen that a very poor milk and a very rich milk will have the same specific gravity; e.g., the normal gravity of whole milk is about 1.031, while the gravity of skim milk will be about 1.035 or 1.036, and that in which cream occurs in large amount may be as low as 1.015 or 1.020. It can be easily seen that starting with whole milk, the addition of cream or the addition of water will both alike reduce the gravity. Hence, taken alone, the gravity tells little or nothing as regards the quality of milk; but, if the gravity is taken together with the fat content, the *two* factors give oftentimes sufficient information.

The relation between the gravity of the fat and the total solids is approximately constant, and the following formula will give the amount of total solids usually within 0.10 or 0.15 of 1%.

$$\text{Total solids} = \frac{\text{Fat} \times 6}{5} + \frac{\text{Sp. gr.}}{4} + 0.46.$$

Reaction. — The reaction of cow's milk, when perfectly fresh, is amphoteric to litmus; i.e., it will both redden blue litmus paper and turn red litmus blue at the same time. This double reaction is due to the presence of various salts, probably the acid and alkaline phosphates.

Cow's milk is acid to phenolphthalein, and this acidity naturally increases by the multiplication of various acid-forming bacteria, which produce lactic acid by hydrolysis of the milk sugar. When the acid strength has increased sufficiently, the caseinogen is decomposed, and casein is produced and precipitated.

This casein constitutes the curd, and the process is the ordinary souring of milk.

Lactic acid is not the only acid produced in the spontaneous fermentation of milk, as traces of formic, acetic, butyric and succinic acids have been demonstrated by different investigators.

The degree of acidity of milk is conveniently determined as suggested by W. Thorner (Chem. Zeit., 1891, page 1108, abst. analyst XVI, 200), 10 c.c. of milk with an equal volume of water and a few drops of phenolphthalein as indicator are titrated with N/10 alkali and every tenth of a degree of alkali used is considered as representing one " degree " of acidity.

By experimenting on samples kept under various conditions, Thorner found that milk coagulates on boiling when the acidity reaches 23°. Adopting 20° as the permissible limit of acidity, he proposes the following test: 10 c.c. of milk, 20 c.c.

of water, a few drops of indicator and 2 c.c. of decinormal alkali are thoroughly mixed; if any red color, however weak, results, the milk will not coagulate upon boiling.*

This method is given partly for its own sake and partly because exactly the same method is used by Dr. Eugene S. Talbot of Chicago and many others for the determination of acidity of urine. By slight modification it may be used for saliva. The record of slight amounts of acidity made in degrees in this way has several practical points in its favor.

Casein is the principal protein found in milk. It exists in combination with calcium salts as caseinogen. This combination is broken up and the casein precipitated by the action of rennin and other enzymes, by acids, and by certain inorganic salts.

Casein is classified as a pseudo-nucleo-albumin. The nucleoproteins, so named because true nuclein may be obtained from them, are constituents of the cell nuclei, and differ in composition from ordinary proteins by containing from 0.5 to 1.6% of phosphorus. Casein from cow's milk contains, according to Hammarsten, 0.85% of phosphorus. It has been classified as a *pseudo*-nucleo-albumin because, upon digestion with pepsin, pseudo-nuclein rather than true nuclein is obtained.

Casein is practically insoluble in water, but dissolves readily in dilute alkaline solutions. Its precipitation as curd is dependent upon the presence of calcium salts.

Lactalbumin is the only other *protein* substance worthy of note in milk. This may be found in the filtrate after separating the casein. The total proteins contained in human milk average from 1.5 to 2.5 per cent, while in cow's milk the proteins are 3.0 to 4.5 per cent. This difference, together with the variation of reaction and sugar-content, makes it necessary to "modify" cow's milk when it is used as an infant food.

The modification usually consists in the addition of lime-

* From Allen's Commercial Organic Analysis, Vol. 4.

water (to change the reaction), of water (to reduce percentage of proteins), and of cream and milk-sugar (to increase fat and lactose).

The following table shows comparative composition:

	Reaction.	Total Solids.	Proteins.	Sugar.	Fat.	Ash.
Human milk..	Alkaline	13.00%	2.70%	6.10%	4.00%	0.20%
Cow's milk...	Acid	14.00%	4.15%	4.90%	4.25%	0.70%

Fat. — The fat of milk exists as microscopic globules apparently inclosed in a protein-like membrane separating substance, the presence of which seems a necessary theory to account for the behavior of milk fat toward various solvents such as ether. The milk fat or butter fat consists largely of olein and palmitin with a slight amount of butyrin and traces of several other fatty acids.

Milk, as has already been stated, undergoes lactic acid fermentation readily and this may be induced by a considerable number of microörganisms. It is not, however, liable to alcoholic fermentation except under peculiar circumstances. Alcoholic fermentation may be induced by certain ferments, such as the Kephir grain used quite largely in the East, the product being known as Kumiss or milk wine. Kumiss originally was produced from mare's milk, but the name has also been applied to any milk which has undergone alcoholic fermentation.

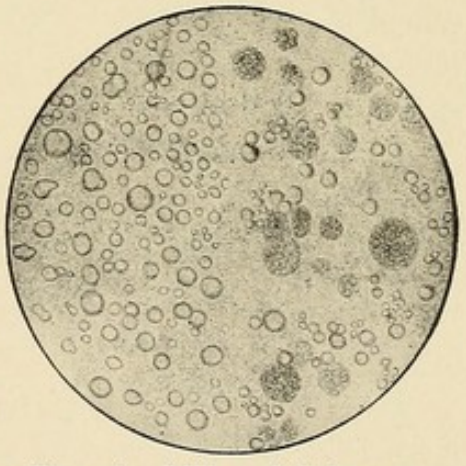


FIG. 18. Milk and Colostrum.

Colostrum is a peculiar substance occurring at the very earliest stages of lactation. Its specific gravity is considerably higher than that of milk, being 1.040 to 1.060. It contains

much more protein substance and is characterized by the presence of granular corpuscles known as colostrum corpuscles. (Fig. 18, on page 289.)

Laboratory Exercise LXVI.

Experiments with Mucin and Milk.

Exp. 178. Examine microscopically whole milk, skim-milk, and cream. Note the relative amounts of fat in the three varieties.

Exp. 179. Shake a little cream with chloroform in a test-tube; separate the chloroform, evaporate, and melt the fat residue obtained; allow it to cool slowly, when fat crystals will be obtained, which may be examined under the microscope and micropolariscope.

Exp. 180. With a lactometer take the specific gravity of whole milk and skim-milk and explain the difference in results.

Exp. 181. Test the reaction of milk with litmus.

Exp. 182. Dilute some milk with six or seven times its volume of water, and add acetic acid drop by drop till the casein is precipitated. Filter and reserve the precipitate. Test the filtrate for proteins, if any remain; determine if possible their character.

Exp. 183. Test another portion of the filtrate for carbohydrates, determining the variety present.

Exp. 184. To 50 c.c. of milk add a few drops of rennin solution; keep at a temperature of 40° C. for a few minutes, and explain results.

Exp. 185. Take a portion of the precipitated casein from Exp. 182, digest at 40° C. with pepsin HCl for twenty minutes or half an hour. While digesting, test other portions of casein, for solubility in water, in dilute acid and dilute alkali. Test also a portion for phosphorus by boiling in a test-tube with dilute nitric acid, cooling to at least 50° C., and adding ammonium molybdate solution.

Exp. 186. To a little skim-milk contained in a test-tube add a saturated solution of ammonium sulphate.

Exp. 187. To a solution of mucin* found on the side shelf add acetic acid till precipitation takes place. Settle, filter, wash, and test solubility in water, dilute alkali solution and 5% HCl.

Exp. 188. Make color-tests for proteins.

Exp. 189. Boil a little mucin solution with dilute HCl for several minutes. Cool, neutralize, and test for sugar.

Derived Proteins.

Meta-proteins — Acid Meta-protein. — The digestive action of the gastric juice on protein substances is the formation of an acid meta-protein, formerly called acid albuminate. The meta-proteins are characterized by the fact that they are precipitated on neutralization and are not coagulated by heat. They may also be precipitated by saturation with common salt.

The Alkali Meta-protein or alkali albuminate is the stronger of these two classes of compounds when considered from a chemical standpoint; that is, the reactions are more marked, and some compounds will be formed with the alkali albuminate which are not produced when the acid albuminate is treated in a similar way. The acid meta-protein from the digestion of meat is known as syntonin.

The Proteoses (albumoses) may be considered as the next well-defined protein product of protein digestion following the albuminate. That is, leaving out the many intermediate products between which sharp lines of demarkation cannot be drawn, the decomposition of albumin brought about by enzymes or digestive ferments gives, first, acid albumin; second, albumose; and third, peptone. Albumose may be taken as a type of this second class of digestive products. Other proteoses, such as globulose, etc., are the substances derived from other proteins

* For preparation of mucin solution from navel cord, see Appendix.

at a corresponding point of decomposition or peptic digestion. Albumose may be coagulated by heat at a temperature ranging upwards from 56° C., but, unlike albumin, as the temperature approaches the boiling-point the albumose goes again into solution, and at a boiling temperature may be separated from albumin by filtration. As the filtrate cools, albumose will again precipitate. The albumose is also precipitated by nitric acid, by ferrocyanid of potassium and acetic acid (the precipitate in both cases being dissolved by heat), and the other general protein precipitates. The biuret test gives a distinctive color with proteoses and peptones, it being a marked reddish shade rather than the violet or blue obtained with other proteins.

Peptones are the final products of *peptic* digestion of the proteins. They are soluble substances which give the biuret test similarly to the proteoses, but are not precipitated by heat, by nitric acid, by potassium ferrocyanid and acetic acid, nor by saturation with ammonium sulphate.

Peptids. — The peptids are the simpler forms of the peptones, many of them being complex amino acids. Upon decomposition or hydrolytic splitting of peptid, the simpler amino acid, which is without the protein characteristics, results.

Laboratory Exercise LXVII.

Experiments with Protein Derivatives.

Preparation of Metaprotein. To a solution of egg-albumin add a few drops of a 0.5% solution of NaOH, and warm gently for a few minutes. With the solution thus obtained perform the following tests:

Exp. 190. (*a*) *Effect of Heating.* — Boil some of the solution and report result.

Exp. 191. (*b*) *Effect of Neutralizing.* — Add a drop of litmus solution, and cautiously neutralize.

Acid Metaprotein.

Exp. 192. Add a small quantity of a 0.2% HCl solution to a solution of egg-albumin, and warm at 40° C. for one half to one hour. Or cover with an excess of 0.2% HCl some meat cut into fine pieces, and expose for a while to a temperature of 40° C. Filter. With either of the solutions thus obtained make same tests as on alkali metaprotein, and compare results. How distinguish between them?

Albumoses (Hemialbumose). — This name includes four closely allied forms of albumose, namely: (1) Protoalbumose; (2) Deuteroalbumose; (3) Heteroalbumose; (4) Dysalbumose, an insoluble modification of heteroalbumose. Commercial peptone, which is substantially a mixture of albumoses and peptones, will be given out for use.

Exp. 193. Make a solution of the peptone in water, filter if necessary, and saturate with solid $(NH_4)_2SO_4$. Filter. The precipitate contains the albumoses, the filtrate the peptones. Reserve the filtrate for subsequent tests for peptone. Wash the precipitate with a saturated solution of ammonium sulphate; dissolve in water, and, with the solution obtained, perform the following tests, noting especially the tendency of albumose precipitates to dissolve upon the application of heat and to reappear upon cooling.

Using this solution of albumose, repeat Exps. 155, 156, 157, 164, 165. If no precipitate forms with HNO_3 in Exp. 164, add a drop or two of a saturated solution of common salt. (Deuteroalbumose gives this reaction only in the presence of HCl.)

Exp. 194. Saturate some of the solution with $(NH_4)_2SO_4$. Report the result.

Exp. 195. To some of the solution add 2 or 3 drops of acetic acid and then a saturated solution of NaCl. A precipitate forms, which dissolves on heating, and reappears on cooling.

Exp. 196. Using the peptone solution prepared in manner

above described from commercial peptone, repeat the experiments indicated in Exp. 193.

Exp. 197. *Effect of heating.* — Boil some of the peptone solution. Report the result.

Exp. 198. *Power of Dialyzing.* — Dialyze some of the peptone solution. Use 10 c.c. of the peptone solution, and in the outside vessel about 100 c.c. of water, which in this case is not to be changed. After twenty-four hours test the outside water for peptone, employing the biuret test.

Exp. 199. *Action of Ammonium Sulphate.* — Saturate some of the peptone solution with solid $(NH_4)_2SO_4$. Report the result.

A number of unknown solutions will be given out to be tested for carbohydrates and proteins. A report of the results, together with the methods employed, is to be made.

BLOOD AND MUSCLE.

Blood.

The blood, carrying oxygen and other forms of nutrition to all parts of the body, and returning carbon monoxid and the waste products of cellular activity, is an exceedingly complex substance. The composition of the blood itself, however, may be grossly described as a fluid (plasma) carrying in suspension the cellular constituents, red and white corpuscles. The plasma contains solid matter to the extent of about 8.9%. This is largely protein, consisting of serum globulin, serum albumin, a slight amount of nucleoprotein, and fibrinogen; also a fibrin ferment, thrombase or thrombin, by the action of which the fibrin is separated as a "clot" which mechanically carries down the corpuscles. As the clot contracts, the "serum" separates as a clear, amber-colored liquid, consisting of serum globulin (paraglobulin), serum albumin, and the fibrin ferment.

Fibrin. — The fibrin may be obtained free from corpuscles by whipping fresh blood. Under this treatment the fibrin separates as shreds, while the remaining fluid constitutes "defibrinated blood." The presence of lime-salts is essential to the coagulation of the blood, i.e., the decomposition of fibrinogen and separation of fibrin, in much the same way as in the decomposition of caseinogen and precipitation of casein from milk.

Fibrin, as usually obtained, is in the form of brown, stringy, and "fibrinous" masses, which are kept under glycerin for laboratory use. It is insoluble in water or alcohol. In dilute acid (HCl) or alkali solutions, it swells and ultimately dissolves, although it may be several days before solution is effected. The fibrins from the blood of different animals differ in composition, as indicated by marked differences in solubility.

The chemistry of the red and white corpuscles is more complex and not so well known as the chemistry of the plasma, which we have considered. The red corpuscles consist of a frame of protoplasm, also called stroma, which contains lecithin, cholestrin, nucleoalbumin, and a globulin. (Hammarsten.) Upon and all through the stroma is the hæmoglobin, which, together with its oxygen compound oxyhæmoglobin, is responsible for the *color* of the blood. Oxyhæmoglobin may be obtained as silky, transparent crystals of blood-red color.

From hæmoglobin may be derived the blood pigment *hæmochromogen*, containing iron, and this by oxidation is converted into hæmatin. The iron from the blood may, by decomposition of the pigment and subsequent combination with sulphur (FeS), cause discoloration of teeth. This is the theory of Dr. Kirk of Philadelphia, and in the author's opinion is perfectly sound, and far more probable than other explanations which have been offered, but which do not recognize the formation of a sulphur compound.

CO Hæmoglobin. — Hæmoglobin forms with carbon monoxid (from water-gas or other sources) a definite and very stable

compound, being even stronger than the oxyhæmoglobin, to which reference has previously been made. Blood containing carbon monoxid hæmoglobin is of a bright-red color, which darkens in the air much more slowly than ordinary blood.

Hæmin, or Teichmann's hæmin crystals, is the hydrochloric acid compound of hæmatin. (See Exp. 206, page 299, also Plate VII, Fig. 2.)

The form of the red corpuscle is that of a biconcave disk without nucleus; by action of water it becomes swollen, and the hæmoglobin may be washed away, leaving the "stroma." The diameter of the red corpuscles of human blood is about 1/3200 of an inch. Of the domestic animals, the corpuscles of the dog approach most nearly to the measurement of the human. The sheep, horse, and ox have smaller corpuscles than man, while those of birds, cold-blooded animals, and reptiles are larger (see Plate VII, Figs. 5 and 6).

The white corpuscles are rather larger than the red, and occur in much smaller numbers, a cubic millimeter containing about 5,000,000 red to 7500 white. The white corpuscles present a much greater diversity of character than do the red. They contain one to four nuclei, and are capable of amœboid movements. The white corpuscles are also called leucocytes, aggregations of which constitute pus. The leucocytes are divided histologically into various classes, — lymphocyte, neutrophiles, eosinophiles, etc., — according as they are acted upon by different staining-fluids or fulfill some particular office; but these are not to be distinguished chemically.

Muscle.

The chemistry of muscle is complex. It changes rapidly upon the death of the animal, so much so that the liquid which may be expressed from living muscle (or from muscle frozen immediately upon the death of the animal) has been called muscle plasma, in distinction from the fluid obtained in the

PLATE VII.—PHYSIOLOGICAL CHEMISTRY.

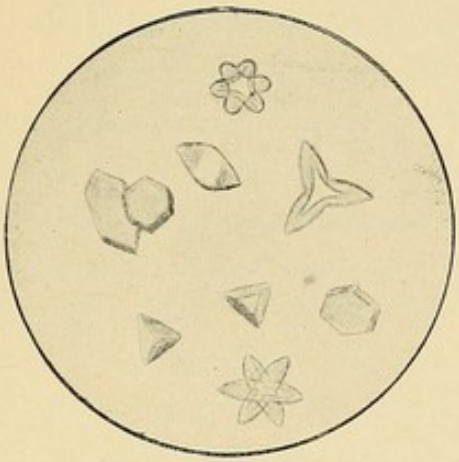


FIG. 1.
Edesten.

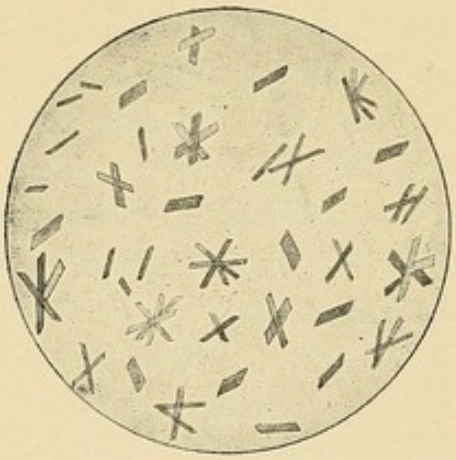


FIG. 2.
Teichmann's Hemin Crystals.

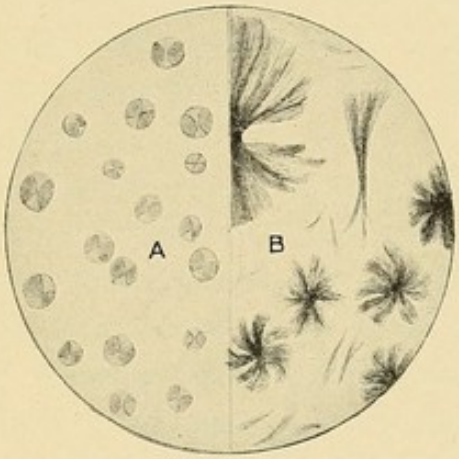


FIG. 3.—Fat Crystals.
A, Butter Crystals; *B*, Lard Crystals.

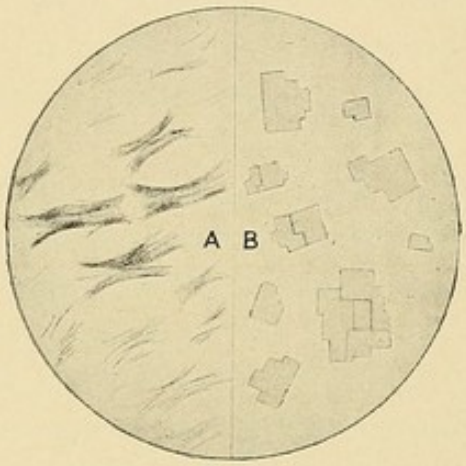


FIG. 4.
A, Fat Acid; *B*, Cholesterin.

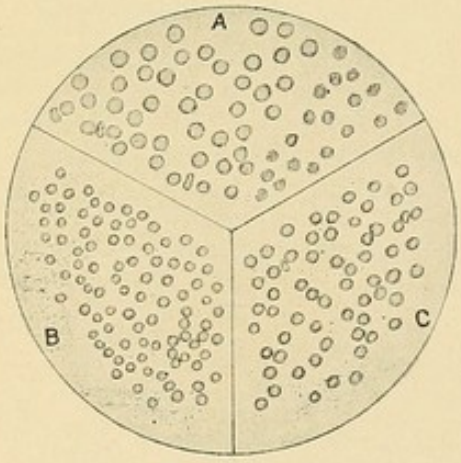


FIG. 5.
A, Human Blood; *B*, Horse Blood;
C, Dog Blood.

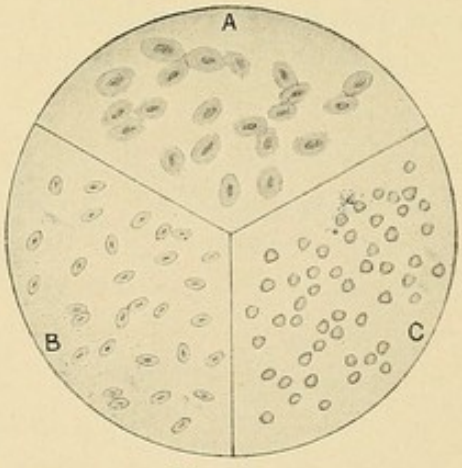


FIG. 6.
A, Frog Blood; *B*, Chicken Blood;
C, Fish Blood.

same manner from dead muscle, which is called muscle serum. The chemical reactions of these solutions differ, due to the formation of sarcolactic acid in the dead muscle. The proteins differ in certain respects. Myosin is the most essential constituent of muscle plasma, and corresponds to the fibrin of the blood-clot. It exists as a parent protein myosinogen, or myogen, from which it may be precipitated by saturation with salt or magnesium sulphate. Myosin has many of the properties of the globulins, but differs in the very important particular of not being precipitated by dialyzation. Among the more important extractive bodies obtained from muscle are creatin, carnin, inosite, glycogen, and lactic acid. Creatin is a xanthin body, being chemically a methyl-guanidin-acetic acid, which may appear in the urine as creatinin. (Creatinin is creatin minus H_2O.)

Carnin is a white crystalline substance obtained from meat extract and converted by oxidation induced or produced by nitric acid, chlorin or bromin into hypoxanthin or sarkin. Its chemical constitution is not positively known.

Inosite, $C_6H_{12}O_6+H_2O$, is a hexahydroxybenzene, $C_6H_6(OH)_6 + H_2O$. It has a sweet taste, and was formerly erroneously classed with the carbohydrates. It is capable of yielding lactic and butyric acids (?).

Glycogen occurs in slight amounts in muscle, but decomposes after death, with formation of a reducing sugar. (Compare page 264.)

Lactic Acid is a constituent not only of muscle but also of various glands, of the bile, and of blood. For the chemistry of this substance, see page 220.

Laboratory Exercise LXVIII.

Experiments on Blood.

Exp. 200. Test the reaction of blood with a piece of litmus-paper which has been previously soaked in a concentrated NaCl solution. To what is reaction due?

Exp. 201. *Blood-corpuscles.* — (*a*) Examine a drop of blood under the microscope. Sketch the red and white corpuscles.

(*b*) Note the difference between the corpuscles of mammals and those of birds and reptiles.

(*c*) Note the effect upon the red corpuscles produced by the addition of (1) water, (2) a concentrated solution of salt.

Exp. 202. *Hæmoglobin Crystals.* — Place a drop of defibrinated rat's blood on a slide; add a drop or two of water; mix, and cover with a cover-glass. Sketch the crystals which separate after a few minutes. Or instead of above add a few drops of ether to some blood in a test-tube; shake thoroughly until the blood becomes "laky," and then place the tube on ice till crystals appear.

Exp. 203. A spectroscope will be found ready for use in the laboratory, and the absorption-bands given by oxyhæmoglobin and hæmoglobin will be demonstrated. The student may prepare solutions for examination as follows:

(*a*) *Oxyhæmoglobin.* — Use dilute blood (one part of defibrinated blood in fifty parts of distilled water).

(*b*) *Hæmoglobin* (reduced hæmoglobin). — Add to blood a few drops of strong ammonium sulphid, or one or two drops of freshly prepared Stokes's reagent.* Note the change in color produced by the addition of the reducing agent. Shake with air and note the rapid change to oxyhæmoglobin.

(*c*) *Hæmochromogen.* — To a little of the hæmochromogen, reduced with ammonium sulphid, add a few drops of concen-

* Stokes's reagent consists of two parts of ferrous sulphate and three parts of tartaric acid dissolved in water and ammonia added to distinct alkaline reaction. There should be no permanent precipitate.

trated NaCl, and note the spectrum of reduced hæmatin or hæmochromogen.

(*d*) *Carbonmonoxid Hæmoglobin.* — Pass a current of illuminating gas through a dilute oxyhæmoglobin solution for a few minutes and filter. Note the change of color. Try the effect on the solution of (1) ammonium sulphid; (2) Stokes's reagent; (3) shaking with air. Note the stability of the compound.

Exp. 204. Take the specific gravity of blood by filling a test-tube one-half full of benzene; add one drop of blood, and then add chloroform, a drop at a time, with careful but thorough mixing, until the drop of blood floats at about the middle of the mixture, indicating that the gravity of the mixture and of the blood are the same. The specific gravity of the benzene and chloroform may be taken in any convenient way.

Exp. 205. Make the guaiacum test for blood on a sample of dried blood; also on potato scrapings. The method is as follows:

To a little *clear solution* of blood or material obtained from potato scrapings, add some fresh tincture of guaiacum; then add a few drops of an ethereal solution of hydrogen peroxid, shake the mixture and note the blue color obtained.

From these two tests what do you gather about the value of the guaiacum test for blood, and what is probably the cause of the coloration?

Exp. 206. *Hæmin Crystals* (*Teichmann's Test*). — Place a bit of powdered dried blood on a glass slide; add a minute crystal of NaCl (fresh blood contains sufficient NaCl) and two drops of *glacial* acetic acid. Cover with a cover-glass and warm *gently* over a flame until bubbles appear. On cooling, dark-brown rhombic crystals, often crossed, separate (chlorid of hæmatin). Similar crystals can be obtained by using an alkalin iodid or bromid in place of NaCl.

Exp. 207. *Coagulation of Blood.* — Observe the phenomena of coagulation as it takes place (*a*) in a test-tube; (*b*) in a drop of blood examined under the microscope. Explain fully.

Exp. 208. *Proteins of Blood-plasma.* — (*a*) Serum-albumin. (*b*) Serum-globulin. Using blood-serum, separate and identify these two proteins.

(*c*) *Fibrinogen.* — Fibrinogen is a globulin found in blood-plasma, lymph, etc., together with paraglobulin. Like paraglobulin it responds to all the general precipitants and tests, and in addition gives the reactions with CO_2, dialysis and $MgSO_4$. It is distinguished from paraglobulin easily by two reactions, viz., its power to coagulate, i.e., to form fibrin when acted on by fibrin ferment, and its temperature of heat coagulation, which will be found to be from 56° to 60° C.

Exp. 209. *Fibrin.* — (*a*) Note its physical properties.

(*b*) Note action of 0.2% hydrochloric acid.

(*c*) Apply the protein color tests.

Laboratory Exercise LXIX.

Experiments with Muscle.

Exp. 210. Place 25 grams of fresh finely chopped muscle in a beaker with 75 c.c. of 5% solution of common salt, and allow to stand for about one hour, with frequent stirring. (In the meanwhile perform Exp. 211.) Then filter off the liquid and make the following tests with the filtrate:

(*a*) Test for proteins.

(*b*) Having found proteins, pour a little of the solution into a beaker of water. Result. Inference (myosin).

(*c*) Make a fractional heat coagulation in the following manner (upon the care with which the temperatures given are adhered to, depends the success of the separation): Warm to from 44° to 50° C., and keep at that temperature for a few minutes. The coagulum is myosin [synonyms: paramyosinogen (Halliburton), musculin (older authors)]. In solutions the myosin, which has the properties of a globulin, becomes insoluble after a time, because it changes to myosinfibrin. In heating the solution as above, a slight cloud may appear at from 30° to 40° C.

This is due to coagulation of soluble myogenfibrin. Now filter off the coagulated myosin.

Heat filtrate to from 55° to 65° C. The coagulum is myogen (synonym: myosinogen). In spontaneous coagulation of its solutions it forms, first, soluble myogenfibrin, and, finally, insoluble myogenfibrin. Filter.

Heat to from 70° to 90° C. Coagulum is serum albumin from the blood within the muscle, and is not a constituent of the muscle plasma. Filter.

Test filtrate for proteins. If it shows a slight biuret test, this is due either to incomplete precipitation by coagulation or to the post-mortem formation of albumose or peptone by auto-digestion (autolysis).

Exp. 211. Make an aqueous extract of muscle, and test for lactic acid by acidulating with H_2SO_4, extracting with ether and testing the ethereal extract with *very* dilute ferric chlorid solution. The presence of lactic acid is shown by a bright-yellow color.

Exp. 212. Creatin may be most conveniently prepared from a strong solution of Liebig's extract. Dissolve the extract in twenty parts of water, add basic lead acetate drop by drop to avoid more than a slight excess, then remove excess of lead; concentrate to a syrup over a water-bath and allow to stand in a cool place, when creatin crystals will separate out. Two or three days' time may be required before the crystals are obtained. They may be washed with 88% alcohol and purified by recrystallization from water. Hypoxanthin and sarcolactic acid may be obtained from the mother liquor.*

Exp. 213. Creatinin may be prepared from creatin by boiling for ten or fifteen minutes with very dilute sulphuric acid. Neutralize the acid with $BaCO_3$, filter, evaporate to dryness on a water-bath, and extract the creatinin with alcohol. Upon evaporation the creatinin is obtained in the form of crystals.

* Lea's Chemical Basis of the Animal Body.

PART VII.

DIGESTION.

CHAPTER XXXIII.

SALIVA PROPERTIES AND CONSTITUENTS.

THE saliva is a mixed secretion from the parotid, submaxillary, and sublingual glands, together with a slight amount obtained from the smaller buccal glands. The chemical composition of the secretion from these various sources differs considerably, but from a chemical standpoint we are much more interested in the mixed saliva and its constituents than the differences in the product of the various glands. The notable differences are that the mucin is practically wanting in the parotid saliva. The alkaline salts seem to be in smaller proportion in the parotid saliva than in the other two. Potassium sulphocyanate is a constituent of all varieties of saliva, although more constantly present in the submaxillary and in the sublingual than in the parotid. The parotid, on the other hand, contains a larger proportion of dissolved gases. The data on the composition of these varieties differ to a considerable extent and comparisons are not wholly satisfactory.

The mixed saliva contains, according to Professor Michaels, all the salts of the blood which are dialyzable through the salivary glands, and hence furnishes a reliable index of metabolic processes which are being carried on within the system. In order for this fact to be of practical values, two things are obviously of prime importance: First, methods of analysis which are not too complicated and at the same time conclusive; second, a

knowledge regarding the source of the various constituents found which will enable us to make a rational interpretation of the results obtained. In both of these fundamentals we are very much hampered by lack of knowledge; as yet there is much to be desired in the way of practical clinical tests for the various salivary constituents, and very much to be learned as to their meanings in order to make deductions which shall be conclusive. We are led to believe from the work of an increasing number of specialists that this subject of salivary analysis promises much and is certainly worthy of careful investigation.

The *quantity* of saliva secreted in twenty-four hours is variously estimated from a few hundred to 1500 c.c.; 1200 to 1500 is the more probable amount. The quantity is diminished in fevers, severe diarrhœa, diabetes, and nephritis, by fear and anxiety, and by the use of atropine. It is increased by smoking, by mastication, by the use of mercury, potassium iodid, or pilocarpin. The flow of saliva is also increased by action of the sympathetic nervous system, during pregnancy, and by local inflammatory process.

Physical Properties. — The physical properties of saliva include its appearance, specific gravity, reaction, color, and odor.

Appearance. — The appearance is clear, opalescent, frothy, or cloudy; normal saliva is usually opalescent. It may become turbid by precipitation of lime-salts caused by the escape of carbon dioxid.

Specific Gravity. — Specific gravity ranges from 1.002 to 1.009, the total solids being only from 0.6 to 2.5 per cent.

Reaction. — The reaction is normally alkaline to litmus-paper or to lacmoid. Normal saliva, however, fails to give an alkaline reaction with phenolphthalein, due to the presence of free CO_2, which may be present to the extent of 19 parts in 100, by volume. If the sample be subjected to even a slight degree of heat the acid gas is expelled; then the usual pink color may be obtained with this indicator. Saliva may be acid upon

fasting, particularly before breakfast and also after much talking. Acid conditions may exist which are local in their character and due to lactic acid fermentation. Acid salivas may also be met with in cases of rheumatism, mercury salivation, and diabetes. By exercise of the glands, as during the chewing of food, the alkalinity is increased; oftentimes the reaction changes from faintly acid to alkaline during this process, the proportion of alkaline salts becoming greater, although the total solids as a whole are slightly diminished. This fact of the change in the reaction from acid to alkaline has been explained by ascribing the acidity due to fermenting particles in the mouth; the continued process of chewing and swallowing washes this away, or, in other words, the change in reaction is a mechanical one rather than a change of the chemical composition of the secretion. This explanation seems to be a superficial one and without sufficient experimental foundation.

The acidity of saliva, as indicated at the opening of this paragraph, is referred to the behavior of the saliva to phenolphthalein, and is in large part due to the presence of free carbon dioxid.

The sources of CO_2 in saliva are probably three. CO_2 dialyzed through the salivary glands, traces from carbohydrate fermentation, and considerable quantities absorbed from contact with expired air.

The saliva obtained by chewing paraffin (a process calculated to furnish the maximum amount from the last two sources), may yield several times the amount of free CO_2 that another sample taken from the same patient by a saliva ejector will give.

Acidity of saliva may be temporary when it may be entirely removed by drawing air through the heated (not boiled) sample. The permanent acidity may be determined by titration of the sample after removal of CO_2.

The apparatus pictured in Fig. 19 has been used by the author for this acidity determination.

The air is drawn from left to right first through a potash bulb (*A*) to absorb atmospheric CO_2, next through 10 c.c. of saliva diluted with 20 c.c. of water contained in a small Soxhlet

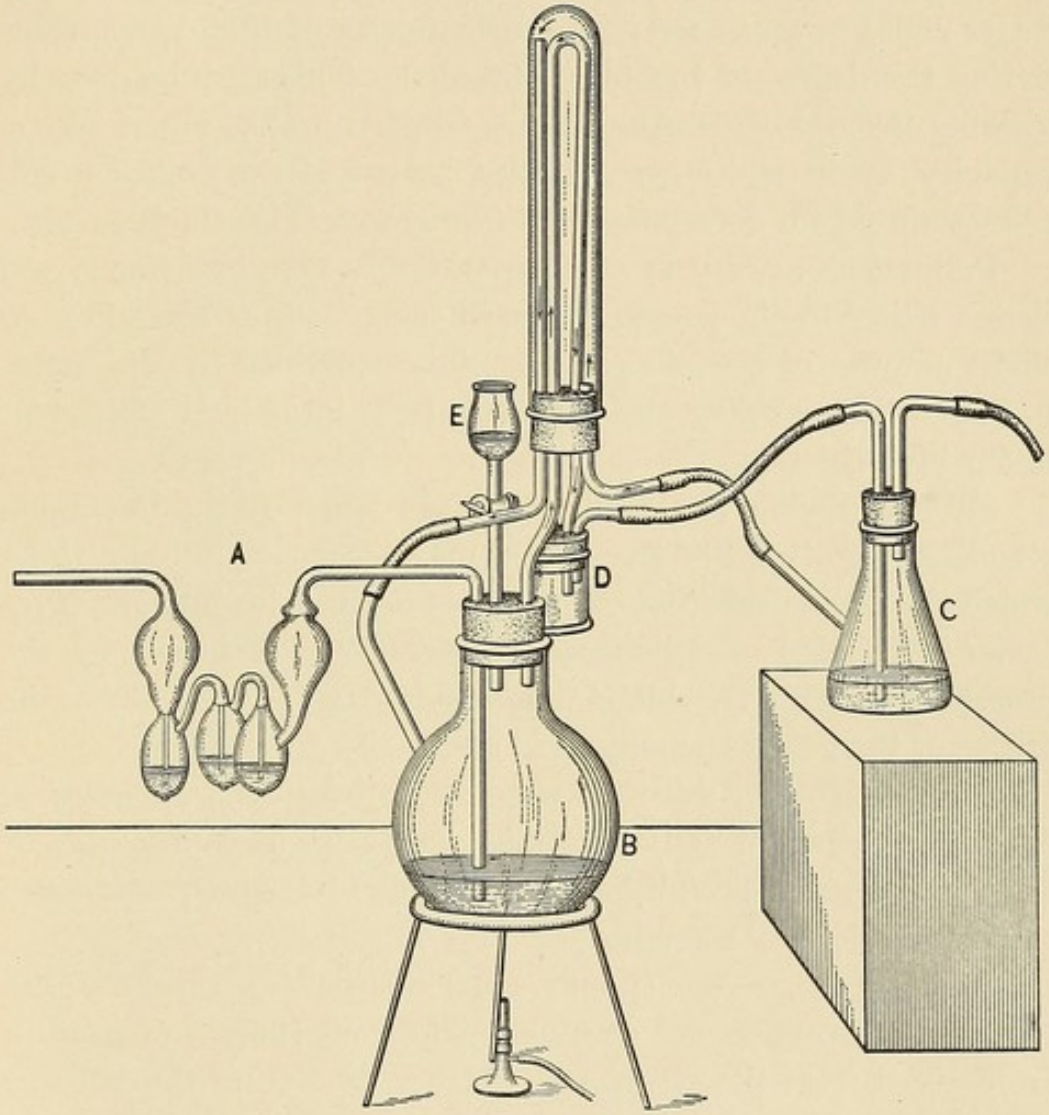


FIG. 19.

flask (*B*) whereby the CO_2 from the saliva is carried through the "test-tube condenser" and collected in baryta water in the Erlenmeyer flask (*C*) at the left. This in turn is connected with a suction pump or aspirator. The "drip cup" (*D*) has been found necessary when working with very viscid samples. The

thistle tube (*E*) holds water for maintaining the volume in (*B*) if the condenser is not used.

The amount of free CO_2 may be determined by adding a standard carbonate solution (N/100 Na_2CO_3) to a volume of baryta water equal to that used in the Erlenmeyer flask and then comparing the degree of turbidity obtained. This may be done by viewing through flat-bottom tubes (shell tubes) of about 20 c.c. capacity, or, in many cases, better, by use of the Duboscq colorimeter used for determination of ammonia (Fig. 20, page 307).

Permanent acidity is of comparatively rare occurrence and is due either to the presence of acid salts, such as NaH_2PO_4, or slight amount of organic acids possibly combined as acid metaprotein. This acidity and its clinical significance is at present under investigation.

Color. — Saliva is usually colorless when fresh, but upon standing for twenty-four hours may assume various tints, which are developed from constituents derived from bile. (Professor Michaels.) Saliva may be colored red or brown by the presence of blood or blood pigments, but in such cases the source of the color is usually local and easily discovered.

Odor. — Normal saliva is practically odorless. In cases of pyorrhœa there is usually a peculiar fetid odor easily recognized. In other pathogenic conditions the odor may be slightly ammoniacal, or occasionally resemble the odor of acetone or garlic.

Constituents. — We should here distinguish carefully between saliva proper and sputum. The constituents of sputum are derived from the air-passages rather than from the salivary glands, and are not at present under consideration. Among the *normal* constituents of saliva are included mucin, albumin, ptyalin, also oxydizing enzymes, ammonium salts, nitrites, potassium sulphocyanate, alkaline phosphates, and chlorids, with traces of carbonates; and, in the sediment, epithelium cells, occasional leucocytes, and fat globules. The *abnormal* constituents will include glycogen, urea, dextrin, rarely sugar,

cholesterin, derivatives from bile, lecithin, xanthin bodies or alkaline urates, acetone, lactic acid, and crystalline elements resulting from insufficient oxidation or perverted glandular function. These latter are recognizable by the micropolariscope.

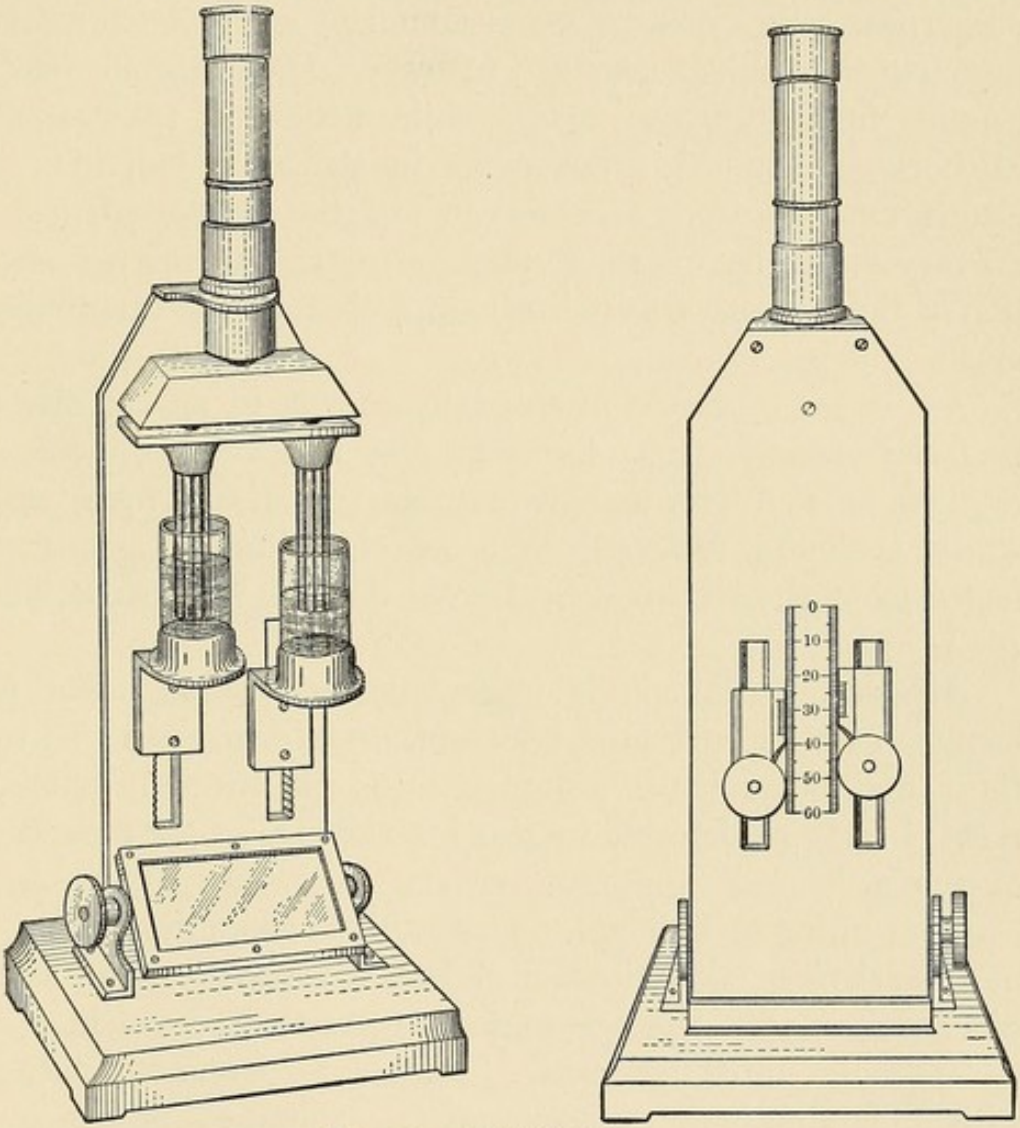


FIG. 20. — Colorimeter.

Mercury and lead may also be found in saliva in cases of poisoning by salts of these metals.

Mucin. — The secretion from the parotid gland contains practically no mucin, but the sublingual saliva contains large amounts. Mucin is, according to Simon, the most important

constituent of the saliva, not excepting ptyalin. The various glands contributing salivary mucin do not in all probability furnish just the same kind of protein; moreover, the mucin from different individuals seems to vary in composition and properties, some yielding more abundant acid decomposition products than others (see article by W. D. Miller, in Dental Cosmos for November, 1905), while, according to Professor Michaels, the mucin varies much in the same individual in health and disease. The changes in the characteristics of salivary mucin have been studied but little, and the investigation of these changes, as indications of diathetic states, promises much.

An excess of mucin in the saliva tends to an increase of bacterial growth, from the fact that it furnishes increased facilities for multiplication; it may also give rise to mucic acid, which, according to Dr. G. W. Cook of Chicago, is a probable factor in tooth erosion. (See Dental Review, May, 1906, page 461.)

Albumin. — Albumin is present in very small quantities, increased during mercurial ptyalism, usually in cases of pyorrhœa, and, according to some authorities, in various albuminurias. It may be detected by usual methods after the separation of mucin.

"According to Vulpian, the quantity of albumin is increased in the saliva of albuminurics of Bright's disease. The saliva of a patient with parenchymatous nephritis had mucin 0.253 and albumin 0.182 per cent. The saliva of another patient, with albuminuria of cardiac origin, contained mucin 0.45, albumin 0.145 per cent. In a healthy man there was found mucin 0.320, albumin 0.05 per cent. This fact has been confirmed by Pouchet, who found these substances in greater quantities." *

* Dr. Joseph P. Michaels. S. S. White's reprint of paper read before International Dental Congress, Paris, 1900.

Ptyalin. — Ptyalin is the principal ferment of the saliva; it converts starch, by hydrolysis through the various dextrins (page 264), to maltose. The maltose in turn is converted into glucose by a second ferment, known as maltase, which exists in saliva in very small quantities.

The activity of ptyalin is greatest at a temperature of 40° C. Very faintly acid saliva is the best media. Neutral and faintly alkaline salivas are next in order.

The amylolytic power of a given sample of saliva may be determined by the action on dilute starch paste. In making comparative tests it is essential that the conditions under which the ptyalin is allowed to act should be exactly the same, especially as regards the temperature and duration of the process. A slight variation in the strength of the starch solution is of no consequence, as starch is supposed to be in excess. (See Exp. 214 on page 327, also method on page 322.)

Ammonium Salts. — Ammonium salts occur chiefly as chlorid, probably to some extent as sulphocyanate, and occasionally as oxalate. Professor Michaels says that ammonia must be considered as a more completely oxidized form of nitrogen than urea; hence its relative increase is observed in all diseases which occasion an excess of nitrogen and urea, as in tuberculosis and all hypoacid diatheses. There is a decrease of ammonia whenever the nitrogen fails to reach the stage of oxidation represented by urea. This condition is accompanied by uric acid and other products of deficient oxidation, and characterizes the hyperacid state. The ammonia may be detected by a microscopical examination of the dried saliva, although the ammonium salts do not polarize light (Plate VIII, Fig. 1, page 327), also by the reaction with Nessler's reagent, which produces a yellow color.

Potassium Sulphocyanate is peculiarly a constituent of the saliva, although it occurs in traces in the blood, urine, etc. In a state of health, according to Dr. Michaels, the ammonium salts and the sulphocyanates are present in very slight amounts,

and the color-tests, with Nessler's solution and with ferric chlorid, respectively, are of about equal intensity. In the hyperacid state the sulphocyanates are in excess of ammonia, while in hypoacid conditions, the ammonia exists in the greater quantity. Sulphocyanate is detected by means of ferric chlorid, and distinguished from meconates and acetates, as indicated by Exp. 216 page 329. The sulphocyanates are normal constituents of saliva, and consequently always present. According to A. Mayer (Deutsch. arch. f. klin. med., Vol. 79, No. 394), the sulphocyanates, without doubt, result from the decomposition of proteins, and exist in the urine in quantities variously estimated from 20 to 80 milligrams per liter, while in saliva it has been estimated from 60 to 100 milligrams per liter. Professor Ludholz of the University of Pennsylvania says that the sulphocyanates are eliminated in increased amounts in conditions where there is a lack of oxygen in the system, thus corroborating statements of Professor Michaels (see Ammonia). Dr. Fenwick (Lancet, 1877, Vol. II, page 303) demonstrated that the quantity of KCNS was directly dependent upon the bile salts in the blood. He found an increase of the salt in liver disorders attended with increase of bile salts in the blood, and marked increase in jaundice. In gout, rheumatism, and conditions producing pyorrhœa, it is also claimed to be present in considerable quantity.

The sulphocyanates are usually present in more than normal quantity in the saliva of people addicted to smoking tobacco.* The claim has been made for this salt that it exerts a specific antiseptic action toward bacteria.

While the sulphocyanates, or, in fact, any salt in sufficient concentration, will have an inhibitory action on the growth of bacteria, it is rather doubtful if this is the particular office of KCyS in the saliva.

Nitrites. — That nitrites exist in most salivas is without ques-

* See article by Dr. J. Morgan Horne in Jour. of the Allied Societies, Vol. 4. Ms. 3, p. 183.

tion. So far as we know at present, the nitrites are apparently incidental, and occur as intermediate products in the oxidation of ammonia to nitrates, just as they do otherwise in nature outside of the animal body.

It is not at all improbable that the proportion of nitrates is dependent upon activities of the oxidases. This has, in some cases at least, been proven to be the case, as the same sample of saliva has frequently given steadily diminishing quantities of nitrates until they have wholly disappeared in cases containing active oxidizing enzymes.

Oxidases. — As a result of the work of Dr. C. F. MacDonald in the author's laboratory, the following conclusions were reached regarding these enzymes:

First. That human mixed saliva contains an oxidizing enzyme distinct from ptyalin.

Second. That the enzyme exhibits the properties of both an oxydase and a peroxydase.

Third. That it is a product of the body (probably glandular) metabolism and may be increased in quantity, or activity by mastication.

Fourth. That it is more resistant to heat than ptyalin, but more easily destroyed by acids.

Fifth. That the color obtained with a freshly prepared 1% solution of pyrocatechol is sufficient test for this enzyme in saliva.

The test for oxidizing enzymes may be made with the pyrocatechol as given on page 323; also by the use of phenolphthalin (reduced phenolphthalein). This last reagent has recently been rendered available by the work of Dr. H. L. Amoss, Harvard Medical School, who has given us a concise and simple method for its preparation. (Jour. Biolog. Chem., 1912.)

Phosphates and Carbonates. — These salts are probably present in both acid and neutral forms; that is, the phosphate may exist as Na_2HPO_4 also as NaH_2PO_4, and at times both of these may be present at once. The acid carbonate, $NaHCO_3$, is an

undoubted constituent, while the neutral carbonate is present in only very slight quantities, if at all. Chittenden says that mixed human saliva contains normally no sodium carbonate whatever.

As explained by Dr. Kirk, the normal reaction by which overacidity of the blood is taken care of by renal epithelium is $H_2CO_3 + Na_2HPO_4 = NaH_2PO_4 + NaHCO_3$, and when conditions are such as to produce larger quantities of carbonic acid than the kidneys can eliminate in accordance with the above reaction, there is an increased acidity of the saliva as well as of the urine.* In the hypoacid individual, the so-called alkaline sodium phosphate, Na_2HPO_4, is present in the greater quantity. In diabetic patients, sugar has very rarely been found in the saliva; one case coming under the observation of the author was that of a woman of middle age, with diabetes of long standing, with 8% of sugar in the urine, and from this case there were obtained a very few osazone crystals by subjecting a considerable quantity of saliva, after concentration, to the phenylhydrazine test.

Urea has been repeatedly found in the saliva of patients suffering from chronic nephritis.

Acetone is of quite frequent occurrence in the saliva. In diabetic patients this substance is often present in comparatively large amounts, sometimes sufficient for the detection of the acetone by its characteristic odor. Acetone may appear in the saliva when it is not present in the urine. In such cases it has usually resulted from disordered digestion and a consequent faulty metabolism. (For further consideration of acetone, see Urine.)

Cholesterin and lecithin have been found by Professor Michaels in pathological saliva, and leucin has been found by Michaels in a case of lupus and, according to Novey, in a case of hysteria.

Of the crystalline salts which may be separated by evapora-

* International Dental Journal, February, 1904.

tion of dialyzed saliva, the sodium oxalate and the lactates and acid lactates of lime and magnesia are of the most importance and have been the most thoroughly studied. As these salts may likewise be separated from urine their significance will be studied under that head.

CHAPTER XXXIV.

ANALYSIS OF SALIVA.

THE analysis of saliva may be taken up from two distinct standpoints, and considering our present lack of positive knowledge on this subject it may for a while be expedient so to study it. First, we will study a few tests of saliva of such a character that they may be made with simple apparatus, and which might be used by any dental practitioner with sufficient time and interest, to contribute to our general knowledge; secondly, we may study saliva by accurate laboratory methods which are not available for general use, but which are necessary for the establishment of positive data, and in fact necessary for an intelligent schedule of tests under division I.

At least two methods are therefore to be considered. The second method should include the standard methods of the National Association but of course is not necessarily confined to them.

We shall introduce a third method in some cases, which will be supplementary to the second.

As it is quite important that the division of salivary analysis into these three methods be clearly understood the following definite classification is given.

Methods marked I are in large part taken from Professor Michaels' methods, and are the simplest methods applicable to small amounts. They will give results of various degrees of value, but may be applied in a few moments by any dentist.

Methods marked II are those given by Dr. Ferris and adopted by the National Dental Association at its annual meeting in 1911, and reported in the Dental Cosmos for November of that same year, on pages 1295, etc.

Methods marked III are those which the author believes to be the most accurate and the most satisfactory in exhaustive determinations.

Physical properties of the saliva should first be noted. In method I, the color and appearance of the perfectly fresh sample is to be carefully compared with the appearance and color after standing for forty-eight hours in a small, tightly covered vial. The color may be yellowish, greenish, or brown, according to the variety of the derivative of biliverdin from which the color is obtained.* The general appearance may also change independently of any color. A saliva that is, when fresh, hypoacid in character, is, after forty-eight hours, usually markedly opalescent and of offensive odor, while a hyperacid saliva may have become clear or cloudy but without odor.

By method II, we should add to this examination a viscosity test which will be of value as indicating the amount of mucin, as probably the mucin content affects the viscosity more than any one constituent.

The **viscosity** may be determined by use of the apparatus pictured in Fig. 21 (page 316).

The essential features of the viscosimeter are a straight graduated tube with the *constriction* (*c*) jacketed so that the conditions under which a given sample will pass through the opening will always be under absolute control.

The apparatus is standardized by partly filling with distilled water in which the bulb of a thermometer is immersed.

The temperature of the distilled H_2O is brought to 25° C. The thermometer is removed to facilitate reading and from 5 to 10 c.c. of the liquid are allowed to run out, the time consumed being accurately determined by a stop watch.

The viscosity of saliva is determined in the same way, except that this sample must be strained through a very fine brass

* Dr. Joseph P. Michaels. S. S. White's reprint of paper read before International Dental Congress, Paris, 1900.

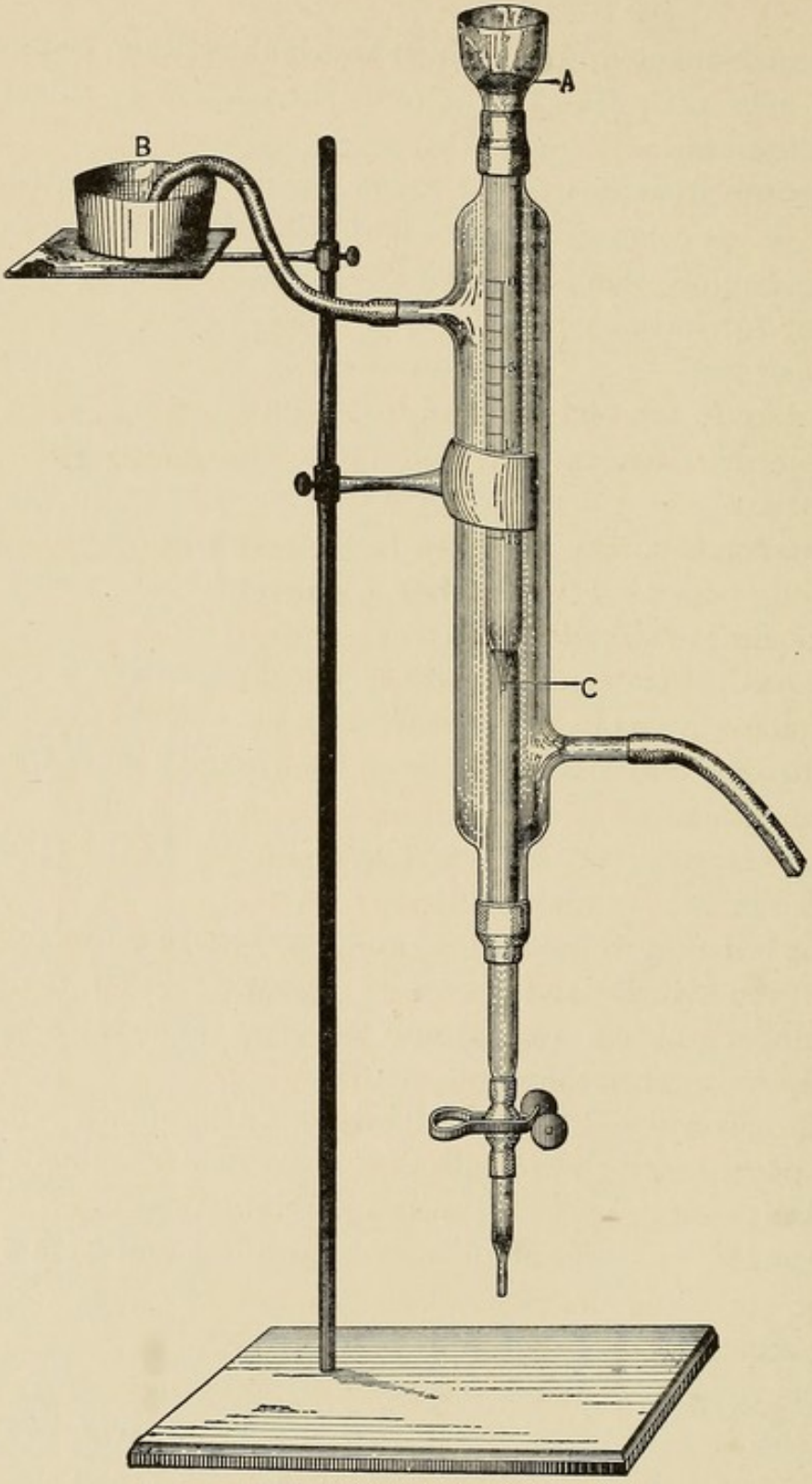


FIG. 21.

sieve (100 meshes to the inch) to prevent clogging of the apparatus.

If the constriction of the graduated tube is sufficiently great, i.e., the opening sufficiently small, comparison may be made by counting drops delivered in a given time. This is not advised, as there is much greater difficulty in obtaining the saliva free enough from suspended particles so as not to clog the tube.

The inner tube should always be filled to the same mark in the determination as that used in the standardization of the instrument.

The **reaction** may be taken in method I by the simple use of litmus paper. This test has a general value, and is sufficient to detect extreme conditions. Our second method should be, in this case as in most others, a quantitative one, and the degree of alkalinity should be determined by titration with N/20 or N/100 acid, using a strong practically neutral litmus solution as an indicator. The degree of acidity, using N/20 or N/100 alkali and neutral phenolphthalein as an indicator, should be determined next. Then the reaction, after driving off carbon dioxid, should be ascertained. The permanent acidity, if such exists, should be found a useful factor in the study of Dental Caries and may be determined by the apparatus pictured on page 305.

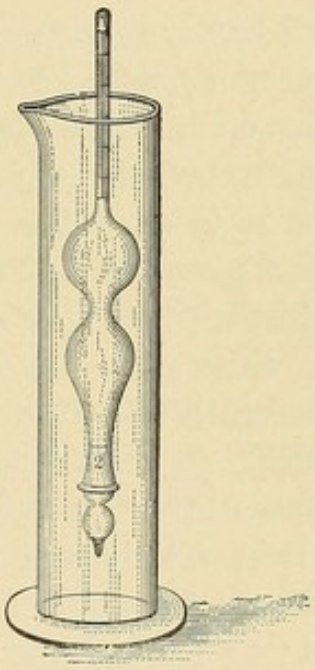


FIG. 22. — Pyknometer.

Specific Gravity may be taken (Method I) by an ordinary urinometer or a specific gravity bulb if the quantity is sufficient, the reading to be made from beneath the surface of the liquid. If the quantity of the saliva is small, it may be diluted with an equal volume of water, and the last two figures multiplied by

two will give the gravity of the undiluted sample, or the gravity may be taken by the pyknometer in which the bulb of the instrument is filled with saliva accurately to the mark *M* (Fig. 22), and then the reading of course on this instrument will be from the bottom up, and the lower the bulb sinks the greater will be the gravity of the sample. This method, claimed to be devised by S. A. De Santos Saxe, M. D., for use in examination of urine, has been suggested by Dr. Ferris and adopted by the National Dental Association as an official method.

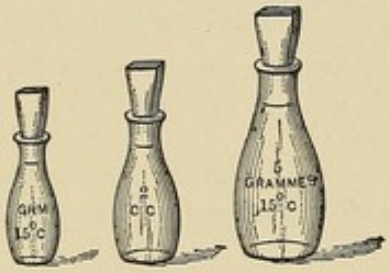


FIG. 23.

For very accurate work the use of specific gravity bottles is recommended. These may be obtained holding one, two and five cubic centimeters (Fig. 23), and with an accurate balance of course the gravity can be accurately obtained.

Thiocyanate (Sulphocyanate) **Tests.** — (Method I.) To a large drop of saliva on a white porcelain surface, add about half as much 5% ferric chlorid, acidified with HCl. A reddish coloration indicates the presence of thiocyanate. "(Method II.) Use a colorimetric scale (Ferris and Schradieck), place 1 c.c. of the specimen in tube *A*; 1 c.c. of 1/2000 ammonia sulphocyanate in tube *B* (Fig. 24); add two drops of a 5% ferric chlorid solution to each tube, add aquo distillata in tube *B*, until its color matches that of the specimen. Read the scale in thousandths and ten thousandths.

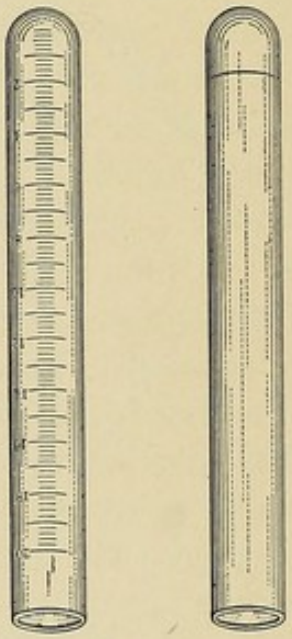


FIG. 24. — Sulphocyanate Tubes.

"Care must be taken to have the bottom of the meniscus on the line. If these tubes are introduced in the colorimeter,

the readings can be made more accurately. If, later, diacetic acid ester is found, a correction is made in the finding."

A much more accurate method than either of these is by use of the Duboscq colorimeter, the detail of the method being as follows:

(Method III.) Fifteen cubic centimenters of a standard thiocyanate solution is placed in one tube, and in the other a filtered mixture of equal parts of saliva and alcohol made fairly acid with HCl. Then two or three drops of acid ferric chlorid are added to each tube, and the color compared. Scale on the back of the instrument makes it possible for very accurate determinations of quantity of the color compound in the unknown solution.

Ammonium Salts. — (Method I.) To a drop of saliva add one drop of Nessler's reagent: a yellow to brown color shows the presence of ammonium salts. If a precipitate forms by the addition of Nessler's reagent, it indicates either a large amount of ammonia or the presence of urobilin. If due to urobilin the precipitate is of a rose color after desiccation. Ammonium salts are usually seen in the evaporated drop examined by polarized light. (Plate VIII, Fig. 1.)

(Method II.) Add one drop of neutralized 1% solution of phenolphthalein to $2\frac{1}{2}$ c.c. saliva, and titrate with N/40 NaOH solution to a permanent color of faintest pink. Ten times the number of cubic centimeters of NaOH used gives the acid index, since N/40 : N :: 2.5 c.c. : 100 c.c., and the acidity is expressed in parts per liter (1000 c.c.).

Now add to the above 1 c.c. of neutralized formalin. The pink color disappears, because the formalin splits off ammonia from the organic matter, liberating free acids. Titrate again to find the amount of combined acids thus liberated, and multiply the reading by 10 as before.

Total acidity is obtained by adding the two findings.

Amino-acids calculated as ammonia may be obtained by multiplying the second findings by 0.0017.

(Method III.) A modification of Dr. Folin's ammonia test in urine, using the Duboscq colorimeter.

Measure out 10 c.c. of saliva in a large Jena test-tube. Add 2 c.c. of a solution containing (*a*) potassium oxalate, (*b*) potassium carbonate (15% of each). By means of an air current, drive the ammonia through a Folin absorption-tube (Fig. 25) into a 100 c.c. wide-mouth bottle containing 2 c.c. N/10 HCl, and about 30 c.c. water. In 20 minutes, all the ammonia should have gone over.

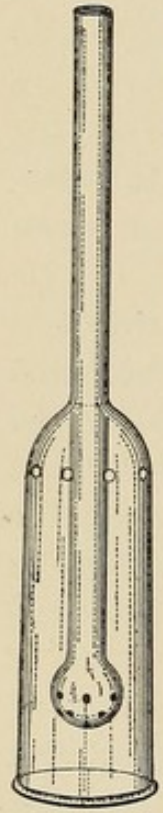


FIG. 25.

Remove the delivery-tube, rinsing it with water, and transfer contents of bottle to 100 c.c. measuring flask, rinsing with sufficient water to make total volume about 60 c.c.

Pipette out 1 c.c. of standard ammonium sulphate into another 100 c.c. measuring flask and dilute with water to about 60 c.c.

Nesslerize both solutions simultaneously in the following manner. Provide two small beakers (100 c.c.) and place from 10 to 15 c.c. of distilled water in each. Add to each 5 c.c. of Nessler's reagent. Mix the reagent with water, and add immediately to the ammonia solutions. Add about one-third of the diluted Nessler reagent at a time, and shake after each addition.

Fill both flasks up to mark with distilled water, mix and compare the colors by means of a Duboscq colorimeter (Fig. 20, page 307).

Urea. — Reagent, sodium hypobromite as used for urea in urine analysis (Appendix, page 380).

Fill the tube of a Ferris modified Doremus ureometer with a saturated salt solution. Close the stopper, and add 1 c.c. of saliva to the upper tube. Allow this to run through the stopper

carefully, then close, and add 1 c.c. of the reagent. When this has gone through, close the stopper quickly, set up the apparatus, and allow to stand one hour or longer. Then, by gently tapping, cause any bubbles adhering to the sides of the tube to rise to the top, and read the amount of gas collected. Each division represents 0.025.

Chlorids. — (Method I.) To a drop of saliva add a small drop of a 5% solution of neutral chromate of potassium, K_2CrO_4. Mix with a glass rod and add one drop of a 1/10% solution of silver nitrate. This constitutes the test for chlorin which, if present in normal quantities, will give a reddish precipitate, gradually becoming white. Should the precipitate remain red it shows the chlorin deficient or less than normal in amount. If the precipitate rapidly turns white, or if a white precipitate is formed to the exclusion of the red, chlorin is increased in amount. High chlorin is indicative of hypoacid diathesis.

(Method II.) To 1 c.c. of the specimen add 4 c.c. of distilled water and two or three drops of potassium chromate; then titrate with N/40 silver nitrate solution, until the first appearance of a permanent reddish tinge. Multiply the number of cubic centimeters of nitrate used by 0.0886 to find the amount of chlorin.

Glycogen. — (Method I.) A drop of saliva may be tested for glycogen by the addition of one drop of an aqueous solution of iodin and potassium iodid. This must be left for some time, as the test is not obtained until the drop is dried; then, if the color is a feeble violet around the edge, glycogen is indicated. If the color is a strong brown-red it indicates erythrodextrin, if gray or black a reducing sugar.

Phosphates. — The phosphates in saliva are determined as in urine except that it is necessary to modify the process slightly as given on page 153.

Acetone. — (Methods I and III.) In the fifth drop dissolve a small crystal of potassium carbonate, then add a drop of

Gram's reagent, when a marked odor of iodoform will indicate the presence of acetone. Should this odor be obtained, it is better to repeat this test upon a microscope slide, and examine carefully for the characteristic hexagonal crystals of iodoform (Plate V, Fig. 1, page 222).

Nitrites. — (Method I.) Nitrites may be detected by adding to a large drop of saliva on porcelain a few drops of freshly prepared reagent, made by dissolving a very little naphthylamin chlorid and an equal amount of sulphanilic acid in distilled water strongly acidulated with acetic acid. A purple coloration is a test for nitrites.

This method could be made quantitative in a manner similar to the colorimetric methods for ammonia, or thiocyanate of potassium; but, at the time of the present writing, there seems to be no particular reason for this amount of work.

Amylolytic Enzymes. — (Method II.)* Preparation of starch paste. Put 15 c.c. of distilled water to boil. Meanwhile, weigh out 3 grams sterile starch and mix with 6 c.c. cold distilled water. Add drop by drop under constant stirring to the boiling water, then rinse out with 5 c.c. of distilled water any particles of starch adhering to the dish and add to the boiling starch solution. Boil one minute under constant stirring. Cool to blood temperature and add gradually 4 c.c. of N/100 iodin solution.

This makes 30 c.c. of a 10% starch solution, which, when colored, is of a dark blue, and can be kept several days in the ice-box.

Filling the Tubes. — Suck up the paste into glass tubes of 1.5 mm. diameter, and cool in the ice-box. Just before using, make a file mark 1 cm. from the end of the tube and break off the piece of tubing so that it is full of the blue starch paste. Be sure that this small tube is broken so as to leave each end square and full of paste. Examine under low-power microscope.

Determination of Enzyme. — Immediately after delivery of

* Method II as usual by Dr. Ferris (see p. 314).

the specimen, measure 2 c.c. of saliva into a test-tube. Place it in the small tube of starch paste, and heat the whole in a thermostat at from 37° to 38° C. for half an hour. The enzyme of the saliva will dissolve the paste from the ends of the tube, leaving a blue column of paste unchanged in the center of the glass tube. After half an hour, measure with a micrometer gauge the total length of the tube and the length of the blue starch paste column remaining undissolved. The difference between these two measurements represents the amount of starch digested by the enzyme. Since the quantity of ferment in any fluid varies with the square of the length of the column digested, the quantity of ferment in the saliva is found by squaring this difference. Multiply by 100 to give the enzymic index.

Proteolytic Enzyme. — (Method II.) Reagent. Dissolve 1 dg. of casein (c.p.) and 1 gram sodium carbonate in 1 liter of distilled water. Mix 1 or 2 c.c. Fehling's copper solution and 5 c.c. Fehling's alkaline solution, and add the mixture to 94 c.c. of the first solution. The color will be a light blue.

Heat 5 c.c. of the reagent in the thermostat at from 37° to 38° C. Then add 1 or 2 c.c. saliva, and watch the color. If there is a strong reaction, the color will turn pink in five seconds, indicating the presence of peptone. If the reaction is medium, a lavender color will result, indicating albumin. If there is no reaction, the color will remain a dirty blue, and will indicate unsplit casein.

Oxidizing Enzyme. — (Oxydase.) Methods I and III consist of treating 5 c.c. of saliva, diluted with an equal volume of water, with about 1 c.c. of a 1% solution of pyrocatechol. The color obtained is a characteristic brown, developing within thirty minutes.

Oxydase. — (Method II.) Take 1 c.c. of saliva, 4 c.c. of aqua distillata, twelve drops of a 10% solution of H_2SO_4, then mix and add drop by drop 0.5% water solution of metaphenylene-diamin. If there is no oxydase, it stays without color. If there

is an oxydase, there is formed triaminphenylin, which makes the solution strongly yellow. Compare the color formed with four drops and ten drops standard in aqua distillata.*

Mucin and Albumin. — (Method I.) *Mucin* may be separated after taking the gravity by the addition of a little acetic acid. It should then be filtered off, but it will be necessary to dilute and agitate, in order that a fairly clear filtrate may be obtained.

Albumin may be demonstrated in the filtrate, from which mucin has been separated by underlaying with strong nitric acid. This is Heller's test for albumin in the urine, and is best performed in a small wine-glass with round bottom and plain sides.

Mucin, Albumin and Sediments. — (Method II.)* I. Centrifuge 10 c.c. of the specimen of saliva for three minutes in a tube graduated to fortieths. Record the amount, percentage, and color of the sediment. Pour off and save the supernatant fluid; record its appearance.

II. To the precipitate add 10 c.c. of limewater, shake vigorously, and let stand for five minutes. Shake again and centrifuge. The difference between the total sediment and this reading gives amount of mucin and nuclear albumin which the limewater has dissolved. Record the percentage of the mucin in the sediment.

III. To 2 c.c. of the fluid saved from I add 8 c.c. distilled water. A cloudy appearance indicates the presence of globulin. Centrifuge, and record the amount.

IV. (*a*) To the fluid remaining from II add 10 drops of glacial acetic acid. A precipitate indicates dissolved mucin. Centrifuge, and record the amount and percentage of mucin.

(*b*) If the saliva is thin, and if it gives only a trace of dissolved mucin that settles easily, repeat, using the whole of the liquid remaining from I. Save the liquid, and subtract the amount of globulin from the percentage of the precipitated mucin.

* Dr. H. C. Ferris.

(*c*) If the saliva is viscid, and if it becomes cloudy in (*a*) without the separation of a precipitate, take 2.5 c.c. of the liquid remaining from I, add 7.5 c.c. neutralized 95% alcohol, shake well, and let stand for five minutes. Then centrifuge and record the amount of dissolved proteins in the saliva. Pour off and save the liquid.

Add limewater to the precipitate, shake well, let stand for two or three hours, and centrifuge to determine the amount of mucin dissolved from this precipitate.

V. (*a*) To the liquid remaining from IV (*a*), or IV (*b*) add 1 c.c. of 10% solution of potassium ferrocyanid. If albumin is present, the specimen will become cloudy. Centrifuge as before, and record the amount of albumin.

(*b*) To the liquid remaining from IV (*c*) add 1 c.c. nitric acid to see if there be a precipitate.

Also to the liquid in IV (*a*), when the precipitate will not settle, add 1 c.c. of 10% solution of potassium ferrocyanid and centrifuge. Subtract the amount of mucin found in IV (*c*) to find the quantity of albumin.

Total Solids and Ash. — (Method II.) These should be determined immediately upon the arrival of the specimen to avoid error through evaporation of moisture.

Use a platinum or fused silica dish of constant weight which has been kept in a desiccator over sulphuric acid. Weigh the dish accurately and rapidly, then introduce $2\frac{1}{2}$ c.c. of the well-mixed specimen and heat in a drying oven, not over 100° C., for two hours. Then place in the desiccator over sulphuric acid for twelve hours or longer, and weigh accurately and rapidly.

The difference between these weights represents the weight of total solids. To calculate the percentage, divide by two and one-half times the specific gravity.

Add to the dish two or three drops of fuming nitric acid, and heat over a flame, keeping the dish two inches above the top of the flame, until the black color has become white. Heat

in the direct flame until glowing, place at once in desiccator to cool for one or more hours, and weigh. Calculate the percentage of ash in same manner as of total solids.

(Method III.) Total solids and ash are best obtained as follows: evaporate over a water bath 5 c.c. of the sample (10 if possible) thoroughly mixed with a weighed amount (half a gram) of ignited magnesium oxid. The weight of residue (less the magnesia) obtained by drying at 100° C., gives the total solids. These may be ignited until white ash is obtained and again weighed. The second weight (less magnesia) gives the ash.

The use of the magnesium oxid serves to retain carbonates and chlorids in the total solids and the chlorids in the ash. It also obviates the necessity of oxidation with nitric acid, which would decompose many of the inorganic constituents of the ash.

To determine weight of sediment. Obtain total solids as above; then if a portion of the saliva is carefully filtered and the solids determined in the clear filtrate by the same method, the difference between the two determinations of solids will be the weight of sediment, epithelium, leucocytes, etc.

Crystals from the Dialyzed Saliva.

To obtain characteristic crystals, as has been explained in considering the subject of micro-chemistry, uniformity as to conditions under which the crystallization takes place is a necessity. In the case of saliva, however, we are not producing new compounds, but simply searching for compounds already formed and existing in unknown proportions in the samples tested. It is therefore necessary to make several preparations of each sample, in order that we may obtain the widest range of possibility for characteristic crystallizations. The following method of procedure will usually give satisfactory results: For a dialyzer use a fairly wide glass tube, over one end of which has been tightly tied a piece of parchment (Fig. 26), or better,

PLATE VIII. — ANALYSIS OF SALIVA.



FIG. 1.
Ammonium Chloride.

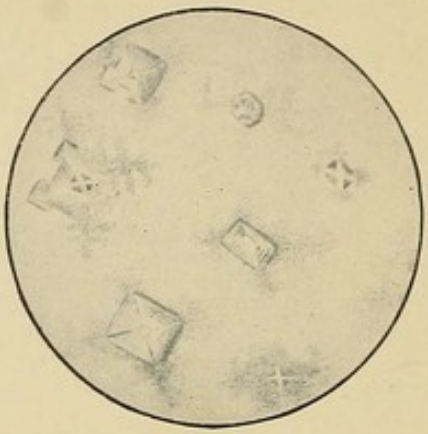


FIG. 2.
Sodium Chloride, $\frac{1}{8}\%$.

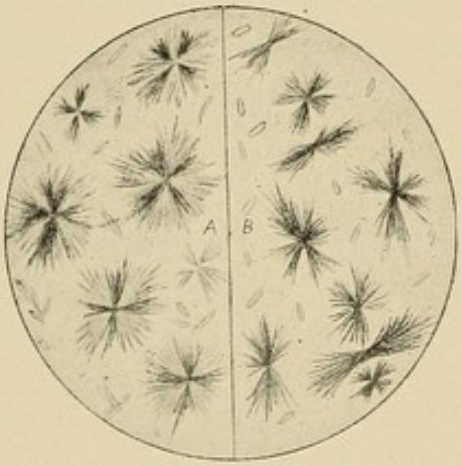


FIG. 3.
A, Magnesium Lactate (P. L.).
B, Calcium Lactate (P. L.).

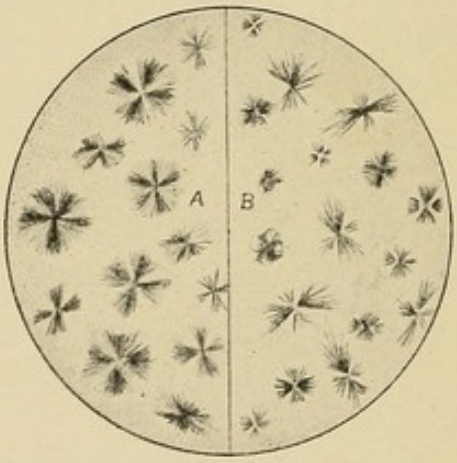


FIG. 4.
A, Magnesium Acid Lactate.
B, Calcium Acid Lactate.

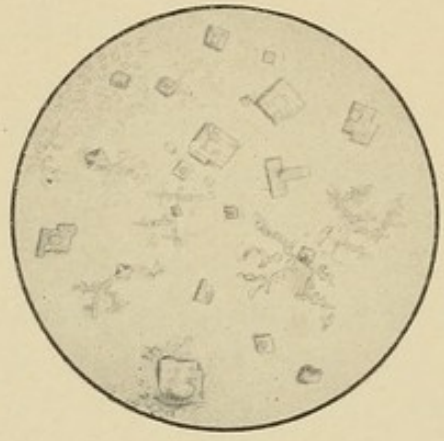


FIG. 5.
Potassium Chlorid, $\frac{1}{8}\%$ Solution.

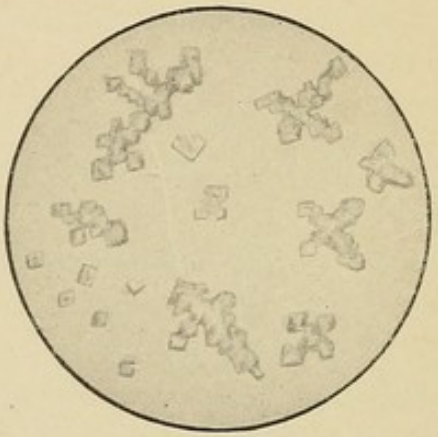


FIG. 6.
Potassium Chlorid, $\frac{1}{4}\%$ Solution.

a small dialyzing tube made entirely of parchment. Place about 15 c.c. of saliva in the dialyzing tube, and suspend it in a small beaker or wine-glass which contains an equal volume of distilled water. At the end of twenty-four hours the distilled water will contain the dialyzable salts in nearly the same concentration as existed in the original saliva. Take four previously prepared cell-slides (microscope slides on which a ring of Bell's or other microscopical cement has been placed) and fill each cell full of the dialyzed saliva. Put number 1 in a warm place that it may evaporate rapidly, leave number 2 exposed to the air at the room temperature and it will dry in from half to three-quarters of an hour. Place number 3 under a large beaker, or small bell-jar, and cover number 4 with a cover-glass, and from time to time examine the crystals that may be formed. Numbers 3 and 4 will probably take several hours, perhaps several days, before crystallization is complete. When the crystals have appeared, the preparation may be preserved by mounting in xylol balsam. In attempting to obtain crystals from the saliva before dialyzation, results are usually unsatisfactory, owing to the presence of mucin and other organic substances which interfere with the crystallization. The crystals obtained by this method are principally sodium oxalate, lactates, and acid lactates of lime and magnesia, and rarely urates of the alkalis. (For forms of these crystals see Plate VIII, Figs. 3 and 4, and Plate II, Fig. 4, pp. 327 and 162.)

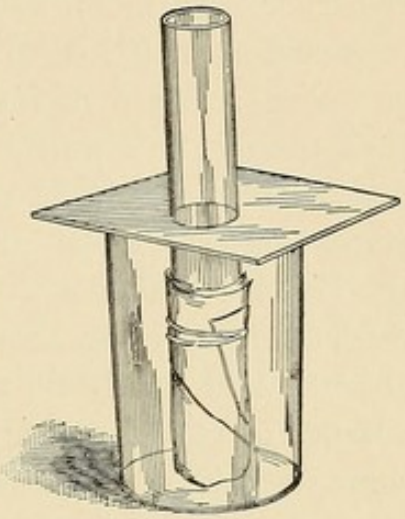


FIG. 26.

LABORATORY EXERCISE LXX.

Exp. 214. *Action of Saliva upon Starch.* — Take some filtered saliva in a test-tube and place in the water-bath at 40° C.,

for five or ten minutes. Put some starch paste into a second test-tube and place this also in the water-bath for a while, then mix the two (10 c.c. of starch paste to 3 c.c. of undiluted saliva) and return to the water-bath. The starch is changed first to soluble starch (if originally a thick paste, it becomes fluid and loses its opalescence), then to erythrodextrin, which gives a red color with iodin, and finally to achroodextrin, which gives no reaction with iodin, and to maltose. Prove these changes as follows: Every minute or two take out a drop of the mixture, place it on a porcelain plate, and add a drop of iodin solution. This gives first a blue color, showing the presence of starch; later a violet color, due to the mixture of the blue of the starch reaction with the red caused by the dextrin; next a reddish-brown color, due to erythrodextrin alone (starch being absent), and finally no reaction at all with iodin, proving the absence of starch and erythrodextrin. The fluid now contains achroodextrin and maltose. Test for the latter with Fehling's solution and with Barfoed's reagent.

Exp. 215. *Influence of Conditions on Ptyalin and its Amylolytic Action.* — Report and explain the results of the following experiments:

(*a*) Boil a few cubic centimeters of the saliva, then add some starch paste, and place in the water-bath at 40° C. After five minutes test for sugar.

(*b*) Take two test-tubes: put some starch paste in one, and saliva in the other, and cool them to 0° C., in a freezing mixture. Mix the two solutions, and keep the mixture surrounded by ice for several minutes, then test a portion for sugar. Now place the remainder in the water-bath at 40° C., and after a time test for sugar.

(*c*) Carefully neutralize 20 c.c. of saliva with very dilute HCl (the 0.2% diluted), and dilute the whole to 100 c.c. Test the action of this neutralized saliva on starch.

(*d*) To 5 c.c. of starch paste add 10 c.c. of 0.2% HCl and

5 c.c. of neutral saliva, and expose the mixture for a while at 40° C., and test for sugar.

(*e*) To 5 c.c. of starch paste add 10 c.c. of a 0.5% solution of Na_2CO_3 and 5 c.c. of neutral saliva, and expose the mixture for a while at 40° C., and test for sugar.

(*f*) Carefully neutralize (*d*) and (*e*), and again test the action of the two on starch.

(*g*) Mix a little uncooked starch with saliva, expose to a temperature of 40° C. for a while, and test for sugar.

Exp. 216. In three separate test-tubes place a few cubic centimeters of dilute solutions of KCNS or NH_4CNS, of meconic acid, and of acetic acid; add to each a few drops of ferric chlorid, and notice that a similar color is obtained in each case. Divide the contents of each tube into two portions, and to one set add HCl; to the other add mercuric-chlorid solution. Formulate a method of distinguishing from the sulphocyanates, meconates, and acetates.

Tests for Abnormal Constituents.

Acetone, glycogen, and dextrin have already been considered. Urea may be demonstrated as follows: To a given volume of saliva add twice as much alcohol. This serves to precipitate proteins. Filter and evaporate on a water-bath till original volume is reached, or evaporate to less than original volume, and make up with distilled water. Then determine urea with Squibb's apparatus, as used for urine, except that in this case it will be necessary to replace the 2-c.c. pipette with a small burette, and introduce 10 c.c. of the prepared saliva. Then it will be necessary to allow for these 10 c.c. by subtracting this amount from the volume of water received in the graduated cylinder, and the remaining number of cubic centimeters, multiplied by two, will correspond to the urea in 20 c.c. of the sample. The percentage shown on the card, divided by ten, will give the per cent of urea required. See also method by Dr. H. C. Ferris on page 320.

Lactic, *butyric*, and *acetic acids* may each be tested for, qualitatively, by the methods given under gastric digestion (q. v.).

Mercury. — A very delicate test may be made for this metal as follows: Collect as large a sample of saliva as possible, dilute with an equal volume of water, acidify with a few drops of HCl, throw in a few very small pieces of copper-turnings, which have been recently cleaned in dilute HNO_3, and boil for at least one-half hour, keeping up the volume by occasional additions of water. Remove the copper-filings, dry thoroughly on filter-paper, and place in a large-sized watch-glass (3 inches). In another watch-glass of similar size place one drop of solution of gold chlorid, and quickly invert so that the drop remains hanging on the under side of the glass. Now place this watch-glass directly over the one containing the copper, so that the chlorid of gold shall be suspended directly above the turnings and perhaps a half inch from them, then gently heat the lower watch-glass with a very small flame, when the slightest trace of mercury, which may have been deposited upon the copper, will be volatilized, reducing the chlorid of gold, and causing a purplish ring to appear around the edge of the drop. If no reduction of the gold occurs, mercury is absent.

Lead, which occasionally occurs in saliva, may be detected by the methods given under urine.

Microscopical examination of the sediment should be made in every instance. Normal saliva will contain epithelium from various parts of the oral cavity, an occasional leucocyte, and occasional mold fungi, leptothrix, etc. Constituents, which perhaps are not properly classed as normal and at the same time are not pathological, are fat globules, a rare blood-corpuscle, sarcinæ, extraneous material as food particles, starch granules, muscle fibers, etc. An excessive amount of blood, fat, pus, or micro-organisms would, of course, indicate pathogenic conditions. The bacteriological investigation of samples of saliva is always of interest, and may be necessary, but the detailed methods of such investigation do not lie within the scope of this work.

CHAPTER XXXV.

GASTRIC DIGESTION.

DIGESTION begins with the action of the saliva upon the carbohydrates, and if mastication is sufficiently prolonged, the ptyalin may convert an appreciable quantity of starchy food into a more soluble form before it reaches the stomach. In the stomach the amylolitic action of the saliva is stopped by the contact with the gastric juice. A certain amount, however, of salivary digestion takes place within the stomach, due to the fact that considerable time necessarily elapses before the acid of the gastric juice has been secreted in sufficient quantity to completely permeate and acidify the mass of food received from the œsophagus. As has been previously shown, a very feeble degree of acidity is conducive to the activity of the amylolytic ferment. The average alkalinity of the saliva, calculated as Na_2CO_3, is about 0.15 of 1%.

The first step in the gastric digestion is probably the union of the stomach HCl with the proteins, forming acid albumins (metaproteins) or allied bodies which are changed by pepsin, which is the active digestive ferment of the stomach, into the albumoses (proteoses), and slight amounts of the various peptones, following practically the changes produced experimentally on page 332.

Pepsin is an active proteolytic enzyme occurring in the cells of the stomach-wall as pepsinogen, which is decomposed by the HCl with the formation of free pepsin. Pepsin works only in faintly acid solutions, and in the stomach carries the digestion of proteins but little beyond the stage of the proteoses.

Hydrochloric acid is obtained from the fundus glands by an

interchange of radicles between alkaline chlorids and the carbonates of the blood.* The quantity present varies from 0 to 3/10 per cent, 0.18% being about the most favorable for peptic activity. Aside from HCl, various organic acids may be present in the stomach contents; lactic acid, butyric acid, and acetic acid are the most important of this class, tests for which are referred to under analysis of gastric contents.

Hydrochloric acid combines with protein substances of the food, forming a rather unstable compound in which condition the acid is known as combined hydrochloric acid in distinction from the free hydrochloric acid which the gastric juice may also contain. The combined HCl possesses only in modified form the properties of free HCl, and hence is less liable to stop the digestive action of ptyalin from the saliva.

Rennin is a second enzyme found in the stomach. This, like pepsin, also exists as a zymogen, and is liberated or developed by the presence of acid. Its action is particularly the curdling of milk, i.e., the decomposition of caseinogen (Exp. 222), and consequent coagulation of the casein. A third enzyme, existing in the stomach in very small quantities, is a gastric lipase, or stomach steapsin, a fat-splitting enzyme, the action of which is comparatively weak and of but slight importance.

Laboratory Exercise LXXI.

Analysis of Gastric Contents and Experiments with Pepsin.

The following solutions will be found in the laboratory:

A. *A 0.2% Solution of HCl.* — This is prepared by diluting 6.5 c.c. of concentrated HCl (sp. gr. 1.19) with distilled water to 1 liter.

B. *A Solution of Pepsin.* — Prepared by dissolving two grams of pepsin in 1000 c.c. of water.

* Long's Physiological Chemistry.

C. *A Pepsin-hydrochloric-acid Solution.* — Prepared by dissolving two grams of pepsin in 1000 c.c. of solution A.

Or, add to 150 c.c. of solution A about 10 c.c. of the glycerol extract of the mucous membrane of the stomach.

Exp. 217. Take five test-tubes and label *a*, *b*, *c*, *d*, *e*. Fill as indicated below. Place in a water-bath at 40° C., and examine an hour later, and again the next day.

(*a*) 3 c.c. pepsin solution + 10 c.c. water + a few shreds of fibrin.

(*b*) 10 c.c. 0.2% HCl + a few shreds of fibrin.

(*c*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, and a few shreds of fibrin.

(*d*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, boil, and then add a few shreds of fibrin.

(*e*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, and a few shreds of fibrin which have been tied firmly together into a ball with a thread.

Make a note of all changes.

Exp. 218. Filter *c*. Neutralize with dilute Na_2CO_3. Filter again. Why? Test the filtrate for the biuret reaction.

Exp. 219. To 5 grams fibrin add 30 c.c. of the pepsin solution and 100 c.c. 0.2% HCl. Set in the water-bath at 40° C., stirring frequently, and leave in the water-bath overnight. Observe the undigested residue, on the following day, and also a slight flocculent precipitate. What is this precipitate?

Filter and carefully neutralize the filtrate. A precipitate varying with the progress of the digestion will form. What is it?

Remove this by filtration, and saturate this filtrate with $(NH_4)_2SO_4$. Filter. Save precipitate and filtrate. Of what does each consist?

Exp. 220. Dissolve the last precipitate of Exp. 219 in water, and try the following tests:

(*a*) Biuret reaction.

(*b*) Effect of boiling.

(*c*) Test with NHO_3, as in performing test for albumin in the urine, page 359.

Exp. 221. To the last filtrate of Exp. 219 add an equal volume of 95% alcohol, and stir thoroughly. The peptones will collect in a gummy mass about the stirring-rod.

(*a*) Determine the solubility of peptones in water.

(*b*) What is the effect of heat when so dissolved?

(*c*) Try the biuret reaction.

Exp. 222. *Demonstration of the Rennet Enzyme.* — Place 10 c.c. of milk in each of three test-tubes. Label the test-tubes 1, 2, 3.

To 1 add a drop of neutralized glycerol extract of the mucous membrane of the stomach (made from the stomach of the calf).

To 2 add a drop of neutralized glycerol extract, and boil at once.

To 3 add a few cubic centimeters of $(NH_4)_2C_2O_4$ solution, and then a drop of a glycerol extract.

Place these tubes in the water-bath at 40° C., and examine after five to ten minutes. Explain results in each case.

Continue heating tube 3 for half an hour, then add 2 or 3 drops $CaCl_2$ solution. The liquid instantly solidifies. Why?

Exp. 223. *Digestion of Casein.* — Determine the products of the digestion of the curd from the last experiment.

Exp. 224. *Tests for Free Hydrochloric Acid.* — Try each of the following tests with (*a*) HCl (0.2%, 0.05%, and 0.01% successively); (*b*) lactic acid (1%); (*c*) mixtures containing equal volumes of (*a*) and (*b*). Tabulate the results.

(*a*) *Dimethylaminoazobenzene.* — Use one or two drops of a 0.5% alcoholic solution. In the presence of free mineral acids a carmine-red color is obtained.

(*b*) *Gunzburg's Reagent.* — Phloroglucin, 2 grams; vanillin, 1 gram; alcohol, 100 c.c. Place two or three drops of the solu-

tion to be tested in a porcelain dish, add one or two drops of the reagent, and evaporate on a water-bath. In the presence of free hydrochloric acid a rose-red color develops.

(*c*) *Boas' Reagent.* — This is prepared by dissolving 5 grams of resublimed resorcinol and a gram of cane-sugar in 100 grams of 94% alcohol. Take three or four drops each of the reagent and the solution to be tested, and cautiously evaporate to dryness. In the presence of a free mineral acid a rose or vermillion red color is obtained. This gradually fades on cooling.

(*d*) *Tropæolin OO.* — Use one or two drops of a saturated alcoholic solution.

(*e*) *Congo-red.* — Use filter-paper which has been dipped into a solution of the reagent and then dried.

Exp. 225. To 5 c.c. egg-albumin in solution add 1 c.c. of 0.2% HCl. Mix thoroughly, and test for the presence of free HCl. What is the result? How do you explain it? Repeat the test, using a solution of peptone in place of the egg-albumin.

Exp. 226. *Tests for Lactic Acid.* — Uffelmann's reagent. Mix 10 c.c. of a 4% solution of carbolic acid with 20 c.c. of water, and add a drop or two of ferric chlorid.

To 5 c.c. of the reagent add a few drops of the lactic-acid solution. Note the canary-yellow color.

Does the presence of free HCl interfere with this reaction?

A more delicate reagent is obtained by adding three or four drops of a 10% ferric-chlorid solution to 50 c.c. of water. Such a solution has a *very faint* yellow color, which is distinctly intensified by lactic acid.

Using 5 c.c. of this nearly colorless solution for each experiment, note the effect of (*a*) 0.2% HCl; (*b*) acid phosphate of sodium; (*c*) alcohol; (*d*) glucose; (*e*) cane-sugar. What conclusions do you reach concerning the value of this test, when applied directly to the gastric contents?

The test is best applied to an aqueous solution of the ethereal extract of the gastric contents. Add to the contents two drops

of HCl, boil to a syrup, and extract with ether. Dissolve the residue obtained upon evaporation of the ether in a little water, and test for lactic acid.

Exp. 227. Test for butyric acid; see ethyl butyrate, page 207.

Exp. 228. Test for acetic acid; see acetates (page 94).

Exp. 229. The acidity of the gastric contents may be determined as follows: To 5 c.c. of the filtered contents, diluted with 25 to 30 c.c. of water in an Erlenmeyer flask, add 2 or 3 drops of a solution of dimethylaminoazobenzene. Titrate with N/10 alkali till the color changes to a yellow which fairly matches the indicator; this represents the free HCl. To this mixture add a few drops of phenolphthalein solution, and continue the titration until a permanent pink color is obtained. The N/10 alkali used will represent the total acidity, combined HCl and organic acids. The organic acids will not be present in gastric contents in the presence of any appreciable amount of free HCl, as they are derived almost entirely from fermentations which are inhibited by the hydrochloric acid.

CHAPTER XXXVI.

PANCREATIC DIGESTION AND BILE.

It may be an aid, in remembering the various digestive ferments, to note that in the saliva we have one principal ferment, ptyalin; in the stomach we have two principal ferments, pepsin and rennin; in the pancreatic juice, three active ferments. The first is a proteolytic enzyme, known as *trypsin*, which continues the work of the gastric juice, and converts the proteoses into peptones, tyrosin, leucin, etc.

Trypsin is the proteolytic enzyme of the pancreatic juice. It is a much more energetic digestive agent than the pepsin found in the stomach, but it differs in that it acts in an alkaline media rather than an acid. Trypsin exists, like other proteolytic enzymes, as a parent enzyme, trypsinogen, which in itself is not a digestive ferment, but which is rendered active (activated) by another substance known as enterokinase.

The enterokinase occurs in the intestinal juice, and seems to be secreted only as it is needed for the activation of the trypsinogen. Enterokinase does not in itself possess digestive power, but its action is destroyed by heat and in this it resembles the enzymes.

Amylopsin is the starch digesting enzyme of the pancreatic juice. Here, again, we have an enzyme much more energetic in its action upon carbohydrates than the ptyalin of the saliva. It converts starch into maltose and to some extent to dextrin. The amylopsin is active in faintly alkaline or very faintly acid solution; more acid, however, retards its action.

Steapsin is the fat-splitting enzyme of the pancreatic juice. It splits the fat, as indicated on page 209, into glycerol and

fatty acids, and also acts as an emulsifying agent. The free fatty acids thus formed unite with the alkaline bases found in the intestines to form soaps, which are also active emulsifying agents.

The pancreatic juice and the bile enter the duodenum in very close proximity, and the digestive action of each is dependent, to a considerable extent, upon the presence of the other.

Bile. — A secretion produced by the liver and stored in the gall-bladder, from which it is delivered to the intestines, where it aids materially in emulsification and absorption of the fats.

Composition of Bile. — Its composition is very complex, but there are two acids and two coloring matters which are of particular importance, and derivatives of which indicate the presence of bile in saliva, urine, blood, etc. The acids are taurocholic and glycocholic, existing principally as sodium or potassium salts. The coloring matters are bilirubin and biliverdin; the former predominates in human bile and the latter in ox bile. Glycocholic acid upon hydrolysis splits into a simpler acid (cholalic) and glycocoll, glycocoll being an amino-acetic acid (page 222), which is undoubtedly an antecedent of urea. Both of the bile-pigments are derived from the coloring matter of the blood. The appearance of either of these or of their derivatives, in either urine or saliva, is indicative of pathological conditions either of the liver- or bile-ducts, causing obstruction to the outflow of the bile or a destruction of the red-blood corpuscles.* The blood pigments, according to Michaels, are easily demonstrable in the desiccated saliva by means of polarized light.

The intestinal juice contains a number of substances playing an important part in the preparation of food material for assimilation. Among them is erepsin (erepase). This is a protein-splitting enzyme acting upon the products of tryptic digestion. It has little power upon the simple proteins, but will

* Ogden.

split the peptones into amino acids. There are also in the intestinal juice certain amylolytic enzymes which continue the digestive action started byamylopsin or by ptyalin of the saliva.

Secretin, excreted by the mucous membrane of the intestine, is a substance differing materially from the digestive ferments in that it is not destroyed by heat. It acts not as an activator in the sense that it starts specific chemical action, but as an essential constituent for the secretion of the various digestive fluids; i.e., the secretin in the blood starts the flow of pancreatic juice, for instance, which contains the parent enzyme, trypsinogen, which in turn requires the action of enterokinase before it is in condition to perform its digestive action. Some authorities claim that the secretin itself exists as a pro-secretin, from which it is liberated by action of acid.

Laboratory Exercise LXXII.

Experiments with Pancreatic Juice.

Exp. 230. *Proteolytic Action.* — To 25 c.c. of a 1% solution of Na_2CO_3 add a few drops of the pancreatic extract. Place some pieces of fibrin in this liquid, and keep in the water-bath at 40° C. till the fibrin has disappeared (one or two hours probably). Observe the digestion from time to time. Note that the fibrin does not swell and dissolve as in gastric digestion, but that it is eaten away from the edges.

Filter. What is the precipitate? Carefully neutralize the filtrate with 0.2% HCl. Another precipitate may appear. What is this?

Again filter, if necessary, and test the filtrate for proteoses and peptones as directed under gastric digestion.

Exp. 231. *Formation of Leucin and Tyrosin.* — Perform a similar experiment, using boiled fibrin and adding a few drops of a 20% solution of thymol, or a few drops of chloroform water.

Why use boiled fibrin, and why add thymol or chloroform? Digest for forty-eight hours, and then examine as follows: Filter, neutralize, and concentrate by evaporation on the water-bath. Crystals of tyrosin (and possibly leucin) usually separate. Examine microscopically.

Exp. 232. *Amylolytic Action.* — To some starch paste in a test-tube add a drop or two of the pancreatic extract and place in the water-bath at 40° C. After a few minutes test for sugar and report the result.

Exp. 233. *The Piolytic (Fat-splitting) Action.* — For the demonstration of this action use natural pancreatic juice, or finely divided fresh pancreas, or a *recently prepared* extract.

To some perfectly neutral olive-oil, colored faintly blue with litmus, add half its volume of the pancreatic extract, shake thoroughly, and keep at 40° C. for twenty minutes. Record the result. Reserve for next experiment.

Exp. 234. *Emulsifying Action.* — To 10 c.c. of a 0.2% solution of Na_2CO_3 add a few drops of the mixture used in Exp. 233. Shake thoroughly, and report the result. Referring to the earlier experiments on emulsification (see Fats), explain the efficacy of the pancreatic juice in emulsifying fats.

Laboratory Exercise LXXIII.

Experiments with Bile.

Exp. 235. *Color.* — Note the difference in color between human bile and ox bile. Explain.

Exp. 236. *Reaction.* — Dilute some bile with four parts of water. Immerse a strip of red litmus-paper, then remove and wash with water. Note the reaction.

Exp. 237. *Nucleo-albumin.* — Dilute bile with twice its volume of water, filter if necessary, and add acetic acid. What is the precipitate? How distinguished from mucin?

Exp. 238. Filter 237 and test the filtrate for proteins. Report the result.

Exp. 239. *Separation of Bile Salts.* — Mix 20 c.c. of bile with animal charcoal to form a thick paste, and evaporate on the water-bath to complete dryness. Pulverize the residue in a mortar, transfer to a flask, add 25 c.c. of absolute alcohol, and heat on the water-bath for half an hour. Filter. To the filtrate add ether till a permanent precipitate forms. Let the mixture stand for a day or two, and then filter off the crystalline deposit of bile salts. Save the filtrate which contains cholesterin. (Plate VII, Fig. 4, page 296.)

Exp. 240. *Bile-pigments.* — (*a*) *Gmelin's Test.* — Take some bile in a wine-glass and underlay with *yellow* HNO_3, in the manner described in testing saliva for albumin. Notice the play of colors, beginning with green and passing through blue, violet, and red to yellow, at the junction of the two liquids. Explain.

(*b*) *Iodin Test.* — Place 10 c.c. of dilute bile in a test-tube, and add slowly two or three cubic centimeters of dilute tincture of iodin, so that it forms an upper layer. A bright green ring forms at the line of contact.

Exp. 241. *Cholesterin.* — Examine under the microscope the crystals obtained by the cautious evaporation of the alcohol-ether filtrate of Exp. 239. For color reactions refer to demonstrations.

Exp. 242. *Action of Bile in Digestion.* — (*a*) Take three test-tubes. In one mix 10 c.c. of bile and 2 c.c. of neutral olive-oil; in the second, 10 c.c. of bile and 2 c.c. of rancid olive-oil; in the third, 10 c.c. of water and 2 c.c. of neutral oil. Shake and place in a water-bath at 40° C. for some time. Note the extent and the permanency of the emulsion in each case.

(*b*) Into each of two funnels fit a filter-paper. Moisten one with water and the other with bile, and into each pour an equal volume of olive-oil. Set aside for twelve hours (with a beaker

under each funnel). Do you notice any difference in the rate of filtration?

(*c*) Add drop by drop a solution of bile salts to (*a*) a solution of egg-albumin; (*b*) a solution of acid-albumin; (*c*) a solution obtained by digesting a bit of fibrin in gastric juice and filtering. Explain the results.

PART VIII.

URINE.

CHAPTER XXXVII.

PHYSICAL PROPERTIES OF URINE.

URINE is a solution of waste products from the blood. It contains, normally, certain coloring matter, urea, uric acid in combination with alkaline bases, various organic constituents in slight amounts, including, perhaps, albumin and sugar, chlorid of sodium, sulphates and phosphates of the alkalis and the alkaline earths. Abnormally the urine may contain albumin, sugar, uric acid as such, bile, salts of the heavy metals, lead, mercury, and arsenic; occasionally albumose, peptones, lactates, acid lactates, oxalates, carbonates, hippuric acid, also organic compounds, resulting from insufficient or imperfect oxidations, as amino-acids, leucin, tyrosin, and acetone bodies.

We are to study the urine, not primarily with a view to the diagnosis of renal disease, which is more particularly the province of the physician, but to detect irregularities or deficiencies in the body metabolism, and, as far as possible, we are to study the methods whereby we may correct and regulate the malnutrition which lies at the foundation of many diseases of the oral cavity. As has been previously stated by the author,* if there are diseases of the oral cavity which may have their etiology in some systemic derangement not easily apparent, and if such diseases are to receive the attention of the dentist, he should obtain all possible light on every case, and at present

* International Dental Journal, January, 1905.

a quantitative analysis of the urine is of greater value than any other laboratory aid. In examining a sample of urine to obtain information as above indicated, it is essential that the sample be a portion of the *mixed* twenty-four-hour quantity, and that the total amount of the twenty-four-hour excretion be known. In collecting samples for such analysis a convenient method is to give the patient a one- or two-dram vial, nearly filled with water, and containing three or four drops of a commercial formaldehyd solution, with instructions to empty this into the bottle, or other receptacle, in which the twenty-four-hour sample is collected. Formaldehyd if used in this amount has no effect on the subsequent analysis and is a sufficient preservative.

Physical Properties.

Quantity. — The quantity of urine passed in twenty-four hours normally is about 1200 to 1400 c.c. for an adult female and 100 or 200 c.c. more than this for the male. The amount is increased in Bright's disease, in diabetes, and various other pathological conditions, also in cold weather when less moisture is given off from the skin. Normally, the quantity passed during twelve day hours, as 8 A.M. to 8 P.M., will exceed the amount overnight from 8 P.M. to 8 A.M. In cases of chronic interstitial nephritis the twelve-hour night quantity exceeds the day, hence it is desirable in collecting a twenty-four-hour sample to divide the time as suggested, and measure the amounts separately, especially if there is any suspicion of any chronic kidney disease. A diminished quantity of urine may indicate simply a diminished amount of water taken into the system. The urine is diminished pathologically in acute conditions, such as fevers, etc., but such samples rarely reach the dental practitioner.

Color. — The normal color of the urine is usually given as straw color or pale yellow. If lighter than this the color is regarded as pale, if darker than normal it is regarded as high.

The urine may also be colored by various abnormal constituents; it may be bright red from the presence of blood, or chocolate colored with a so-called coffee-ground sediment from decomposed-blood coloring matter. It may be brown to yellow, bright blue or green, due to the ingestion of various drugs. If bile is present in any quantity in the urine it will have a dark or smoky appearance, and, upon shaking, the foam will have a distinctly yellowish or yellowish-green tint.

Appearance. — In addition to the colors mentioned above urine may sometimes have a smoky appearance, due to the presence of hematoporphyrin or iron-free hematin, often found in cases of lead-poisoning. It may have a milky appearance, due to presence of finely divided fat globules, as in chylous urine, due to parasitic disease of the blood. It may be cloudy from four principal causes: first, amorphous urates; second, amorphous phosphates; third, pus; and fourth, bacteria. These may easily be distinguished. The application of a slight degree of heat (insufficient to cause coagulation of albumin) will redissolve the urates, and clear a urine which is cloudy from this cause. A deposit of phosphates is increased by the application of heat, but clears easily upon the addition of a few drops of acetic acid. A urine cloudy from the presence of pus is not cleared by either of these methods, but the cloud settles with comparative rapidity and pus corpuscles are easily recognized by microscopical examination of the sediment. If bacteria are present in sufficient quantity to cause cloudiness, the sample is apt to be alkaline in reaction and will not clear upon filtering. If it is necessary to obtain a clear solution, a little magnesium mixture may be added to the urine, then a little sodium phosphate; warm gently with agitation, when the precipitated ammonium magnesium phosphate will mechanically carry down the bacteria, and a filtrate may be obtained which, after acidifying with dilute acetic acid, will be suitable for an albumin test.

Specific Gravity. — The gravity is most conveniently taken with a urinometer (Fig. 27). Care should be taken in the selection of this instrument so that the scale graduation may be accurate. The fact that the instrument will sink in distilled water at the proper temperature (usually 60° F., 15½° C.) to the 0 mark, is not a sufficient proof of its accuracy, as many cheap instruments will do this, and give erroneous readings at the higher markings of the scale. Distilled water is represented by 1000, and the relative increase in the comparative gravity of urines will be easily represented on the scale ranging from 1000 to 1050. As the first two figures of the specific gravity are always the same (10), they are usually omitted from the scale which is made to read from 0 to 50 or 60. The reading should be made, if possible, from underneath the surface of the liquid, as the liquid is usually drawn around the stem by adhesion, so that accurate readings from the surface are difficult. The specific gravity of normal urine is from 1018 to 1022; it decreases in cases where the quantity is much above the normal (polyurias), unless sugar is present. It is increased by the presence of sugar or by concentration, whereby the normal solids are relatively increased. In case the quantity of urine is too small for the determination of the gravity in the usual way, the urinopyknometer, devised and recommended by Dr. Saxe in his "Examination of the Urine," may be employed. See page 317, on specific gravity of saliva.

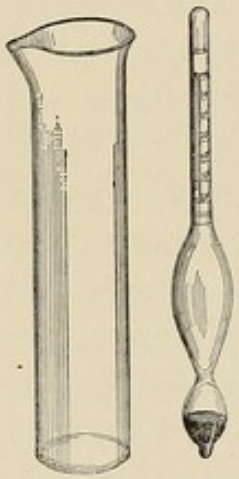


FIG. 27.

Reaction. — The reaction of urine is normally acid to litmus-paper, due to the presence of acid sodium phosphate. The degree of acidity is roughly indicated by the intensity of color produced with the carefully prepared litmus-paper. More accurate results may be obtained by a regular volumetric examination (with N/20 alkali), or by the test for urinary acidities

given by Freund and Topfer who suggest the following method:

" To 10 c.c. of the urine add two to four drops of a 1% solution of alizarin. If the resulting color is pure yellow, free acids are present; if deep violet, combined acid salts. If none of these colors appear, there are present acid salts of the type of disodic phosphate. The amount of one-tenth normal HCl standard solution required to produce a pure yellow color represents the alkaline salts, while the amount of one-tenth normal sodium hydrate required to cause a deep violet represents the acid salts."

CHAPTER XXXVIII.

NORMAL CONSTITUENTS OF URINE.

THE more important normal constituents of the urine are urea, uric acid (combined as urates), chlorids, phosphates, sulphates, indoxyl, coloring matters; traces of mucin, organic acids, carbonates, hippuric acid, creatin, and creatinin may also be present. The total normal solids are composed approximately of 50% urea, 25% chlorid of sodium; at least one half of the remainder are phosphates and sulphates. We see that the constituent which most influences the specific gravity is the urea, and in normal samples the specific gravity is an index of the amount of urea present. The total solids may be calculated by multiplying the last two figures of the specific gravity by $2\frac{1}{3}$,* which will give approximately the number of grams of solids in one liter of urine; from this the solids in the twenty-four-hour amount may be easily calculated.

UREA.

The chemistry of urea has been already considered (page 232).

Detection. — A qualitative test for this substance is obviously superfluous, although such may be made by obtaining the crystals of urea nitrate or oxalate (page 233). The quantity of urea is of great importance, especially in cases where there is any question in regard to the body metabolism or the amount of nitrogen excreted. By far the greater proportion of all nitrogenous waste is eliminated by the kidneys in the form of urea, a comparatively slight amount as other nitroge-

* Coefficient of Haeser.

nous constituents of the urine, a still smaller amount in the feces, and traces only by other avenues. The urea may be quantitatively determined by various methods, the hypobromite method being the most practical.

Quantitative Determination. — There are various forms of apparatus used in connection with this process.

The one devised by Dr. Squibb is pictured in Fig. 28. It has been quite generally used; hence its description is given. It is not recommended, because a source of considerable error

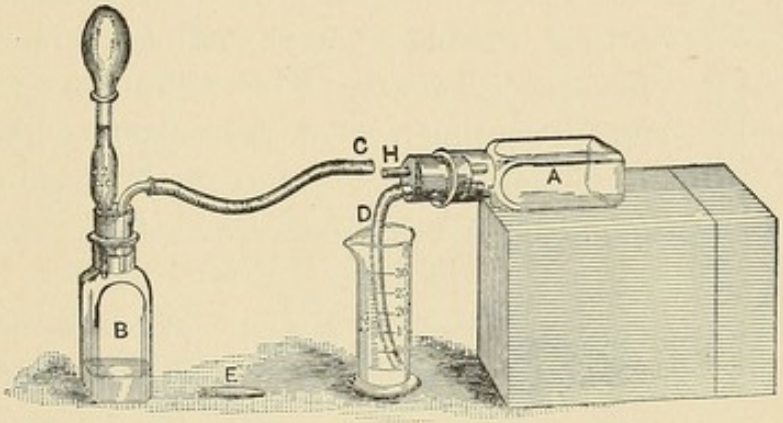


FIG. 28.

lies in the fact that the gases (CO_2 and N) evolved from the urea are very apt to be driven over into bottle *A* *before all* the CO_2 has been absorbed by the reagent in *B* and consequently the results are higher than they should be.

The first step in the use of this apparatus is to completely fill the bottle *A*, including the tubes *D* and *H*, with water, with the glass plug *E* closing the lower end of *D*. Next put 5 c.c. each of a 40% solution of caustic soda and a bromine solution in potassium bromide* into *B*. Place the stopper in *B* and connect the tube *C* at *H*, then fill accurately the 2-c.c. pipette with urine. Place in position in the stopper of *B* as shown in the cut, remove *E* from the rubber tube *D*, and

* For preparation of this solution see Appendix.

allow *D* to fall to the *bottom* of the graduate as indicated. Pressure is now applied to the bulb of the pipette, so that the 2 c.c. of urine is forced with moderate rapidity into the bottle. As the pressure on the bulb is released, water will be drawn back into *A*, and it is essential that the end of *D* be under water during this part of the process. Bottle *B* should be agitated to insure complete decomposition of the urea. Nitrogen and carbon dioxid are at once evolved according to the reaction on page 233. The 40% solution of caustic soda is strong enough to absorb and hold the CO_2. The nitrogen passes into *A*, forcing a corresponding volume of water into the graduate. This volume of gas, read in cubic centimeters of the water, will give the percentage of urea in the sample examined, 1 c.c. of nitrogen being equivalent to 0.126 gram of urea.

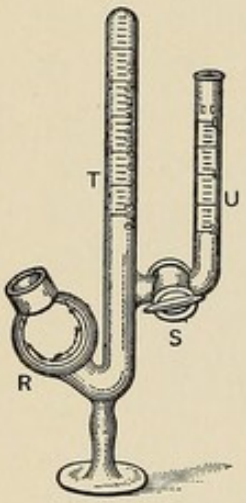


FIG. 29.

The Doremus-Hinds apparatus shown in Fig. 29 gives a perfectly satisfactory method for the estimation of urea by the hypobromite method. The reagent, equal parts of bromin solution and 40% NaOH (Appendix, page 380), is introduced into *R* and the tube completely filled. The tube *U* is next filled exactly to the 0 mark, then by means of the stop-cock *S* 1 c.c. of urine is allowed to enter *T* a few drops at a time and slowly enough to prevent any escape of gas through *R*. The gas rises in small bubbles through a comparatively long tube and remains in contact with the reagent which insures perfect absorption of CO_2, thus overcoming the greatest objection to the Squibb's apparatus.

The tube *T* is graduated to read centigrams of urea in 1 c.c. of urine.

URIC ACID.

Uric acid and its antecedents, the xanthin bases, are derived from the decomposition of nuclein and nucleoprotein. For

chemistry of this substance, see pages 235 to 237. The uric acid is increased by a highly nitrogenous diet and certain vegetable substances which contain purin (page 235) derivatives, such as coffee, tea, and cocoa. The so-called red meats, beef, mutton, etc., are regarded as the most abundant source of uric acid and urates. As previously suggested uric acid does not occur in normal urine as such, but is combined with the alkaline bases.

Detection. — It is unnecessary to make a qualitative test in urine, as urates are always present. If a qualitative test is desired the murexid test, as given on page 239, is available. Uric acid is most conveniently determined quantitatively by the centrifugal method as devised by Dr. R. Harvey Cook.* The detail of this method is as follows: Measure 10 c.c. of urine into a graduated tube, used in the centrifugal machine, add a few grains of sodium carbonate, and about 3 c.c. of strong ammonium hydrate. Place in the centrifuge, and allow to run for one or two minutes, then carefully decant the clear urine into another graduate tube, leaving the precipitate which consists of earthy phosphates. The bulk of this precipitate may be noticed and an idea obtained as to whether the earthy phosphates are present in normal quantities or not. To the clear urine add 2 or 3 c.c. of ammoniacal silver-nitrate solution ($AgNO_3$, 5 grams; distilled water, 80 c.c.; strong ammonia, 20 c.c.), and run in the centrifuge till the precipitate of silver urate has reached its lowest obtainable reading. The ammonia will prevent the precipitation of chlorids and, unless iodids or bromids are present, the precipitate will be fairly pure silver urate, each tenth of a cubic centimeter of the precipitate being equivalent to 0.001176 gram of uric acid in the 10 c.c. of urine used, or 0.01176%.

The silver precipitate is by no means pure silver urate, many of the other nitrogenous bases in urine forming insoluble silver salts. These occur only in very slight traces; so, for

* Medical Record, Mar. 12, 1898, p. 373.

clinical purposes, the method is available unless the sample contains bromids or iodids, when iodid or bromid of silver will be formed, insoluble in the amount of ammonia usually used. More accurate results may be obtained by either Hopkins' or Folin's method. These are somewhat similar and consist of precipitation of the uric acid as ammonium urate. 100 to 200 c.c. of urine is used and the precipitation effected by a saturated solution of NH_4Cl (Hopkins' method) or 10 grams ammonium sulphate (Folin's method).

The precipitate is washed in the reagent and dissolved in boiling water and the amount of uric acid determined by titration with N/20 permanganate of potassium. Each cubic centimeter of $KMnO_4$ used is equal to 0.00375 grams of uric acid.

Ammonia Determination.

The amount of ammonia normally present in urine is about 0.7 gram in the 24-hour amount. Ammonia is increased in any systemic condition resulting in an increase of acidic elements (Acidosis), or upon ingestion of ammonium salts of inorganic acids, i.e., salts not easily oxidized to urea.

Normally, the quantity of NH_3 follows more or less closely the urea and the protein metabolism, and amounts to about one-half of one per cent or about 0.7 gram in 24 hours.

Determination may be made as follows:

Folin's New Method. — Measure by use of standardized "Ostwald pipette" 1 or 2 c.c. of urine into a large Jena test-tube. Then proceed exactly according to method given for saliva on page 320.

Formaldehyd Method. — Place 10 c.c. urine in a 250 c.c. Erlenmeyer flask, add 50 or 60 c.c. H_2O, titrate with N/10 NaOH with phenolphthalein as an indicator. The amount of NaOH used will represent total acidity of sample.

After exact neutralization add 10 c.c. of previously neutralized commercial formaldehyd solution and titrate *again* with

N/10 NaOH. The *second* amount of alkali added represents ammonia as follows:

$$4\,NH_4Cl + 6\,CH_2O + 4\,NaOH = N_4(CH_2)_6 + 10\,H_2O + 4\,NaCl.$$

As the ammonium salts and the caustic soda react molecule for molecule it is possible to make calculation for quantity of NH_3 by multiplying the N/10 factor (0.0017) by the number of cubic centimeters of N/10 NaOH used.

In cases of diabetes when the ammonia reaches a comparatively large amount the figures obtained by this process will be found to be a little high, as amino-acids are also acted upon by the NaOH, and will be calculated as ammonia, but for ordinary work or clinical comparisons this method is very simple and sufficiently accurate.

This method is not affected by urea, uric acid, creatin, creatinin, purin bases or hippuric acid.*

Chlorids.

The chlorids are represented in the urine chiefly by sodium chlorid. This is present to the extent of from 12 to 20 grams in twenty-four hours. An increase above this quantity is unusual, although it simply indicates an increase in the ingested salt, and is without clinical significance. The chlorin is diminished in dropsy, acute stages of pneumonia, and in fevers generally.

Detection. — The usual qualitative test with silver nitrate and nitric acid is employed for detection of chlorid in the urine. If one drop of a strong solution of silver nitrate (1 to 8) is allowed to fall into the wine-glass in which the albumin test has been made (q. v.), the appearance of the resulting precipitate will give a rough idea of the quantity of chlorin present. If a solid ball of silver chlorid is formed which does not become

* Dr. Hans Malfatti in Zeit. für Anal. Chemie, 47, page 273.

Note. — See also the Vacuum Distillation Method, giving very exact results when properly carried out:

H. Björn Andersen und Marius Lauritzen, Zeit. für Physiol. Chemie, 64, page 21.

diffused upon gently agitating the contents of the glass, the chlorin is normal or increased. If the precipitate falls as a cloud distributed throughout the liquid, the chlorin is diminished. The chlorin may be determined by precipitation with silver nitrate in 10 c.c. of urine, and the precipitate settled in a centrifuge-tube to constant reading, but this method is not recommended, as the precipitate is a bulky one, and usually takes a long time for thorough settling. The titration with silver nitrate, using potassium chromate as an indicator, really takes less time, and is much more accurate. This titration is made in the usual way (see page 149), except that, inasmuch as phosphates and urates are also precipitated, from three-tenths to 1 c.c. may be deducted from the amount of the silver-nitrate solution used according as it is much or little, thus allowing for these substances. An accurate titration of chlorin may be made by acidifying the urine with nitric acid, adding an excess of standard silver-nitrate solution, and titrating back with a standardized sulphocyanate solution (preferably of the same strength as the $AgNO_3$ solution), using ferric sulphate as an indicator. But, as a rule, the simpler method gives results which for clinical purposes are equally valuable with those of this more tedious though more accurate process.

Phosphates.

The phosphates in the urine are of two kinds, the alkaline phosphates, Na_2HPO_4 and NaH_2PO_4, etc., and the earthy phosphates represented by the magnesium and the calcium phosphates. The phosphates are normally present to the extent of two and a half to three and a half grams, calculated as P_2O_5 (in twenty-four hours).

The triple phosphates, ammonium magnesium phosphates (Plate IV, Fig. 2, p. 163), are the forms in which phosphoric acid is usually found in urinary sediment. Crystals of acid calcium phosphate are occasionally found, and resemble the acid sodium

urate in form (Plate X, Fig. 3, p. 368), except that they are usually a little broader and more often occur in fan-shaped clusters. They may be distinguished by treatment with acetic acid, which dissolves the calcium phosphate promptly, while the urate is slowly dissolved and crystals of uric acid appear after a little time. The phosphates are deposited from neutral or alkaline urines and when this precipitation takes place within the body, the crystals cause more or less irritation to the urinary tract and may form aggregations which result in calculi. Phosphates are supplied by either a cereal or meat diet. They may be much increased in diseases accompanied by nervous waste, or by softening and absorption of bone. Phosphates are diminished in gout, in chronic diseases of the kidney, and during pregnancy.

Detection. — A qualitative test for earthy phosphates (E.P.) may be made by taking a test-tube half-full of urine, and making alkaline with ammonium hydrate. When the precipitate has thoroughly settled, if it is about 1/4 to 1/2 inch in depth, it represents normal, earthy phosphates. If this mixture is now filtered, the alkaline phosphates (A.P.) may be determined in the filtrate by the addition to the solution of one-third its volume of magnesium mixture.* The precipitate after settling will be 1/2 to 3/4 of an inch in depth if normal. The total phosphates may be determined in the centrifugal machine by adding 5 c.c. of magnesium mixture to 10 c.c. of urine. Each tenth of a cubic centimeter of the centrifugalized sediment will be equivalent to 0.0225 of P_2O_5.

A more accurate determination of the total phosphoric acid may be made by the titration with uranium nitrate or acetate solution as follows:

Reagent Required. — *First.* A standard solution of uranium nitrate or acetate made by dissolving 35.5 grains of pure salt (the molecular weights of the two salts differ so little that the

* See Appendix.

same weight of either may be used) in sufficient water to make 1000 c.c.

Second. A sodium acetate solution containing 100 c.c. of 30% acetic acid and 100 grams of sodium acetate in enough distilled water to make 1000 c.c.

Third. An indicator consisting of a saturated solution of potassium ferrocyanid.

Process. — Place 50 c.c. of urine with 5 c.c. of sodium acetate solution above described in a small Erlenmeyer flask and heat nearly to the boiling-point. Titrate, while hot (80° or above), with the standard uranium solution till a drop of the mixture placed on a white porcelain tile with a drop of the indicator (K_4FeCy_6) gives a distinct brown color. This method of determining the end point is known as "spotting" and with a little practice gives very accurate results.

The number of cubic centimeters of uranium solution multiplied by 0.01 will give the weight of P_2O_5 in 100 c.c. of urine (1 c.c. of reagent being equal to 0.005 gram P_2O_5).

Sulphates.

The sulphates in the urine are present as alkaline sulphates, K_2SO_4 and Na_2SO_4; also as ethereal sulphates, represented by such compounds as indoxyl potassium sulphate, page 250.

Detection and Determination. — The sulphates may be detected by precipitation with barium chlorid in HCl solution. If the precipitate is obtained from 10 c.c. of urine and centrifugalized to constant reading, the per cent of sulphuric acid by weight will be one fourth of the volume per cent of the precipitate. The sulphates follow rather closely the urea, and their determination is not of great importance. They are increased in acute fevers, diminished in chronic diseases generally, and markedly diminished in carbolic-acid poisoning. (Ogden.)

Coloring Matter. — Urobilin, an important coloring matter of the urine, exists as a parent substance or chromogen to which

has been given the name urobilinogen. This undergoes decomposition by action of light with liberation of urobilin.

Urobilin is without doubt derived from the bilerubin of the bile, which, in turn, comes from the hemochromogen of the blood. Dr. J. B. Ogden is authority for the statement that "it is safe to infer that the amount of urobilin in the urine is a measure of the destruction of the hemoglobin or blood pigment."

Urochrome is a pigment to which the yellow color of urine is chiefly due. Uroerythrin and urorosein are less important, existing only in very slight quantities, but they are responsible for colors of some sediments and of decomposition products which are noticed in analysis.

Indoxyl.

The indoxyl is of considerable importance, as an increase above the normal amount is indicative of increased putrefaction of nitrogenous substances taking place in the small intestine. Indoxyl may also be increased by acute inflammatory process of the peritoneal cavity. Ordinary constipation does not increase the indoxyl. The test for indoxyl depends upon the oxidation of the indoxyl potassium sulphate to indigo blue according to the following reaction:

$$2\,C_8H_6NKSO_4 + O_2 = 2\,C_8H_5NO + 2\,KHSO_4.$$

Indoxyl potassium sulphate. Indigo.

Detection and Determination. — 15 c.c. of strong HCl is placed in a wine-glass, and a single drop of concentrated nitric acid added; then 30 drops of urine are stirred into the mixture. If indoxyl is present, an amethyst color develops in from five to fifteen minutes. If the color is purple, the indoxyl is increased. Variation of the amount of indoxyl within normal limits is rather wide, and the indoxyl may be reported as high or low normal, increased, or diminished.

CHAPTER XXXIX.

ABNORMAL CONSTITUENTS OF URINE.

THE principal abnormal constituents are albumin, sugar, acetone, bile, and various crystalline salts, discoverable either by microscopical examination of the sediment, or by evaporation of a clear fluid, and examination with the micropolariscope.

Metallic substances, arsenic, lead, and mercury are occasionally present, and tests should be made for them when general symptoms or the conditions of the kidney indicate metallic poison. ALBUMIN is probably present in minute traces in the majority of urines. When in sufficient quantity to be detected by the usual laboratory methods, it is essential that we learn the source from which it has been derived, for the simple presence of even a considerable trace of albumin may be of but slight clinical importance. Albumin may indicate either a pathological condition of the kidney, which allows the entrance into the renal tubules of serum-albumin from the blood, or it may indicate a change in the composition of the blood, whereby the albumin passes more easily through the renal membranes, or its presence may be due to irritations from various sources of the urinary tract; and, as regards the bearing of albuminurias on dental disease, it is sufficient simply to determine whether renal disturbance is primary or secondary to some other trouble, such as heart disease; or purely local, as when caused by irritation due to crystalline elements.

Detection. — Albumin may be detected by either of two simple methods. It is often desirable to use both of these methods, thereby eliminating possible confusion from the

presence of substances other than albumin, which may respond to one of the two tests, but not to both.

The first consists simply in underlaying about 25 c.c. of *filtered* urine in a wine-glass with concentrated nitric acid. The wine-glass should be tipped as far as possible and the acid allowed to run very slowly down the side. This method is preferable to the use of the apparatus known as the albuminoscope or Horismascope (Fig. 30). As this latter method does not



FIG. 30.

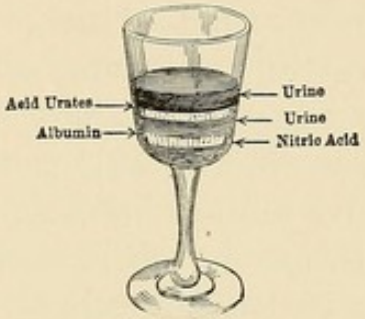


FIG. 31.

provide for sufficient mixing of nitric acid with the sample, the albumin is shown by a narrow white ring *at* the plane of contact of the two liquids. A white ring *above* the plane of contact is not albumin, but is composed of acid urates, indicating an excess of urates in the sample (Fig. 31). The albumin, in distinction from this band, occurs directly above the acid and is usually reported as the slightest possible trace when just discernible; as a slight trace, when well marked, but not dense enough to be seen by looking through the liquid from above; as a trace, when the white cloud may be seen by looking down into the glass from above and a large trace if plainly visible in this way.

Acetic acid and heat method of testing for albumin is the other method referred to in the preceding paragraph. It is of about the same delicacy as the nitric acid test, and is less liable to respond to substances other than albumin. It is made as follows:

A test-tube is filled two thirds full of perfectly clear filtered urine, one drop of acetic acid added and the upper half of the sample boiled. The tube can easily be held in the hand by the lower end. After boiling, if the tube is examined before a black background, a slight cloudiness or turbidity resulting from coagulated albumin can be easily detected in the upper part of tube. Anything more than a trace should be determined in the centrifugal machine by mixing 10 c.c. of filtered urine with about 2 c.c. of acetic acid and 3 c.c. of potassium ferrocyanid solution. Each tenth of a cubic centimeter of the precipitated albumin, when settled to constant reading, indicates one sixtieth of one per cent albumin by weight. This factor is fairly correct up to four or five tenths of a cubic centimeter of precipitate; beyond this it is of little value, and the albumin is best determined quantitatively by measuring 50 or 100 c.c. of urine into a small beaker, adding a drop of acetic acid, and boiling, which will completely precipitate the albumin. It may then be filtered into a counterpoised filter, thoroughly washed, first in water, next in alcohol, and lastly in ether, dried at a temperature a little below the boiling-point of water, and weighed. Esbach's method may be of value in some instances, and is carried out as follows:



FIG. 32.

Fill the albuminometer (Fig. 32) with urine to the line *U*, and then add the reagent* to the line *R*; close the tube, mix the contents thoroughly, and allow to stand in an upright position for twenty-four hours. At the end of that time the depth of precipitate may be read by the figures on the lower part of the tube, these figures representing tenths of one per cent of albumin, or grams of albumin in a liter of urine. If a sample of urine contains more albumin than is easily estimated by the

* Esbach's reagent consists of picric acid, 10 grams; citric acid, 20 grams, and distilled water sufficient to make one liter.

centrifugal or Esbach's method, approximate results will be obtained by diluting with several volumes of distilled water, until the quantity of albumin precipitated is within the limit of the test. The proteoses occasionally occur in the urine, and are distinguished from albumin by the fact that they redissolve at a boiling temperature. If filtered while hot, albumin, which usually accompanies them, will remain on the paper, while albumose will separate out from the clear filtrate as it cools.

Sugar.

Sugar in urine represents a perverted process of oxidation for which the liver is largely responsible. The pancreas also often plays an important part in cases of diabetes, but just how this is done is not clearly known. Sugar in the urine does not of necessity indicate diabetes any more than albumin indicates Bright's disease. Many cases of glycosuria are of a temporary nature and respond readily to dietary treatment. Whenever sugar is found it is desirable to make tests upon both a fasting and an after-meal sample, such as might be obtained before breakfast and one hour after dinner. If the fasting sample is comparatively free from sugar, it indicates that the glycosuria is of a temporary nature and due to faulty metabolism, rather than to any organic disease of the liver or pancreas.

Detection. — Sugar in the urine may be detected by several general carbohydrate tests, as previously given. The one which is most valuable and most generally employed is Fehling's test (Exp. 136, page 262). It is best to modify this test by bringing the Fehling's solution to active ebullition, adding from 5 to 30 drops of the suspected sample and allowing to stand without further heating. This prevents possible reduction of the sugar by xanthin bases or other occasional constituents of the urine, which might give misleading results if the mixture were boiled after addition of the sample. There is less danger of trouble of this sort if the gravity of the urine is below normal.

If it is necessary to make a rapid test, the mixture may be boiled after the urine is added, and in case the result is negative there is no need of further test; if, however, a slight reduction of the copper solution takes place, it will be necessary to repeat the test, using the precaution above given. The fermentation test (Exp. 140, page 262) may also be used to detect the presence of sugar and, approximately, the amount. The phenyl-hydrazine test may be used as a confirmatory test or in cases where very minute quantities are suspected. This test is considered about ten times as delicate as the Fehling's test; consequently, it may show small amounts of sugar which are not detected by the more rapid process. Quantitatively, sugar may be determined by the use of Fehling's solution as follows:

If the urine contains more than a trace of albumin, this substance should be removed by adding a drop of acetic acid and heating; after filtration the sample should be cooled and restored to original volume with distilled water. If specific gravity of the urine is more than 1025, it should be diluted to ten times its volume with distilled water (urine, one part; water, nine). If the gravity is less than 1025 dilute it to five times its volume, mix, and fill a 25 c.c. burette. In a 250 c.c. flask place 10 c.c. each of the alkaline tartrate and copper sulphate solutions (Fehling's solution), and add about 100 c.c. of distilled water. Place the flask over a Bunsen burner, and bring to a boil. If no change takes place after a minute or two of boiling, add the solution from the burette gradually, until the precipitate becomes sufficiently dense to obscure the blue color of the solution. Continue to boil for one or two minutes, then remove from the flame and watch carefully the line directly beneath the surface of the liquid, which will appear blue until all of the copper has been reduced to the red suboxid. The solution should be kept at the boiling-point throughout the entire operation, except in making the examination of the meniscus between the additions of the diluted urine. These additions must be

made very carefully, and as the process nears completion not more than one or two drops should be added at a time. When the blue color has entirely disappeared, and the line of meniscus has become colorless, note the number of cubic centimeters of dilute urine used, and calculate that in that quantity there is an equivalent of 0.05 gram of glucose; in other words, 0.05 gram of glucose will exactly reduce the amount of Fehling's solution used, and from this fact the amount of glucose in the entire twenty-four hour amount of urine is easily calculated. If the titration is carried beyond the proper "end point" the meniscus will appear yellow instead of colorless.

The fermentation test for sugar is a convenient and easily made qualitative test, it being only necessary to fill a fermentation tube (Fig. 17, page 263) absolutely full of urine to which a small portion of yeast has been added, and to allow the tube to stand in a warm place for several hours. Any collection of gas in the top of the tube will indicate the presence of sugar. This method may also be used as a quantitative test for sugar by taking two portions of the same sample, adding yeast to one, and using the other as a control. At the end of twenty-four hours, CO_2 is removed from fermented sample, the specific gravity of both samples is carefully taken, and the loss of density in the fermented sample is calculated as sugar by multiplying the number of degrees lost in gravity by 0.23, water being considered as 1000.

The optical analysis for sugar may be made with a polariscope, preferably constructed for use on urine. This determination depends upon the ability of glucose to rotate the plane of polarized light toward the right, the degree of rotation indicating the amount of sugar in a pure solution. Of course, allowance or correction must always be made for the presence of any substances which will rotate the light in the opposite direction, such as albumin, lævulose and β oxybutyric acid.

For the detail of construction and use of the polariscope,

the student is referred to the more complete works on urine analysis by Ogden, Holland, or Purdy.

Acetone.

Acetone may occur in the urine as a result of various pathological conditions and according to von Noorden they are all due to some one-sided perversion of nutrition. The acetonurias attendant on diabetes, scarlet fever, pneumonia, smallpox, etc., are of less practical interest to the dental practitioner than those more often overlooked by the medical profession, and which indicate improper diet, possibly resulting in serious malnutrition. The following points may be noted: In advanced stages of diabetes, acetone appears in the urine accompanied by diacetic acid. An increased ingestion of proteins may result in the appearance of acetone, in which case the direct cause is more an "insufficient utilization of carbohydrates"* than the increase of protein. Acetone may result from the oxidation of β oxybutyric acid. Diacetic acid is first formed, and subsequently the carboxyl group is replaced by an atom of hydrogen, as shown by the following graphic formulæ:

β oxybutyric acid: $CH_3–CHOH–CH_2–COOH$.
Diacetic acid: $CH_3–CO–CH_2–COOH$.
Acetone: $CH_3–CO–CH_3$.

Detection. — Acetone may be detected in the urine by the production of iodoform, as described under analysis of saliva on page 321, but it is not in this case nearly so delicate a test on account of the odor and acid character of the urine. A more useful test is known as Legal's test and is made as follows: To a third of a test-tubeful of urine add a few drops of a freshly prepared and fairly concentrated solution of sodium nitroprussid, next add two or three drops of strong acetic acid, and then a considerable excess of ammonia. If the contents of the

* Von Noorden's Diseases of Metabolism and Nutrition.

tube are mixed by a rather rapid rotary motion without inverting or violent shaking, the ammonia will not reach the bottom of the tube, and the presence of acetone will be indicated by a violet-red band above the layer of acid liquid. If much acetone is present a deep violet to purple color is obtained.

Diacetic Acid occasionally occurs in urine as an abnormal constituent most commonly in advanced stages of diabetes, usually accompanied by acetone and β oxybutyric acid. It may be detected by adding to the urine a little ferric chlorid, when a dark wine red color is produced. If a precipitate of ferric phosphate is obtained, filter the urine and examine the filtrate for color. This test may be made fairly distinctive for diacetic acid by boiling and cooling a second portion of the urine previous to making the test, when the result will be negative if the color at first produced was due to diacetic acid.

Bile.

Bile may occur in the urine as such, due to pathologic conditions of the liver- or bile-ducts, as stated on page 338. The coloring matters of the bile may also occur from causes aside from lesions of the liver. A urine containing bile or bile-pigments is always more or less highly colored, and upon shaking the foam will be of a yellow or greenish-yellow color. Albumin and high indoxyl accompany the presence of bile and there is also usually considerable renal disturbance. It may be detected by carefully adding to one-half a wine-glass of the suspected sample a few cubic centimeters of the alcoholic solution of iodin (tincture of iodin). A green color will be observed just beneath the line of contact of the two liquids (page 341). The test may be conveniently made by placing the iodin first in the wine-glass and then with a pipette introducing the urine beneath the iodin solution.

Metallic Substances.

Arsenic, mercury, and lead are the three metals which it may be necessary to look for in a sample of urine. The method for the detection of mercury, given on page 330, is applicable for this purpose.

Arsenic may be detected by the Marsh-Berzelius test (page 29), after oxidizing all organic matter. The process may be carried out as follows: Evaporate to dryness a liter of urine, to which 200 c.c. of strong nitric acid has been added; add to the residue, while still hot, from 15 to 20 c.c. of concentrated sulphuric acid. This must be done in a large porcelain evaporating-dish, or else the acid must be added very slowly to prevent frothing over and loss of a portion of the sample. After the action has quieted down the whole mixture may be transferred to a 500 c.c. Kjeldahl flask and heat applied gradually at first, and then more strongly. It will be necessary to add from time to time small portions of nitric acid and possibly a little more sulphuric acid; as the oxidation progresses the liquid in the flask becomes lighter in color and at the completion of the process is water-white, even when the temperature is increased so that sulphuric-acid fumes are given off. After cooling, the strongly acid liquid is diluted with four or five times its volume of water, filtered, if necessary, to remove excessive amounts of earthy sulphates, and is then ready for the arsenic test.

Lead. — The sample of urine to be tested for lead should measure at least 1000 c.c., and should be tested for iodin to insure the fact that the patient has been under treatment with potassium iodid to dissolve lead salts, otherwise a negative result may be obtained when lead is actually present and poisoning the system. Oxidize the sample in precisely the same manner as when making the arsenic test, up to the point of diluting the strong acid solution with water; then, in this case, use rather less water for the dilution, allow to cool, and neutralize with Squibb's

ammonia, acidify quite strongly with acetic acid, and pass H_2S gas into the solution. It is desirable to leave the solution saturated with H_2S for at least twelve hours. Then filter, and without washing dissolve the precipitate in warm dilute nitric acid, evaporate the HNO_3 solution to dryness, add 5 c.c. of water, make alkaline with a drop or two of ammonia, and again acidify with acetic acid and add a solution of bichromate of potash.* Allow to stand several hours, filter off the chromate of lead, wash several times with distilled water, and lastly with H_2S water when the lead chromate will blacken from the formation of lead sulphid. This stain is a superficial one and disappears upon standing, but when the process is conducted in this way it constitutes a very delicate and satisfactory test for lead in either urine or saliva.

Urinary Sediments.

The sediment which settles from a sample of urine upon standing consists normally of a slight amount of mucin and epithelial cells. It may contain also bacteria and a considerable variety of extraneous matter, including starch grains, various vegetable spores, yeast cells, fibers from various fabrics, cotton, wool, flax from linen, etc., diatoms, scales from insects' wings, and other particles which may occur as dust (see Plate IX, Fig. 6; also Plate X, Fig. 4). Under abnormal conditions the sediment may contain crystalline elements, including uric acid and urates, phosphates, oxalates, cystin, tyrosin, leucin, etc., also organized elements such as epithelium, renal or other casts (Plate IX, Fig. 4), blood globules, pus cells (Plate IX, Fig. 3), spermatozoa (Plate IX, Fig. 2), fat, mucin (Plate IX, Fig. 5), etc. Urinary sediment may be thrown down from a fresh specimen by the use of the centrifugal machine, or it may be allowed to stand in a glass tube with rounded bottom for several hours, when the sediment settles to the bottom by gravity. If possible

* Natural chromate of potash will precipitate copper, the acid chromate precipitates lead only of the second group metals.

it is best to examine sediments settled in both of these ways, as the centrifuge will show elements, such as small casts, that would settle slowly, possibly not at all, by the gravity method. On the other hand, the sediment allowed to settle spontaneously will often give a more correct idea of comparative numbers of the various elements observed, than when settled in a centrifuge-tube. A drop or two of formalin may be used to preserve urinary sediment, as suggested on page 344, but if too much of this substance is used, especially in urines containing high percentages of urea, a compound is liable to be formed which has been called formaldehydurea (Plate X, Fig. 5), which settles with the sediment and seriously interferes with the microscopical examination. This compound may form sheaf-like crystals similar to tyrosin and may be mistaken for crystals of sodium oxalate, especially when examined with a low power objective.

Uric Acid. — Uric acid is deposited from normal urine, upon standing, with an excess of free acid (HCl). Urines that have a high degree of acidity will also produce a like deposit, and the finding of uric-acid crystals does not necessarily signify that the crystallization took place within the body, unless special care has been taken that the sample examined was perfectly fresh, although the *tendency* to deposit uric acid is, of course, indicated. The urine from which uric acid separates, as such, is usually rather concentrated and of strong acid reaction. These crystals vary in appearance (Plate X, Figs. 1 and 2), but are almost always colored yellow to red. Colorless crystals are sometimes observed. They are usually quite small, but of the peculiar whetstone shape in which this acid most usually crystallizes. The presence of uric acid has practically no effect upon the acidity of the sample; for, if the acid separates in a crystalline form, it is insoluble, and if it does not separate it is in combination as urates, possibly, of course, as acid urates. Uric acid exists normally in proportion to urea as about 1 to 50,

PLATE IX. — URINE.

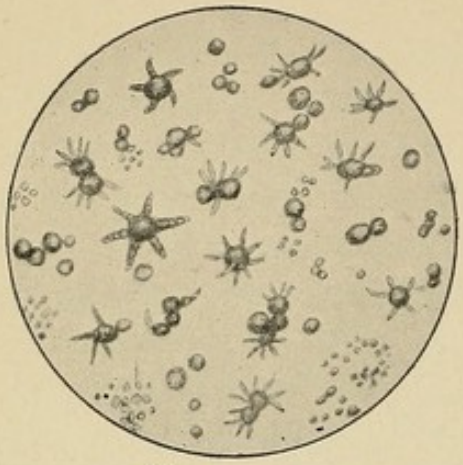


FIG. 1.
Ammonium Acid Urate.

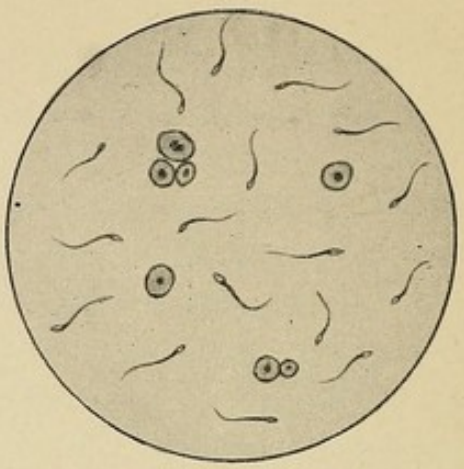


FIG. 2.
Spermatozoa.

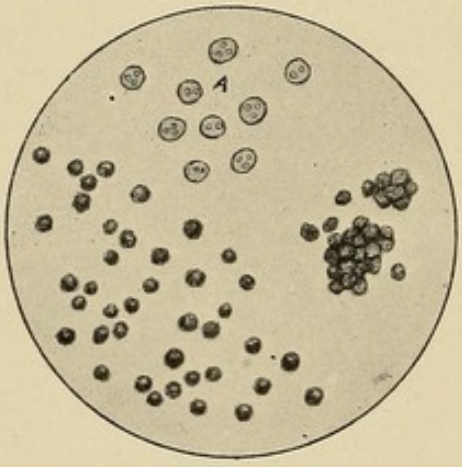


FIG. 3. — Pus.
A, After addition of Acetic Acid.

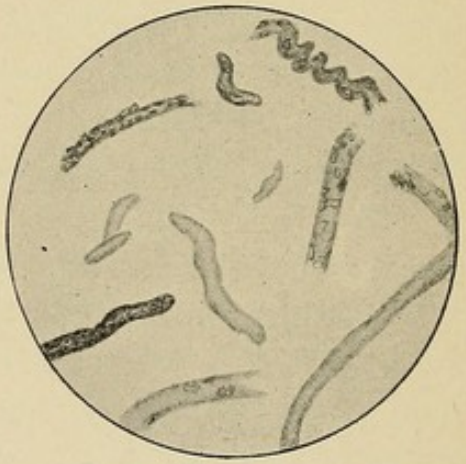


FIG. 4.
Renal Casts.



FIG. 5.
False Casts and Mucin.

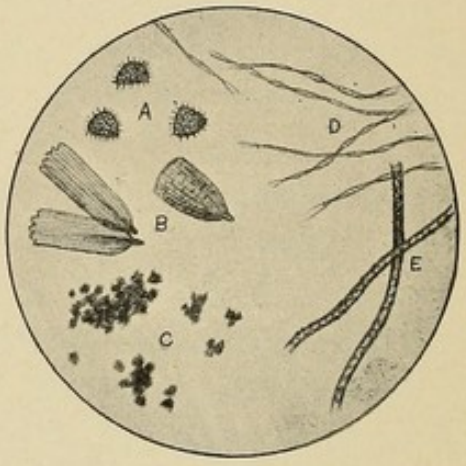


FIG. 6.
A, Lycopodium; *B*, Moth-scales; *C*, Cork; *D*, Cotton-fibres; *E*, Wool-fibres.

but there is no necessary relationship between the quantities of the two substances, and the one may be diminished while the other is increased.

Urates. — Urates may occur as crystalline or amorphous precipitates. The crystalline urates are urate of sodium rarely, acid urate of sodium (Plate X, Fig. 3, p. 368), and acid ammonium urate (Plate IX, Fig. 1, p. 367). The amorphous urates are of the alkaline bases, usually sodium, and are frequently precipitated by lowering of the temperature after the sample has been passed, in such cases the urine assumes a cloudy appearance which is cleared up by the application of heat. A sediment consisting of urates is usually of a pinkish color.

Phosphates. — Phosphates in the urinary sediment may be amorphous or crystalline. They are of the alkaline earths rather than of the alkaline metals, as the latter are soluble in both the acid and neutral forms. The amorphous phosphates deposit with the change of reaction from acid to alkaline, and usually in the form of a so-called triple phosphate of ammonia and magnesia (Plate IV, Fig. 2, p. 163). This salt crystallizes in two forms. The prismatic form is the ultimate form; that is, if the crystallization takes place very slowly, the prismatic form is the one in which the salt is thrown out. If it takes place rapidly it may be precipitated in the feathery form, but this slowly changes over to the prismatic form. The acid phosphates may be precipitated closely resembling in appearance the acid urates (Plate X, Fig. 3), but may be distinguished from them by their ready solubility in acetic acid and failure to produce, after solution in acetic acid, any crystals of uric acid such as are obtained from the urates.

Acid Lactates. — These are soluble salts, and are found in urine only by evaporation of a drop of the clear fluid and an examination of the residue by polarized light. When found in the urine, the significance is quite different from that when found in the saliva, as in the urine they may possibly be formed from

lactates, which indicate a faulty action of the liver, and of course they have no connection with tooth erosion. The lactates furnish evidence of similar character.

Oxalates. — Oxalates if found in the sediment usually occur as calcium oxalates. These crystals assume a variety of forms, as shown in Plate II, Fig. 1, p. 162. Sodium oxalate (Plate II, Fig. 4) may occur in the urine (not, however, in the sediment), and is detected only by evaporating a drop of the clear liquid and examining with polarized light. Dr. Kirk claims that an oxaluria may be in this way detected for a considerable time before the appearance of the oxalate of lime crystals, and hence such examination becomes a valuable aid to diagnosis.

Cystin. — Cystin occurs as six-sided plates. It is a comparatively rare crystal, and indicates insufficient oxidation, particularly of the organic sulphur compounds.

Epithelium. — Epithelium occurs in the urinary sediment from any part of the urinary tract. In the male urine it is much easier to determine the character of the epithelium than in the female, as in the latter the comparatively large amount of mucous surface, from which epithelium may be gathered, furnishes a great variety of forms which are, of course, without clinical significance. The epithelium from the vagina may be quite readily distinguished as very large cells with small nuclei, lying usually in masses overlapping one another but with comparatively slight density. Renal epithelium may be found as small, round cells, differing but slightly in size from a leucocyte. They may be a little larger, a little smaller, or about the same size. They are round and more or less granular in appearance.

Epithelium from the bladder varies considerably, but the majority of cells would properly come under the general head of squamous epithelium, rather large and flat with a distinct nucleus of medium size. Epithelial cells from the neck of the bladder in male urine are quite typical, being round and comparatively dense with a prominent nucleus. They are four

PLATE X.—URINE.

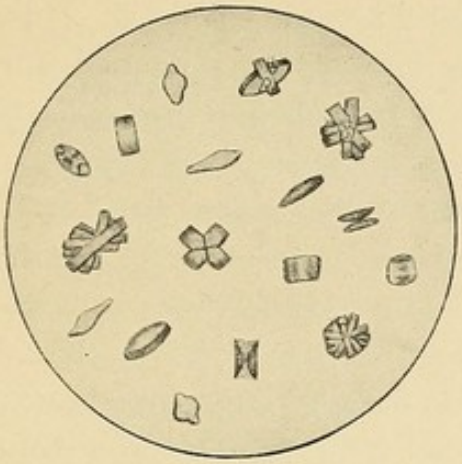


FIG. 1.
Uric Acid.

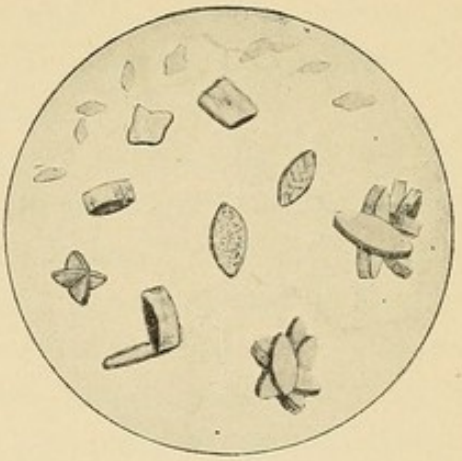


FIG. 2.
Uric Acid.

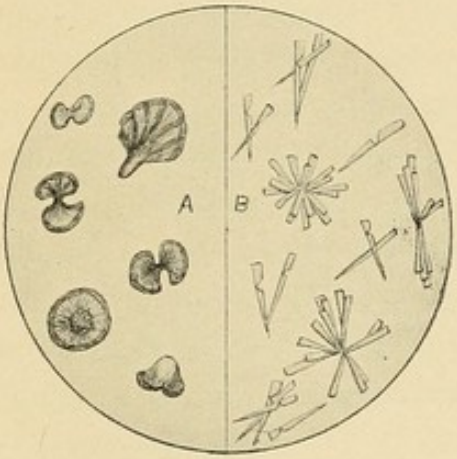


FIG. 3.
A, Sodium Urate; *B*, Sodium Acid Urate.



FIG. 4.
Yeast Cells and Molds.

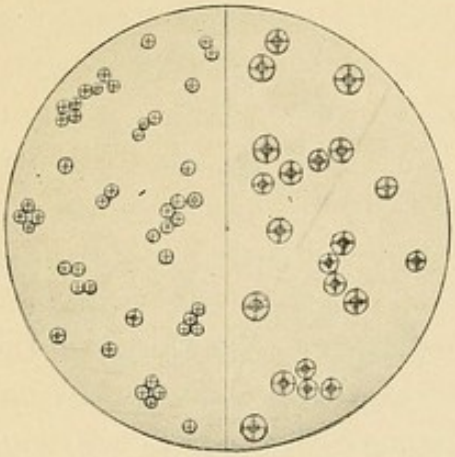


FIG. 5.
Formaldehyd Urea (P. L.).

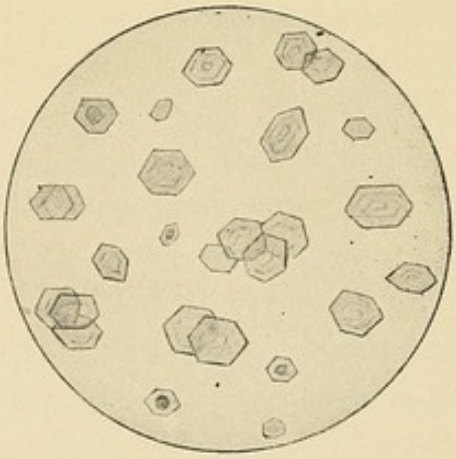


FIG. 6.
Cystin.

or five times the size of a leucocyte and, in cases of irritation at the neck of the bladder, are usually present in considerable numbers and of quite uniform appearance.

Renal casts consist of molds formed within the tubules of the kidneys which retain the form of the tubules after expulsion into the bladder. According to Ogden the most probable theory of their formation is "that they are composed of coagulable elements of blood that have transuded into the renal tubules, through pathologic lesions of the latter, and have there solidified to be later voided with the urine, as molds of the tubules." Casts are termed blood casts, pus casts, epithelial or fat casts according as these elements may adhere with more or less profusion to the cast itself. Pure hyaline casts are pale, perfectly transparent cylinders, with at least one rounded end which can be plainly seen, and may occur occasionally in urine from perfectly healthy individuals. Fibrinous casts are highly refractive and when seen by white light are of a yellowish color and indicate acute renal disturbance. Waxy casts resemble the so-called fibrinous as regards density, but they have no color, and usually indicate advanced and serious stages of kidney disease, while the presence of fibrinous casts has no necessarily serious significance.

Blood and Pus are readily recognized under the microscope after a very little practice. The blood disks are circular and show a characteristic biconcavity in the alternate shading of the edge and center by slight changes of focus. The red corpuscles usually show a shade of color by white light. The pus corpuscles or leucocytes are larger than the red corpuscles, and are granular in appearance. Treatment with acetic acid destroys the granular matter and brings into prominence the cell nuclei, two or three in number. If the leucocytes are free and scattered they should not be regarded as pus but be reported simply as an excess of leucocytes; if they are very numerous and occur in clumps they constitute pus.

Spermatozoa. — Occasional spermatozoa may be found in sediment from either male or female urine and are without clinical significance. If persistent and in considerable numbers, seminal weakness is indicated (Plate IX, Fig. 2, p. 367).

Fat occurs in urinary sediment as small globules, highly refractive and varying greatly in size. They are frequently adherent to cells or to casts. Fatty casts indicate a fatty degeneration, which may or may not result from chronic disease. Fat may be demonstrated by staining with osmic acid which is reduced by the double-bonded fatty constituent (olein), leaving a black deposit which stains the globule.

Mucin appears in the sediment as long and more or less indistinct threads. An excessive amount usually indicates irritation of some mucous surface. The source would have to be determined by other more characteristic elements (Plate IX, Fig. 5).

The salts which may be obtained by evaporation of a drop of clear urine and detected by the micropolariscope are similar to those occurring in the saliva; sodium oxalate is probably most frequently found. If the gravity is above normal the urea often crystallizes, making it somewhat difficult to pick out the abnormal crystalline constituents. Phosphates are also usually observed, but these crystals are large and as a rule prismatic, not easily mistaken for anything else.

Interpretation of Results.

As stated at the beginning of the chapter on urine, our object has been the study of this secretion from the standpoint of general metabolism, rather than with a view to differentiate various forms of renal disease, and while it is important that the *presence* of renal disease should be recognized, its further investigation constitutes a proper study for the physician rather than for the dentist, and when such conditions are found to exist a patient's physician should be apprised of the fact.

The discussion of a few examples based upon actual analyses, may serve to show deductions which may be drawn from analyses of saliva and urine.

No. 1.*

URINE. NAME. DATE,

Anal. for Dr. C. A. J.			Per cent.	Grams in 24 hours.
24 h. Am't. 2000 c.c.		Urea	0.88	17.6
Sp. Gr. 1013.	Reaction Ac.+(50°)	Uric Ac.	0.034	0.68
Color =N.	Sulph.	Ammon.		
Ind. =+	E. Phos.−	Chlor.	0.455	9.1
Bile.	A. Phos.−	Phos. Ac.	0.09	1.8
Diac. Ac.	Acetone=abs.	Sugar=abs.		

Alb.=Sl. possible trace. Uric Ac. to Urea=1 to 24.
Soluble Salts (cryst.) Occasional sodium oxalate.
Sediment. Occasional leucocytes, few neck of bladder cells, an excess of mucin.

ANALYSIS OF SALIVA.

Dr. C. A. J. February, 1906.

Appearance = cloudy.
Odor = slight.
Reaction = strongly acid.
Specific gravity = 1003.
Mucin = slight.
Albumin = marked.
Ammonia = increased, but inferior to sulphocyanate which is very high.
Glycogen = negative.
Chlorin = normal or slightly increased.
Soluble salts = lactates, alkaline chlorids.
Abnormal constituents = lactic acid.
Sediment = heavy, excess of leucocytes, mucin, and squamous epithelium.
Indicated diathesis = hyperacid.

As we study these analyses, we notice first in the urine an increased quantity with low urea. These things accompany chronic kidney disease, but inasmuch as in this case we find no casts in the sediment, and no more albumin than can be accounted for by the slight irritation at the neck of the bladder, we consider the dilution unimportant. The uric acid is high in proportion to the urea, and the chlorin being nearly normal for the twenty-four-hour amount would indicate a full diet

* The abbreviations used in this analysis are as follows: N = normal, Ac.= acid, Sl.=slight. The minus sign=diminished or decreased, the plus sign=excessive or increased, Abs.=absent.

with perverted oxidation. These indications are of probabilities rather than positive conclusions, although in this particular case the actual facts were as indicated. The high indoxyl in the absence of any acute disease would indicate an increased putrefaction in the small intestine, probably due to defective intestinal digestion.

The condition of the saliva, together with the urine analysis, would indicate a condition favorable to erosion of the teeth and the development of pyorrhœa. It was found that the patient was not suffering from erosion of the teeth, except in a very slight degree, but the evidences of pyorrhœa were quite marked at the time of the first examination some weeks before the analyses were made.

No. 2.

URINE.	NAME.	DATE,		
Anal. for			Per cent.	Grams in 24 hours.
24 h. Am't. 1200 c.c.		Urea	2.27	25.24
Sp. Gr. = 1023	Reaction = Ac.	Uric Ac.	0.051	0.61
Color = Sl. high.	Sulph.	Ammon.		
Ind. N.	E. Phos. = N.	Chlor.	0.834	10.1
Bile.	A. Phos. = N.	Phos. Ac.	0.112	1.3
Diac. = Ac.	Acetone = Abs.	Sugar Abs.		
Alb. Sl. possible trace.		Uric Ac. to Urea = 1 to		
Soluble Salts (cryst.)				

Sediment. — Numerous large calcium oxalate crystals, occasional uric-acid crystals, excess of mucin, rarely a blood globule.

The saliva accompanying this sample indicated a hyperacid diathesis and a slight amount of pus in the sediment, otherwise nothing abnormal. In this sample we notice a concentrated urine with a tendency to precipitation of crystalline elements which have apparently produced a slight irritation of the urinary passages, as indicated by the blood globules, and the slightest possible trace of albumin. The patient in this case was a young man in good general health, a student at the Dental School. An incipient pyorrhœa had been noticed, and, as a result of information gained by this analysis, the red meat, coffee, and other uric-acid-producing foods were wholly elimi-

ated from the diet, and improvement of the conditions of teeth and gums followed. It is not necessary to assume that the next case of this character would respond to similar treatment.

No. 3.

URINE. NAME. F. J. DATE, Dec. '05. PHYS. Dr. R.

					Grams in 24 hours.	N.
24 h. Am't. = 2200 c.c.			Sp. Gr. = 1026	N.%		
Color = N.	Reaction = Ac. +		Urea	= 2.65 (2.0)	58.3	(28.0)
Uph. = Sl. −			Uric Ac.	= 0.047 (0.033)	1.03	(0.5)
Ind. = Sl. −	E. Phos. = N.		Chlor.	= 0.625 (0.67)	13.7	(10.0)
Bile = Abs.	A. Phos. = N.		Phos. Ac.	= 0.16 (0.18)	3.5	(2.7)

Acetone very slight trace. Sugar = slight trace present.
Alb. = Sl. possible trace.
Sediment. — Calcium oxalate crystals very numerous, occasional leucocyte, occasional blood globule with rarely a hyaline cast.
(The numbers in parentheses are the average normal.)

This urine was from a patient with a tendency to diabetes who was living almost exclusively on a protein diet. This accounted for the high uric acid and high urea. There was a slight irritation of the kidneys which was secondary to the glycosuria. There was no trouble with the teeth and no examination of saliva was made.

The following sample indicates a chronic disease of the kidneys, and it was thought wise to have the day and night twelve-hour quantities measured separately as, in cases of chronic kidney disease, the night quantity usually exceeds the day quantity, and this fact is often a valuable aid in determining the character of kidney disturbances. The metabolism in this case is good, the nephritis being only at an early stage.

No. 4.

URINE. NAME. DATE,

			Per cent.	Grams in 24 hours.
Anal. for				
24 h. Am't. 2500 c.c.		Urea	1.01	25.25
Sp. Gr. 1012.	Reaction N.	Uric Ac.	0.020	0.50
Color pale.	Sulph.	Ammon.		
Ind. −	E. Phos. −	Chlor.	0.315	7.87
Bile.	A. Phos.	Phos. Ac.	0.90	2.25
Diac. Ac.	Acetone Abs.	Sugar Abs.		
Alb. Sl. trace.		Uric Ac. to Urea = 1 to		

Soluble Salts (cryst.).
Sediment. — Squamous epithelium with several hyaline and fine granular casts.

The following is a case of chorea and is of interest, particularly, on account of the large number of sodium oxalate crystals which were persistently present.

No. 5.

URINE. NAME. M.G. DATE, March 28, 1912.

Anal. for			Per cent.	Grams in 24 hours.
24 h. Am't. 473 c.c.		Urea	2.31	10.93
Sp. Gr. 1021.	Reaction Ac.	Uric Ac.	0.053	0.251
Color, Sl. high.	Sulph.	Ammon.		
Ind. N.	E. Phos.	Chlor.	0.588	2.781
Bile.	A. Phos.	Phos. Ac.	0.135	0.638
Diac. Ac.	Acetone Abs.	Sugar Abs.		
Alb. Sl. possible trace.		Uric Ac. to Urea = 1 to		

Soluble Salts (cryst.). Sodium oxalate crystals, phosphatic crystals.
Sediment. — Leucocytes, epithelium.

As seen by these examples, it is necessary to take the whole analysis into consideration, often in conjunction with an analysis of the saliva, in order to know just what the system is doing, and whether there is possible systemic derangement which may have an important bearing on conditions found in the oral cavity. Experience and study alone will enable one to correctly interpret the results of such analyses, but it has been our aim to give sufficient groundwork for the prosecution of such study, and to show that in many cases the knowledge derived from thorough examinations may be of the greatest importance in the successful treatment of diseased conditions.

APPENDIX.

Ammonia (dilute). — Strong ammonia one part, distilled water two parts.

Ammonium Molybdate Solution for Phosphates. — This may be made by dissolving 20 grams of ammonium molybdate in a mixture of 250 c.c. NH_4OH and 250 c.c. of water. Then this solution is added to 1000 c.c. of nitric acid making 1500 c.c. of reagent. In using this solution as a test for phosphates it is necessary to heat the mixture to about 60° C. The test is less delicate than if made with reagent prepared as follows:

Dissolve 100 grams of molybdate trioxid (molybdic acid) in 400 c.c. of dilute NH_4OH (10%). Allow to cool and add all at once 1000 c.c. of dilute HNO_3 (HNO_3 3 parts, H_2O 2 parts). The precipitate first formed is immediately redissolved and the product should be a perfectly clear, nearly colorless solution. This reagent acts in the cold, is more sensitive than that produced by the first formula and is recommended as the better of the two.

Barfoed's Reagent. — Dissolve one part of copper acetate in fifteen parts of water; to each 200 c.c. of this solution add 5 c.c. of acetic acid containing 38 per cent of glacial acetic acid.

Congo Red. — Two per cent aqueous solution.

$CuSO_4$ Solution. — One per cent for Biuret test.

Preparation of Cystin, Tyrosin, and Leucin.

Cystin. — 1. Clean 200 grams of hair by washing with dilute HCl and then with ether. Boil the clean hair with 600 c.c. of concentrated HCl (specific gravity, 1.19) for four hours (in a

three-liter flask with condenser) on a sand-bath in hood. Then let cool.

2. Add concentrated NaOH solution (750 c.c. H_2O, 500 grams NaOH) till the reaction is only faintly acid.

3. Add to the solution, which has begun to boil on neutralization, plenty of animal charcoal, and boil three-quarters of an hour.

4. Filter hot, being careful to moisten filter and funnel with hot water to prevent funnel from cracking.

5. The filtrate should be faintly yellow. On cooling, a crystalline precipitate forms, mainly cystin, with some tyrosin and leucin. If this is not the case, or if the precipitate is slight, the solution must be concentrated. Save the filtrate, which with the filtrate from 6 is to be worked up later for tyrosin and leucin.

6. After standing overnight filter off the precipitate.

7. Dissolve this precipitate in 350 c.c. of hot 10 per cent NH_4OH (hood) and let cool. Then continue the cooling with finely chopped ice or with snow. Filter off any tyrosin that may have precipitated, and combine it with the filtrate of 6.

8. Add glacial acetic acid, being careful not to acidify. The precipitate is a mixture of tyrosin and cystin. Filter.

9. Make filtrate from 8 quite acid with glacial acetic acid. The precipitate is almost pure cystin. Let stand twenty-four hours. Then filter, and wash with H_2O and alcohol.

10. Recrystallize by redissolving in as little hot 10 per cent ammonia as is necessary to effect solution, cooling and precipitating with glacial acetic acid.

The preparations should be pure and contain no tyrosin, for which test may be made with Millon's reagent.

Reactions. — Put a trace of cystin into a test-tube with some dilute NaOH and a little lead acetate. Boil. H_2S is formed because S is split off.

Tyrosin. — 1. Concentrate the neutralized filtrate of 6 of cystin preparation till, on cooling, tyrosin crystallizes out.

2. Filter, and save filtrate for the preparation of leucin.

3. Dissolve the tyrosin crystals in very little hot water.

4. Add amyl alcohol till a heavy precipitate forms.

5. Filter precipitate.

6. Redissolve in very little hot water, and let crystallize out by cooling.

Examine crystals under the microscope.

Test with Millon's reagent.

Leucin. — 1. Take the filtrate of 2 in the preparation of tyrosin, and evaporate to dryness on the water-bath.

2. Extract with alcohol.

3. On standing, the leucin crystallizes out of the alcoholic extract as it evaporates.

4. Filter, and dry the crystals.

Examine under the microscope.

Dimethyl-amino-azobenzene.—0.5 per cent alcoholic solution.

Esbach's Reagent. — See page 360.

Fehling's Solution. — The Fehling's solution recommended for experiments in this book is one-half the strength frequently employed, and is prepared in separate solutions as follows: Dissolve 34.639 grams of pure crystallized copper sulphate in water, and make solution up to one liter. This constitutes the first part of the reagent. The second part may be made by dissolving 173 grams of Rochelle salt and 52.7 grams of caustic soda (NaOH) in water and making up to one liter. When prepared in this way 10 c.c. of each of these solutions mixed together will be reduced by 0.05 gram of glucose.

Ferric Chlorid. — 2.5 per cent. Solution acidified with HCl.

Glycogen $(C_6H_{10}O_5)_n$. — Use a liver taken from an animal just killed, or, if the season permits, oysters just removed from the shell. Cut an oyster, as rapidly as possible, into small pieces, and throw it into four times its weight of boiling water,

slightly acidulated with acetic acid. After boiling the first portion for a short time, remove the pieces, grind in a mortar with some sand, return to the water, and continue the boiling for several minutes. Filter while hot. The opalescent solution thus obtained is an aqueous solution of glycogen and other substances.

If a purer solution is desired, continue as follows: Add to the filtrate alternately a few drops of HCl and potassiomercuric iodid, until a precipitate of protein ceases to form. This may be determined more conveniently by filtering off a small portion of the liquid from time to time, and adding to the clear filtrate the HCl and potassiomercuric iodid. When the precipitation of the proteins is complete, filter, and to the milky filtrate add double its volume of alcohol; the glycogen will precipitate as a white powder. Filter this off, wash with 66 per cent alcohol (one part of water to two of alcohol), and dissolve in water.

Gram's Solution. — Same as Iodin Solution given below.

Gunzburg's Reagent. — Phloroglucin, 2 grams; vanillin, 1 gram; alcohol, 100 c.c.

Hydrochloric Acid (dilute). — Hydrochloric acid, strong, (sp. gr. 1.20) one part; distilled water, two parts.

Hypobromite Solution for Urea. — Consists of a mixture of equal parts of the following solutions:

Bromin Solution for Urea. — 125 grams KBr and 125 grams Br to one liter water.

NaOH Solution for Urea. — A 40-per cent solution.

Iodin Solution. — 10 grams iodin, 20 grams KI, made up with water to one liter.

Iodin Tincture. — See tincture.

Invertase. — Mix 500 gms. of "beer yeast," 200 c.c. of water and 10 gms. of sugar, allow to stand one hour. Add 50 c.c. of 60% alcohol and a little thymol. Filter, press or allow to dry, put the nearly dry mass in a flask, add 20 gms. of sugar and shake till solution is effected. Keep in ice chest.

If "beer yeast" is not available a solution of invertase, rather less satisfactory than the above, can be made as follows: Take one dozen compressed yeast cakes, grind with sand and mix with 500 c.c. of water, and a little chloroform as preservative. Allow to stand twelve hours and filter.

Leucin. — See under Cystin, pages 377, 379.

Lipase. — From castor bean. Remove the shells from 10 grams of fresh beans, break them up as fine as possible and allow to stand overnight in a loosely stoppered test-tube full of alcohol ether mixture. Pour off; grind the beans to a powder in a small mortar, transfer to a test-tube and let stand under ether overnight. Filter with suction filter and wash two or three times with small amounts of the alcohol ether mixture.

Fat Digestion with Lipase (castor bean). — Grind with the powder, in the order named, 5 c.c. N/10 sulphuric acid (supplied), 5 c.c. of neutral cotton oil (sp. gr. 0.92) and 5 c.c. lukewarm water. The water should be added a little at a time and thoroughly worked into the mixture so that at the end of the operation a good emulsion is secured. Cover the evaporating dish and let stand in a warm place overnight.

Add 50 c.c. of alcohol, 10 c.c. ether, and a few drops phenolphthalein and titrate with N/1 sodium hydrate. Calculate the amount of fatty acid and the per cent of fat digestion.

Lipase. — From pancreas. Take a pig's pancreas, remove all fat, grind and allow to stand overnight. Then add four times its weight of 25% alcohol and allow to stand three days. Syphon off clear fluid and neutralize with sodium carbonate. The solution will contain a fat-splitting enzyme.

Magnesia Mixture. — 125 grams of ammonium chlorid, 125 grams of magnesium sulphate, dissolved in sufficient water to make one liter of solution, then add 125 c.c. of strong ammonia water.

Mercuric Chlorid Solution. — Five per cent $HgCl_2$ in distilled water.

Millon's Reagent. — To one part of mercury add two parts nitric acid of specific gravity 1.4, and heat on the water-bath till the mercury is dissolved. Dilute with two volumes of water. Let the precipitate settle, and decant the clear fluid.

Mucin Solution. — Cut a portion of a navel-cord into small pieces. Shake in a flask with water, changing the water several times. This removes salts and albumin. Extract for twenty-four hours with lime-water or baryta-water in a corked flask. Filter. To filtrate add acetic acid, which precipitates the mucin. Let settle, filter, and wash with water.

Mucin may also be prepared from the saliva by precipitation with acetic acid.

Nessler's Solution. — This is an alkaline solution of mercuric iodid, made as follows: Dissolve 35 grams of potassium iodid in about 200 c.c. of water. Dissolve 17 grams of mercuric chlorid in 300 c.c. of hot water. Add the potassium iodid to the mercuric chlorid, until the precipitate at first formed is nearly all redissolved. If the precipitate should entirely dissolve, add a few cubic centimeters of a saturated solution of mercuric chlorid, until a slight permanent precipitate is obtained. After the mixture is cold, make up to one liter with a 20-per-cent solution of caustic potash. Allow to settle and use the clear solution.

Nitric Acid (dilute). — Strong HNO_3 (Sp. gr., 1.42) one part, and water three parts.

Pancreatic Extract. — Obtain a fresh pancreas and soak in four times its weight of 25% alcohol for two or three days. Filter and make the solution neutral or very slightly alkaline with sodium carbonate. This solution will contain the fat-splitting enzyme.

Phenoldisulphonic Acid. — Phenoldisulphonic acid, for estimation of nitrates in water analysis, may be prepared by heating on a water-bath for several hours a mixture of 555 grams of concentrated sulphuric acid and 45 grams of pure carbolic-acid crystals.

Phenyl-hydrazine Solution. — 1 gram phenyl-hydrazine hydrochlorid and 2 grams sodium acetate dissolved in 10 c.c. water.

Picric-acid Solution (Esbach's Reagent). — Picric acid, 10 grams; citric acid, 20 grams; dissolved in sufficient water to make one liter.

Potassium Ferrocyanide Solution. — Ten per cent $K_4Fe(CN)_6$ in distilled water.

Potassium Cyanid (KCNO). — Melt in an iron ladle, of at least 50 c.c. capacity, five grams of commercial potassium cyanid, and stir in gradually 20 grams of litharge. When the entire amount has been added, pour the mass out upon an iron plate, and allow to cool. Separate as far as possible the reduced lead from the potassium cyanid that has been formed, powder the latter, and dissolve in 25 c.c. of cold H_2O. Filter if necessary and purify by repeated crystallization.

Silver-nitrate Solution. — Drop solution, 1:8.

Quantitative Solution for Chlorin Titration in Urine. — 29.075 grams $AgNO_3$, made up to one liter with water. 1 c.c. of this solution corresponds to 0.01 gram NaCl or 0.00607 gram Cl.

Starch Paste (thin). — Rub about one-half gram of starch to a thin paste with cold water. Add sufficient boiling water to dissolve, then dilute to 100 or 150 c.c.

Sulphuric Acid (dilute). — Twenty per cent strong H_2SO_4 in distilled water.

Tincture Iodin for Bile Test. — Dilute until just transparent in test-tube.

Tropæolin oo. — Saturated alcoholic solution.

Tyrosin. — See paragraph under Cystin, pages 377, 379.

Uffelmann's Reagent. — Mix 10 c.c. of a 4-per-cent solution of carbolic acid with 20 c.c. of water, and add a drop or two of ferric chlorid.

Urea. Synthesis of. — Add to the filtered solution of KCNO (above) a cold saturated solution of ammonium sulphate, con-

taining at least six grams of $(NH)_2SO_4$. Heat the mixture slowly on a water-bath at a temperature of 60° C., and maintain at that point for one hour. By this process ammonium cyanate is formed and then changed to urea, which may be obtained in an impure state by evaporating the solution to dryness on a water-bath, and extracting the residue with hot, strong alcohol. The urea will crystallize from the alcohol as it cools.

INTERNATIONAL ATOMIC WEIGHTS, 1912.

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	*Nitron (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromin	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
*Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorin	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
*Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorin	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.07
Glucinum	Gl	9.1	*Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204.0
Indium	In	114.8	Thorium	Th	232.4
Iodin	I	126.92	Thulium	Tm	168.5
Iridium	Ir	193.1	Tin	Sn	119.0
*Iron	Fe	55.84	Titanium	Ti	48.1
Krypton	Kr	82.92	Tungsten	W	184.0
Lanthanum	La	139.0	Uranium	U	238.5
Lead	Pb	207.10	*Vanadium	V	51.0
Lithium	Li	6.94	Xenon	Xe	130.2
Lutecium	Lu	174.0	Ytterbium (Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
*Mercury	Hg	200.6	Zirconium	Zr	90.6

* Values that have been changed.

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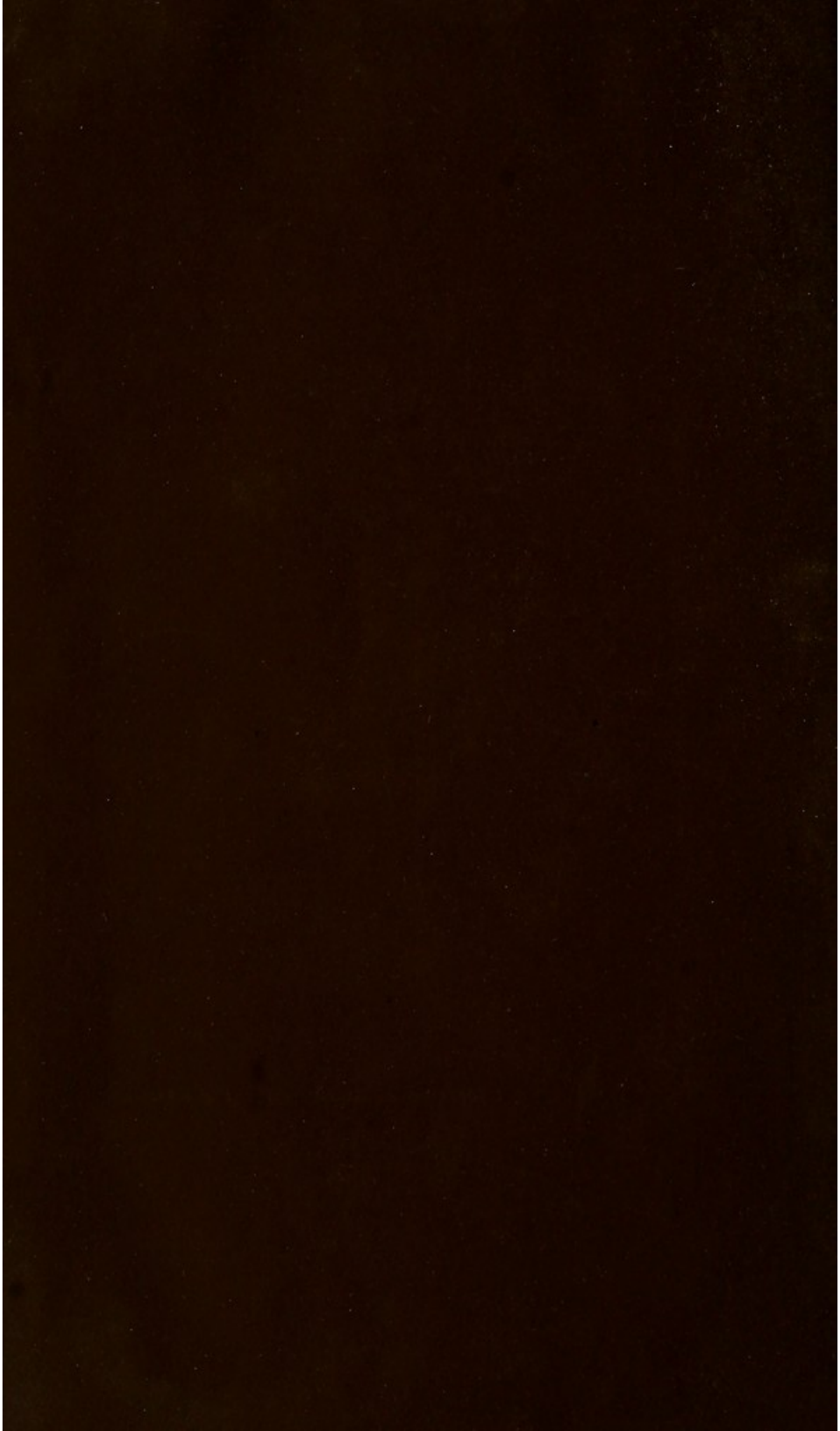
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