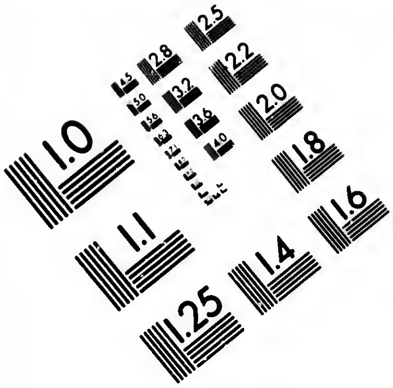

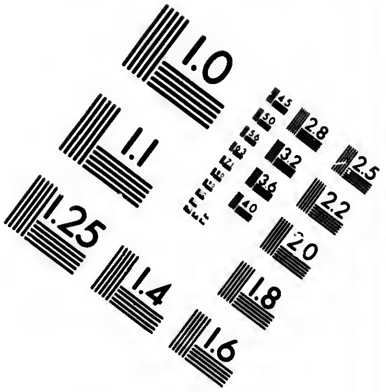

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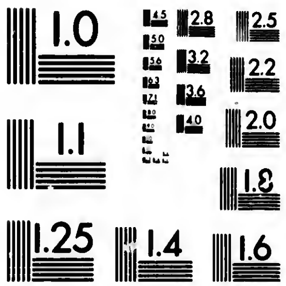

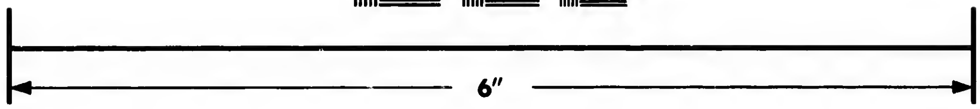

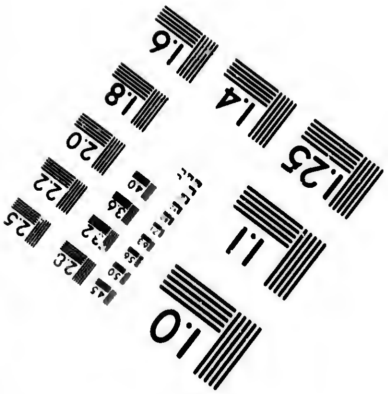

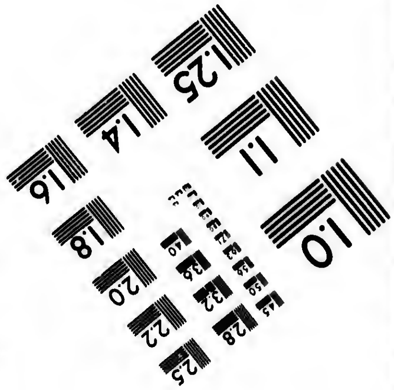

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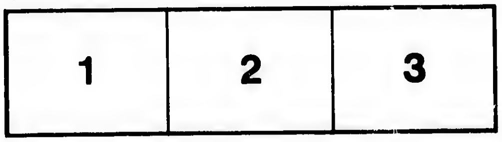

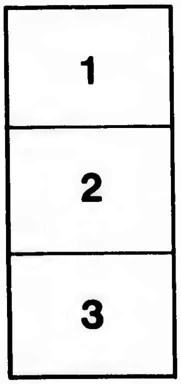

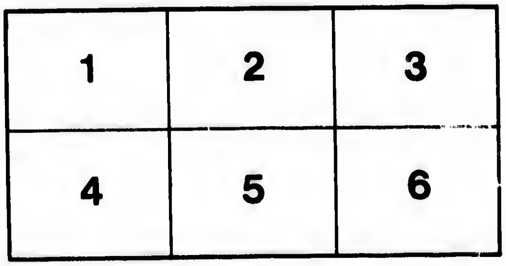

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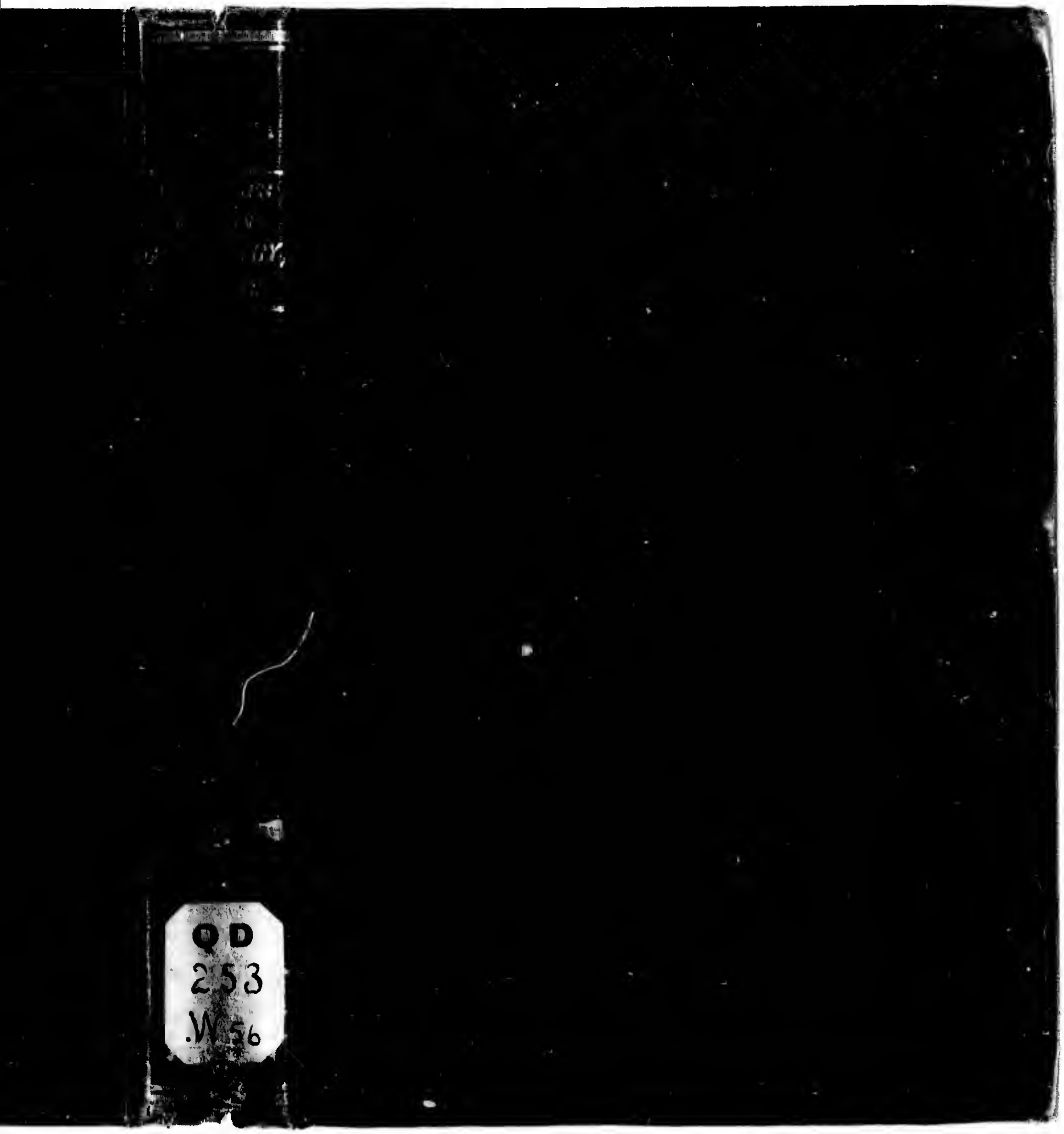

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OUTLINES

OF

MODERN CHEMISTRY,

ORGANIC,

BASED IN PART UPON RICHES' MANUEL de CHIMIE,

BY

C. GILBERT WHEELER,

Professor of Chemistry in the University of Chicago.

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PREFACE.

Organic chemistry has not as yet secured in American colleges sufficiently pronounced attention to create a demand for text-books of considerable size or extended scope. In these simple Outlines, therefore, no more has been attempted than this circumstance would appear to warrant. It is hoped that the necessary conciseness in method and form of expression has not resulted in any important sacrifice of perspicuity in thought or arrangement.

It would have been easier to prepare a larger work. From the bewildering wealth of results afforded by the labors of investigators in this branch of science, the appropriate selection of that suited to the wants of students was by no means an easy task.

It is assumed in these Outlines that those entering upon the study of Organic Chemistry have previously made themselves acquainted with Inorganic Chemistry as taught by some modern author, such as Miller or Barker, or have at least become familiar with the general principles of modern chemical philosophy. The author taking this for granted, has not, therefore, encumbered the work with a restatement of that which appertains to the theory of chemistry in general.

In addition to the organic portion of Riche's Manuel de Chimie, a translation of which by the author has served in part as basis for these Outlines, the works of Miller, Fownes, Williamson, Roscoe, and others have been freely used, while the chemical journals of Europe and America, including their latest numbers, have been consulted and the data which they afforded utilized.

For the benefit of any who may care to read the full original papers from which are taken the abridged excerpta of recent articles there are given references, within parentheses, to a list of authorities to be found in the author's work on Medical Chemistry.

Lest any regard the number of characteristic reactions of the more important compounds as insufficient, it should be stated, that it was not within the plan of the author to adapt this work to the requirements of an analytical manual. Not more than two or three analytical tests are therefore given as a rule, and even this number only in the case of the leading compounds. A similar explanation might be proffered to any who may miss the full technical details relative to certain compounds which are usually given in works on applied, or technological chemistry.

Throughout the work, the centigrade thermometer and the metric system of weights and measures are employed, unless otherwise specifically stated.

C. GILBERT WHEELER.

UNIVERSITY OF CHICAGO, October, 1877.

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CONTENTS.

ORGANIC CHEMISTRY.

INTRODUCTORY.

Organic chemistry is the science of the compounds of carbon.

Only a small number of other elements are met with in natural organic substances; they are hydrogen, oxygen and nitrogen, sometimes also, sulphur, phosphorus, and very rarely certain other elements.

Chemists have succeeded in incorporating most of the elemental substances in organic bodies, yet the larger number even of the artificial compounds include only the four elements first named.

Paraffine is found by analysis to contain only carbon and hydrogen, and is therefore called a *hydrogen-carbide.* The hydrocarbides are compounds so stable and fundamental that some chemists, as Schorlemmer for instance, have even defined organic chemistry as "the chemistry of hydrocarbons and their derivatives."

From alcohol, or sugar, we may obtain carbon and water. These bodies therefore are composed of three elements: carbon, hydrogen and oxygen, and are called *carbohydrates* ; though by some chemists, this term is restricted to those compounds containing carbon with hydrogen, and oxygen in such proportions as would form water.

If albumen is decomposed by heat, the result is not only carbon and water, but also ammonia; this substance accordingly is *nitrogenous.*

The number of organic bodies is very great. As they are composed of a small number of elements only, it may be concluded that the latter unite in a very great variety of proportions; it is therefore of much importance to know the molecular grouping of these elements. The mere fact that the kind and number of elements entering into a compound are known, is not sufficient proof that its molecular structure is really determined. Synthesis must often be employed to confirm the results of analysis.

Berthelot has specially occupied himself with the synthesis of organic bodies, and has artificially produced a great number of them. Other chemists have experimented in the same direction during the last 15 or 20 years. However, Gerhardt's opinion advanced in 1854; viz., "The vital force alone operates by synthesis and reconstructs the edifice demolished by chemical affinity," has ceased to be held as true.

ISOMERISM.

Carbon, hydrogen, oxygen and nitrogen are not only capable of uniting in a great variety of proportions, but these elements also furnish numerous *isomeric* bodies; these comprise substances which, while composed of the same elements, have different properties. Sometimes the physical properties alone are different; we then have *physical isomerism.*

When the chemical properties themselves are modified, this is denominated *chemical* isomerism. Of the latter, two kinds are recognized.

I. *Polymerism;* cyanogen and paracyanogen are examples of this variety of isomerism; the latter is to be considered as cyanogen, CN condensed, thus (CN)n; it is a polymeride of cyanogen. The weight of the molecule of these two substances is therefore different.

II. *Metamerism.* At other times the isomerism results from a different grouping of elements in the compound, the molecular weight remaining the same.

We will illustrate this by two examples:

a) Methyl acetate,
and b) Ethyl formiate.

Acetic acid = $H\text{-}O\text{-}C_2H_3O$.

Methyl hydrate, or methyl alcohol=$H\text{-}O\text{-}CH_3$.

When these two bodies react they furnish water and methyl acetate, $CH_3\text{-}O\text{-}C_2H_3O = C_3H_6O_2$.

Formic acid=$H\text{-}O\text{-}CHO$.

Ethyl hydrate, or ethyl alcohol=$H\text{-}O\text{-}C_2H_5$.

Now formic acid contains CH_2 less than acetic acid, and hydrate of ethyl contains one molecule of CH_2 more than does hydrate of methyl. As these substances in reacting lose one molecule of water, it is therefore clear that the compound obtained will have, like the preceding one, the formula $C_3H_6O_2$. But these two products are not identical substances, for the former treated with alkalies regains the molecule of water which it had lost, reforming acetic acid and methyl hydrate, while the latter regenerates formic acid and ethyl hydrate.

These bodies accordingly differ in the arrangement of their molecule; they are called *metameric bodies.*

Finally there exist bodies which are *isomeric, properly so-called*, possessing the same formula, having the same general reactions, the same chemical functions, and which differ only in a very few, chiefly physical, properties: such are oil of turpentine and oil of lemon, each having the formula $C_{10}H_{16}$.

CLASSIFICATION OF ORGANIC COMPOUNDS.

Chemical Types.—The idea of referring organic bodies to some simple *model*, or *type*, was originally worked out by Laurent and Gerhardt, 1846-53, though the germs of their ideas on classification are to be found in the earlier papers of the distinguished American chemist T. Sterry Hunt. (*Am. Jour. Sci.* [2] xxxi.)

The four principal types are:

I. The hydrogen type, $\left.\begin{matrix}H'\\H'\end{matrix}\right\}$ or H_2.

II. The oxide or water type, $\left.\begin{matrix}H'\\H'\end{matrix}\right\}O''$ or H_2O.

III. The nitride or ammonia type, $\left.\begin{matrix}H'\\H'\\H'\end{matrix}\right\}N'''$ or H_3N.

IV. The marsh gas type $\left.\begin{matrix}H'\\H'\\H'\\H'\end{matrix}\right\}C^{IV}$ or H_4C.

Of the leading groups of organic bodies, we refer to the hydrogen type: hydrocarbides, aldehyds and the compounds of metals and metalloids with organic radicals.

To the water type are referred the alcohols, ethers, mercaptans and anhydrides.

To the ammonia type belong the amides, amines, and alkalamides, all of which are denominated *compound ammonias.*

Marsh-gas is the type to which carbon dioxide is referred, as well as some of the more complex organometallic bodies.

Further details as to the relation of each of these classes of compounds to their respective types will be given as each particular class is studied.

Besides the simple type, Kekulé has proposed compound types formed by the combination of two of the four types already given. Thus the types of ammonia and water combined serve as a pattern for carbamic and oxamic acids:

$$\begin{matrix} & \text{Carbamic acid.} & \text{Oxamic Acid.} \\ \left.\begin{matrix}H'\\H'\\H'\end{matrix}\right\}N''' & \left.\begin{matrix}H\\H\end{matrix}\right\}N, & \left.\begin{matrix}H\\H\end{matrix}\right\}N \\ \left.\begin{matrix}H'\\H'\end{matrix}\right\}O'' ; & \left.\begin{matrix}CO''\\H\end{matrix}\right\}O & \left.\begin{matrix}(C_2O_2)''\\H\end{matrix}\right\}O . \end{matrix}$$

HOMOLOGOUS SERIES.

The members of a series of compounds which have the common difference of CH_2 are said to be *homologous*. Two or more such homologous series are termed *isologous*.

The first idea of progressive series in organic chemistry was enunciated by James Schiel, of St. Louis, Mo., in 1842. It was afterwards adopted by Gerhardt unchanged, save only in name. (100-5-195.)

The subjoined table will illustrate the nature of these series. Each vertical column forms a homologous series in which the terms differ by CH_2, and each horizontal line an isologous series in which the successive terms differ by H_2. The bodies of these last series are designated as the monocarbon, dicarbon group, etc.

$C\,H_4$	$C\,H_2$					
C_2H_6	C_2H_4	C_2H_2				
C_3H_8	C_3H_6	C_3H_4	C_3H_2			
C_4H_{10}	C_4H_8	C_4H_6	C_4H_4	C_4H_2		
C_5H_{12}	C_5H_{10}	C_5H_8	C_5H_6	C_5H_4	C_5H_2	
C_6H_{14}	C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6	C_6H_4	C_6H_2

The terms of the same homologous series resemble one another in many respects, exhibiting similar transformations under the action of given re-agents, and a regular gradation of properties from the lowest to the highest ; thus, of the hydro-carbons, C_nH_{2n+2}, the lowest terms CH_4, C_2H_6, and C_3H_8, are gaseous at ordinary temperatures, the highest containing 20 or more carbon-atoms, are solid, while the intermediate compounds are liquids, becoming more and more viscid and less volatile, as they contain a greater number of carbon-atoms, and exhibiting a constant rise of about 20° C. (36° F.) in their boiling points for each addition of CH_2 to the molecule.

The individual series are given in the following table, with the names proposed for them by A. W. Hoffmann:

Methane CH_4	Methene CH_2			
Ethane C_2H_6	Ethene C_2H_4	Ethine C_2H_2		
Propane C_3H_8	Propene C_3H_6	Propine C_3H_4	Propone C_3H_2	
Quartane C_4H_{10}	Quartene C_4H_8	Quartine C_4H_6	Quartone C_4H_4	Quartune C_4H_2
Quintane C_5H_{12}	Quintene C_5H_{10}	Quintine C_5H_8	Quintone C_5H_6	Quintune C_5H_4
Sextane C_6H_{14}	Sextene C_6H_{12}	Sextine C_6H_{10}	Sextone C_6H_8	Sextune C_6H_6

The formulæ in the preceding tables represent hydrocarbons all of which are capable of existing in the separate state, and many of which have been actually obtained. They are all derived from saturated molecules, C_nH_{2n+2}, by abstraction of one or more *pairs* of hydrogen-atoms.

But a saturated hydrocarbon, CH_4, for example, may give up 1, 2, 3, or any number of hydrogen-atoms in exchange for other elements; thus marsh gas, CH_4, subjected to the action of chlorine under various circumstances, yields the substitution-products,

$$CH_3Cl, \qquad CHC_2Cl_2, \qquad CHCl_3, \qquad CCl_4,$$

which may be regarded as compounds of chlorine with the radicles,

$$(CH_3)', \qquad (CH_2)'', \qquad (CH_3)''', \qquad C^{iv};$$

and in like manner each hydrocarbon of the series, C_nH_{2n+2}, may yield a series of radicles of the forms,

$$(C_nH_{2n+1})', \ (C_nH_{2n})'', \ (C_nH_{2n-1})''' \ \ (C_nH_{2n-2})^{iv}, \&c.$$

each of which has an equivalent value, or combining power, corresponding with the number of hydrogen-atoms abstracted from the original hydrocarbon. Those of even equivalence contain even numbers of hydrogen-atoms, and are identical in composition with those in the table above given; but those of uneven equivalence contain odd numbers of hydrogen-atoms, and are incapable of existing in the separate state, except, perhaps, as double molecules.

These hydrocarbon radicles of uneven equivalence are designated by Hoffmann, with names ending in *yl*, those of the univalent radicles being formed from methane, ethane, &c., by changing the termination *ane* into *yl;* those of the trivalent radicles by changing the final *e* in the names of the bivalent radicles, methene, &c., into *yl;* and similarly for the rest. The names of the whole series will therefore be as follows :

CH_4	$(CH_3)'$	$(CH_2)''$	$(CH)'''$
Methane	Methyl	Methene	Methenyl
C_2H_6	$(C_2H_5)'$	$(C_2H_4)''$	$(C_2H_3)'''$
Ethane	Ethyl	Ethene	Ethenyl
C_3H_8	$(C_3H_7)'$	$(C_3H_6)''$	$(C_3H_5)'''$
Propane	Propyl	Propene	Propenyl
&c.		&c.	&c.

From these hydrocarbon radicles, others of the same degree of equivalence may be derived by partial or total replacement of the hydrogen by other elements, or compound radicles. Thus from propyl, C_3H_7, may be derived the following univalent radicles:—

C_3H_6Cl	$C_3H_3Cl_4$	C_3H_5O
Chloropropyl	Tetrachloropropyl	Oxypropyl
$C_3H_2Cl_3O$	$C_3H_6(CN)'$	$C_3H_6(NO_2)$
Trichloroxypropyl	Cyanopropyl.	Nitropropyl
$C_3H_4(NH_2)O$	$C_3H_6(CH_3)$	$C_3H_5(C_2H_5)_2$
Amidoxypropyl	Methylpropyl	Diethylpropyl.

From the radicles above mentioned, all well-defined organic compounds may be supposed to be formed by combination and substitution, each radicle entering into combination, just like an elementary body of the same degree of equivalence.

TABLE TO ILLUSTRATE THE ARRANGEMENT OF THE MORE

Series.	Hydro-carbons.	Sulphides.	Chlorides or Haloid Ethers.	Alcohols.
General Formula.	C_nH_{2n}	$\left.\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\right\}S$	$C_nH_{2n+1}Cl$	$\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O$
	1. $C\ H_2$	$(C\ H_3)_2S$	$C\ H_3\ Cl$	$C\ H_3\ HO$
	2. $C_2\ H_4$	$(C_2H_5)_2S$	$C_2H_5\ Cl$	$C_2H_5\ HO$
	3. $C_3\ H_6$		$C_3H_7\ Cl$	$C_3H_7\ HO$
	4. $C_4\ H_8$		$C_4H_9\ Cl$	$C_4H_9\ HO$
	5. $C_5\ H_{10}$	$(C_5H_{11})_2S$	$C_5H_{11}Cl$	$C_5H_{11}HO$
	6. $C_6\ H_{12}$			$C_6H_{13}HO$
	7. $C_7\ H_{14}$			
	8. $C_8\ H_{16}$		$C_8H_{17}Cl$	$C_8H_{17}HO$
	9. $C_9\ H_{18}$			
	10. $C_{10}H_{20}$			
Types	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$

THE MORE

IMPORTANT ORGANIC COMPOUNDS IN HOMOLOGOUS SERIES.

rs.	Alcohols.	Mercaptans.	Aldehyds.	Acids.	Simple Ethers.	Compound Ethers.	
1	$\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}S$	$\left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\right\}O$	$\left.\begin{matrix}C_nH_{2n+1}\\C_nH_{2n-1}O\end{matrix}\right\}O$	
	CH_3HO	CH_3HS	CHO,H	$HCHO_2$	$(CH_3)_2O$	CH_3CHO_2	1.
	C_2H_5HO	C_2H_5HS	C_2H_3O,H	$HC_2H_3O_2$	$(C_2H_5)_2O$	$C_2H_5C_2H_3O_2$	2.
	C_3H_7HO		C_3H_5O,H	$HC_3H_5O_2$		$C_2H_5C_3H_5O_2$	3.
	C_4H_9HO	C_4H_9HS	C_4H_7O,H	$HC_4H_7O_2$		$C_2H_5C_4H_7O_2$	4.
	$C_5H_{11}HO$	$C_5H_{11}HS$	C_5H_9O,H	$HC_5H_9O_2$	$(C_5H_9)_2O$	$C_5H_{11}C_5H_9O_2$	5.
	$C_6H_{13}HO$		$C_6H_{11}O,H$	$HC_6H_{11}O_2$		$C_2H_5C_6H_{11}O_2$	6.
			$C_7H_{13}O,H$	$HC_7H_{13}O_2$		$C_2H_5C_7H_{13}O_2$	7.
	$C_8H_{17}HO$			$HC_8H_{15}O_2$		$C_2H_5C_8H_{15}O_2$	8.
				$HC_9H_{17}O_2$		$C_2H_5C_9H_{17}O_2$	9.
			$C_{10}H_{19}H,O$	$HC_{10}H_{19}O_2$	$(C_{10}H_{19})_2O$	$C_2H_5C_{10}H_{19}O_2$	10.
	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	

CARBIDES OF HYDROGEN.

The origin or preparation of these compounds, also called *hydrocarbides*, and their properties, physical and chemical, all differ largely.

They are unlike the hydrogen combinations studied in inorganic chemistry inasmuch as they possess but feeble chemical energy Among the carbides are: acetylene, marsh-gas or methane, ethylene, oil of turpentine and of lemon, benzol, naphthalin, petroleum, caoutchouc, gutta-percha, etc.

The hydrocarbides will be divided into six series, they are all built upon the type of a molecule of hydrogen, or $\left.\begin{matrix}H'\\H'\end{matrix}\right\}$.

FIRST SERIES.

General Formula, C_nH_{2n-2}.

ACETYLENE, OR DIHYDROGEN DICARBIDE.

Discovered by Davy and composition determined by Berthelot.
Formula, C_2H_2.
Specific Gravity, 0.92. Density, 13. Molecular weight, 26.

Direct combination of Carbon and Hydrogen. Up to comparatively recent times it has been considered impossible to unite carbon and hydrogen directly. Berthelot, however, succeeded in doing this in the year 1863.

Preparation.—The apparatus which he employed in this remarkable synthesis, consisted of a glass flask, provided with two lateral tubulures through which passed two metallic rods, terminating in carbon points, and which approached so as to form, when connected with a powerful battery, an electric arc. The corks through which these rods passed were provided with another opening each, to which a tube was adapted. Through one of these tubes hydrogen was admitted and through the other the products of the reaction passed as they were formed.

The gas was collected in a solution of cuprous chloride in ammonia. A red-precipitate, acetylide of copper was formed, which was thrown upon a filter and treated with hydrochloric acid in a flask, whereupon acetylene was set free.

Many organic compounds produce acetylene on subjecting their vapors to the action of electric discharges.

Acetylene is also produced, as a rule, whenever organic matter is decomposed by heat.

PROPERTIES.—Acetylene is a colorless gas, having a disagreeable odor. It is moderately soluble in water, and has not been liquified. It is decomposed, at about the temperature at which glass melts, into carbon, hydrogen, ethylene, ethyl hydride and condensed hydrocarbides, among which Berthelot has found benzol. Thenard has recently obtained it both as a liquid and a vitreous solid. (9—78--219.)

Acetylene burns with a fuliginous flame. It detonates violently and without residue when mixed with

2.5 volumes of oxygen. Cuprous acetylide is an explosive body. It is sometimes formed in brass gas-pipes, and has been the cause of fatal accidents.

Chlorine acts upon acetylene with extreme energy; there is often detonation accompanied by light. On moderating the action the compound $C_2H_2Cl_2$ can be obtained, which, as well as the body $C_2H_2Cl_4$, can also be prepared by the action of antimonic chloride upon acetylene.

As acetylene is not uncommonly studied in connection with inorganic compounds, a more detailed account of this hydrocarbide need not be given here.

Acetylene is the prototype of a homologous series of hydrocarbides, of which the general formula is,

$$C_n\,H_{2n-2}$$

The following members of this series are known:

Allylene, - - - -	$C_3\,H_4$
Crotonylene, - - -	$C_4\,H_6$
Valerylene, - - -	$C_5\,H_8$
Rutylene, - - -	$C_{10}H_{18}$
Benzylene, - - -	$C_{15}H_{28}$.

SECOND SERIES.

General formula, C^nH_{2n}.

ETHYLENE.

Synonyms: Elayl, Olefiant gas.
Formula $C_2 H_4$
Sp. Gr. 0.97. Molecular weight, 28.

This gas, for no good reason other than custom, is always studied in inorganic chemistry, usually in connection with the consideration of illuminating gas, of which, with methane, it forms a prominent constituent.

Ethylene is the type of a class of homologous hydrocarbides, of which the general formula is:

$$C_n H_{2n}.$$

Each member of the series is related to an alcohol from which it may be obtained on treatment with bodies having a great affinity for water, as sulphuric acid or zinc chloride.

$$C_n H_{2n-2} + O_2 - H_2O = C_nH_{2n}.$$

We note the following members of this series :

Ethylene,	$C_2 H_4$
Propylene,	$C_3 H_6$
Butylene,	$C_4 H_8$
Amylene,	$C_5 H_{10}$
Hexylene,	$C_6 H_{12}$
Heptylene,	$C_7 H_{14}$
Octylene,	$C_8 H_{16}$
Nonylene,	$C_9 H_{18}$
Paramylene,	$C_{10}H_{20}$
Cetene,	$C_{11}H_{22}$
Duodecylene,	$C_{12}H_{24}$
Tridecylene, (Paraffin?)*	$C_{13}H_{26}$
Tetradecylene,	$C_{14}H_{28}$.

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*A. G. Pouchet (66—[3] 4—868) has prepared from paraffin, by oxydation with nitric acid, paraffin acid, $C_{24}H_{48}O_2$, from which he deduces $C_{24}H_{50}$ as the formula for paraffin.

THIRD SERIES.

General formula, $C_n H_{2n+2}$.

METHANE.

Discovered by Volta in 1778.
Synonyms; Methyl hydride, Marsh gas, Formene.
Formula CH_4 or CH_3, H.
Sp. Gr. 0.559. Molecular weight, 16.
Permanent gas, not liquifiable, neutral.

Not discussed in detail here for the same reasons as given under Ethylene.

Methane is the first member of the following very important homologous series:

$C H_4$	methyl	hydride,	or	methane.
$C_2 H_6$	ethyl	"	"	ethane.
$C_3 H_8$	propyl	"	"	propane.
$C_4 H_{10}$	butyl	"	"	butane.
$C_5 H_{12}$	amyl	"	"	amane.
$C_6 H_{14}$	hexyl	"	"	hexane.
$C_7 H_{16}$	heptyl	"	"	heptane.
$C_8 H_{18}$	octyl	"	"	octane.
$C_9 H_{20}$	nomyl	"	"	nonane.
$C_{10} H_{22}$	decyl	"	"	decane.
$C_{11} H_{21}$	undecyl	"	"	undecane.
$C_{12} H_{26}$	bidecyl	"	"	bidecane.

$C_{13}H_{28}$	tridecyl "	"	tridecane.
$C_{14}H_{30}$	tetradecyl "	"	tetradecane.
$C_{15}H_{32}$	pentadecyl "	"	pentadecane.
$C_{16}H_{34}$	hexadecyl "	"	hexadecane.

Nearly all the members of this series have been found in American petroleum, mixed with members of the preceding, or ethylene, series.

Crude petroleum, refined by fractional distillation, is still a mixture of various hydrocarbons.

The commercial names given to the products separated at the different boiling points, do not appertain to chemical compounds, or bodies having a definite composition.

Subjoined is a table based on Dr. C. F. Chandler's Report on Petroleum, (100—'72–41) showing the

PRODUCTS OF THE DISTILLATION OF CRUDE PETROLEUM.*

NAME.	PERCENTAGE YIELDED.	SPECIFIC GRAVITY.	BOILING POINT.	CHIEF USES.
Cymogene			0°C.	Generally uncondensed—used in ice machines.
Rhigolene		.625	18.3	Condensed by ice and salt—used as an anæsthetic.
Gasolene	1½	.665	48.8	Used in making "air-gas."
C Naphtha	10	.706	82.2	Used for oil-cloths, cleaning, adulterating kerosene, etc. For paints and varnishes,
B Naphtha		.724	104.4	
A Naphtha		.742	148.8	
Benzine	4			Used to adulterate kerosene oil.
Kerosene oil	55	.804	176.6	Ordinary oil for lamps.
Mineral sperm		.847	218.3	
Lubricating oil		.843	301.6	Lubricating machinery.
Paraffin	19½	Solid.		Manufacture of candles.

*Re-arranged from Dr. C. F. Chandler's Report on Petroleum, presented to the Board of Health, of the City of New York, 1870.

UNSAFE KEROSENE.

Many accidents occur by explosion of lamps, when kerosene oil contains too much of the lighter oils, benzine and naphtha. This makes the oil too readily inflammable, for the lighter oils are driven out by heating (as when a lamp or kerosene stove is burning), and their vapors mixed with the oxygen of the air form a dangerous explosive mixture. There is a law requiring manufacturers to keep kerosene oil free from these lighter oils, unfortunately not always faithfully enforced.

The temperature at which kerosene, on heating in an open vessel, emits vapors which readily catch fire on approaching a burning body, is called, technically, the "flash point," and that at which the kerosene itself inflames is called the "burning point."

FOSSIL RESINS, AND BITUMEN.

These substances include amber, retinasphalt, asphalt, retinite, and many other allied bodies which are chiefly contained in the tertiary strata. In many instances they are the products of the action of an elevated temperature upon vegetable bodies; and when this is the case, they form irregular deposits which impregnate the strata around. In many cases the bitumens occur in regular beds, which appear to have been formed in a manner similar to the deposits of true coal.

Certain important building stones have been found to be more or less impregnated with bitumen.

Such is the limestone obtained at the artesian well quarry in the city of Chicago, and the celebrated Buena Vista, (Ohio,) sandstone used extensively in Cincinnati; also employed at Chicago in various prominent public buildings, as the post-office and Chamber of Commerce. The author, in making a chemical examination of the latter stone for the United States Treasury Department, found it to contain 2.3 per cent. bituminous matter.

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FOURTH SERIES.

General formula $C_n H_{2n-6}$.

BENZOL.

Synonyms ; Benzene, Benzine.
Formula $C_6 H_6$.
Sp. Gr. 0.88. Molecular weight, 78.
Sp. Gr of vapor 2.70.
Density " " 39.
Solid at 4°. Boils at 80.5°

Benzol is obtained, with acetylene and ethylene, in the decomposition of organic substances by heat, and its production is especially favored when the temperature is kept at a high point for some time.

Ethylene and methane form at a tolerably low temperature. Acetylene, which is richer in carbon, is produced at a higher temperature. Benzol and especially napthalin, being still more carbonaceous, are formed at an extremely high temperature.

Berthelot has prepared benzol synthetically by conducting methane tribromide, $CHBr_3$, over red-hot copper:

$$6(CHBr_3)+9Cu=C_6H_6+9CuBr_2$$

Benzol may be considered as condensed acetylene: $C_6H_6=(C_2H_2)_3$

Originally, benzol was prepared by a process analogous to that which furnishes methane, *i. e.*, by distilling benzoic acid with lime,

$$C_7H_6O_2+CaO = Ca\ C\ O_3+C_6H_6.$$

At present it is obtained in immense quantities from the tar which is formed as an accessory product in the manufacture of illuminating gas.

At the high temperature of the gas-retort other products, homologous with benzine, are formed as well; viz.:

Toluene	$C_7\ H_8$	boils at	110°
Xylene	$C_8\ H_{10}$	" "	139°
Cumene	$C_9\ H_{12}$	" "	165°
Cymene	$C_{10}H_{14}$	" "	180°

and other hydrocarbides, as napthalin $C_{10}H_8$, anthracene, also various sulphur compounds, notably carbon bisulphide; several oxygenated compounds, as phenol C_6H_6O, cresylol C_7H_8O; nitrogenous compounds, as aniline C_6H_7N, and various members of its homologous series.

Benzol is a colorless, neutral liquid, with a specific gravity of 0.89, almost insoluble in water but soluble in alcohol and ether.

It dissolves sulphur, phosphorus, iodine, the different resins, and fatty substances; this latter property causes it to be employed similarly with commercial "benzine" for cleansing purposes. Care must be taken to rub with a piece of cloth having an open texture, that it may remove the benzol by absorption, without which the spot would reappear after evaporation of the solvent.

Benzol burns with a fuliginous flame. Nascent oxygen gives with it various products, and notably oxalic acid and carbon dioxide.

Chlorine and bromine yield crystalline compounds with benzol. Benzol is the simplest member of a group of bodies known as the *aromatic compounds*, of which we shall proceed to describe some of the more important.

For distinguishing benzol from the benzine of commerce, which is made from petroleum, Brandberg recommends to place a small piece of pitch in a test tube, and pour over it some of the substance to be examined. Benzol will immediately dissolve the pitch to a tar-like mass, while benzine will scarcely be colored.

NITRO-BENZOL $C_6H_5NO_2$.

This body is obtained by treating benzol with fuming nitric acid.

$$C_6H_6+HNO_3 = C_6H_5(NO_2)+H_6O.$$

Nitro-benzol is a yellowish oil, crystallizing at 3°, has a sweet taste and an odor which has led to its use in perfumery under the name of *essence of mirbane.* Taken internally it acts as a poison.

On treatment of nitro-benzol with nascent hydrogen, hydrogen sulphide, or other reducing agent, we obtain *aniline*, which is a colorless liquid, boiling at 182°. It does not act upon litmus, yet combines with the acids, forming crystallizable compounds.

Aniline gives with chlorine, bromine and nitric acid products of substitution which are very numerous and well defined. It reacts upon the iodides of methyl, ethyl, etc., forming the corresponding *amines, or bodies constructed on the type of ammonia, having one or more of the hydrogen atoms replaced by an organic compound radicle:*

Aniline

$$C_6H_7N = N\left\{\begin{matrix}C_6H_5\\H\\H\end{matrix}\right.$$

Methylaniline

$$C_7H_9N = N\left\{\begin{matrix}C_6H_5\\CH_3\\H\end{matrix}\right.$$

Ethylmethylaniline

$$C_9H_{13}N = N\left\{\begin{matrix}C_6H_5\\CH_3\\C_2H_5\end{matrix}\right.$$

C_6H_5 or, when free, $(C_6H_5)_2$, is the radicle *phenyl*, hence aniline is properly *phenylamine.*

Aniline has, during the last score of years, acquired great importance, as, under the influence of oxydizing bodies, it forms most remarkable tinctorial compounds.

If a small quantity of aniline is added to a solution of chloride of lime, the liquid is colored violet, which color disappears in a few moments. In 1858, Perkins obtained, by the action of potassium bichromate and sulphuric acid, a beautiful purple, which is known in commerce as *mauve.* Shortly after, Verguin obtained a magnificent red coloring matter on heating aniline with tin dichloride.

This substance, known under the names of *aniline-red, fuchsin, magenta,* etc., is now very economically obtained with arsenic oxide in place of the tin dichloride, which is reduced to arsenous oxide by the reaction.

Hoffmann has shown that aniline-red is a salt of a colorless base, which he calls rosaniline; this substance has the formula $C_{20}H_{21}N_3O$, or $C_{20}H_{19}N_3,H_2O$.

In the past few years there have been produced green, yellow and black colors, all originating from aniline. These substances dissolve in alcohol, and dye wool and silk without in any way weakening the fabric. They have a magnificent lustre, but their permanency is not of the highest grade.

The consumption of aniline for dyeing has now come to something enormous, amounting in Germany alone to over 15,000 tons per annum.

The aniline colors are employed in injecting tissues for microscopic preparations.

For a fuller account of the aniline colors, a larger work should be consulted.

The history of aniline affords one of the most remarkable instances of the value of scientific chemical research, when perseveringly and skillfully applied, for at first few substances seemed to promise less; and the gigantic manufacturing industry at present connected with this compound, in its applications as a tinctorial agent, offers a singular contrast to the early experiments upon this body, when a few ounces furnished a supply which exceeded the most sanguine expectations of the early discoverers of this body.

PHENOL, C_6H_5O.

Synonyms: Hydrate of phenyl, carbolic acid or phenic acid.

It occurs in castoreum, though usually procured from the portions of coal-tar distilling over between 170° and 195°. They are agitated with caustic soda, water added to separate the insoluble oils, and the phenol dissolved in the alkali is liberated as a crystalline mass, on decomposing the potassium compound with hydrochloric acid.

Salicylic acid, distilled with an excess of lime, also furnishes phenol;

$$C_7H_6O_3 + CaO = CaCO_2 + C_6H_6O.$$

If phenyl-sulphuric acid, $\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}SO_4$, obtained by direct action of sulphuric acid upon phenol, is heated with potassium hydrate to about 300°, potassic phenol C_6H_5KO is obtained. Phenol is therefore obtained from benzol under the same conditions as alcohol is obtained from ethylene, the corresponding hydrocarbide.

Phenol crystallizes in handsome needles, fusible at 34° and boiling at 188°. It is little soluble in water, very soluble in alcohol and ether. Phenol furnishes with chlorine, bromine and iodine numerous substitution products.

Phenol has come, like alcohol, to have a generic signification, there being a number of analogous compounds, though only this, the ordinary phenol, is an important body. Heated with concentrated nitric acid, it furnishes yellow, very bitter, crystals of the body known as

Picric or Carbazotic acid.

Picric acid is also formed when silk, benzoin, aloes, indigo, etc., are treated with nitric acid.

This acid is very largely used in dyeing, either directly to produce a yellow color, or, combined with indigo, to produce a green.

Phenol, though called carbolic acid, does not decompose the carbonates, or combine with the metals to form true salts. Phenol dissolves in sulphuric acid without coloration, if pure, and forms phenyl-sulphuric acid or sulpho-carbolic acid

$$\left.\begin{matrix} C_6H_5 \\ H \end{matrix}\right\} SO_4,$$

which gives definite salts with the metals. One of these, the phenyl-sulphate or sulpho-carbolate of sodium $NaC_6H_6SO_4$, is claimed to have valuable properties as a prophylactic against scarlet fever.

Phenol gives certain reactions of the alcohols; this somewhat explains the origin of the name given it by Berthelot. This body is the type of a class of compounds which contains:

Cresylol obtained from creosote C_7H_8O
Phlorylol " " " $C_8H_{10}O$
Thymol " " essence of thyme $C_{10}H_{14}O$.

PHYSIOLOGICAL ACTION OF PHENOL.

Phenol attacks the skin, producing a white stain. It coagulates albumen and is employed with great success as an antiseptic and disinfectant. It is used externally in a diluted state to dress wounds which suppurate, also in many surgical cases.

It is sometimes used internally. Large doses of it are poisonous. Carbonate and especially saccharate of calcium are considered as antidotes for phenol. Grace Calvert has announced that olive or almond oil is a still better antidote.

FIFTH SERIES.

General Formula, $C_n H_{2n-4}$.

ESSENCE, OR OIL OF TURPENTINE.

Formula $C_{10}H_{16}$.
Density of vapor compared with air 4.7.
Molecular weight, 136.
Boils at 160.

Turpentine is extracted from several varieties of the family of *conifera*, notably from the pine, fir and larch.

The products vary somewhat with the nature of the tree, but they have many common characteristics; their composition is the same, their density is nearly identical and their boiling point very nearly so. Their rotary action on the solar ray varies largely.

Isomeric carbides are found in other families of plants, in the *aurantiaceæ* family for instance, as the lemons and oranges. These contain carbides very different, as evidenced by their odors and other physical properties, also different in certain chemical relations, yet having the same composition as oil of turpentine. There are also various polymers of this carbide.

This entire series of hydrocarbons can be divided into three groups. The first contains carbides having the formula $C_{10}H_{16}$, their boiling points being below 200°, and including :

	Density.	Boiling at
Oil of turpentine,	0.86	157° to 160°.
" cloves,	0.92	140° " 145°.
" lemon,	0.85	170° " 175°.
" orange,	0.83	175° " 180°.
" juniper,	0.84	about 160°.
" bergamot,	0.85	" 183°.
" pepper,	0.86	" 167°.
" elemi,	0.85	" 180°.

The carbides of the second group have the formula $C_{20}H_{32}$, their boiling is above 200°, they are :

Oil of copaiva,	0.91	245°.
" cubebs,	0.93	240°.

The third group contains the non-volatile carbides, such as

	Density
Caoutchouc, - - - -	0.92.
Gutta-percha, - - -	0.98.

The rotary power, constant for each, varies with the different species.

French oil of turpentine causes the plane of polarization to deviate to the left; the American variety turns it 13° to the right; oil of lemon causes a deviation of 50° to the right; in the case of essence of elemi the deviation amounts to 100°. Some of the essential oils of the first group contain oxygen compounds as well as the carbohydrides.

The principal chemical differences between the members of the group are the facility with which they are oxydized and their reaction with hydrochloric acid. Essence of turpentine becomes resinous rapidly when exposed to the air and finally solidifies. Essence of lemon becomes viscid after a considerable time. Hydrochloric acid produces, with essence of turpentine, a liquid and a solid compound, having each the same composition, $C_{10}H_{16}, HCl$, which, after a few weeks, becomes a dichlorhydride, (by some denominated a dichlorhydrate), $C_{10}H_{16}, 2HCl$. Essence of lemon also gives two dichlorhydrides at once, one liquid, the other solid.

Oil of turpentine may be obtained in a pure state, on distilling the commercial article in a vacuum. Thus obtained, turpentine is colorless, limpid, very volatile, and has a characteristic odor. It is insoluble in water; very soluble in alcohol and ether. It burns with a smoky flame; on exposure to the air it oxydizes and becomes resinous. The same effect is produced more rapidly with oxide of lead and some other oxides which render the oil siccative and suitable for use in painting. J. M. Merrick (100-4-289) has noticed the circumstance, important in its technical applications, that oil of turpentine attacks metalic lead quite strongly; tin, on the other hand, not at all. Turpentine, if exposed to the air, mixed with a solution of indigo, absorbs oxygen and transfers it to the indigo, which loses its color, yielding a product of oxydation called *isatin*. Under these circumstances, the turpentine does not change, and a given quantity of the essence can absorb several hundred times its volume of oxygen, and oxydize an indefinite quantity of indigo. This oxygen is probably the active modification, or ozone. Heated to 300° in a hermetically sealed tube, it changes into two products, one, isomeric, called *isoturpentine*, which boils at 177°, and which exerts a rotatory power of 10° to 15° to the left; the other, a polymer called *meta-terebenthene*, $C_{20}H_{32}$ boiling at 360°.

OTHER SERIES OF HYDROCARBIDES.

Cinnamene C_8H_8 is a very refractive liquid with a density of 0.924, boiling at 146°. *Styrol* which is produced from storax is converted at 205°, into a polymeric solid, termed *Meta-styrol* or *Draconyl*. If styrol is made to act upon acetylene, or ethylene, at a red heat, there is obtained the very important hydrocarbide *naphthalin* $C_{10}H_8$. This is a body crystallizable in very handsome plates, and is ordinarily obtained from coal tar by distillation between 200° and 300°; heavy oils pass over, out of which naphthalin crystallizes; on cooling, the mass is pressed and purified by sublimation. It fuses at 79° and distils at 220°.

Naphthalin is associated in coal tar with a hydrocarbide, beautifully crystallizing in long needles, fusing at 93° and boiling at 285°. This is *acenaphtene*

$C_{12}H_{10}$. Another hydrocarbide is also found in this tar, *anthracene.* Its formula is $C_{14}H_{10}$. It forms very diminutive crystalline plates fusing at 210° and boiling at 360°. Its vapor is extremely acrid.

This body has recently enabled chemists to reproduce the coloring principle of madder; *alizarin* $C_{14}H_8O_4$. It is obtained on oxydizing anthracene by means of a mixture of bichromate of potassium and sulphuric acid, which gives *oxyanthracene* $C_{14}H_8O_2$. This, with fused potassa, furnishes a combination of potassium and alizarin, from which the latter is precipitated by an acid. It has the form of brilliant bronze-colored needles, identical with natural alizarin obtained from madder.

Alizarin sublimes at 215° and is very stable, little soluble in cold water, but readily soluble in boiling water. It is easily dissolved in alcohol, ether and carbon bisulphide.

Its chemical character, not quite well defined as yet, appears to place it among the phenols. (See page 33.)

The artificial production of alizarin from anthracene, thus furnishing a cheap substitute for madder, the chief dye-stuff used in printing calicoes, is one of the latest and most noteworthy triumphs of organic chemistry. Thousands of acres of land in Europe, especially in Alsatia, now devoted to the culture of madder, may be restored to cereal or other food agriculture.

Before leaving the hydrocarbons proper, it should be stated that compounds of carbon and hydrogen of extra-terrestrial origin have been found in certain meteorites, by J. Lawrence Smith. (80-76-388.)

CAMPHOR.

Camphor is usually considered at this point, on account of its intimate relation to the oxydized essential oils in composition, and to turpentine in many chemical reactions.

Berthelot regards camphor as an aldehyd. Kekulé places it among the ketones.

Camphor exists in various parts of the *Laurus camphora.* To obtain it, the wood is finely divided and heated with water in a metallic vessel, closed by a cover filled with straw. The camphor is condensed in grayish crystals on the straw, forming the crude camphor of commerce; it is afterwards sublimed in a glass retort as a further purificatio. .

Camphor is a crystallized body, having a burning taste and an aromatic odor. Its density is 0.99 at 10°. It is elastic and with difficulty pulverized, which can, however, be easily effected on moistening with a few drops of alcohol. Water dissolves only about $\frac{1}{1000}$ part of it; thrown upon pure water it floats on the surface with a gyratory motion. It is soluble in alcohol, ether, acetic acid and essential oils; it is sublimed at ordinary temperatures where kept in close vessels, and deposits again on the cooler side of the receptacle.

It burns with a smoky flame and oxydizes on being boiled with nitric acid, yielding *camphoric acid* $C_{10}H_{16}O_4$ which is bibasic. Heated with zinc chloride or anhydrous phosphoric acid, it furnishes *Cymol* $C_{10}H_{14}$.

The author found (1-146-73) that on treatment of camphor with hypochlorous acid he obtained the new body, $C_{10}H_{15}ClO$, which he denominates *monochlorcamphor*; this, on treatment with alcoholic potassium hydrate, yielded *oxycamphor* $C_{10}H_{16}O_2$.

Camphor is very extensively employed in medicine and pharmacy.

RESINS, BALSAMS, GUM-RESINS.

These bodies are products of the oxidation of essential or volatile oils. The name of *gum-resin* is applied to those which contain a gum, and *balsam* to those which contain essential oils and an acid, usually cinnamic or benzoic, in addition to the resin which is present in both. A. B. Prescott, the eminent authority on proximate analysis, defines balsams as "natural mixtures of volatile oils with their oxidation products,—resins and solid volatile acids."

They are substances more or less colored, hard and brittle. They are fusible, non-volatile, and burn with a fuliginous flame. They are insoluble in water, generally soluble in alcohol, ether and essential oils.

Several of them are acid. This is the case with the most important of them, as the resin of the pine, called *colophony*, from which three isomeric acids have been obtained—the *pinic*, *sylvic*, and *pimaric*, $C_{20}H_{30}O_2$.

This resin constitutes the fixed residue obtained on distilling crude turpentine. It is used for preparing varnish, in soldering, and in certain combinations with the alkalies, called resin-soaps.

Subjoined are given the names and the origin of the principal resins, oleo-resins, gum-resins and balsams. With some, the position assigned them in this classification is not definitely settled.

RESINS.

Amber is found in the lignites and in the alluvial sands of the Baltic.

Arnicin, the active principle of Arnica Root.

Cannabin, the active principle of *Indian Hemp*.

Castorin, a secretion of the Beaver (*Castor*).

Ergotin(?), the active principle of Ergot of common rye.

Mastic, a resinous exudation of the Mastic, or Lentisk tree.

Burgundy Pitch, an exudation of the Spruce Fir, *Abies excelsa*.

Pyrethrin, the active principle of the Pellitory root.

Rottlerin, a crystalline resin from Kamala, the minute glands which cover the capsules of *Rottlera tinctoria*.

OLEO-RESINS.

Copaiva, a resinous juice of the *copaifera officinalis* found in Spanish America.

Wood-oil, an oleo-resin from the *Dipterocarpus turbinatus*.

Elemi, an exudation of an unknown tree, (probably *Cannarium commune*).

Common Frankincense, a concrete turpentine of the *Pinus tæda*.

Canada balsam, the turpentine of the Balm of Gilead Fir, (*Abies balsamea*).

Storax, from the *Liquidambar orientale*.

GUM-RESINS.

Ammoniacum, an exudation of the *Dorema ammoniacum*.

Assafœtida, a gum resin obtained by incision from the living root of the *Narthex assafœtida*.

Gamboge, obtained from the *Garcinia morella*.

Galbanum, from the *galbanum officinale*.

Myrrh, an exudation of the *Balsamodendron myrrha*.

BALSAMS.

Benzoin, obtained from incisions of the bark of *Styrax benzoin*.

Balsam of Peru, from the *Myroxylon Pereiræ*.

Balsam of Tolu, obtained from incisions of the bark of *Myroxylon tuluifera*.

Caoutchouc is the hardened juice of *Ficus elastica*, *Jatropha elastica*, *Siphonia cahuchu*, and other plants.

Gutta-percha is the concrete juice of the *percha* (Malay) tree the *Isonandra percha*, a sapotaceous plant.

ALCOHOLS.

GENERAL DEFINITION AND CHARACTERISTICS.

This name is given to a class of neutral bodies as important as they are numerous. Their essential characteristic is that of reacting upon acids so as to form water and a class of bodies called *ethers*.

The number of alcohols is very considerable. There are several distinct varieties of alcohol recognized.

I. Those built on the type of one molecule of water:

$$\left.\begin{matrix}C_2H_5{}' \\ H\end{matrix}\right\} O, \text{ ethyl or common alcohol.}$$

II. On two molecules of water:

$$\left.\begin{matrix}C_2H_4{}'' \\ H_2\end{matrix}\right\} O_2, \text{ ethylene alcohol or glycol.}$$

III. On three molecules of water:

$$\left.\begin{matrix}C_3H_5{}''' \\ H_3\end{matrix}\right\} O_3, \text{ glycerine and thus on.}$$

They may be defined as bodies built on the type of one or more molecules of water having one-half of the hydrogen replaced by a hydrocarbide radicle.

MONATOMIC ALCOHOLS,

or those formed on the type of one molecule of water.

of which ordinary alcohol is the best studied, are characterized by the fact that they contain one atom of oxygen only, and that by reaction with the monobasic acids they form only a single ether.

They may be obtained synthetically, as well as by various indirect processes.

Subjoined is a classified list of the more important monatomic alcohols:

FIRST SERIES,

$C_nH_{2n+2}O$.

Methyl alcohol (wood spirit),	$C\ H_4\ O$
Ethyl alcohol, (spirit of wine)	$C_2\ H_6\ O$
Propyl alcohol	$C_3\ H_8\ O$
Butyl alcohol,	$C_4\ H_{10}O$
Amyl alcohol,	$C_5\ H_{12}O$
Setyl alcohol	$C_6\ H_{14}O$
Octyl alcohol	$C_8H_{18}O$
Sexdecyl alcohol	$C_{16}H_{34}O$
Ceryl alcohol	$C_{27}H_{56}O$
Myricyl alcohol	$C_{30}H_{62}O$

SECOND SERIES,

$C_nH_{2n}O$.

Vinyl alcohol	$C_2\ H_4\ O$
Allyl alcohol	$C_3\ H_6\ O$

THIRD SERIES,

$C_n\ H_{2n-2}O$.

Borneol alcohol	$C_{10}H_{18}O$

FOURTH SERIES,

$$C_nH_{2n-6}O.$$

Benzyl alcohol	C_7H_8O
Xylyl alcohol	$C_8H_{10}O$
Cumol alcohol	$C_9H_{12}O$
Cymol alcohol	$C_{10}H_{14}O$

FIFTH SERIES,

$$C_nH_{2n-8}O.$$

Cinnyl alcohol	$C_9H_{10}O$
Cholesteryl alcohol	$C_{26}H_{44}O$

MONATOMIC ALCOHOLS HAVING THE GENERAL FORMULA,

$$C_nH_{2n+2}O.$$

METHYL ALCOHOL, OR WOOD-SPIRIT.

$$CH_4O = \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O.$$

This substance is found in the liquid obtained on distilling wood. The distillate contains in addition, water, acetic acid, tar, and various oils. In order to extract the methyl alcohol, it is again distilled and that portion which passes over at 90° is collected; this is diluted with water, the oil which precipitates separated, and the liquid agitated for a considerable time with olive oil. This oil is then removed, the liquid redistilled several times and only that portion collected which passes over above 70°. On being again distilled with calcium chloride it furnishes methyl alcohol, nearly pure, boiling at 66.5°.

There are other methods of rectifying besides the one here given.

This body possesses most of the general properties of ordinary alcohol. Under the action of the oxides it furnishes an aldehyd and formic acid.

With the acids it produces ethers; viz., with hydrochloric acid, methyl chloride, $CH_3Cl = \left.\begin{array}{l}CH_3\\ Cl\end{array}\right\}$; with acetic acid,

methyl acetic ether, $C_3H_6O_2 = \left.\begin{array}{l}CH_3\\ C_2H_3O\end{array}\right\} O$.

CHLOROFORM, $CHCl_3$.

Methyl chloride produces with chlorine a regular series of products of substitution. One of these terms, $CHCl_3$, is the very important body, *chloroform*, discovered in 1831 by Soubeiran and Liebig.

To prepare this compound, 40 litres of water, 5 kilos of recently slacked lime, and 10 kilos of chloride of lime are heated to 40°; 1500 grams of 90 per cent. alcohol are then added and the retort luted with clay.

It is now heated for a moment to the boiling point and the fire then at once slackened.

The ebullition having ceased there will be found two layers in the receiver. The upper layer is formed of water and alcohol, the lower one is chloroform nearly pure. The latter is washed with water, agitated with a dilute solution of potassium carbonate, or with fused calcium chloride for twenty-four hours, and distilled to four-fifths.

Chloroform is a colorless liquid. When first prepared it has a sweetish penetrating taste, and an agreeable, ethereal odor.

Its density is 1.48; it boils at 60.5°, is soluble in alcohol and ether and difficultly so in water.

It burns, though not readily; its flame having a green margin. It dissolves iodine, sulphur, phosphorus, fatty substances and resins.

An alcoholic solution of potassa decomposes it into chloride and formiate:

$$CHCl_3 + 4KHO = 3KCl + CHKO_2 + 2H_2O.$$

PHYSIOLOGICAL ACTION.

Chloroform is at present very generally used as an anesthetic. Opinions as to its manner of acting are divided. Formerly it was thought that the insensibility produced was the commencement of asphyxia. Since then it has been ascertained that the heart, in case of poisoning by chloroform, immediately loses all power of contraction. and it is now generally admitted that paralysis of the muscles and nerves of the heart is produced.

As the vapor of chloroform is very dense, care should be taken that in its use, access of air to the lungs be not wholly prevented, or serious consequences may result. Probably the fatal accidents that have occurred may, in some instances at least, be attributed to lack of care in this regard.

It is of great importance that the chloroform used should be quite pure. In some cases it has been found to have undergone spontaneous decomposition after exposure to a strong light. It ought to communicate no color to oil of vitriol when agitated with it. The liquid itself should be free from color or any chlorous odor. When a few drops are allowed to evaporate on the hand no unpleasant odor should remain.

Shuttleworth (100, 4, 339) states that partially decomposed chloroform can be rectified by agitating it with a solution of sodium hypo-sulphite.

ORDINARY ALCOHOL.

ETHYLIC, OR VINIC ALCOHOL.

Formula: C_2H_6O.
Density of vapor 23.
Density .81.
Boils at 78.4°.
Cannot be solidified.

It is prepared by the fermentation of saccharine liquids at a temperature of 25° to 30°, in the presence of a small quantity of a ferment. Cane sugar does not *directly* become alcohol under the influence of a ferment. It is first transformed into two other sugars, glucose and levulose.

$$C_{12}H_{22}O_{11} + H_2O = \underbrace{C_6H_{12}O_6}_{\text{Glucose.}} = \underbrace{C_6H_{12}O_6}_{\text{Levulose.}}.$$

In its final fermentation nearly all the sugar is changed into alcohol and carbon dioxide,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

This equation accounts for the transformation of 94 to 96 per cent. of the sugar employed, but besides alcohol and carbon dioxide, succinic acid is always formed as well as glycerine, and in most cases "fusel oil," consisting chiefly of amyl alcohol.

Fermentation is a phenomenon correlative with the development and growth of cells of the fungus *Mycoderma* (*Torula*) *cerevisiæ* which constitutes yeast. Sometimes the sugar is furnished as a natural product by fruits; often glucose is produced from the starch of cereals, potatoes, etc., and then changed into alcohol afterwards. Corn is the leading original source in this country.

Alcohol obtained by fermentation is concentrated by distillation. This operation is performed in retorts, the construction of which is based upon a principle developed by A. de Montpellier, and improved by Derosne, Dubrunfant and others. The object is to prevent the distilling over of the water with the alcohol, and is quite well accomplished by the improved methods now employed. The details are not suited to the scope of this work.

The application of this rational method of distilling admits of obtaining liquids containing up to 90 per cent. of alcohol, but it is difficult to go beyond that point of concentration.

In order to prepare alcohol more concentrated, substances having a great avidity for water must be used. Calcium chloride is not suitable, as it unites with the alcohol. Anhydrous sulphate of copper, carbonate of potassium or quicklime do not produce absolute alcohol. But it is very rare that perfectly anhydrous alcohol is required. Alcohol of 97 per cent. is obtained in treating alcohol of 85 per cent. during two days with lime, or better, with a sixth or seventh part of its weight of dry potassium carbonate, and then distilling. If it is desired to procure absolute alcohol, very concentrated alcohol is treated with caustic baryta until the liquid is colored yellow and then distilled.

Alcohol in fresh bread made with yeast has been found by Bolas (8-27-271) to the amount of .314 per cent. Slices of bread a week old contained .12 to .13 per cent.

Absolute alcohol is a colorless liquid, more limpid than water, of an agreeable odor and a burning taste. It boils at 78.4°, is neutral, combustible and burns with a flame but little luminous. It heats on coming in contact with water, and attracts the moisture of the air very rapidly.

It contracts upon mixing with water; the maximum of contraction takes place at a temperature of 15° when 52.3 vol. of absolute alcohol are mixed with 47.7 vol. of water; instead 100 vol. one obtains

96.3 vol. At the moment of admixture numerous air bubbles escape and the mixture becomes heated.

The alcoholic strength of the liquids consumed as beverages varies considerably.

Madeira	wines,	about	20	per cent.
Malaga	"	"	14 to 16	"
Bordeaux	"	"	5 to 12	"
Rhine	"	"	10 to 12	"
California	"	"	7	"
Cider		"	2 to 7	"
Beer		"	1 to 8	"

Spirits are distilled from fermented liquids; *brandy* from wine; *whisky* from a mash of corn or rye; *rum* from molasses, etc. They contain about 50 per cent. of alcohol.

The term *proof spirits* was originally given to alcohol sufficiently strong to fire gunpowder when lighted. The strength of proof spirits now varies in different localities, and it would be well were this ambiguous designation no longer employed.

Alcohol dissolves the caustic alkalies, certain nitrates, chlorides and other salts, also various gases. With some of these, genuine chemical combinations are produced, and not mere solutions; this is the case with calcium chloride and magnesium nitrate. Alcohol can be mixed with ether in all proportions; it dissolves the resins, essential oils, and a great number of other organic bodies.

The chemical properties of alcohol are very interesting. Vapor of alcohol is decomposed on passing through a tube heated to redness; hydrogen, marsh-gas, oxide of carbon, small quantities of naphthalin, benzol, and phenol are formed. In presence of air and water it slowly oxidizes and yields acid compounds. This action is rapid, if a hot spiral of platinum is placed in the alcoholic vapor.

Experiment.—Place a small platinum spiral in the wick of an alcohol lamp, light and then blow out the flame. It will be seen that the spiral remains incandescent. Spongy platinum acts still more energetically; if very concentrated alcohol is poured drop by drop into a capsule containing spongy platinum, or platinum black, it will be seen to redden, fumes are produced and an acid liquid is formed containing chiefly aldehyd and acetic acid. The same oxidation occurs if diluted alcohol is exposed to the air in the presence of *mother of vinegar*, a cryptogamic plant, (*Mycoderma aceti*). In fact, this is the basis of the manufacture of wine-vinegar and alcohol.

Fuming nitric acid reacts upon alcohol with explosive energy. Aldehyd is formed, also acetic ether, nitrous ether and acetic, formic, glycollic, oxalic and carbonic acids. Alkaline hydrates attack alcohol even in the cold potassium acetate being the chief product formed. If alcoholic vapor is made to pass over lime heated to 250°, hydrogen gas and calcium acetate are produced; the latter is decomposed at a more elevated temperature into marsh gas and water. If silver or mercury is dissolved in nitric acid, and 90 per cent. alcohol added to the cooled solutions, a lively ebullition results, and a crystalline precipitate is deposited which explodes at 185°, or by percussion. This body is the *fulminate of silver or mercury*, respectively, which is considered as derived from methyl cyanide, CH_3Cy, by the substitution of 1 molecule of nitryl, and of 1 atom of mercury, or 2 of silver for 3 atoms of hydrogen. The formulæ are $C(NO_2)HgCy$; $C(NO_2)Ag_2Cy$.

Potassium attacks absolute alcohol, and is dissolved liberating hydrogen; on cooling, potassium ethylate is deposited. Sodium acts in the same manner. These compounds, if brought in contact with water, regenerate alcohol and the respective alkaline hydrates.

Acids attack alcohol and furnish compound ethers, which we will study later. Ozone, according to A. W. Wright, (80—[3]7—184) oxydizes alcohol to acetic acid.

PHYSIOLOGICAL ACTION OF ALCOHOL. USES OF ALCOHOL.—Alcohol coagulates the blood; injected into the veins it produces instantaneous death. It is a very powerful poison, as are all alcohols of the series $C_nH_{2n+2}O$. Rabuteau (9—81—631) has shown that they are more poisonous in proportion as their molecules are complex. Cases have been observed where a large dose of alcohol has caused death in half an hour.

The worse than worthless character of distilled liquors as beverages is no longer an open question. With regard to their value as food or medicine, a more authoritative or competent expression of opinion cannot be desired than that of the International Medical Congress, which at its session in Philadelphia in 1876, said:

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"1. Alcohol is not shown to have a definite food value by any of the usual methods of chemical analysis or physiological investigation.

"2. Its use as a medicine is chiefly that of a cardiac stimulant, and often admits of substitution.

"3. As a medicine, it is not well fitted for self-prescription by the laity, and the medical profession is not accountable for such administration, or for the enormous evils arising therefrom.

"4. The purity of alcoholic liquors is, in general, not as well assured as that of articles used for medicine should be. The various mixtures when used as medicine, should have definite and known composition, and should not be interchanged promiscuously."

The dissolving power of alcohol renders it very serviceable in the arts. Solutions in this menstruum are called *alcoholic tinctures*. Only the purest alcohol ought to be used in pharmacy, though of course, various strengths are requisite, as it should be of a degree to suit the nature of the matter to be dissolved. If the substance to be treated is a resin, or some substance absolutely insoluble in water, a very concentrated alcohol is preferable. A weaker alcohol is made use of, it the matter is one that is soluble, both in alcohol and water.

Alcohol acts not only as a solvent, but also as a preventative of decay. This is a property which renders it especially valuable in the preparation of remedies.

AMYL ALCOHOL.

$$C_5H_{12}O = \left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O.$$

Synonyms: Fousel (or Fusel) Oil, Potato Spirit.

The amylic compounds derive their name from *Amylum*, starch, the chief constituent of the potato. They are formed in some proportion in almost every instance of alcoholic fermentation of sugar. Amylic alcohol is usually prepared on fractionally redistilling the oil which remains when the alcohol, prepared from potatoes, barley, corn, etc., is distilled. The product which comes over at 132°, is that collected. Cahours and Balard first established the analogy, in constitution and properties, of this compound with ordinary alcohol. It is a monatomic alcohol, giving with oxidizing re-agents, *valeric acid.*

$$\underbrace{C_5H_{12}O+O_2}_{\text{Amylic alcohol.}} = \underbrace{C_5H_{10}O_2}_{\text{Valeric acid.}}+H_2O,$$

and with acids, compound ethers, as

Chloride of amyl,	$C_5H_{11}Cl.$
Acetate of amyl or amyl-acetic ether,	$\left.\begin{matrix}C_5H_{11}\\C_2H_3O\end{matrix}\right\}O.$

MONATOMIC ALCOHOLS.

Having the general Formula $C_nH_{2n}O$.

ALLYLIC ALCOHOL $C_3H_6O = \left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}O.$

This is a body giving the same reactions as ordinary alcohol. The radicle it contains is the same as that in the triatomic alcohol, glycerine. Among its derivatives there are two which are of considerable importance:

Allyl sulphide, $\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}S.$

Sulpho-cyanide, $\left.\begin{matrix}C_3H_5\\CN\end{matrix}\right\}S.$

The former is oil of garlic; the latter oil of mustard. OIL OF GARLIC is prepared by the following method: allylic alcohol is treated with phosphorus iodide which furnishes allyl iodide C_3H_5I. This iodide is afterwards mixed with an alcoholic solution of potassium sulphide and the whole is distilled; the product which passes over is identical with the essential oil obtained in distilling garlic, onions, assafœtida, etc., with water.

OIL OF MUSTARD, OR SULPHO-CYANIDE OF ALLYL.

This body is prepared by causing iodide of allyl to react upon potassium sulpho-cyanide, $\left.\begin{matrix}CN\\K\end{matrix}\right\}S$, and may be regarded as sulpho-cyanic acid, $\left.\begin{matrix}CN\\H\end{matrix}\right\}S$, having the hydrogen replaced by the radicle of allyl alcohol, C_3H_5. The product which distills over is an irritating liquid which boils at 145°, like the oil prepared from mustard directly. This substance may also be obtained by the action of allylic alcohol upon potassium sulpho-cyanide. It is likewise obtained by the fermentation of mustard seeds.

Sulpho-cyanide of allyl does not exist already formed in black mustard (*Sinapis nigra*), but according to Bussy, its formation is due to a particular ferment.

Oil of mustard combines directly with ammonia, forming a crystalline substance called *thiosinnamine*, $C_4H_8N_2S$, which, in contact with mercuric oxide, changes into an alkaloid called *sinnamine*, of which the composition is $C_4H_6N_2$. It reacts upon lead oxide producing a substance called *sinapoline* whose formula is $C_7H_{12}N_2O$.

BORNEO CAMPHOR, OR BORNEOL $C_{10}H_{18}O$.

This body exudes from the *dryobalanops camphora* (Borneo). It is crystalline and has an odor between that of camphor and pepper. It fuses at 195°, and boils at about 220°. It is dextrogyrate. Heated with nitric acid it furnishes common camphor $C_{10}H_6O$.

DIATOMIC ALCOHOLS OR GLYCOLS.

$$C_nH_{2n+2}O_2.$$

Ordinary Glycol, $(C_2H_4)-O_2-H_2=C_2H_6\ O_2$
Propyl “ $(C_3H_6)-O_2-H_2=C_3H_8\ O_2$

Butyl Glycol, $(C_4H_8)—O_2—H_2=C_4H_{10}O_2$
Amyl " $(C_5H_{10})—O_2—H_2=C_5H_{12}O_2$
Hexyl " $(C_6H_{12})—O_2—H_2=C_6H_{14}O_2$
Octyl " $(C_8H_{16})—O_2—H_2=C_8H_{18}O_2$.

TRIATOMIC ALCOHOLS.

Glycerine, $(C_3H_5)—O_3—H_3=C_3H_8O_3$.

TETRATOMIC ALCOHOLS.

Erythrite, $(C_4H_6)—O_4—H_4=C_4H_{10}O_4$.

OTHER COMPLEX ALCOHOLS.

Glucose and its isomerides, $(C_6H_6)—O_6—H_6=C_6H_{12}O_6$.
Mannite, - - $(C_6H_8)—O_6—H_6=C_6H_{14}O_6$.
Dulcite, - - - $(C_9H_8)—O_6—H_6=C_6H_{14}O_6$.

$$\left.\begin{matrix}\text{Quercite,}\\ \text{Pinnite,}\end{matrix}\right\} C_3H_6O_2 = \left.\begin{matrix}(CH_2)_2\\ H_2\end{matrix}\right\} O_2—C_6H_{12}O_5.$$

ORDINARY GLYCOL.

$$C_2H_6O_2 = \left.\begin{matrix}(CH_2)_2\\ H_2\end{matrix}\right\} O_2.$$

The discovery of the glycols was an event of great importance. It was achieved by Wurtz in 1856, and the glycol of which we are treating was the first discovered.

In a flask surmounted by a condenser, two parts of potassium or sodium acetate, are dissolved in weak alcohol and one part of ethylene bromide added. This mixture is heated in a water bath as long as the precipitate of alkaline bromide continues to form, care being taken at the same time to keep the worm well cooled, in order that the vapors of alcohol may continually flow back into the flask. The alcohol is distilled off in a water bath, and the residue afterwards also distilled at a higher temperature, and that part collected which passes over between 140° and 200°. This portion which contains monacetic glycol, is heated with a saturated solution of baryta until the liquid acquires a strong alkaline reaction. The excess of baryta is removed by passing carbon dioxide through the solution which is then filtered and evaporated. The barium acetate is precipitated completely by strong alcohol, and the alcohol subsequently removed by distillation. The retort is now heated in an oil bath, and that portion set aside which boils above 150°. This is redistilled and the distillate between 190° and 198° is the product sought. Zeller and Huefner have lately (18, 10, 270) obtained the purest glycol by simply heating a solution of potassium carbonate with ethylene bromide.

Glycol is a colorless, odorless liquid, somewhat viscid and having a sweetish taste. Its density is 1.12; water and alcohol dissolve it in all proportions. Ether dissolves it with difficulty.

It is not oxydized in the air under ordinary conditions, but if dilute glycol be made to fall on platinum black, it becomes heated and is transformed into *glycolic acid.* Its equivlence is shown by the follow-

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ing: glycol attacks sodium forming two sodium glycols;

$$\left.\begin{matrix}C_2H_4\\NaH\end{matrix}\right\}O_2, \qquad \left.\begin{matrix}C_2H_4\\Na_2\end{matrix}\right\}O_2.$$

These glycols furnish two ethyl glycols on being heated with ethyl iodide.

$$\underbrace{\left.\begin{matrix}C_2H_4\\C_2H_5\end{matrix}\right\}O_2.}_{\text{Ethyl-glycol.}} \qquad \underbrace{\left.\begin{matrix}C_2H_4\\(C_2H_5)_2\end{matrix}\right\}O_2}_{\text{Diethyl-glycol.}}$$

With hydrogen bromide it furnishes two different products according to the number of molecules of HBr taken.

$$C_2H_6O_2 + HBr = \underbrace{C_2H_5BrO}_{\text{Monobromhydric ether.}} + H_2O.$$

$$C_2H_6O_2 + 2HBr = \underbrace{C_2H_4Br}_{\text{Ethylene bromide.}} + 2H_2O.$$

It is evident that mixed ethers may be obtained by treating glycol not with two molecules of the same acid, but with two molecules of different acids. Thus aceto-chlorhydric glycol is formed $\left.\begin{matrix}C_2H_4\\(C_2H_3O)Cl\end{matrix}\right\}O.$

These ethers, in the presence of alkalies, are reformed into their respective acids and glycol, in the same manner in which ethers of ordinary alcohol regenerate alcohol.

Monochlorhydric and aceto-chlorhydric glycol form an exception to this rule; they form oxide of ethylene in presence of alkalies.

OXIDE OF ETHYLENE, C_2H_4O,

a polymer of $(C_2H_4)_2O_2$, is related to glycol as ordinary ether to alcohol. It is not obtained like the latter by the action of hydrogen sulphate on the alcoholic compound, but is produced by the action of potassa on monochlorhydric glycol. A solution of potassa is gradually poured into chlorhydric glycol placed in a glass, or a tubulated retort.

$$KHO + C_2H_5ClO = KCl + H_2O + C_2H_4O.$$

The oxide of ethylene distills over with the water; the latter is absorbed by causing the vapors to pass through a flask containing anhydrous calcium chloride, and the oxide is condensed in a receptacle placed in a refrigerating mixture.

It is a colorless, ethereal, fragrant liquid; boiling at 13°. Its density is 0.89. Ethylene oxide is very soluble in water, alcohol and ether. It burns with a luminous flame and reduces silver salts. It has the composition but not the properties of aldehyd, of which it is an isomeride.

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Oxide of ethylene is a very remarkable body. It combines directly with oxygen, hydrogen, chlorine and bromine, also combines directly with acids, often even with the disengagement of heat, forming the ethers of glycol and polyethylenic alcohols. This body is therefore a true non-nitrogenous basic oxide.

TRIATOMIC ALCOHOLS OR GLYCERINES.

ORDINARY GLYCERINE, $C_3H_8O_3 = \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\} O$.

This body, discovered by Scheele, in 1779, and called by him, on account of its sweet taste, *the sweet principle of oils*, has been specially studied by Chevreul and by Pelouze. Berthelot discovered its real nature and proved it to be a triatomic alcohol.

Glycerine is prepared by decomposing neutral fatty bodies, in the soap and candle industry by alkalies, or better still by superheated steam. (*Tilghman's process.*) It is obtained in pharmacy, whenever lead plaster is prepared and remains in the water with which the latter is washed.

It is much employed in pharmacy and perfumery and as a solvent for many substances. Crude glycerine may be purified by boiling with animal charcoal and filtering before being evaporated to the required consistency. The best process consists in distilling the crude condensed glycerine in a current of steam. Pasteur has shown that glycerine is produced in a very small quantity in alcoholic fermentation. We owe to Wurtz, a remarkable synthetical reproduction of glycerine. Propylene C_3H_6 furnishes an iodide C_3H_5I, called iodide of allyl. This body produces with bromine the

YCERINES.

$\left.\begin{matrix} I_5 \\ I_3 \end{matrix}\right\} O$.

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compound $C_3H_5Br_3$ which, treated with potassa, or oxide of silver, yields glycerine.

$$C_3H_5Br_3+3KHO = 3\ KBr.+\underset{\text{Glycerine.}}{C_3H_8O_3}$$

Glycerine is a syrupy liquid, colorless, of a sweetish taste and destitute of odor; its density is 1.28 at 15°. Sarg has obtained crystals of glycerine, whose angles have been measured by Victor Lang (2-152-637). They are rhombic in form and very deliquescent. Glycerine is soluble in alcohol and water in all proportions; it is not dissolved by ether. It dissolves alkalies, alkaline sulphates, chlorides and nitrates, copper sulphate, silver nitrate and many other salts.

Glycerine distills at 280°, but is thereby partially decomposed. It may, however, be distilled in a vacuum without change. It is decomposed at a temperature above 300°, and oils, inflammable gases, carbon dioxide, and a product very irritating to the eyes, called *acrolein*, acrylic aldehyd, are formed; this last substance may be obtained pure by distilling glycerine with sulphuric, or phosphoric acid. The formula of acrolein is $C_3H_4O_2$; it is also produced in the dry distillation of all fatty bodies which contain glycerine. If glycerine be made to fall drop by drop upon platinum black, it unites, like alcohol and glycol, with O_2 and *glyceric acid* is formed.

$$C_3H_8O_3+O_2=C_3H_6O_4+H_2O.$$

The oxidation of the glycerine does not stop here;

there is subsequently formed, acetic, formic, and carbonic, but chiefly oxalic acid. The action of acids on glycerine demonstrates two facts; first, that glycerine is an alcohol; second, that it is a triatomic alcohol. On treating glycerine with hydrochloric acid the first reaction is similar to that between alcohol and this acid,

$$HCl+C_3H_8O_3=C_3H_7ClO_2+H_2O.$$

Monochlorhydric ether,
or
Monochlorhydrin.

The continued action of phosphorous perchloride upon glycerine, or the dichlorhydrate of glycerine, effects the elimination of additional molecules of water and the formation of trichlorhydrin.

$$3HCl+C_3H_8O_3=C_3H_5Cl_3+3(H_2O)$$

Trichlorhydrin.

Berthelot has studied the acetines, butyrines (tributyrine exists in butter), valerines, and many other ethers of glycerine. If glycerine is mixed with cold nitric acid, and sulphuric acid added drop by drop, an oily substance separates out which is *trinitroglycerine* $C_3H_5(NO_2)_3O_3$. This body detonates with great violence. It acts very energetically on the system. A few drops placed on the tongue produce violent megrim. Glycerine forms compounds with lime analogous to those formed by sugar, according to P. Carles, (1–174–87).

USES.—The uses of glycerine in the arts, and especially in pharmacy, are numerous and important, many of which are based upon the solvent power of this compound. Henry Wurtz (31–195–58) has made valuable suggestions as to its economical applications.

TABLE SHOWING THE SOLUBILITY OF SOME CHEMICALS IN GLYCERINE, (FROM KLEVER.) ONE HUNDRED PARTS OF GLYCERINE DISSOLVE THE ANNEXED QUANTITIES OF THE FOLLOWING CHEMICALS:

Arsenous oxide,	20.00
Arsenic oxide,	20.00
Acid, benzoic,	10.00
" oxalic,	15.00
" tannic,	50.00
Alum,	40.00
Ammonium carbonate,	20.00
" chloride,	20.00
Antimony and potassium tartrate,	5.50
Atropia,	3.00
Atropia sulphate,	33.00
Barium chloride,	10.00
Brucia,	2.25
Cinchonia,	0.50
" sulphate,	6.70
Copper acetate,	10.00
" sulphate,	30.00
Iron and potassium tartrate.	8.00
" lactate,	16.00
" sulphate,	25.00
Mercuric chloride,	7.50
Mercurous chloride,	27.00
Iodine,	1.90
Morphia,	0.45
Morphia acetate,	20.00
" chlorhydrate,	20.00
Phosphorus,	0.20
Plumbic acetate,	20.00
Potassium arsenate,	50.00
" chlorate,	3.50
" bromide,	25.00
" cyanide,	32.00
" iodide,	40.00
Quinia,	0.50
" tannate,	0.25

Sodium arsenate,	50.00
" bicarbonate,	8.00
" borate,	60.00
" carbonate,	98.00
" chlorate,	20.00
Sulphur,	0.10
Strychnia,	0.25
" nitrate,	4.00
" sulphate,	22.50
Urea,	50.00
Veratria,	1.00
Zinc chloride,	50.00
" iodide,	40.00
" sulphate,	35.00

ETHERS.

SIMPLE ETHERS.

Ethers are products formed by the action of alcohols upon acids.

By most chemists they are looked upon as referable to the oxides of metals; thus $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$ and $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$, may be regarded as the oxides respectively of methyl and ethyl. They bear the same relation to alcohols that oxides of the metals do to the hydrates.

Potassium hydrate	KOH.
Ethyl hydrate, or ethyl alcohol	C_2H_5OH.
Potassium oxide	$\left.\begin{matrix}K\\K\end{matrix}\right\}O$.
Ethyl oxide or ethyl ether	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$.

The simple ethers are mostly liquid. They are very slightly soluble in water, while they are readily soluble in alcohol. Exposed to the action of alkaline solutions they regenerate alcohol.

$$C_4H_8O_2+KHO = C_2H_6O+KC_2H\,O_2.$$

ETHYL ETHER.

Synonyms: Vinic ether, sulphuric ether, common ether.

$$C_4H_{10}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\} O.$$

Density .736.
Density of vapor, 37.
Specific gravity of vapor, 2.586.
Boiling point, 35.5°.

To prepare this compound, sulphuric acid is heated with alcohol in a retort, placed in a sand-bath. The ether distills, its vapor being received in a well cooled condenser, provided with a long tube which conducts the uncondensed vapor into a chimney.

The cork adapted to the tubulure of the retort is provided with two openings; in one is fixed a thermometer, through the other a tube passes which furnishes the supply of alcohol. All the connections should close perfectly. When the apparatus is arranged in this manner, pour 700 grams of 85 per cent. or 90 per cent. alcohol into the retort, and add, little by little, 100 grams sulphuric acid of 1.84 sp. gr., then heat. When the thermometer attains 130°, cause the alcohol to flow from the upper vessel at a rate sufficient to keep the temperature between 130° and 140°. The weight of alcohol capable of being transformed into ether is from 13 to 15 times the weight of the mixture first introduced into the retort. The distilled liquid is mixed with 12 parts, to every 100 of its weight, of a solution of soda having a specific gravity of 1.32, and agitated from time to time, during 48 hours.

The ether is decanted by means of a glass siphon, redistilled and four-fifths of the liquid collected. The remainder may serve for a future operation.

This furnishes ordinary ether. To further purify, wash with water, decant and treat for two days with equal parts of quick lime and fused calcium chloride. Williamson has clearly shown that etherification takes place in two stages or successive reactions as follows:

$$C_2H_6 + H_2SO_4 = H_2O + \underbrace{(C_2H_5)HSO_4}_{\text{Ethylsulphuric acid.}}$$

$$(C_2H_5)HSO_4 + C_2H_6O = C_4H_{10}O + H_2SO_4.$$

This explains how a small quantity of sulphuric acid etherizes a large amount of alcohol, since sulphuric acid is constantly regenerated. This is confirmed by the following experiment. Iodide of ethyl is made to react upon potassium alcohol; ether is obtained as indicated by the reaction;

$$C_2H_5I + C_2H_5OK = C_4H_{10}O + KI.$$

Ether is a neutral, volatile liquid, colorless, having a burning taste and a strong agreeable odor. When agitated with water it rises to the surface, but the water dissolves about one ninth of its own weight of the ether. It is miscible with alcohol in all proportions and with wood spirit. Ether is frequently adulterated with the latter substance. Next to alcohol it is the most generally employed solvent for organic substances. It dissolves resin, oils and most compounds rich in carbon and hydrogen.

Bromine, iodine, chloride of gold and corrosive sublimate are soluble in this liquid. It dissolves phosphorus and sulphur in small quantity.

W. Skey, (8—Aug. 3, '77,) has shown that contrary to the usual statement in standard works, ether dissolves notable quantities of the alkalies.

At a red heat it is decomposed and furnishes carbon monoxide, water, marsh gas and acetylene.

It is exceedingly inflammable, and burns with a bright flame.

Its extreme volatility, the density of its vapor, its insolubility in water and its great inflammability render its use dangerous, and explosions caused by it are of frequent occurrence. It should never be brought near a fire or light in open vessels. In case ether inflames, it is best, if possible, to at once close the vessel containing it, and thus avoid the more serious consequences ensuing from an explosion. Exposed to the air it experiences a slow combustion as in the case of alcohol, and the same compounds are the result.

Chlorine acts violently upon it; in moderating the action, the whole or a part of the hydrogen may be replaced atom for atom by chlorine.

Uses.—It is used in pharmacy in preparing etherial tinctures, and as an antispasmodic and stimulant in the well-known Hoffmann's anodyne. Its most important use in medicine is as an anesthetic, than which none is safer or more reliable in efficient hands. It is extensively employed in the laboratory and in photography.

COMPOUND ETHERS

are bodies built up on the type of water, having one half the hydrogen replaced by a hydrocarbide and the other half by a compound radicle containing oxygen, or, in other words, by the radicle of an acid.

ACETIC ETHER, $\left.\begin{matrix}(C_2H_5)\\(C_2H_3O)\end{matrix}\right\}O.$

To prepare this ether 8 parts of very concentrated alcohol are distilled with 7 parts of sulphuric acid and 10 parts of anhydrous sodium acetate, which may be replaced by 20 parts of dry lead acetate. The distillate is agitated with a solution of calcium chloride containing milk of lime, decanted, dried over calcium chloride and finally distilled.

Seven parts of water dissolve one part of this body. Alcohol and ether dissolve it in all proportions. It is a solvent for many organic bodies. It is easily decomposed on contact with water. Potassa also effects this decomposition very readily. A prolonged action of ammonia transforms it into acetamide and alcohol.

OXALIC ETHERS.

Oxalic acid, being a bibasic acid, furnishes with alcohol two combinations, one being acid and capable of combining with bases; the other is neutral, $C_6H_{10}O_4$.

Only the latter is of interest. It may be prepared by introducing four parts of 90 per cent. alcohol and four parts of oxalic acid into a retort, adding to this mixture three to six parts of sulphuric acid and then rapidly distilling; the product is washed several times, dried, then redistilled, collecting only the liquid which passes over at 184°. This ether is aromatic, oily, and gradually decomposes in water.

Potassium changes it into carbonic ether.

If oxalic ether is agitated with ammonia, a white powder, *oxamide*, and ethyl alcohol are produced.

$$\left.\begin{matrix}(C_2H_5)_2\\(C_2O_2)''\end{matrix}\right\}O_2+N_2\left\{\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right. =$$

$$2\left(\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O\right)+N_2\left\{\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right.$$

Oxamide may be considered as derived from two molecules of ammonia, and belongs to a class of bodies called *diamides*.

It is a white substance, insoluble in cold water and alcohol. Heated with mercuric oxide it is transformed into carbon dioxide and urea. (Williamson.)

Oxalic ether treated with ammonia in solution in alcohol furnishes *oxamic ether*.

In this connection the compound of the organic radicles with the haloid elements are usually studied: they are not unfrequently denominated ethers of the hydracids. Their type is a molecule of

hydrogen, $\left.\begin{matrix}H\\H\end{matrix}\right\}.$

CHLORIDE OF ETHYL OR CHLORHYDRIC ETHER.

$$C_2H_5Cl=\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}.$$

This body is formed in small quantity when ethylene is made to react upon hydrochloric acid.

To prepare it, alcohol contained in a flask surrounded by cold water, is saturated with hydrochloric acid gas and the mixture then distilled.

$$C_2H_6O+HCl=C_2H_5Cl+H_2O.$$

It is also obtained by pouring into a flask containing 2 parts common salt, a mixture of 1 part alcohol, and 1 part sulphuric acid: it is then gently heated and the ether collected as previously shown.

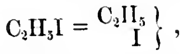
It is a liquid of an agreeable odor, and very volatile, having a boiling point of 12° and a vapor density of 64°. A red heat decomposes it into ethylene and hydrochloric acid gas. It is combustible and burns with a green, smoky flame; water dissolves the fiftieth part of its volume, alcohol dissolves it completely.

With chlorine it furnishes a complete and regular series of products of substitution which are not identical, but isomeric with the chlorine products of ethene.

Their formulæ are:

$$\begin{array}{l} C_2H_4Cl_2 \\ C_2H_3Cl_3 \\ C_2H_2Cl_4 \\ C_2H\ Cl_5 \\ C_2\ Cl_6. \end{array}$$

IODIDE OF ETHYL OR HYDROIODIC ETHER.



$$C_2H_5I = \left.\begin{array}{c} C_2H_5 \\ I \end{array}\right\} ,$$

is obtained on causing alcohol to react upon iodide of phosphorus; the action is violent with white phosphorus, considerably less so with red phosphorus.

Six hundred grams of concentrated alcohol are introduced into a retort with 140 grains of amorphous phosphorus, and to this mixture 450 grams of iodine are added. The distilling is carried nearly to dryness. The product, condensed in the receiver, is washed with water containing a little potassa; afterwards with pure water. It is then dried over calcium chloride and again distilled.

Iodide of ethyl is a colorless liquid Its density is 1.975. It becomes colored on exposure to light, being slightly decomposed; it is again rendered colorless on agitating it with an alkaline solution, which absorbs the acid formed. It burns with a green flame, leaving a residue of iodine. Ammonium compounds in alcoholic, or aqueous solution, furnish ethylamine. This amine can be attacked in its turn by iodide of ethyl and yields diethylamine and oxide of tetrethylammonium. The knowledge of these reactions and their application to other iodides are the basis of a general mode for the preparation of organic bases originated by Hoffmann. Iodide of ethyl, unlike the chloride, is readily decomposed by solutions of silver nitrate, giving a precipitate of silver iodide.

$$C_2H_5I + AgNO_3 = (C_2H_5)\,NO_3 + AgI.$$

CYANIDE OF ETHYL, OR CYANHYDRIC ETHER.

$$C_3H_5N = \left.\begin{matrix} C_2H_5 \\ C\,N \end{matrix}\right\}.$$

This ether is obtained on distilling in an oil-bath 1 part of potassium cyanide, with 1-5 part of an alkaline sulpho-vinate. To the product, redistilled in a bath of salt-water, nitric acid is slowly added in excess; it is then subjected to another distillation. Finally, it is dried over calcium chloride, and that which passes over from 195° to 200° is collected on redistillation.

Cyanide of ethyl is a colorless liquid of an alliaceous odor, boiling at 97°.

Cyanide of ethyl is decomposed by potassium hydrate; ammonia is produced, and the acid obtained corresponds with a higher homologous alcohol.

$$CN(C_2H_5)+2H_2O=NH_3+\underbrace{C_3H_6O_2}_{\text{Propionic acid.}}.$$

M. Meyer observed some years ago, that if cyanide of silver is treated with iodide of ethyl, a liquid is formed, boiling at 82°, of an odor which is not that of ordinary cyanhydric ether. Gautier has shown that this is an isomeric body, and that there are two isomeric series of cyanhydric ethers. Hoffmann has given a distinctive character to these bodies: under the influence of the alkalies they produce a fixed substance, but this is formic acid and not ammonia, and a volatile substance which is a compound ammonia.

$$CN(C_2H_5)+2H_2O=\underbrace{CH_2O_2}_{\text{Formic acid.}}+\underset{\text{Ethylamine.}}{\left.\begin{matrix}H\\C_2H_5\\H\end{matrix}\right\}N}.$$

ORGANO-METALLIC COMPOUNDS.

Iodide of ethyl attacks the metals and furnishes a class of bodies called *organo-metallic* radicles. None of these bodies are found in nature. They are formed from the iodohydric ethers by the substitution of a metal for the iodine;

$$Zn+2(C_2H_5I)=(C_2H_5)_2Zn+ZnI_2,$$

$$2Sn+2(C_2H_5I)=(C_2H_5)_2Sn+SnI_2.$$

Practically these metallic radicles are obtained by various reactions:

1. By the action of the metal upon the iodide, for example;

$$2C_2H_5I + Zn = (C_2H_5)_2Zn + ZnI_2.$$

In certain cases, with tin for instance, the reaction is not as distinct, and there is formed in addition to stannethyl iodide, stannethyl iodides variously condensed.

2d. The metal is treated with another radicle; thus sodium-ethyl is prepared by the action of sodium upon zinc ethyl,

$$(C_2H_5)_2Zn + Na_2 = Zn + 2C_2H_5Na.$$

3d. On decomposing a metalloid compound radicle with a metallic chloride,

$$3ZnCl_2 + (C_2H_5)_3P = 3(C_2H_5)Zn + 2PCl_3.$$

4th. Stannethyl is obtained by plunging a plate of zinc into a soluble salt of this radicle: the radicle is precipitated in the form of an oily liquid.

Cacodyl, $As(CH_3)_2$ was the first discovered of this class of bodies. It was obtained by Bunsen on distilling arsenous acid with potassium nitrate. The organic radicles combine with metalloids with more or less energy; zinc-ethyl and cacodyl take fire in the air; they also decompose water. The products of oxidation vary with the nature of the compounds employed; zinc-ethyl furnishes the body, C_2H_5ZnO, zinc-ethylate, which, in contact with water, produces alcohol and oxide of zinc. The metals which are less readily oxydized, such as tin, lead and mercury, give oxides which play the parts of bases, and these latter comport themselves like the oxides of the metals they contain. Finally, the radicles formed by the elements, phosphorus, arsenic, and antimony, give, with oxygen, compounds which generally have the character of acids.

Some of the organic derivatives containing phosphorus are very complex. For instance, J. Auanoff (60–'75–493) has obtained a body he denominates, *methyldiethylphosphoniumphenyloxidehydrate!*

To prepare *zinc-ethyl*, we introduce into a flask connected with a condenser inclined in such a manner that the vapors find their way back into the flask, 100 grams iodide of ethyl, 75 grams of zinc, and 6 to 7 grams of an alloy of zinc and sodium, and heat in the water bath until the zinc is dissolved; then the condenser is inclined as usual, and the distilling is effected over a direct fire, collecting the liquid product in a flask filled with dry carbon dioxide. Finally it is again distilled in this gas, and that collected which passes over from 116° to 120°. All the vessels and all the substances should be absolutely dry, and it should always be collected and distilled *in vacuo*, or in carbon dioxide. It is a colorless liquid, whose density is 1.182, boiling at 118°, inflammable on exposure to the air.

With sodium this body furnishes sodium-ethyl, and with chloride of phosphorus or arsenic, it furnishes triethyl phosphine, $P(C_2H_5)_3$, and triethyl arsine, $As\,(C_2H_5)_3$.

Mercury-methyl, treated with iodine, furnishes a hydrocarbide which has the formula of methyl, CH_3.

Professors Crafts and Friedel (72–[4]19–334) have prepared a large number of compounds of silicon with compound radicles, from which they have deduced valuable theoretical considerations.

MISCELLANEOUS ETHERS.

Formic, butyric, valerianic ether, and other ethers of the fatty series are prepared in the same manner as acetic ether, and have the general properties of this ether. The odor of these ethers is agreeable. Butyric ether has the odor of pine-apple, and valerianic ether that of pears; œnanthylic ether has the aroma of wine, etc. They are used in the manufacture of syrups, flavoring extracts, and for imparting an odor to liquors.

If the difference between the points of ebullition of these ethers is examined it will be seen that the addition of the elements CH_2 causes an elevation of about 20° in the point of ebullition. Kopp has shown that this fact is a general one and applies to the alcohols, and acids of the same series, and to the homologous bodies in general.

	Point of ebullition.	Difference.
Formic ether, - -	55°	
Acetic " - -	74°	19°
Propionic " - -	95°	21°
Butyric " - -	119°	24°
Valerianic " - -	133°	14°

The boiling point of one of these bodies may accordingly be predicted, if that of one of its homologous substances is known. There is a certain close relation between the point of ebullition of an ether and that of the acid whose radicle it contains:

	Point of ebullition.	Difference.
Formic acid,	105°	50°
" ether,	55°	
Acetic acid	118°	44°
" ether,	74°	
Propionic acid,	140°	45°
" ether,	95°	
Butyric acid,	163°	44°
" ether,	119°	

The solubility in water of the ether formed by homologous acids varies with the molecular weight; thus formic ether is quite soluble, acetic ether is less soluble, butyric ether is but slightly so, and valerianic ether, which follows it, is nearly insoluble.

MERCAPTANS AND THEIR ETHERS.

On substituting sulphur, selenium, or tellurium for oxygen in the alcohols of different atomicity, sulphur, selenium, or tellurium alcohols are obtained, which are designated as mercaptans, selenium mercaptans, and tellurium mercaptans.

Ethers proper correspond to these as to ordinary alcohols. These ethers are derived either by the substitution of an alcohol radicle for the typical hydrogen, as happens with monatomic mercaptans, or by the elimination of H_2S, as is the case with biatomic mercaptans.

One only of each of these two classes will be alluded to here.

Ethyl sulphide, or hydrosulphuric ether, $C_4H_{10}S = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\} S.$

Ethyl mercaptan, $C_4H_6S = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\} S.$

To prepare the sulphide a current of ethyl chloride, is passed into an alcoholic solution of potassium sulphide.

The mercaptan is prepared by the action of potassium hydro-sulphide or ethyl sulphide.

In either case potassium chloride is formed.

$$K_2S + C_2H_4Cl = C_4H_{10}S + 2KCl$$
$$KHS + C_2H_5Cl = C_2H_6S + KCl.$$

These bodies are afterwards separated by distillation. Like all the sulphur derivatives of alcohol, they have a nauseous odor. The sulphide boils at 91° the mercaptan at 36°.

MIXED ETHERS

containing two different radicles, are obtained by acting, for instance, with ethyl iodide upon potassium methylate, thus:

$$\underbrace{C_2H_5I}_{\text{ethyl iodide.}} + \underbrace{\left.\begin{matrix}CH^3\\K\end{matrix}\right\}O}_{\text{potassium methylate.}} = \underbrace{KI}_{\text{potassium iodide.}} + \underbrace{\left.\begin{matrix}C\,H_3\\C_2H_5\end{matrix}\right\}O}_{\text{methyl-ethyl ether.}},$$

or by acting on hydric methyl sulphate $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}SO_4$ with ethyl alcohol. The following is a list of some of the more important mixed ethers of the monatomic series;

TABLE OF MIXED ETHERS.	BOILING POINT.
Methyl-ethyl ether $C_3H_8O = \left.\begin{matrix}C\,H_3\\C_2H_5\end{matrix}\right\}O$	+11°
Methyl-amyl ether $C_6H_{14}O = \left.\begin{matrix}C\,H_3\\C_5H_{11}\end{matrix}\right\}O$	92°
Ethyl-butyl ether $C_6H_{14}O = \left.\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right\}O$	80°
Ethyl-amyl ether $C_7H_{16}O = \left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$	112°
Ethyl-hexyl ether $C_8H_{18}O = \left.\begin{matrix}C_2H_5\\C_6H_{13}\end{matrix}\right\}O$	132°

ALDEHYDS.

The following are the principal aldehyds, arranged in series:

$C_nH_{2n}O$.

Formic aldehyd	$C\,H_2\,O$
Ethylic aldehyd	$C_2\,H_4\,O$
Propylic aldehyd	$C_3\,H_6\,O$
Butylic aldehyd	$C_4\,H_8\,O$
Valeric aldehyd	$C_5\,H_{10}O$
Œnanthylic aldehyd	$C_7\,H_{14}O$
Caprylic aldehyd	$C_8\,H_{16}O$
Caproic aldehyd	$C_{10}H_{20}O$
Rutic aldehyd	$C_{11}H_{22}O$
Ethalic aldehyd	$C_{16}H_{32}O$

$C_nH_{2n-2}O$.

Allylic aldehyd (*acrolein*)	$C_3\,H_4\,O$

$C_nH_{2n-4}O$.

Campholic aldehyd (*camphor*)	$C_{10}H_{16}O$

$$C_nH_{2n-8}O.$$

Benzoic aldehyd (*oil of bitter almonds*)	C_7H_6O
Tolnic aldehyd - - - -	C_8H_8O
Cuminic aldehyd - - - -	$C_{10}H_{12}O$
Sycocerylic aldehyd - - -	$C_{18}H_{28}O$

$$C_nH_{2n-10}O.$$

Cinnamic aldehyd (*oil of cinnamon*) - C_6H_8O.

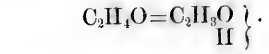
Aldehyds may be regarded as bodies built upon the type of one or more molecules of hydrogen, in which one half the hydrogen atoms are replaced by one or more molecules of an oxidized carbohydride.

The formation of aldehyd, (*al*cohol *dehyd*rogenated), may be illustrated by the following equation:

$$\underbrace{C_2H_6O-H_2}_{\text{Ethyl alcohol.}} = \underbrace{C_2H_4O}_{\text{Ethyl aldehyd.}}$$

Aldehyds are obtained by the oxydation of alcohols, but they are only the first products of oxydation. They are capable of combining with an additional molecule of oxygen, forming acids; hence the aldehyds are intermediate between alcohols and acids.

ORDINARY ALDEHYD.



$$C_2H_4O = \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}.$$

This substance is formed by the slow oxydation of alcohol.

C_7H_6O
C_8H_8O
$C_{10}H_{12}O$
$C_{18}H_{28}O$

C_6H_8O.

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Alcohol is treated with a mixture of manganese binoxide, or of potassium bichromate, and sulphuric acid, and distilled, care being taken to keep the receiver well cooled. Besides aldehyd, acetyl, acetic ether, acetic acid and water are formed. The product is again distilled, care being taken to collect only that portion which passes over above 60°. This liquid is mixed with ether, and, when cool, a stream of dry ammonia gas is caused to pass through the solution. Crystals of ammonium aldehyd are formed, $C_2H_3(NH_4)O$, which are decomposed by dilute sulphuric acid. The mixture is then distilled.

Aldehyd is a colorless, very volatile liquid. It is soluble in water, alcohol and ether, and possesses a strong, somewhat stifling odor.

The salient property of aldehyd is its avidity for oxygen. If a few drops are poured into water the latter becomes acid; it is therefore a valuable reducing agent.

If aldehyd, or ammonium aldehyd, $\left.\begin{matrix} C_2H_3O \\ NH_4 \end{matrix}\right\}$, is poured into an ammoniacal solution of silver nitrate, on slightly elevating the temperature, metallic silver is deposited. This silver adheres to the sides of the tube, and covers it with a mirror-like coating. This property is the basis of a process of silvering glass globes and other hollow articles of glass.

Aldehyd is attacked by chlorine and bromine, and furnishes, by substitution, various products, of which

CHLORAL C_2HCl_3O, is the most important. *Hy-*

drate of chloral, or $C_2HCl_3O + H_2O$, hasbeen prepared now for several years in very large quantities, for medicinal purposes. Its name is derived from *chlor*ine *al*cohol.

Absolute alcohol is saturated, first cold, then hot, with dry chlorine. The liquid obtained is mixed with its volume of concentrated sulphuric acid. The supernatant liquid is decanted, and distilled in an earthern retort, with one-fourth its weight of sulphuric acid. The anhydrous chloral obtained is re-distilled twice with calcium carbonate and 7 to 8 per cent. of water. The hydrate is then obtained in handsome crystals, $C_2HCl_3O + H_2O$, soluble in water. It has been known for some time that this body is decomposed in presence of alkalies or alkaline carbonates, into chloroform and formic acid,

$$C_2HCl_3O + H_2O + KHO = \underbrace{KCHO_2}_{\text{Potassium formiate.}} + \underbrace{CHCl_3}_{\text{Chloroform.}} + H_2O.$$

The question appeared pertinent whether a similar transformation would be affected in the human body, under the action of the alkaline fluids there present, notably those of the blood, and thus develop chloroform.

Liebreich was the first to administer chloral, and he at once obtained the anesthetic effects of chloroform. His experiments were repeated in different countries, and hydrate of chloral soon came into general use as a hyponotic.

Chloral hydrate for medical use must be crystalline and possess the following properties: it should be colorless, transparent, and have an aromatic odor, a caustic taste, readily soluble in water without furnishing drops of oil, also soluble in alcohol, ether, naphtha, benzol, and carbon bisulphide; it should fuse at 56° to 58°, solidify at about 15°, boil and volatilize completely at 95°. With caustic potassa it should furnish chloroform, and with sulphuric acid, chloral, without becoming brown. Its aqueous solution should be neutral and not produce any turbidity with silver nitrate and nitric acid. Exposed to the air it should not become moist. According to recent investigations by Liebreich, (60-69-673) chloral produces the opposite physiological effects of strychnine, hence, these bodies may be used as antidotes one for the other.

The remaining aldehyds are not sufficiently important for a work of this scope. Camphor has already been considered in connection with turpentine.

ORGANIC ACIDS.

ACIDS CONTAINING TWO ATOMS OF OXYGEN.

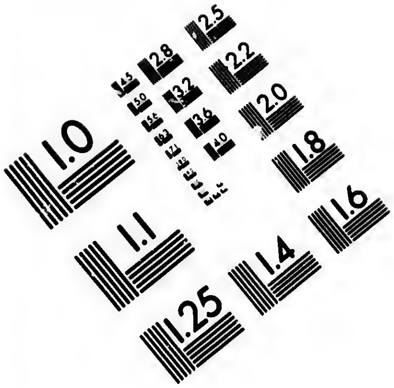
FATTY ACID SERIES.

$C_nH_{2n}O_2$.

Formic	acid,	$C H_2 O_2$
Acetic	“	$C_2 H_4 O_2$
Propionic	“	$C_3 H_6 O_2$
Butyric	“	$C_4 H_8 O_2$
Valeric	“	$C_5 H_{10} O_2$
Caproic	“	$C_6 H_{12} O_2$
Œnanthylic	“	$C_7 H_{14} O_2$
Caprylic	“	$C_8 H_{16} O_2$
Pelargonic	“	$C_9 H_{18} O_2$
Capric	“	$C_{10} H_{20} O_2$
Lauric	“	$C_{12} H_{24} O_2$
Coccinic	“	$C_{13} H_{26} O_2$
Myristic	“	$C_{14} H_{28} O_2$
Palmitic	“	$C_{16} H_{32} O_2$
Margaric	“	$C_{17} H_{34} O_2$
Stearic	“	$C_{18} H_{36} O_2$
Arachidic	“	$C_{20} H_{40} O_2$
Cerotic	“	$C_{27} H_{54} O_2$
Melissic	“	$C_{30} H_{60} O_2$.

YGEN.

$H_2 O_2$
$H_4 O_2$
$H_6 O_2$
$H_8 O_2$
$H_{10}O_2$
$H_{12}O_2$
$H_{14}O_2$
$H_{16}O_2$
$H_{18}O_2$
$H_{20}O_2$
$H_{24}O_2$
$H_{26}O_2$
$H_{28}O_2$
$H_{32}O_2$
$H_{34}O_2$
$H_{36}O_2$
$H_{40}O_2$
$H_{54}O_2$
$H_{60}O_2$.



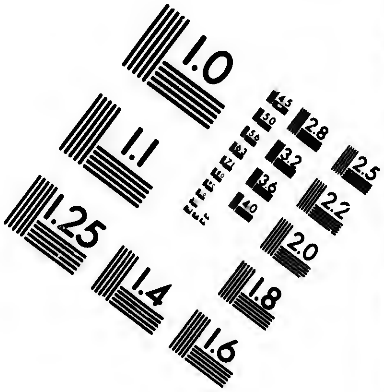
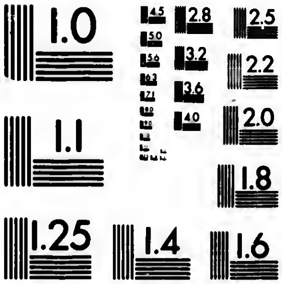
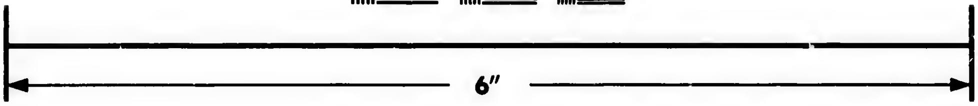
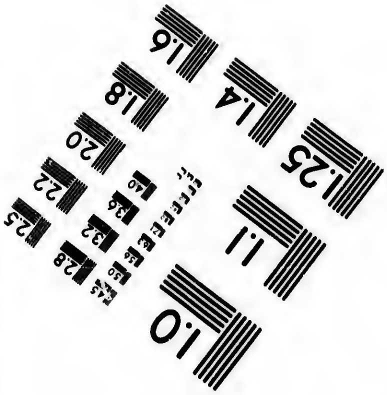
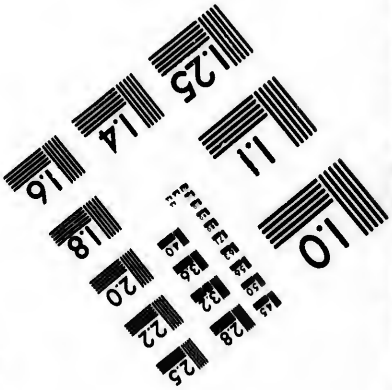


IMAGE EVALUATION
TEST TARGET (MT-3)









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$C_nH_{2n-2}O_2$.

Acrylic acid	$C H_4 O_2$
Crotonic "	$C_4 H_6 O_2$
Angelic "	$C_5 H_8 O_2$
Pyroterebic "	$C_6 H_{10} O_2$
Campholic "	$C_{10} H_{18} O_2$
Moringic "	$C_{15} H_{28} O_2$
Physetoleic "	$C_{16} H_{30} O_2$
Oleic "	$C_{18} H_{34} O_2$
Doeglic "	$C_{19} H_{36} O_2$
Erucic "	$C_{22} H_{42} O_2$.

$C_nH_{2n-4}O_2$.

Sorbic acid	$C_6 H_8 O_2$
Camphic "	$C_{10} H_{16} O_2$

AROMATIC ACID SERIES.

$C_nH_{2n-8}O_2$.

Benzoic acid	$C_7 H_6 O_2$
Toluic "	$C_8 H_8 O_2$
Xylic "	$C_9 H_{10} O_2$
Cumic "	$C_{10} H_{12} O_2$
Alpha-cymic acid	$C_{11} H_{14} O_2$.

$C_nH_{2n-10}O_2$.

Cinnamic acid	$C_9 H_8 O_2$
Pinic "	$C_{20} H_{30} O_2$.

ACIDS CONTAINING THREE ATOMS OF OXYGEN.

$C_nH_{2n}O_3$.

Carbonic	acid	$C\ H_2O_3$
Glycolic	"	$C_2H_4O_3$
Lactic	"	$C_3H_6O_3$
Oxybutyric	"	$C_4H_8O_3$
Oxyvaleric	"	$C_5H_{10}O_3$
Leucic	"	$C_6H_{12}O_3$
Œnanthic	"	$C_{14}H_{28}O_3$.

$C_nH_{2n-2}O_3$.

Pyruvic	acid	$C_3H_4O_3$
Scammonic	"	$C_{15}H_{28}O_3$
Ricinoleic	"	$C_{18}H_{34}O_3$.

$C_nH_{2n-4}O_3$.

Guaiacic	acid	$C_6H_8O_3$
Lichenstearic	"	$C_9H_{14}O_3$.

$C_nH_{2n-6}O_3$.

Pyromeconic	acid	$C_5H_4O_3$.

$C_nH_{2n-8}O_3$.

Salicylic	acid	$C_7H_6O_3$
Anisic	"	$C_8H_8O_3$
Phloretic	"	$C_9H_{10}O_3$
Oxycuminic	"	$C_{10}H_{12}O_3$
Thymotic	"	$C_{11}H_{14}O_3$.

$C_nH_{2n-10}O_3$.

Coumaric acid - - - $C_9H_8O_3$.

ACIDS CONTAINING FOUR ATOMS OF OXYGEN.

$C_nH_{2n}O_4$.

Glyceric acid $C_3H_6O_4$.

$C_nH_{2n-2}O$.

Oxalic	acid	$C_2H_2O_4$
Malonic	"	$C_3H_4O_4$
Succinic	"	$C_4H_6O_4$
Pyrotartaric	"	$C_5H_8O_4$
Adipic	"	$C_6H_{10}O_4$
Pimelic	"	$C_7H_{12}O_4$
Suberic	"	$C_8H_{14}O_4$
Anchoic	"	$C_9H_{16}O_4$
Sebic	"	$C_{10}H_{18}O_4$
Roccellic	"	$C_{17}H_{32}O_4$.

$C_nH_{2n-4}O_4$.

Fumaric	acid	$C_4H_4O_4$
Citraconic	"	$C_5H_6O_4$
Terebic	"	$C_7H_{10}O_4$
Camphoric	"	$C_{10}H_{16}O_4$
Lithofellic	"	$C_{20}H_{36}O_4$.

$C_nH_{2n-6}O_4$.

Mellitic	acid	$C_4H_2O_4$
Terechrysic	"	$C_6H_6O_4$.

$C_nH_{2n-8}O_4$.

Veratric acid	$C_9H_{10}O_4$.

$C_nH_{2n-10}O$.

Phtalic	acid	$C_8H_6O_4$
Insolinic	"	$C_9H_8O_4$
Choloidic	"	$C_{24}H_{38}O_4$.

$C_nH_{2n-14}O$.

Oxynaphthalic	acid	$C_{10}H_6O_4$
Piperic	"	$C_{12}H_{10}O_4$.

ACIDS CONTAINING 5, 6, 7 AND 8 ATOMS OF OXYGEN.

$C_nH_{2n-2}O_5$.

Tartronic	acid	$C_3H_4O_5$
Malic	"	$C_4H_6O_5$.

$C_nH_{2n-4}O_5$.

Mesoxalic acid	$C_3H_2O_5$.

$CnH_{2n-6}O_5$.

Cholesteric acid	$C_8H_{10}O_5$.

$$C_nH_{2n-8}O_5.$$

Croconic	acid	$C_5H_2O_5$
Comenic	"	$C_6H_4O_5$
Gallic	"	$C_7H_6O_5$
Cholalic	"	$C_{24}H_{40}O_5$.

$$C_nH_{2n-2}O_6.$$

Tartaric	acid	$C_4H_6O_6$
Quinic	"	$C_7H_{12}O_6$.

$$C_nH_{2n-4}O_6.$$

Carballylic acid	$C_6H_8O_6$.

$$C_nH_{2n-6}O_6.$$

Aconitic acid	$C_6H_6O_6$.

$$C_nH_{2n-10}O_6.$$

Chelidonic	acid	$C_7H_4O_6$

$$C_nH_{2n-10}O_7.$$

Meconic	acid	$C_7H_4O_7$
Citric	"	$C_6H_8O_7$
Mucic	"	$C_6H_{10}O_8$.

Organic acids are bodies built upon the type of one or more molecules of water, having one half the hydrogen replaced by an organic compound radicle con-

taining oxygen. There are some acids whose composition is not definitely fixed. We shall first examine the monatomic acids, and study the other series in the order of their atomicity.

The organic acids possess the general properties of the mineral acids. Many among them, like acetic acid, have a very decided action upon litmus. Generally, they are solid and crystallizable; however, formic, propionic, butyric acids, etc., are liquid. Acids whose molecules are comparatively simple, are ordinarily soluble in water—the others are little, or not at all, soluble in this solvent. The monobasic acids are volatile, at least where their molecules are not very complex. The polybasic acids are decomposed by heat. Their salts are ordinarily crystallizable.

METHODS OF PREPARATION.

I. The acids of the so-called fatty series are obtained by the oxidation of the corresponding alcohol, or aldehyd, which latter is the first product of oxidation of the respective alcohol.

$$C_2H_6O + O_2 = \underbrace{C_2H_4O}_{\text{Acetic aldehyd.}} + H_2O.$$

$$C_2H_4O + O_2 = \underbrace{C_2H_4O_2}_{\text{Acetic acid.}}.$$

II. These acids are also produced by the action of alkalies upon the cyanide of the radicle appertaining to the homologous inferior alcohol.

$$\underbrace{(CH_3)CN}_{\text{Methyl cyanide.}}+KHO+H_2O=NH_3+\underbrace{KC_2H_3O_2}_{\text{Potassium acetate.}}$$

III. Acids are likewise formed by the union of the elements of carbon monoxide and carbon dioxide with hydrogen carbides and water. The remarkable synthesis of formic acid by Berthelot is, according to this method:

$$CO+H_2O=CH_2O_2.$$

Pelouze has shown that heat, carefully applied to polyatomic acids, causes them to part with a certain number of molecules of water, of carbon dioxide, or of both, and furnishes acids more simple and of a lower equivalence, which he designates by the name of *pyro*-acids.

$$\underbrace{2C_4H_6O_6}_{\text{Tartaric acid.}}=\underbrace{C_5H_8O_4}_{\text{Pyro-tartaric acid.}}+2H_2O+3CO_2.$$

Of all the series of acids, the most numerous and the most important are those of the so-called *fatty series*. We shall presently indicate the methods by which they are obtained.

Their boiling point increases from 15° to 20° with each addition of CH_2 to their molecule. Certain of their salts, those of calcium, for instance, are decomposed by heat, furnishing compounds called *acetones*.

$$\underbrace{Ca(C_2H_3O_2)_2}_{\text{Calcium acetate.}}=CaCO_3+\underbrace{C_3H_6O.}_{\text{Ordinary acetone.}}$$

FORMIC ACID.

$$CH_3O_3=\left.\begin{array}{r}CH_2O\\H\end{array}\right\}O.$$

Red ants made to pass over moistened blue litmus paper produce red stains. The acid secreted by these insects was first obtained by Gehlen, and has received the name of *formic acid.*

I. Berthelot has obtained it from carbon monoxide by synthesis.

II. It is prepared by distilling a mixture of 10 parts of starch, 30 parts of sulphuric acid, 20 parts of water, and 37 parts of manganese binoxide in a large retort connected with a condenser.

The mass swells considerably, and at first must be heated but gently. The formic acid is distilled over and saturated with lead carbonate. The formiate of lead is caused to crystallize in boiling water, then placed in a retort and decomposed by a current of hydrogen sulphide and thereupon heated; the formic acid is then distilled off.

III. One kilo of glycerine, 150 to 200 grams of water and 1 kilo. of oxalic acid are introduced into a retort and heated for 15 hours at a temperature of about 100°. The oxalic acid is decomposed, but only carbon dioxide is disengaged. Water is added from time to time, and the mixture then distilled until 8 litres have passed over. The glycerine remains unchanged in the retort, and can again be used.

Formic acid is a colorless liquid, of a very acid reaction, a pungent odor and crystallizing at about 0° and boiling at 104°.

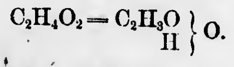
It reduces oxide of mercury, furnishing mercury, as a brown powder, also carbon dioxide and water. Its salts are usually soluble, though that of lead is very little soluble in cold water, but quite soluble in boiling water.

On heating with sulphuric acid, carbon monoxide and water are formed.

Experiment.—Introduce into a test-tube a small quantity of formic acid or a formiate. Add sulphuric acid and heat; a regular liberation of a gas takes place, which may be ignited, producing a blue flame.

$$CH_2O_2 = CO + H_2O.$$

ACETIC ACID.



$$C_2H_4O_2 = \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O.$$

Sp. Gr. 1.08. Density of vapor 30.
Glacial acetic acid melts at 17°; boils at 118°.

This is the acid of vinegar, and of which it forms the essential part. It is found in the juices of many plants and in certain fluids of the body. It is formed by synthesis from methyl, sodium, or potassium formiate, and by the oxidation of acetylene; also by the action of nitric acid upon fatty substances, and by the reaction of potassa upon tartaric, malic and citric acids.

It is further produced:

I. By the oxidation of alcohol in the following way:

Wine in vats, or casks, is placed in a cellar maintained at a temperature of about 30°; every sixth or eighth day several litres of vinegar are withdrawn and replaced by an equal quantity of wine.

Pasteur has established that the oxydation of alcohol is produced by a minute plant, the *Mycoderma aceti*. In fact, acetification commences only when this plant has been formed in the liquid. If its development is interrupted the oxydation stops; it renders the service of taking oxygen from the air and transferring it to the alcohol.

This process is very slow. It may be rendered more rapid by pouring dilute alcohol on beach-wood shavings placed in barrels. The air penetrates through openings made in the lower portion. The alcohol, after having been passed over the shavings four times, will be found sufficiently acetified, if the temperature is maintained at about 25°.

II. Distillation of wood. Pyroligneous acid. Wood is distilled in retorts; yielding vapors and gases. The former are condensed by causing them to pass through a condenser; the gases are conducted under the retorts, where they are burned, and the heat utilized in the distillation of the wood.

The condensed liquids are water, acetic acid, wood spirit and tar; the greater portion of the tar is mechanically removed and the remaining liquid distilled in a water bath. The wood spirit, which boils at 63° passes into the receiver. The water and acetic acid remaining in the retort are saturated with sodium carbonate, the product is evaporated to dryness and heated from 250° to 350°; this temperature, while not effecting the decomposition of the sodium acetate, is sufficient to carbonize the tarry substance remaining in solution. The mass is thereupon dissolved in water, filtered, and the acetate allowed to crystallize. If it is desired to obtain the acetic acid uncombined, the solution of the salt is distilled with a slight excess of sulphuric acid.

The acetic acid which distils over contains a large amount of water. Normal, or anhydrous acid may be obtained from it by saturating half of the liquid with sodium carbonate, then adding the remainder to this solution; acid sodium acetate is thereby produced, which is evaporated to dryness and distilled with sulphuric acid. This liquid, cooled with ice, gives crystals of normal acetic acid, which can be separated on decanting the liquid, furnishing the so-called *glacial acetic acid.*

Acetic acid is liquid above 17°; below that it crystallizes in handsome plates. It is a strong acid, has a pronounced odor, and is very caustic, producing blisters on the skin. It is soluble in water, alcohol and ether in all proportions. It dissolves resin and camphor, also fibrin and coagulated albumen. On uniting with water it contracts in volume. A red heat destroys it, many products being formed; methane, acetylene, acetone, benzol, naphthalin, etc., also carbon, which remains in the retort.

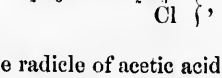
If a flask containing chlorine gas and a small quantity of acetic acid, is exposed to the sunlight, trichloracetic acid is formed. $\left.\begin{matrix}C_2Cl_3O\\H\end{matrix}\right\}O$. This experiment of Dumas served as a basis for the theory of substitution. Le Blanc has also obtained monochloracetic acid $\left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O$. These chlorine products are reduced to the state of acetic acid by reducing agents, such as sodium amalgam in presence of water,

$$(H_2)_3+C_2HCl_3O_2=3HCl+C_2H_4O_2.$$

In the same manner as acetic acid, heated with an excess of a base, furnishes marsh gas, trichlor, acetic acid produces trichlorinated marsh gas, which is chloroform,

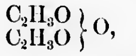
$$C_2H_4O_2+BaO=BaCO_3+CH_4$$
$$C_2HCl_3O_2+BaO=BaCO_3+CHCl_3.$$

Perchloride of phosphorus, in the hands of Gerhardt, has become the means of an important discovery, that of acetic anhydride and in general of the anhydrides of the monobasic acids. If dry sodium acetate (3 parts) is mixed with the perchloride, or better, with oxychloride of phosphorus, (1 part), and then distilled, a chloride is obtained called acetyl chloride,



$$C_2H_3OCl=\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\},$$

acetyl being the radicle of acetic acid. This chloride, subjected to the action of an excess of sodium acetate, is decomposed and furnishes *acetic anhydride*,



$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O,$$

(also called acetate of acetyl) or acetic oxide, which boils at 139°. Water destroys it, acetic acid being produced. Chloride of acetyl is an irritating liquid, boiling at about 158°, decomposable by water into acetic and hydrochloric acids.

A derivative of acetic acid of considerable theoretical importance is cyanacetic acid $C_3H_3NO_2=\left.\begin{matrix}C_2H_3O\\CN\end{matrix}\right\}O,$ a crystalline body forming salts with the metals, which have been studied by T. Menies. On acting with sulphuric acid and zinc on cyanacetic acid, the author [82-67-69] obtained formic and acetic acids and ammonia.

Vinegar. This name is given to the mixture which is obtained by the acetification of wine, whiskey, infusion of malt, etc. Good acetic vinegar is of an agreeable taste and aroma. Wood vinegar has a very strong disagreeable taste and odor. It is frequently adulterated with sulphuric acid. An addition of $\frac{1}{1000}$ of its weight of this acid is, however, not considered fraudulent, as its presence is regarded necessary to prevent moulding.

A ready method of detecting mineral acids, proposed by M. Witz (77–75–268), is based upon the use of methyl-aniline, which undergoes no change in contact with acetic acid, but promptly changes to a greenish-blue in presence of the least trace of mineral acid.

Vinegar and concentrated acetic acid are employed in medicine as stimulants.

An acetate, or acetic acid, can be recognized by heating it slightly with sulphuric acid and alcohol; a fragrant odor, characteristic of acetic ether, is observed. Heated with sulphuric acid alone, the acetates liberate a vapor which has the odor of vinegar.

The following reaction permits of the detection of mere traces of acetic acid; it is saturated with potassium carbonate and heated with arsenous oxide in a test tube; fumes and a nauseating odor are given off.

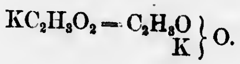
The author finds that one of the simplest tests for acetic acid, is to direct a fine, yet powerful stream of water into a test-tube, containing a few drops of the liquid to be tested. The very fine, white effervescence resulting is entirely characteristic of this acid, none of the other ordinary acids producing the same effect.

Alcohol should not be present, as it causes a similar effervesence. If the acetic acid is combined it should be set free with a strong mineral acid. By this test, perhaps more physical than chemical, acetic acid, diluted with 1000 parts of water, can be readily recognized, and with practice, one part in 1500.

ACETATES.

Acetic acid is monobasic; there are, however, alkaline biacetates and some basic acetates of copper and lead.

POTASSIUM ACETATE.



$$KC_2H_3O_2 = \left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O.$$

This salt, distilled with its weight of arsenous oxide, furnishes a very inflammable liquid, formerly called the "liquor of Cadet," and in which Bunsen has found a radicle spontaneously inflammable, *cacodyl*, $C_4H_{12}As_2$.

Potassium acetate forms, as well as sodium acetate, an acid acetate when treated with acetic acid. It is a very deliquescent salt, difficultly crystallizable.

AMMONIUM ACETATE

$$NH_4C_2H_3O_2,$$

Is prepared by saturating ammonium carbonate with acetic acid. Its solution constitutes the *spirit of Mindererus*; treated with phosphoric oxide it forms cyanide of methyl. There is also an acid salt, $NH_4C_2H_3O,C_2H_4O$. In compounds of this character, acetic acid must be considered as acting the same part as the water of crystallization in salts.

SODIUM ACETATE.

$NaC_2H_3O_2+3H_2O$.

This is used in preparing marsh gas and concentrated acetic acid. It is recommended by Tommase (52-72-23), as a solvent for plumbic iodide, of which two grams are readily dissolved in 0.5 c. c. of a strong solution of sodium acetate.

CALCIUM ACETATE.

$Ca(C_2H_3O_2)_2$.

This salt, subjected to distillation, furnishes a liquid containing a large proportion of *acetone* C_3H_6O.

ALUMINUM ACETATE.

$Al(C_2H_3O_2)_3$.

This body is employed at present by dyers, as a mordant. It is prepared by causing aluminum sulphate to react upon lead acetate. Lead sulphate, which is insoluble, is separated on filtering the liquid.

FERRIC ACETATE.

This salt (*pyrolignite*) has been, and is still, somewhat employed for the preservation of wood.

COPPER ACETATES.

Normal acetate $Cu(C_2H_3O_2)_2$ is called *verditer.* It forms beautiful green crystals (*crystals of Venus*), which, subjected to distillation, furnish acetic acid mixed with acetone. During this operation, a white sublimate is formed, which deposits in the neck of the retort. This latter is cuprous acetate, and is carried over into the receiver, oxydizes, and changes into cupric acetate, which colors the distillate blue. There remains in the retort, after this decomposition, very finely divided copper which takes fire when slightly heated in the air. Solutions of this acetate reduce the salts of the oxide, CuO, and serve to prepare the suboxide, Cu_2O.

A basic acetate, designated by the name of *verdigris*, is obtained by exposing to the air sheets of copper moistened with vinegar, or surrounded by the *marc* of grapes. The metal becomes covered with a greenish incrustation whose formula is,

$$Cu(C_2H_3O_2)_2,CuO+6H_2O.$$

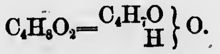
LEAD ACETATE.

The normal acetate $Pb(C_2H_3O_2)_2$ is prepared by treating litharge with acetic acid in slight excess. This salt, known by the name of *sugar of lead*, crystallizes in oblique rhombic prisms, soluble in two parts of water and eight parts of 95 per cent. alcohol. It has a sweet taste, and is very poisonous. It is employed as a re-agent, also to prepare aluminum acetate and lead chromate.

In digesting acetic acid with an excess of litharge, it furnishes a hexabasic acetate of lead. If ten parts of normal acetate, with seven parts of litharge are taken and this mixture digested with 30 parts of water, there are formed minute needles of a tribasic salt $Pb(C_2H_3O_2)_2$, $PbO2,H_2O$. Finally this salt, dissolved in normal acetate, gives a sesquibasic acetate, which is deposited in crystals, $2(Pb2C_2H_3O_2),PbO,H_2O$.

Goulard's extract is a solution containing a mixture of normal and of sesquibasic acetate of lead, which is prepared by boiling 30 parts of water, 7 parts of litharge and 6 parts of normal acetate of lead.

BUTYRIC ACID.



$$C_4H_8O_2 = \left.\begin{matrix} C_4H_7O \\ H \end{matrix}\right\} O.$$

It is usually prepared as follows: a mixture of 10 parts of sugar, 1 part of white cheese, 10 parts of chalk, and some water, is maintained at a temperature of 30° to 35°. First, lactate of lime is formed, which causes the mass to thicken, then that salt changes into butyrate, disengaging hydrogen and carbon dioxide. When the mixture has become clear, the liquor is evaporated and the butyrate separated with a skimmer. This salt is decomposed by concentrated hydrochloric acid which separates the butyric acid in the form of an oil, which is distilled off. It boils at 163°. It is of a fetid odor, and soluble in water, alcohol and ether.

VALERIANIC, OR VALERIC ACID $C_5H_{10}O_2 = \left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O.$

It can be obtained by oxydizing amylic alcohol by a mixture of potassium bichromate and sulphuric acid, or by distilling valerian root with water acidulated with sulphuric acid. The best method is to boil porpoise oil with water and lime. The oil saponifies and the valerianate of calcium alone is dissolved. This liquid is concentrated and hydrochloric acid added in excess. The valerianic acid separates out in the form of an oil which is distilled, and that portion collected which passes over at 175°.

Pierre and Puchot have lately devised a process for preparing valeric acid from amyl alcohol. (3–[3]5–40.)

BENZOIC ACID, $C_7H_6O_2$.

Density, 61.
Density of its vapor compared with air, 4.27.
Melts at 120°; boils at 250°.

It is obtained by a dry, as also by a wet process. To prepare it by the former method, equal weights of sand and gum benzoin are placed in an earthen vessel, the mixture covered with a sheet of filter paper, which is pasted down round the edge, and a long cone of white cardboard placed over the whole. The earthen vessel is then heated over a slow fire for two hours, and when cool the cone is removed. The benzoic acid is found to have condensed on the interior of the cone in handsome blades, or needles.

It is obtained in the wet way, by pulverizing gum benzoin, mixing it with half its weight of lime, and boiling for half an hour in a cast-iron kettle, with six times its weight of water, care being taken to agitate the mixture. It is thrown upon a piece of linen and the residue treated twice with water. The liquids are reduced in volume to two-thirds that of the water used during the first treatment, then saturated with hydrochloric acid. The benzoic acid separates out, and is recrystallized from a solution in boiling water.

It is also procured from the urine of herbivorous animals. This secretion, evaporated to a small bulk and treated with hydrochloric acid, yields a deposit of hippuric acid, which, on being heated with dilute sulphuric acid, is transformed into benzoic acid.

Benzoic acid is also produced on a large scale from naphthalin.

Benzoic acid crystallizes in lustrous blades, or needles, is little soluble in cold water, quite soluble in boiling water, and still more so in alcohol and ether. On passing its vapors through a tube heated to redness, it is decomposed into benzol and carbon dioxide, $C_7H_6O_2 = C_6H_6+CO_2$. Chlorine, bromine and nitric acid transform it into substitution products.

Chlorbenzoic acid, C_7H_5ClO.
Dinitrobenzoic " $C_7H_4(NO_2)_2O_2$.

Ammonium benzoate furnishes, on distillation, *benzonitrile* $C_7NH_9O_2 = C_7H_5N + 2H_2O$.

The alkaline benzoates heated with chloride, or oxychloride of phosphorus, furnish benzyl chloride, which, submitted to the action of potassium benzoate in excess, gives benzoic anhydride,

$$3(KC_7H_5O_2)+POCl_3=\underbrace{3(C_7H_5OCl)}_{\text{Chloride of benzyl.}}+K_3PO_4.$$

$$C_7H_5OCl+KC_7H_5O_2=\underbrace{C_{14}H_{10}O_3}_{\text{Benzoic anhydride.}}+KCl.$$

The rational formula of benzoic anhydride is,

$$\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O.$$

Calcium benzoate heated to a high temperature furnishes *benzone*,

$$\underbrace{Ca(C_7H_5O_2)_2}_{\text{Calcium benzoate.}}=CaCO_3+\underbrace{CO(C_6H_5)_2}_{\text{Benzone.}}.$$

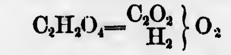
Benzoic acid is monobasic, and the benzoates are generally soluble. Benzoic acid taken into the stomach, is transformed into hippuric acid.

Kolbe and von Meyer have observed that benzoic acid has antiseptic power, though less than salicylic acid, (18–[2]12–133).

CINNAMIC ACID. In certain balsams there exists an acid called *cinnamic acid*, whose formula is $C_9H_8O_2$. It exists in the balsams of Peru, benzoin, tolu and in liquid storax. It fuses at 129° and boils at 290°. It has striking features of resemblance to benzoic acid, and is produced like the latter by the oxydation of an aldehyd. This aldehyd is the essence of cinnamon prepared by distilling cinnamon with water.

POLYATOMIC ACIDS.

OXALIC ACID.



$$C_2H_2O_4 = \left.\begin{matrix} C_2O_2 \\ H_2 \end{matrix}\right\} O_2$$

Preparation. In the burdock and sorrel is found an acid salt, commonly called *salt of sorrel*, which is a mixture of binoxalate and quadroxalate of potassium. Sodium oxalate is found in several marine plants, calcium oxalate in the roots of the gentian and rhubarb, and in certain lichens. Salt of sorrel is extracted from the burdock (*Prunex*), in Switzerland, and in the Black Forest of Germany, by expressing the plant, clarifying the expressed liquid by boiling with clay, and evaporating; crystals of salt of sorrel are deposited.

The oxalic acid may be obtained free by decomposing a solution of these crystals with lead acetate; the oxalate of lead which precipitates is treated with a suitable quantity of sulphuric acid; the lead is completely precipitated as lead sulphate; this is filtered off, and the liquid evaporated and allowed to crystallize.

At present this acid is chiefly prepared by the action of oxydizing agents upon certain organic substances; the substances best suited for this purpose are those which contain oxygen and hydrogen in the proportion to form water. One part of starch, or sugar, is boiled with eight parts of nitric acid diluted with ten parts of water, until nitrous vapors cease to be disengaged, and the liquid then evaporated. The crystals of oxalic acid which separate out are freed from the excess of nitric acid, by being several times recrystallized in water. It is also obtained on a large scale by the action, at a high temperature, of potassa or soda on saw dust.

Oxalic acid has been obtained synthetically, by Drechel, on passing carbon dioxide over sodium heated to 320°.

$$2CO_2+Na_2=Na_2C_2O_4.$$

Properties.—Oxalic acid crystallizes in prisms, which effloresce in the air, and which are very soluble in water and alcohol.

It fumes at 98°; at 170° to 180° it is partially sublimed, but the greater portion is decomposed into carbon monoxide, carbon dioxide, formic acid and water.

$$2(C_2H_2O_4)=CO+2CO_2+CH_2O_2+H_2O.$$

Chlorine, hypochlorous acid, fuming nitric acid and hydrogen peroxide, convert oxalic acid into carbon dioxide.

Sulphuric acid causes it to split up into carbon monoxide and carbon dioxide, and this reaction is made use of in preparing the former gas.

Oxalic acid is bibasic.

Normal potassium oxalate, $K_2=O_2=CO_2$.

Acid potassium oxalate, $KH=O_2=C_2O_2$.

USES.—Oxalic acid is employed in removing ink spots from cloth, and in cleaning copper. It owes these properties to the fact that it forms with iron and copper soluble salts, hence it is also employed in calico-works for removing colors.

Toxic action of oxalic acid. On account of the use of oxalic acid in the arts, and its physical resemblance to certain salts, particularly to magnesium sulphate, poisoning with it has often occurred, either through design or imprudence.

It acts powerfully upon the system. Tardieu mentions the case of a young man, sixteen years of age, who was poisoned by two grams of this substance.

The symptoms observed are similar to those produced by other corrosive agents; great prostration followed by unconsciousness and a persistent numbness in the lower extremities. The blood of the patient becomes abnormally red.

In cases of poisoning, the acid should be removed from the stomach with promptness, and milk of lime, or magnesium, or ferric hydrate administered. Lime is to be preferred, as it forms a salt completely insoluble in vegetable acids.

SUCCINIC ACID.

$$C_4H_6O_4 = \left.\begin{matrix}C_4H_4O_2\\ H_2\end{matrix}\right\} O_2.$$

This acid is produced by the oxydation of butyric acid, and by subjecting amber, *succinum*, to dry distillation or by the action of iodhydric acid on malic or tartaric acids.

Succinic acid crystallizes in rhomboidal prisms which melt at 180° and boil at about 235°, at a higher temperature they are decomposed into water and succinic anhydride $C_4H_4O_3$. It is soluble in 5 times its weight of cold water, soluble in ether and very soluble in alcohol.

It is used in the artificial preparation of malic and tartaric acids. Succinic acid has been found in the fluid of the hydrocele and of certain hydatids.

MALIC ACID.

$$\left.\begin{matrix}C_4H_3O_2\\ H,H_2\end{matrix}\right\} O_3$$

This acid, discovered by Scheele in sour apples, is found in many plants; in the berries of the service-tree, in cherries, raspberries, gooseberries, rhubarb, tobacco, etc. Malic acid is levogyrate, deliquescent and crystallizable; it is soluble in alcohol and fuses at about 100°.

At a temperature above 130°, it is decomposed into various acids and especially *paramalic acid*, $C_4H_4O_4$, which is identical with the acid of the *fumaria*. It is bibasic like oxalic acid, but triatomic and is distinguished from this acid by not producing a turbidity with calcium compounds.

TARTARIC ACID.

$$\left.\begin{matrix} C_4H_2O_2 \\ H_2, H_2 \end{matrix}\right\} O_4.$$

This acid, obtained from wine tartar by Scheele, in 1770, occurs free and combined with potassium in many vegetable products; in the sorrel, berries of the service-tree and tamarind, in the gherkin, potato, Jerusalem artichoke, etc. The grape is the chief original source of this acid.

One method of preparing tartaric acid is to purify crude tartar by dissolving and clarifying with clay, which throws down the coloring matters: then filtering and adding calcium carbonate, which precipitates half of the tartaric acid as a calcium salt.

$$\underbrace{2KHC_4H_4O_6}_{\text{Hydro-potassic tartrate.}}+\underbrace{CaCO_3}_{\text{Calcium carbonate.}}=\underbrace{CaC_4H_4O_6}_{\text{Calcium tartrate.}}+\underbrace{K_2C_4H_4O_6}_{\text{Potassium tartrate.}}+CO_2+H_2O$$

The solution which contains the potassium tartrate, is filtered and calcium chloride added : the remainder of the tartaric acid is thus precipitated as a tartrate and added to the preceding.

$$\underbrace{K_2C_4H_4O_6}_{\text{Potassium tartrate}}+CaCl_2=\underbrace{CaC_4H_4O_6}_{\text{Calcium tartrate.}}+2\,KCl.$$

These precipitates are washed and decomposed with sulphuric acid, the calcium sulphate is filtered off, and the liquid evaporated to the point of crystallization. This acid is also called right tartaric, or *dextroracemic*, as it turns the plane of polarization to the right.

Kistner has obtained from certain tartrates a tartaric acid which is optically inactive. This acid, called *paratartaric* or *racemic acid*, is somewhat less soluble than dextrotartaric acid, while the reverse is the case with its salts. It contains, moreover, one molecule of water of crystallization, but does not crystallize, as does the dextrogyrate acid, in hemihedral crystals.

Levogyrate tartaric acid is prepared by evaporating a solution of racemate of cinchonia; the levogyrate tartrate precipitates while the dextrogyrate remains in solution; or a solution of racemic acid is allowed to stand with a small quantity of calcium phosphate, and a few spores of the *Pencilium glaucum;* fermentation sets in, which destroys the dextroracemic acid.

Dextrotartaric acid crystallizes in beautiful oblique prisms with a rhombic base. Cold water dissolves twice its weight of this acid; alcohol dissolves it with equal facility. It is insoluble in ether.

Tartaric acid melts at about 180°; and furnishes different pyrogenous acids, chiefly:

Tartaric anhydride, or *Tartrelic* acid, $C_4H_4O_5$, and *Pyrotartaric acid*, $C_5H_8O_4$.

Simpson synthesized pyrotartaric acid and Lebedeff has recently (60-75-100) shown that this acid is identical with that obtained by heating tartaric acid.

Tartaric acid does not precipitate calcium salts. It produces a turbidity with lime water, but an excess of acid dissolves it; by these reactions it may be distinguished from malic and oxalic acids.

Tartrates. Tartaric acid is bibasic. The two tartrates of potassium are:

Normal potassium tartrate, $K_2C_4H_4O_6$
Hydro " " $KC_4H_5O_6$.

This latter salt is obtained by purifying the tartar of wine casks, and is called *cream of tartar.* It is used in the preparation of black flux, white flux, potassium carbonate, and tartaric acid, also largely in baking powders.

Rochelle Salt. $KNaC_4H_4O_6+4aq$. This salt is a double tartrate of potassium and sodium, which was formerly much used as a purgative. It may be prepared by mixing in a porcelain dish, 3500 grams of water and 1000 grams of cream of tartar, this is brought to boiling and sodium carbonate added as long as effervescence is produced. This solution is then filtered and evaporated until it has a density of 1.38.

The salt crystallizes in regular rhomboidal prisms; it is soluble in 2½ times its weight of water, but insoluble in alcohol.

Tartar emetic. Tartaric acid forms, with bases, a a class of salts called *emetics*, the type upon which they are formed being that of tartar emetic. The ordinary tartar emetic has been generally assigned the formula $(SbO)'K=O_2=C_4H_4O_4$, in which the monad radicle *stibyl* takes the place of one of the basic hydrogen atoms. It is prepared by boiling for an hour in 100 parts of water, 12 parts of cream of tartar, and 10 parts of antimony oxide. This mixture is then filtered, evaporated and allowed to crystallize. This salt crystallizes in rhombic octahedrons; it has a metallic taste, a slight acidity, and is soluble in 14 parts of cold, and about 2 parts of boiling water.

Crystals of tartar emetic effloresce on exposure to the air.

A strip of tin precipitates the antimony as a brown powder. Tannin, and most astringents, precipitate the antimony, hence tartar emetic should not be administered in connection with this class of bodies. This salt is the most used of the antimony compounds.

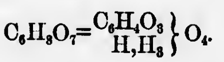
Ferro-potassium tartrate.—Cream of tartar is digested with ferrous hydrate for two hours at a temperature of 60°. For every 100 parts of cream of tartar, a quantity of hydrate should be used containing 43 parts of ferrous oxide.

The product is filtered, the liquid received in shallow plates, and kept at a temperature of about 45°; the salt thus crystallizes in brilliant scales of a garnet red color. It dissolves in water, but is insoluble in strong alcohol. Tartaric acid is often adulterated with alum, potassium bisulphate and cream of tartar; these substances may all be detected by means of alcohol, in which they are not soluble.

Tartaric acid is used in making effervescing drinks, and as a *discharge* by calico printers.

Tartaric acid produces the same toxical effects as oxalic acid, though requiring *much larger* doses. The blood of the poisoned person becomes red and very fluid.

CITRIC ACID.

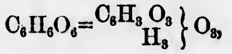


$$C_6H_8O_7 = \left.\begin{matrix} C_6H_4O_3 \\ H,H_3 \end{matrix}\right\} O_4.$$

This acid is found associated with oxalic and tartaric acids in many plants. It occurs in cherries, currants, raspberries, oranges and lemons.

It is ordinarily extracted from the juice of lemons. This juice is allowed to stand until fermentation commences, then filtered and treated with chalk and milk of lime; an insoluble citrate of calcium is formed, which is decomposed by sulphuric acid; the calcium sulphate is filtered off and the filtrate evaporated and left to crystallize. Citric acid crystallizes in regular rhombic prisms; it is soluble in three fourths its weight of cold water; this solution, in time, becomes covered with mould.

Citric acid is soluble in alcohol and ether. Heated to about 175° it furnishes *aconitic acid*,



$$C_6H_6O_6 = \left.\begin{matrix} C_6H_3\,O_3 \\ H_3 \end{matrix}\right\} O_3,$$

losing H_2O on increasing the temperature. Another pyrogenous acid, *itaconic acid* $C_5H_6O_4$ is formed, which, if heated, is transformed into *citraconic acid* isomeric with the last mentioned.

Oxydizing bodies destroy citric acid, carbon dioxide, acetone, etc., being produced. Fused caustic potassa resolves it into acetic and oxalic acids.

$$C_6H_8O_7+H_2O=\underbrace{C_2H_2O_4}_{\text{Oxalic acid.}}+2\underbrace{C_2H_4O_2}_{\text{Acetic acid.}}.$$

Citric acid is tetratomic and tribasic. It may be distinguished from oxalic and tartaric acids by its action on lime water, which it does not precipitate in the cold, but if boiled with an excess of lime water, a precipitate of basic calcium citrate is obtained.

MAGNESIUM CITRATE.—This salt is prepared by treating magnesium carbonate with a strong solution of citric acid and precipitating this salt with alcohol. It is much used in medicine as a purgative.

CITRATE OF IRON.—Hydrated ferric oxide is dissolved in a luke-warm solution of citric acid, and the liquid evaporated to dryness.

This body varies in its composition; it occurs in brilliant amorphous scales, of a garnet-red color.

AMMONIA CITRATE OF IRON.—One hundred grams citric acid are digested for some time with a quantity of ferric hydrate, representing 53 grams of iron, and 16 to 20 grams of aqua ammonia. The liquid is then filtered and evaporated to the consistency of a syrup, and transferred to very shallow vessels which are placed in drying ovens. This substance solidifies in scales, if the temperature at which it is dried is not too high and the layers of liquid are extremely thin.

LACTIC ACID.

$$C_3H_6O_3 = \left.\begin{matrix} C_3H_4 \\ H,H \end{matrix}\right\} O^3.$$

This acid was discovered by Scheele, who extracted it from sour milk. It exists in many products after fermentation, as sauerkraut, beet juice, and various vegetables, also nux vomica. It is found in many animal fluids, in the blood and in the fluids which permeates the muscular tissues. It is to this body that the acid reaction of sour milk is due. Lactic acid extracted from flesh forms, with certain bases, salts which differ in solubility, etc., from those formed with ordinary lactic acid, hence this acid is sometimes called *paralactic acid*, also *sarko-lactic acid*, from σαρκος flesh.

Lactic acid may be prepared by dissolving sugar of milk in butter-milk, adding chalk to the mixture, and allowing it to stand for eight or ten days at a temperature of 30° to 35°

The sugar of milk is sometimes replaced by glucose, or cane sugar and fermentation favored by the addition of cheese.

A special ferment (*lactic ferment*) is developed which is transformed into sugar and lactic acid, but the fermentation is arrested as soon as the liquid becomes acid, and it is in order to prevent this acidity that an excess of calcium carbonate or sodium bicarbonate is always maintained.

Wurtz has produced this acid artificially by the action of platinum black on propylglycol.

$$O_2 + \underbrace{C_3H_8O_2}_{\text{Propylglycol.}} = C_3H_6O_3 + H_2O.$$

Lactic acid is a colorless, syrupy liquid; at about 130° it is changed into the anhydride of lactic acid, $C_6H_{10}O_5$, and at about 250° it furnishes a crystalline body called *lactide* whose formula is $C_3H_4O_2$.

Lactic acid posseses the property of dissolving calcium phosphate. The lactates are soluble in water. Lactate of iron, $(C_3H_5O_3)_2Fe$, is employed in medicine.

URIC OR LITHIC ACID, $C_5H_4N_4O_3$.

Discovered in 1776, by Scheele.

This acid exists in human excretions, and in those of the carnivora. In the excretions of herbivora, the uric acid is replaced by hippuric acid. Uric acid is present in normal human urine only in small quantity. The urine of sedentary persons, and of those whose food is very nitrogenous and quite substantial, contains more of this substance than that of individuals who lead an active life, and whose diet is less nourishing. In the latter case the uric acid is oxydized and converted into urea, hence, the proportion of the acid decreases as the quantity of urea increases: whereas calculi of uric acid are frequently formed in persons whose diet is very nourishing, and whose occupation necessitates but little muscular exertion. The excreta of birds contains a large proportion of uric acid, and that of snakes is formed almost exclusively of this body.

This acid may be prepared by boiling a dilute alkaline solution with guano, excreta of the boa constrictor, or uric calculi finely pulverized.

The liquid is filtered and the filtrate supersaturated with hydrochloric acid; the uric acid precipitates in flakes, which become crystalline on standing.

The author having had occasion in 1858 to prepare large quantities of uric acid from guano, found that in order to obtain the purest product, as free from coloring matter as possible, it was preferable to use sodium hydrate as a solvent, and carbon dioxide as a precipitant, the latter in sufficient excess to transform the hydrate into bicarbonate.

Crystals of uric acid are colorless and odorless. They are nearly insoluble in ether and alcohol. About 1500 parts of boiling water are necessary to dissolve one part of the acid.

On distillation uric acid yields urea and other cyanic compounds. Uric acid heated with water and lead dioxide furnishes urea and a substance called *allantoin*, which has been found in the urine of sucking calves. Its formula is $C_4H_6N_4O_3$.

The same derivative of uric acid was obtained by the author in 1858, also parabanic acid, on heating uric acid with manganese dioxide and sulphuric acid. (80—[2]44—218.)

If 1 part of uric acid be added to 4 times its weight of nitric acid of a specific gravity of 1.45, the solution being kept cool, small crystals of a substance called *alloxan* separate out, whose formula is

$$C_4H_4N_2O_5+3H_2O.$$

Woehler and Liebig obtained from this body a number of very interesting derivations, *alloxantin*, *alloxanic acid*, *parabanic acid*, *thionuric acid*, *dialuric acid*, and finally a magnificent purple crystalline body, *murexide*. A large number of other derivatives have also been obtained by other chemists, especially Bayer. The rich color, *murexide*, is made use of in detecting uric acid. For this purpose, traces of uric acid are heated in a watch glass for a few minutes, with one or two drops of nitric acid; the excess of acid is evaporated, and the dry residue exposed to the vapors of ammonia, when a purple, or very beautiful rose color, will appear.

HIPPURIC ACID

$$C_9H_9NO_3.$$

The urine of herbivora contains a large percentage of this acid, which also exists in a small quantity in human urine. A frugivorous diet augments the proportion of this body. It is prepared by boiling the fresh urine of the horse (hence the name, from ἵππος, a horse), or better from that of a cow, with milk of lime, which is then filtered and evaporated to one-tenth its volume; this is mixed with a large excess of hydrochloric acid and left to stand 10 or 12 hours. The impure hippuric acid which precipitates is re-dissolved in soda and re-precipitated with hydrochloric acid. Animal charcoal may be added to the saline solution if the brown color still remains. Putrid urine yields only benzoic acid. Dessaignes has prepared this acid artificially by causing zincic glycocol to act on benzoyl chloride.

$$Zn(C_2H_4NO_2)_2+2C_7H_5OCl= \\ ZnCl_2+2C_2H_3[NH(C_7H_5O]O_2.$$

Hippuric acid crystallizes in colorless crystals, which require 600 parts of cold water for their solution, but are very soluble in hot water and alcohol.

It is decomposed at 240°, benzoic and cyanhydric acids being found among the products of distillation. Under the action of oxydizing agents it furnishes benzoic compounds; with nitrous acid it yields benzo-glycolic acid.

ALKALOIDS.

ARTIFICIAL BASES OR ALKALOIDS.

PRIMARY.

$C_nH_{2n+3}N$.

Methylamine - - -	$C\ H_5N$
Ethylamine - - -	C_2H_7N
Propylamine - - -	C_3H_9N
Butylamine - - -	$C_4H_{11}N$
Amylamine - - -	$C_5H_{13}N$
Caprylamine - - -	$C_8H_{19}N$.

$C_nH_{2n+1}N$.

Acetylamine - - -	C_2H_5N
Allylamine - - -	C_3H_7N.

$C_nH_{2n-5}N$.

Phenylamine, *aniline* - -	C_6H_7N
Toluidine - - - -	C_7H_9N
Xylidine - - - -	$C_8H_{11}N$
Cumidine - - - -	$C_9H_{13}N$.

$C_nH_{2n-7}N$.

Phtalidamine - - -	C_8H_9N.

$C_nH_{2n-11}N$.

Naphthalamine	$C_{10}H_9N$.

SECONDARY.

Dimethylamine	C_2H_7N
Methylethylamine	C_3H_9N
Diethylamine	$C_4H_{11}N$.

TERNARY.

Trimethylamine	C_3H_9N
Dimethylethylamine	$C_4H_{11}N$
Methylethylamylamine	C_6H_9N.

PHOSPHINES.

Methylphosphine	CH_5P
Dimethylphosphine	C_2H_7P
Trimethylphosphine	C_3H_9P.

ARSINES.

Triethylarsine	$C_6H_{15}As$.

STIBINES.

Triethylstibine	$C_6H_{15}Sb$.

PRINCIPAL NATURAL ALKALOIDS.

OF THE CINCHONAS.

Quinia, Quinicia and Quinidia	$C_{20}H_{24}N_2O_2$
Cinchonia and Cinchonidia	$C_{20}H_{24}N_2O$
Aricina	$C_{23}H_{26}N_2O_4$.

OF OPIUM.

Morphia	$C_{17}H_{19}N\,O_3$
Codeia	$C_{18}H_{21}N\,O_3$
Thebaia	$C_{19}H_{21}N\,O_3$
Narcotina	$C_{22}H_{23}N\,O_7$
Papaverine	$C_{20}H_{21}N\,O_4$
Narceia	$C_{23}H_{29}N\,O_9$.

OF THE STRYCHNOS.

Strychnia	$C_{21}H_{22}N_2O_2$
Brucia	$C_{23}H_{26}N_2O_4$.

OF THE SOLANACEÆ.

Nicotina	$C_{10}H_{14}N_2$
Atropia	$C_{17}H_{23}N\,O_3$
Hyosciamine	$C_{17}H_{23}N\,O_3$
Solania	$C_{43}H_{71}N\,O_{16}$.

OF THE HEMLOCK.

Conylia	$C_8H_{15}N$.

OF PEPPER.

Piperidine - - -	$C_5H_{11}N$.

MISCELLANEOUS.

Aconitina - - -	$C_{27}H_{40}N\ O$
Veratria - - -	$C_{32}H_{52}N_2O_8$
Theobromine - -	$C_7\,H_8\,N_4O_2$
Caffeia - - -	$C_8\,H_{10}N_4O_2$.

The first organic base isolated was morphia, obtained in 1816, by Sertuerner. In 1819, Pelletier and Caventou extracted quinia from cinchona bark, and showed that the very active plants used in pharmacy owed their energy to compounds capable of uniting with the acids, and of forming with them definite crystallizable salts.

From that epoch, the number of organic alkaloids has become very considerably augmented; and methods have been discovered by which many of the alkaloids are prepared artificially. It was Fritsche who, in 1840, obtained the first artificial alkaloid on distilling indigo with potassa ; he named it *aniline*. Gerhardt by similar methods prepared *quinoleine*, Cahours *piperidine*, and Chantard *toluidine*.

The distillation of organic matter also furnishes alkaloids. Thus several of them have been obtained from a product of the distillation of bones, the oil of Dippel ; also as products of the distillation of various other organic compounds.

A very general method is due to Zinin, which consists in causing a reducing substance to act upon nitrous compounds as nitrobenzol, for example. The nitrous compound is introduced into an alcoholic solution of ammonium sulphide, and the mixture allowed to stand; sulphur is soon deposited, and the hydrogen of the hydrogen sulphide combines with the oxygen of the nitrous compound. Example:

$$\underbrace{C_6H_5NO_2}_{\text{Nitrobenzol.}} + 3H_2S = 2H_2O + 3S + \underbrace{C_6H_7N}_{\text{Aniline.}}.$$

For this mode of reduction, as it is not very practical, and is tedious in execution, there is at present substituted the action of iron upon acetic acid, or that of zinc or tin, on hydrochloric acid.

Wurtz has given a very interesting method, which has led to the discovery of alkaloids much resembling ammonia, for that reason called *compound ammonias.* It consists in causing potassa to react upon the cyanic ethers, these bodies being decomposed much like cyanic acid.

Thus methylamine is obtained by the action of potassa upon cyanate of methyl:

$$\underbrace{\left.\begin{matrix}CO\\CH_3\end{matrix}\right\}}_{\text{Cyanate of methyl.}} N + 2KHO = \underbrace{K_2CO_3}_{\text{Potassium carbonate.}} + \underbrace{\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N}_{\text{Methyl-amine.}}.$$

Hofmann made known, very shortly after the publication of Wurtz' process, a method for the preparation of the compound ammonias, by which not only a simple equivalent of hydrogen is replaced by the radicles (CH_3), (C_2H_5), etc., but all the hydrogen of the ammonia. Hofmann's method consists in causing ammonia to react upon hydrochloric as well as bromhydric or iodhydric ethers, particularly the latter.

Let us take, as an example, iodide of ethyl in connection with the study of

ETHYLAMINE.

Ten to 15 grams of iodide of ethyl and 50 grams of aqua ammonia are heated in sealed tubes of green glass placed in a water bath. The following reaction occurs:

$$C_2H_5I + NH_3 = C_2H_8NI.$$

When the liquid has become homogeneous it is allowed to cool, then decomposed by a solution of potassium hydrate, the vapors being collected in water, containing hydrochloric acid. The hydrochloric acid solution is evaporated to dryness, and the residue treated with pure alcohol, which dissolves the chlorhydride of ethylamine and leaves in an insoluble state the ammonium chloride derived from the excess of ammonia used. The solution of chlorhydride of ethylamine is evaporated to dryness, and the deliquescent crystals obtained decomposed by potassium hydrate, with the aid of a gentle heat. The volatilized product is condensed in a cooled receiver. In this reaction there is also formed diethylamine, triethylamine and oxide of tetrethylammonium from which the ethylamine is separated by distillation.

It may be obtained more readily by first distilling 1 part potassium cyanate with 2 parts potassium sulphovinate, then by decomposing the cyanic ether obtained with a boiling solution of potassium hydrate contained in a flask connected with a cool receiver.

Ethylamine is a limpid liquid, with a strong odor resembling that of ammonia. It has not been solidified. It boils at 18.7°, and dissolves in water, producing a very caustic solution. Ethylamine is equally soluble in alcohol and ether. It is combustible, burning with a blue flame, yellow at the margin.

It displaces ammonia from its combinations. Its solutions give reactions similar to those of ammonia; for instance, with salts of copper it gives a bluish white precipitate, which is dissolved in an excess producing a deep-blue solution.

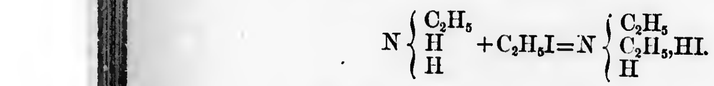
It differs from ammonia in the following reaction: ethylamine precipitates alumina from its salts, and the precipitate is soluble in an excess of ethylamine, which is not the case with ammonia.

CLASSIFICATION OF THE ALKALOIDS, OR ORGANIC BASES.

AMINES.—Hofmann has given the names of *primary amines*, or *monamines*, to ethylamine, which we have just studied, and the compound ammonias in which a single atom of hydrogen has been replaced by a radicle.

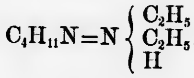
The same chemist, having prepared ethylamine by the action of ethyl iodide upon ammonia, subsequently succeeded in obtaining diethylamine by similar means.

The reaction is the following:



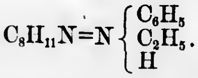
$$N\left\{\begin{array}{l}C_2H_5\\H\\H\end{array}\right. + C_2H_5I = N\left\{\begin{array}{l}C_2H_5\\C_2H_5,HI.\\H\end{array}\right.$$

This hydroiodide obtained, treated with potassium hydrate or lime, furnishes a second base, which is biethylammonia, or diethylamine;

Diethylamine 

$$C_4H_{11}N = N\left\{\begin{array}{l}C_2H_5\\C_2H_5.\\H\end{array}\right.$$

A similar compound is,

Ethylaniline 

$$C_8H_{11}N = N\left\{\begin{array}{l}C_6H_5\\C_2H_5.\\H\end{array}\right.$$

These bases have been given the name of *secondary amines* or *imides.*

The secondary ammonias are attacked by ethyl iodide and other ethers, and a reaction takes place, identical with that which gives rise to the primary and secondary amines and *tertiary amines*, also called *nitrile* bases, are thus obtained.

Such bodies are:

$$\text{Triethylamine } C_6H_{15}N=N\left\{\begin{array}{l}C_2H_5\\C_2H_5.\\C_2H_5\end{array}\right.$$

$$\text{Methylethylphenylamine } C_9H_{13}N=N\left\{\begin{array}{l}C\,H_3\\C_2H_5\\C_6H_5\end{array}\right.$$

These bases are related to the alcohols in the same manner as the primary amines. Thus diethylamine is derived from the action of 2 molecules of alcohol on 1 molecule of ammonia and the elimination of 2 molecules of water:

$$2(C_2H_6O)+NH_3—2H_2O=C_4H_{11}N.$$

In like manner the ternary amines may be considered as derived from 3 molecules of alcohol and 1 molecule of ammonia with the elimination of 3 molecules of water.

There are also bodies built upon the type of two and three condensed molecules of ammonia, and are denominated, respectively, di-amines and tri-amines; as

$$\text{Secondary ethylene diamine } N_2\left\{\begin{array}{l}(C_2H_4)''\\(C_2H_4)'',\\H_2\end{array}\right.$$

$$\text{Ternary ethylene diamine } N_2\left\{\begin{array}{l}(C_2H_4)''\\(C_2H_4)''.\\(C_2H_4)''\end{array}\right.$$

Triethylamine attacks hydroiodic ether, and there is formed the compound $C_8H_{20}NI = N(C_2H_5)_4I$. This body treated with oxide of silver, furnishes an oxygenated *quaternary* base,

$$C_8H_{20}NI + Ag\,HO = Ag\,I + C_8H_{21}NO.$$

This substance is very caustic, soluble in water and acts as an inorganic alkaline base like potassium hydrate, with which body it is also analagous in composition.

$$\left.\begin{matrix}K\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}(C_2H_5)_4N\\H\end{matrix}\right\}O.$$

AMIDES, ALKALAMIDES.—The amides are bodies built upon the type of ammonia, in which one or more of the hydrogen atoms are replaced by an acid compound radicle; thus,

$$\text{acetamide } N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right. .$$

There are also mixed combinations of amides and amines, called *alkalamides*, as

$$\text{acetanilide } N\left\{\begin{matrix}C_6H_5\\C_2H_3O.\\H\end{matrix}\right.$$

NATURAL ALKALOIDS.

Many of the natural alkaloids appear to possess a composition analogous to that of the compound ammonias. Some are not attacked by iodide of ethyl, and should be classified among the *ammoniums*, bodies having the same relation to the compound ammonias as does ordinary ammonium hydrate to ammonia. Others are acted upon by iodide of ethyl, and, from the number of bases furnished, it may be ascertained whether they belong to the primary, secondary or ternary compound ammonias.

The properties of the natural alkaloids in general, resemble those of the artificial bases or alkaloids. They contain nitrogen; those that do not contain oxygen are ordinarily volatile, while those with oxygen are non-volatile; they are very soluble in alcohol, ether and chloroform.

Certain ones are dissolved by the hydrocarbides, which are now considerably used in the preparation of the alkaloids. Water does not dissolve any of the artificial alkaloids, except those having a very low molecular weight, like ethylamine; this liquid, however, dissolves codeia and narceia quite readily. With the exception of quinia and cinchonia, they turn the plane of a polarized ray of light to the left.

They react like ammonia, or potassa, with vegetable colors, and furnish, with platinum bichloride, crystallizable double chlorides, little soluble and yellow in color. They combine equally well with auric and mercuric chlorides.

The natural alkaloids have ordinarily a bitter taste. Among their salts the sulphates, nitrates, chlorides and acetates are mostly soluble, while the oxalates, tartrates and tannates are insoluble.

The harmless character of tannic acid, and the insolubility of the compounds formed by it, with the alkaloids, render tannin and astringent vegetable substances generally very efficacious antidotes.

The precipitates they produce are soluble in acid and alkaline liquids.

The alkaloids are partially precipitated from their solutions by potassa, soda and ammonia. Iodine water and solutions of iodine in potassium iodide, precipitate them completely.

According to Schultze, the liquid obtained by adding antimony perchloride to a solution of phosphoric acid, is a re-agent which precipitates most of the organic bases.

A delicate re-agent for the alkaloids is the double iodide potassium and mercury. According to Meyer, the best proportions are 49 grams of potassium iodide and 135 grams of mercury dichloride, to 1 litre of water. It is best to *add the re-agent* to the solution of the alkaloid, which may be neutral, acid, or even feebly alkaline.

It must be borne in mind that the presence of sugar, tartaric acid and of albumen may mask the reactions of a number of alkaloids.

NICOTINA OR NICOTYLIA.

$C_{10}H_{14}N_2$.

Nicotina is obtained from tobacco (*Nicotina tabacum.*) For this purpose a decoction of tobacco is made, and the liquor evaporated to a syrup. The extract is treated with twice its volume of 85 per cent. alcohol, which precipitates the salts present and certain organic substances.

The alcoholic solution is distilled and the residue submitted to a second similar treatment. The alcoholic extract thus obtained, is mixed with a concentrated solution of potassium hydrate, and the nicotina liberated is re-dissolved in ether. This ethereal solution is evaporated in a water bath, and the residue distilled in an oil bath, in an atmosphere of hydrogen.

Nicotina is a colorless liquid when pure, remaining liquid at -10°, boiling at about 245°, with decomposition. It has the odor of an old pipe. Exposed to the air it becomes brown, then resinous; water, alcohol and ether dissolve it; its solutions are strongly levogyrate.

Nicotina is a powerful base; it fumes when a rod moistened with hydrochloric acid is brought near it; it precipitates the metallic oxides. Nicotina requires two molecules of a monobasic acid for saturation. The chloride, $C_{10}H_{14}N_2 2HCl$, is crystallizable, though deliquescent. The hydrogen it contains is not replaceable by methyl, ethyl, etc. It may be considered as having the rational formula,

$$N_2 \left\{ \begin{matrix} (C_5H_7)''' \\ (C_5H_7)'''; \end{matrix} \right.$$

$(C_5H_7)'''$ being the compound radicle *nicotyl.*

Proportion of nicotina in different tobaccos:

Havana, - -	2.0 per ct.
Maryland, - -	2.3 "
Virginia, - - -	6.9 "
Lothringen, - -	8.0 "

(Schloesing.)

POISONING BY TOBACCO OR BY NICOTINA.

The injection of a concentrated decoction of tobacco, causes serious results in a few minutes: intense headache is produced, with nausea and vomiting, violent pain in the abdomen, pallor, and, finally, extreme prostration.

An infusion of tea, unroasted coffee, or any astringent substance (pulverized nut-galls, or oak-bark) are the only antidotes known, and they are far from being wholly reliable.

The pure nicotina is one of the most dangerous poisons. It manifests itself immediately on being taken, since it is entirely soluble in water.

The nervous system is especially affected. Two or three drops suffice to cause death.

Two drops introduced into the throat of a dog will almost instantaneously cause the following series of symptoms: respiration becomes difficult, the animal staggers, falls without the power of rising again, throws the head back and, in a few moments, is perfectly paralyzed, and death ensues.

PIPERIDINE.

$C_5H_{11}N$.

There has been obtained from the pepper (*Piper longum*, *Piper nigrum* or *Piper caudatum*), a body crystallizing in colorless prisms called *piperine*, whose formula is $C_{17}H_{19}NO_3$. It is a neutral substance. When distilled with three times its weight of soda-lime it furnishes *piperidine*, a limpid liquid having the taste of pepper, and also its odor, soluble in water and alcohol, boiling at 106°.

This body is alkaline and saturates acids. It contains a single atom of hydrogen replaceable by methyl, ethyl, etc.

CONIA, CONYLIA. OR CONINE.

$C_8H_{15}N$.

This body is obtained from hemlock (*Conium maculatum*); the crushed seeds are distilled in a large glass retort, with a solution of potassa, or soda, whereupon an alkaline distillate is obtained. The distilled product is treated with a mixture of two parts of alcohol and one part of ether, which dissolves the sulphate of conia and leaves the insoluble sulphate of ammonium. The ethereal alcohol is separated by distillation, potassa is added to the residue, and the mixture distilled. Water and conia pass over; the latter is dehydrated with potassa, and rectified *in vacuo*, or in a current of hydrogen gas.

Conia is a colorless, oily liquid; emitting an odor of hemlock. Water dissolves it but little, and this better when cold than warm. It is very soluble in alcohol and ether. It boils at about 210°, yet emits vapors even when cold, for if a glass rod, moistened with hydrochloric acid, is brought near it, white fumes are produced. It is a monacidic base, very alkaline, and forms crystallizable salts. One of its atoms of hydrogen is replaccable by ethyl or methyl.

This base is very poisonous. According to Christiason, ten centigrams would suffice to cause death. It is classified among the narcotics; its action is characterized particularly by its effect on the organs of respiration and the left ventricle of the heart.

ALKALOIDS OF THE PAPAVERACEÆ.

The seeds of the poppy (*Papaver somniferum*) yield, on incision, a milky sap, which dries up in a day or two; this sap, when solidified, constitutes *opium*. There are three leading varieties of opium:

I. *Opium of Smyrna* is found in small cakes of 100 to 150 grams, frequently distorted and agglutinated together by reason of their soft nature, and contain 7 to 10 per cent. of water. The surface is brown, but the interior has a fawn color. Sometimes it is found to contain 14 to 15 per cent. of morphia, but in other instances only 5 to 6. Good Smyrna opium should contain not less than 10 per cent.

II. *The opium of Constantinople* is drier than the preceding. It appears in commerce in flattened, irregular cakes, almost always surrounded with poppy-leaves. It contains 5 to 10 per cent. of morphia.

III. *The opium of Egypt* is still dryer; it is rarely enveloped in leaves. Its odor is feeble, and it contains no more than 2 to 7 per cent. of morphia.

Recently, attempts have been made to cultivate the poppy in Europe, especially in France.

Opium contains the alkaloids morphia, codeia, thebeia, papaverine, opianine, narcotine and narceia, an acid combined with these alkaloids called *meconic acid* (from *μηκων*, a poppy), a crystallized neutral substance called *meconine*, which, according to Berthelot, is a complex alcohol, and finally, various gummy and resinous compounds.

MORPHIA OR MORPHINE.

$$C_{17}H_{19}NO_3,\ H_2O.$$

Preparation. Ten kilos. of opium are treated repeatedly with water, and the liquors evaporated to the consistency of a syrup.

The mass is redissolved in water, filtered, and again evaporated. To the lukewarm liquid are added 1200 grams of anhydrous calcium chloride, dissolved in twice its weight of water. A complex precipitate is formed, containing resins, coloring matters, and sulphate and meconate of calcium, which is thrown upon a filter.

The filtered liquid is evaporated over a water-bath. During the concentration, a fresh quantity of meconate of calcium is separated by filtering, and the liquid evaporated to the consistency of syrup. The liquid is then acidulated with a small quantity of hydrochloric acid, and set aside in a cool place.

At the end of a few days, it contains brown crystals of the double chlorhydrate of morphia and codeia, contaminated with a blackish liquid; these crystals are drained, pressed, and again dissolved in as little boiling water as possible. The chlorhydrate, on cooling, deposits crystals, which are again dissolved in hot water and decolored with animal charcoal. After heating to 80° or 85°, the solution is filtered, and the liquid, on being concentrated, deposits the double chlorhydrate in pure white crystals.

This salt is again dissolved in boiling water, and the hot liquid treated with ammonia; the codeia remains in solution, while the morphia is precipitated. This deposit is thrown upon a filter washed with cold water, dried, and dissolved in boiling alcohol; the morphia separates out in crystals on cooling.

It frequently contains some narcotina, from which it is freed by washing once or twice with ether, or chloroform, which dissolves the narcotina, and does not affect the morphia.

Pure morphia, (from *Morpheus*, in allusion to its narcotic qualities,) crystallizes in regular prisms with a rhombic base, is colorless, soluble in 500 parts of boiling water, scarcely soluble in cold. Forty to forty-five parts of cold 90 per cent. alcohol are required to dissolve one part of morphia; it is insoluble in ether. Solutions of morphia are very bitter.

Morphia is little soluble in ammonia, while it is dissolved very readily by alkaline solutions, and even by lime water.

Under the action of heat, it fuses in its water of crystallization, the latter escaping, and the alkaloid recrystallizes on cooling.

Morphine is an energetic reducing agent, reducing gold and silver salts, setting free the respective metals. It separates the iodine from solutions of iodic acid. If a solution of starch is poured into a test-tube, and a solution of iodic acid and traces of morphia added, the blue color of iodide of starch appears.

If morphia is put into a few drops of a concentrated and slightly acid solution of a ferric salt, a beautiful blue color is produced, which subsequently changes to green.

Morphia, moistened with nitric acid, is colored orange-red, which rapidly changes to yellow.

These four reactions are characteristic of morphia.

If iodine and morphia are mixed in equal proportions and the mixture treated with boiling water, a brown liquid is formed which deposits a reddish-brown powder called *iodomorphia*. Morphia fused with alkalies yields methylamine. (p. 127). It is attacked by ethyl iodide at 100°, a single molecule of ethyl entering into the group.

Morphia forms crystallizable salts, from the solutions of which it is precipitated by the fixed alkalies.

Chlorhydrate of morphia, $C_{17}H_{19}NO_3HCl+3H_2O$. To prepare this salt, 100 parts of pulverized morphia are treated with a little warm water, then hydrochloric acid is added in sufficient quantity to dissolve the alkaloid. The solution is afterwards evaporated in a water bath until it crystallizes.

This salt is soluble in 20 parts of cold water, very soluble in alcohol. It is the salt of morphia most used, and contains 76 per cent. of morphia.

Sulphate of morphia, $(C_{17}H_{19}NO_3)_2H_2SO_4+5H_2O$ is prepared like the preceding salt, which it resembles in appearance as well as in properties.

Morphia and its salts are used in very small doses, as in larger doses they are energetic poisons.

Codeia, $C_{18}H_{21}NO_3,H_2O$.

Discovered in 1832 by Robiquet. This base, whose name is derived from *κώδη* poppy head, exists in the ammoniacal solution obtained in the preparation of morphia. On evaporation the ammonia is driven off and the codeia is precipitated by potassa. The codeia is at first precipitated in the form of a sticky mass which soon becomes pulverescent. It is washed with and dissolved in hydrochloric acid. The liquid is then boiled with washed animal charcoal, and the codeia precipitated with potassa.

Codeia is crystalline, very soluble in alcohol and ether. It dissolves in 80 parts of cold and in 20 parts of boiling water.

Codeia is very soluble in ammonia, and nearly insoluble in potassa. With chlorine, bromine and nitric acid it forms products of substitution. With iodine it furnishes ruby-red crystals, whose formula is

$$C_{18}H_{21}NO_3I.$$

Codeia is somewhat used as an anodyne. It is easily distinguished from morphia, since:

I. Codeia is soluble in ether and ammonia.
II. It is insoluble in solutions of potassa.
III. It does not reduce iodic acid or ferric salts.
IV. Nitric acid does not impart to it any color.

NARCOTINA, $C_{22}H_{23}NO_7$.

Narcotina crystallizes in rhombic prisms. It is almost insoluble in cold water, somewhat soluble in alcohol, quite so in ether. It fuses at 170°, and is decomposed before reaching 200°. Dilute nitric acid transforms it into various products of oxydation, the most important of which are *meconine*, *cotarnine* and *opianic acid* Narcotina unites with acids, but the compounds are decomposed on evaporation.

It is distinguished from morphia in that it does not reduce iodic acid and ferric salts, and from codeia in giving with nitric acid a blood red coloration. This substance is also insoluble in potassa and ammonia. It is not as poisonous as morphia.

THEBAIA.

$C_{19}H_{21}NO_3$.

This alkaloid, sometimes called *paramorphia*, is the most poisonous of the bases of opium.

It is crystallizable, insoluble in water, soluble in alcohol and ether. Fuming nitric acid attacks it in the cold, and a yellow liquid is obtained, which becomes brown on contact with alkalies, and which disengages an alkaline vapor. Concentrated sulphuric acid gives it a red hue.

PAPAVERINE.

$C_{20}H_{21}NO_4$.

This body is crystallizable, insoluble in water, quite soluble in boiling alcohol and ether. It forms crystalline salts.

Under the action of strong sulphuric acid it assumes a deep blue color, though Hesse and Dragendorff have recently ascertained that when absolutely pure no color is obtained, the ordinary article found in trade not being pure.

NARCEIA.

$C_{23}H_{29}NO_9$.

This alkaloid crystallizes in silky needles, insoluble in ether, soluble in alcohol and boiling water, little soluble in cold water. It forms crystallizable salts.

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Narceia fuses at 95°, and commences to decompose at about 110°. It is attacked in the cold by concentrated sulphuric acid, a red liquid being produced which rapidly becomes green, especially if slightly heated. The best means of distinguishing narceia is to cause a solution of iodine to act upon the pulverized substance. According to Roussin, the operation is most easily performed with one part of iodine and two parts of potassium iodide dissolved in ten parts of water. A blue color is produced, which disappears on coming in contact with alkalies, or on heating.

PHYSIOLOGICAL ACTION OF OPIUM. NARCOTIC POISONS.

Opium in small doses is a very highly-prized anodyne. Continued use of this substance produces a peculiar state of inebriation, an excited sleep and hallucinations of various sorts.

The bodies of opium-eaters are lean and cadaverous, their eyes are lustrous, their forms bent; their appetite diminishes, and they exist only by increasing the dose of the poison which destroys them. In larger doses it is highly poisonous, and acts in a different manner from that of the poisons already studied. It may be considered as the type of the narcotic poisons. It is not unfrequently used for criminal purposes, and the imprudent administration of laudanum and other solutions of this substance often causes serious effects.

Claude Bernard has made a careful study of the action of the various alkaloids of opium upon the system, and has tabulated their soporific, toxic, and convulsive actions as follows:

Toxic.	Convulsive.	Soporific.
Thebeia,	Thebeia,	Narceia,
Codeia,	Papaverine,	Morphia,
Papaverine,	Narcotina,	Codeia.
Narceia,	Codeia,	Without action.
Morphia,	Morphia,	
Narcotina.	Narceia,	

Those at the head of each column are the most marked in the respective characteristic action.

Subjoined are tabulated the principal chemical characteristics of the opium alkaloids:

	WATER.	ALCOHOL.	ETHER.	AMMONIA.
Morphia.	But little soluble.	Quite soluble.	Almost insoluble.	Nearly insoluble.
Codeia.	Soluble.	Very soluble.	Very soluble	Soluble.
Narcotina.	Insoluble.	Soluble.	Soluble.	Insoluble.
Thebeia.	Insoluble.	Soluble.	Soluble.	Insoluble.
Papaverine.	Insoluble.	Soluble.	Soluble.	Insoluble.
Narceia.	Slightly sol'ble	Soluble.	Insoluble.	Insoluble.

QUINIA OR QUININE.

$C_{20}H_{24}N_2O_2,3H_2O$.

This alkaloid was discovered in 1820 by Pelletier and Caventou. The following is the modern process by which it is prepared.

Yellow Peruvian bark is carefully pulverized and thoroughly mixed with 30 per cent. of its weight of lime, previously slacked. The mass is then lixiviated three or four times with refined petroleum (petroleum ether) or amylic alcohol, (wood spirit) which dissolves the alkaloids.

POTASSA.	NITRIC ACID.	SULPHURIC ACID.	IODIC ACID.
Soluble.	Orange-red coloration.	Colored violet on heating with dilute acid.	Reduced.
Nearly insoluble.	Orange-red coloration.	Colored violet on heating with dilute acid.	Is not reduced.
Insoluble.	Blood-red coloration.	Yellow coloration.	Is not reduced.
Insoluble.	Yellow coloration.	Red coloration.	
Insoluble.		Dark-blue coloration.	
Insoluble.		Red color, which becomes green.	

The united extracts are agitated with water, acidulated with sulphuric acid, making the liquid only slightly acid.

When the solution is completed, animal charcoal is added, and the liquid brought to boiling, filtered while still hot, and allowed to cool. The quinia sulphate which is formed, $2(C_{20}H_{24}N_2O_2)$, $H_2SO_4+7aq.$, being but slightly soluble, is deposited on cooling.

After being allowed to stand 24 hours, the sulphate is collected, expressed and redissolved in as small a quantity of water as possible, containing a few drops of sulphuric acid.

The liquid on cooling, deposits crystals, which are dried at 35°. The mother liquors are treated with ammonia, or sodium carbonate, which precipitates a certain quantity of the alkaloid. The precipitate is lightly washed with water, redissolved in dilute sulphuric acid, boiled with washed animal charcoal, and allowed to cool. A second crop of crystals of quinia sulphate is thus obtained. The mother liquor contains cinchonia sulphate. This sulphate is dissolved in 30 times its weight of boiling water, allowed to cool, and a slight excess of ammonia added.

The cinchonia which is precipitated is collected on a filter, and washed with lukewarm water until the filtrate no longer gives with barium chloride a white precipitate insoluble in acids; it is then dried at a temperature of 30° to 40°.

Quinia is white, amorphous and very friable. It may be obtained in a crystalline condition, by adding an excess of ammonia to a dilute solution of quinia sulphate, and allowing the solution to stand.

This crystallized quinia melts at 57°, losing its water of crystallization, solidifies and remelts at 176°. It requires 250 parts of boiling and 460 parts of cold water for its solution.

It dissolves in 2 parts of boiling absolute alcohol, 2 parts of chloroform or 50 to 60 parts of ether. Its solutions are very bitter, levogyrate, and for the most part fluorescent.

Heated on platinum foil, quinia swells up and inflames, leaving a deposit of carbon. Heated with potassa it produces hydrogen and *quinoleine;* (cinchonlein); it also furnishes a brown compound on being triturated with iodine.

Quinia is recognized by the following reactions. It is first saturated with very dilute sulphuric acid and chlorine water; then an excess of ammonia is added, whereupon a green color is obtained.

On adding powdered potassium ferrocyanide before the aqua ammonia a rose coloration is produced, which afterwards becomes dark red.

Quinia has a basic reaction; it forms with acids crystallizable salts from which the alkalies precipitate quinia. It is a base which saturates two molecules of a monobasic acid.

SULPHATES OF QUINIA. Two sulphates of quinia are known; that obtained by the process we have above described, is the neutral sulphate, though generally known as the basic sulphate. Its formula is

$$2C_{20}H_{24}N_2O_2.H_2SO_4+7H_2O.$$

This salt contains 74.3 per cent. of quinia.

It crystallizes in very delicate needles belonging to the clinorhombic system, and which effloresce in dry air. It dissolves in 30 parts of boiling and 740 parts of cold water; also in 60 parts of cold absolute alcohol. It is very nearly insoluble in ether. Its solutions are extremely bitter. It becomes phosphorescent on being heated, and subsequently fuses.

Heated in the air it burns, leaving a carbonaceous residue.

On adding quinia to water acidulated with sulphuric acid, it rapidly dissolves and another sulphate, often called the acid sulphate, is formed, whose formula is

$$C_{20}H_{24}N_2O_2,H_2SO_4+7H_2O.$$

It is on account of the difficult solubility of the preceding salt, and the great solubility of this latter one, that we cautioned against the employment of an excess of sulphuric acid in the preparation of quinia.

This salt dissolves in 11 parts of water at 12°, and in 9 parts at 18°. Sulphate of quinia, heated to 130° with acidulated water for several hours, is transformed into an isomeric dextrogyrate base called *quinicine*, which is likewise a febrifuge.

Medicinal sulphate of quinia always contains sulphate of cinchonia, and its presence is not considered fraudulent, even when it contains 3.5 per cent. of the latter substance, as this salt is necessarily produced in the preparation of quinia. Cinchonia appears to be of little therapeutic value, and is often added to sulphate of quinia.

This adulterant is detected by weighing out 0.5 grams of the salt, and adding to it 5 grams of ether. The mixture is agitated and 1.5 grams of concentrated ammonia added. If no cinchonia is present, two liquid layers are obtained; if it is present, a layer of this alkaloid is formed directly above the ammonia. Good commercial sulphate of quinia should give only a very thin layer.

The amount of quinia may be directly determined by decanting and evaporating the ethereal solution, and weighing the residue. This result may be verified by replacing the ether in another determination, by chloroform, which dissolves both bases; the residue obtained by the evaporation of this liquid furnishes the weight of the quinia and cinchonia together.

Sulphate of quinia sometimes contains sulphate of quinidia; this base is precipitated, together with cinchonia, by ether. Its presence may be detected by dissolving one gram of the sulphate in 30 grams of boiling water, and adding to the solution ammonium oxalate. Oxalate of quinidia, which is the only soluble oxalate of these bases, remains in solution, and, on filtering, a bitter liquid will be obtained, in which the quinidia may be precipitated by ammonia.

In case sulphate of quinia has been adulterated with calcium sulphate, or other inorganic substance, it may be recognized by a residue which will be obtained on heating the sulphate to redness on platinum foil.

Sulphate of quinia should dissolve in 80 per cent. alcohol. If it dissolves in water, but does not dissolve in 56 per cent. to 60 per cent. alcohol, it may be regarded as not pure.

If adulterated with starch, or fatty bodies, a clear solution cannot be obtained, even in very large quantities of water.

Should it contain sugar it will emit an odor of caramel on ignition, and blacken in contact with sulphuric acid.

Quinia sulphate to which salicin, a common adulterant, has been added, is colored red by sulphuric acid.

Quinia sulphate is chiefly employed in cases of intermittent fevers.

CINCHONIA OR CINCHONINE.

$$C_{20}H_{21}N_2O.$$

Cinchonia was discovered by Duncan in 1803, though first recognized as an organic base by Pelletier and Caventou in 1820.

It differs from quinia in containing one atom less of oxygen ; it has never been converted into quinia.

It is prepared in the same manner as quinia, but from the Gray Peruvian Bark. Cinchonia separates out in crystals on the evaporation of the alcohol with which the calcic precipitate is washed.

The crystals of cinchonia are collected, allowed to drain, and the liquid which runs off will furnish additional crystals on being evaporated. To this mother liquor sulphuric acid is added in excess, and the solution slightly evaporated.

The first crystals obtained are sulphate of quinia, which is less soluble than sulphate of cinchonia. When nothing remains but a very concentrated mother-liquor, the cinchonia is precipitated by ammonia, and freed from quinia by washing with ether. The quinia dissolves, while the cinchonia remains insoluble.

The latter crystallizes in brilliant colorless crystals, which are insoluble in cold water and ether, soluble in 2,500 parts of boiling water, in 30 parts of boiling 90 per cent. alcohol, and 40 parts of chloroform.

Its solutions are very bitter and dextrogyrate.

Cinchonia melts at about 257°; on heating to a slightly higher temperature in a current of nitrogen, or hydrogen, it is completely sublimed.

With chlorine and bromine, it furnishes dichloride and dibromide of cinchonia. With iodine, a yellow crystalline body is obtained, whose formula is $C_{20}H_{24}N_2OI$.

Heated with fused potassa, it produces *quinoleine*.

Cinchonia has an alkaline reaction. It unites with acids, forming salts which correspond to the salts of quinia, though generally more soluble.

Cinchonia sulphate, heated to about 135°, furnishes the sulphate of an isomeric alkaloid, *cinchonicia* or *cinchonicine*.

Cinchonia is employed as a febrifuge in Holland, and a few other countries, but its action is regarded as inferior to that of quinia.

QUINOIDINE.—*Quinidia* is a base obtained from the last mother-liquor in the preparation of quinia, by precipitation with sodium carbonate. It is often mingled with another alkaloid, *cinchonidia* or *cinchonidine*, and it is this mixture, containing chiefly quinidia, which is called *quinoidine* in commerce.

Quinidia is isomeric with quinia; it melts at 160°. It is difficultly soluble in water, very soluble in boiling alcohol, and slightly soluble in ether. Its solutions are dextrogyrate. Quinidia acts as a febrifuge. With chlorine and ammonia, it gives the same reactions as quinia, and forms corresponding salts.

Quinoidine contains, as we have said, cinchonidia, a substance isomeric with cinchonia. This body is crystalline, fusible at about 150°, almost insoluble in water, slightly soluble in ether and chloroform; boiling alcohol is the best solvent for cinchonidia.

ALKALOIDS OF THE STRYCHNOS.

The two chief alkaloids are strychnia and brucia. Desnoix extracted from the nux vomica another alkaloid, which he named *igasuria*; but according to Schützenberger, this body is a mixture of several bases.

These alkaloids are extracted from the fruit of the *Strychnos nux vomica*; from St. Ignatius' beans, fruit of the *Strychnos Ignatii*; from the wood of Coulevre, root of the *Strychnos colubrina*; from the upas, the poison of indian arrows, extracted from the *Strychnos tieuté*; from the False Angustura Bark, and the bark of the *Strychnos nux vomica*, which contains principally brucia.

STRYCHNIA.

$C_{21}H_{22}N_2O_2$.

Nux vomica is pulverized and boiled with three successive portions of water containing sulphuric acid, and these decoctions evaporated in a water bath. When the liquid is reduced to a small volume, 125 grams of quicklime slacked to a thin paste are added for each kilo. of nux vomica. The precipitate is collected on a cloth, washed, dried, and treated with 90 per cent. alcohol.

The alcoholic solution is distilled to three-fourths its volume and left to crystallize. The crystals obtained are chiefly strychnia; these are allowed to drain, then dissolved in water containing $\frac{1}{10}$ its weight of nitric acid, and the solution concentrated in a water bath.

The nitrate of brucia remains dissolved and the nitrate of strychnia crystallizes out. These crystals are re-dissolved in water, animal charcoal added, the solution brought to boiling and then filtered.

Ammonia is added to this liquid, the precipitate washed, dried, and dissolved in boiling alcohol, which deposits the alkaloids on cooling.

This method is at present very advantageously supplanted by the process given for the production of quinia, which, briefly stated, consists in treating the substance with lime directly and employing a solvent for the alkaloids, which is insoluble in water, such as petroleum or amylic alcohol.

Strychnia crystallizes in octahedrons or in prisms of the rhombic system; they are colorless, very bitter, and almost insoluble in water or ether, but readily soluble in ordinary alcohol diluted with 75 per cent. of water. Strychnia treated with potassa furnishes a small quantity of quinoleine. Iodide of ethyl produces with this base the compound

$C_{21}H_{22}(C_2H_5)N_2O_2I$.

Chlorine gas renders even a dilute solution of this alkaloid turbid and the liquid becomes acid; this reaction is characteristic. Bromine also forms derivatives by substitution. Iodine combines directly with the molecule of strychnia.

Strychnia dissolves in strong sulphuric acid; the solution is colorless and becomes dark blue in contact with potassium bichromate or lead dioxide. The color rapidly passes to red and finally to a yellow.

Strychnia is colored yellow by hydrogen nitrate only when it contains brucia, a trace of which is sufficient to produce the change.

Strychnia forms with acids crystallizable salts. The nitrate $C_{21}H_{22}N_2O_2,HNO_3$ crystallizes in fine needles very soluble in hot water.

Strychnia is among the most powerful poisons, 2 to 3 centigrams being sufficient to cause death. There is believed to be no reliable antidote for strychnia though F. M. Peirce claims that small doses of prussic acid are efficient for the purpose. (44-'68-335.)

BRUCIA.

$C_{23}H_{26}N_2O_4,4H_2O$.

To obtain this alkaloid the alcoholic liquids from which strychnia has been removed, are saturated with oxalic acid and evaporated. The crystals of oxalate of brucia which are formed, are washed with 95 per cent. alcohol and redissolved in water. The solution is decomposed by lime, the precipitate collected, dried and dissolved in boiling alcohol; brucia then crystallizes out and is purified by two recrystallizations.

Crystals of brucia are large and of the clinorhombic system; they are soluble in alcohol, insoluble in ether, but soluble in 850 parts of cold, or 500 parts of boiling water.

Concentrated sulphuric acid strikes a rose color with brucia which afterwards changes to green. Nitric acid colors it red, and if heated it gives off nitrous ether, methyl alcohol and carbon dioxide.

Brucia is much less poisonous than strychnia.

It may be distinguished from strychnia by its reaction with nitric acid. A red color is produced by brucia, which passes to violet on the addition of stannous chloride. This latter coloration does not take place with morphia. Brucia is also one of the best reagents for nitric acid.

CURARINA.—From the arrows of the Indians living on the shores of the Amazon and Orinoco, a brown resinous matter is collected, from which crystals of a substance have been obtained whose poisonous action is exceedingly rapid. Preyer, to whom we owe this discovery, regards its formula as $C_{10}H_{15}N$, and has named it *curarina*.

The Indians of Dutch Guiana poison their arrows with two other substances no less dangerous: *urari* and *tikunas*. These three substances paralyze the action of the muscles by destroying the motor nerves

(Claude Bernard). It appears that urari, though a fatal poison when introduced into the blood by a wound, may yet be swallowed with impunity.

DRASTIC POISONS.

We shall not describe the preparation of the following alkaloids, on account of their minor importance. The process in general is similar to that by which the preceding ones are prepared: The alkaloid is dissolved in an inorganic acid, precipitated by a base, and redissolved in an appropriate solvent.

The roots of the white hellebore (*Veratrum album*) and its seeds, furnish an alkaloid called *veratria*, $C_{32}H_{52}N_2O_8$. It crystallizes in prisms having a rhombic base. They are very bitter, insoluble in water, soluble in alcohol and ether, and melt at 115°. Veratria is dissolved by strong nitric acid, the solution being violet. Sulphuric acid colors it first yellow, then red.

Three other poisonous bases, *sabadillia*, *colchinia*, and *jervia*, are found associated with veratria in the *Veratrum album*. Jervia, $C_{30}H_{46}N_2O_32H_2O$, (Gerhardt and Wills' analysis) is white, crystalline and fusible.

These bodies are very corrosive poisons, producing great irritation of the alimentary canal.

ALKALOIDS OF THE POISONOUS SOLANACEÆ.

The belladona, *Atropa belladona*, and the thornapple, *Datura stramonium*, furnish each an alkaloid called, respectively, *atropia* and *daturia*, the formula of which is $C_{17}H_{23}NO_3$.

This substance crystallizes in fine needles, which are fusible at about 90°, and are partially sublimed at about 135°. It is difficultly soluble in water, but very soluble in alcohol and ether.

Heated with an oxydizing agent, such as potassium bichromate, or sulphuric acid, it disengages essence of bitter almonds, easily recognizable by its odor, and crystals of benzoic acid are sublimed. With sulphuric acid a violet color is produced, accompanied by a fragrant odor resembling that of a rose.

Hydrochloric acid furnishes two acids with atropia, *tropic* $C_9H_{10}O_3$, and *atropic* $C_9H_8O_2$.

Cases of poisoning by atropia are rare, but instances in which persons are poisoned by the berries of belladona are of frequent occurrence.

The black henbane, *Hyosciamus niger*, furnishes silky needles of a substance, *hyosciamine*, which has much resemblance to atropia, but whose action as a poison appears to be less violent.

Its physiological action is on the nerves rather than on the muscles. It causes less dilation of the pupil of the eye, and produces a sombre delirium.

Belladona and atropia, the datura, the henbane and hyosciamine, as well as the poisonous solanaceæ in general, should be classed among the narcotic poisons.

Poisoning produced by belladona, and by most of the poisonous solanaceæ, is characterized by great dilation of the pupils of the eyes. The patient is also seized with vertigo and strange hallucinations followed by a turbulent delirium and convulsions. The face is congested, respiration difficult, and the skin often breaks out in an eruption similar to that in rubeola (measles).

No antidote is known for these poisons; an infusion of unroasted coffee. tea, or other astringent substances is recommended. but the use of energetic emetics and purgatives is the most efficient method of treatment.

The chemical characters of these alkaloids has not been as yet very fully studied.

Desfosse has extracted from the woody nightshade, *Solanum dulcamara*, from the berries of the felonwort and from the young sprouts of the potato, *Solanum tuberosum*, a substance called *solanine*, $C_{43}H_{71}NO_{16}$, a highly poisonous alkaloid. On being boiled with acids, it furnishes a stronger base *solanidine* and glucose.

ACONITINA.

Aconitina is extracted from the monk's-hood, *Aconitum napellus*, as a colorless amorphous, bitter powder, soluble in alcohol, slightly soluble in ether, and almost insoluble in water. It fuses at 120°, and is alkaline. It is a very active poison. Planta gives its formula as $C_{30}H_{47}NO_7$ (?).

Duquesnel has extracted from the *Aconitum napellus* a crystalline alkaloid, whose formula is $C_{27}H_{40}NO$.

DIGITALIN.

This substance was long ago obtained in an amorphous condition from the purple fox-glove. In 1871 Nativelle succeeded in obtaining it in a crystalline form. An extract of fox-glove is first prepared, concentrated by distillation and dilluted with 3 times its volume of water.

A precipitate is formed which contains two bodies, *digitalin* and *digitin.* This deposit, washed with boiling alcohol, furnishes crystals composed of these two substances, which are easily separated by chloroform, as digitalin is dissolved by it in all proportions, while digitin is insoluble.

The proportion of digitalin in *Digitalis* grown in different countries, has been made the subject of special investigation by Prof. S. P. Duffield, of Detroit. (94–1868.)

Digitalin is very bitter to the taste. It powerfully irritates the nostrils, and is an active poison. If digitalin be moistened with strong sulphuric acid and then exposed to the vapors of bromine, it assumes a purple color, which is darker or lighter according to the proportions employed. Hydrochloric acid produces with digitalin a very intense emerald green color.

One-fourth of a milligram is sufficient to produce the ordinary poisonous effects ot digitalis. A milligram produces, in from three to five days, a marked change in the circulation. Three milligrams produce most dangerous effects within 24 hours.

It is much to be desired that physicians substitute this crystalline substance, which is invariable, for the amorphous digitalin, which varies greatly, both as to character and effectiveness. Tardieu places digitalin among the hyposthenic poisons.

Poisoning by digitalin has often been produced through imprudence.

The *upas antiar*, with which the Indians poison their arrows, is obtained from the *Antiaris toxicaria.*

EMETIA.

This body is obtained from the roots of the ipecacuanha, *Cephæles ipecacuanha;* it also exists in the *Richardsonia braziliensis*, in the *Phsychtria emetica*, and in the roots of the *Cainca* (madder tribe). These materials, reduced to a powder, are treated with concentrated alcohol, and the alcohol then distilled off. The extract is diluted with five times its volume of water, and filtered. To the filtrate 2 per cent. of caustic potassa is added, and this mixture agitated with chloroform. The chloroform is decanted and distilled ; the emetia crystallizes out. It is dissolved in dilute sulphuric acid, and precipitated from the solution with ammonia. A. Glenward (105-[3] 6—201) gives $C_{15}H_{22}NO_2$ as the formula of emetia.

It is amorphous, yellowish, fusible at 50°, soluble in water and alcohol. Its solutions are slightly bitter. It is a very weak base, and its salts are not crystalline. A few centigrams suffice to produce vomiting.

CANTHARIDIN

is a very poisonous crystalline substance, obtained from Spanish flies, (*Lytta vesicatoria*, and other varieties) and has the composition $C_5H_6O_2$. It is present in nearly all parts of the flies, varying in amount from 0.5 to 1.2 per cent. R. Wolff has of late given this substance a very full investigation. (95, May, '77–102.)

CAFFEINE (CAFFEIA) OR THEINE (THEIA).

$$C_8H_{10}N_4O_2,H_2O.$$

Alcohol is added to a mixture of 5 parts coffee and 1 part slacked lime, until nothing further is dissolved, and the solution distilled. The residue is treated with water, which causes an oil to separate out. The watery liquid furnishes crystals which are purified by treating with animal charcoal, and recrystallizing in hot water.

The extractive matters of the *kola-nut* and *maté* possess the same properties as caffeine.

Caffeine crystallizes in fine needles, fusible at 178°, and is volatile at a slightly higher temperature. These crystals are but little soluble in ether and cold water, yet dissolve very readily in alcohol and boiling water.

It is remarkable that the instinct of man should have led him to select, as the bases of common beverages, just the four or five plants, which out of many thousands are the only ones, as far as we know, containing caffeine.

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It is recognized by boiling with fuming nitric acid; a yellow liquid is produced. On being evaporated to dryness, and ammonia added to the residue, a purple coloration is produced, resembling murexide. (p. 125.) *Amalic acid* and *Cholestrophan* are products of the action of oxidizing agents upon caffeine; bodies linking this alkaloid to the uric acid group.

THEOBROMINE.

There is extracted from the caco, *Theobroma cacao*, a principle crystallizing in microscopic crystals, volatile at 295°, soluble in alcohol and ether, and slightly so in water. It furnishes salts which are decomposed by water. It is called *theobromine*; its formula is $C_7H_8N_4O_2$.

PICROTOXIN.

$C_5H_6O_2$.

From the Indian berry, *Cocculus Indicus*, there is extracted a white crystalline matter of extreme bitterness, called *picrotoxin*, (from πικρός bitter τοξικόν.) This body is neutral, difficultly soluble in water, and easily soluble in alcohol and ether; its solutions are levogyrate.

The physiological action of picrotoxin is analogous to that of strychnia, but it differs from it in that it renders the action of the heart slower, and produces vomiting.

Prof. J. W. Langley, of Pittsburg, has contributed much to (87–1862) our knowledge of the chemical character of picrotoxin.

POLYATOMIC ALKALOIDS.

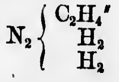
There are polyatomic bases which are to the monatomic bases what polyatomic alcohols are to monatomic alcohols.

They are built upon the type of several molecules of ammonia, or condensed ammonia, in the same manner that polyatomic acids and alcohols are derived from several molecules of water.

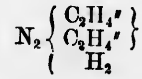
Cloez obtained the former by the action of ethylene bromide upon potassa dissolved in alcohol.

Hoffmann established their true formula. They are called *polyamines*.

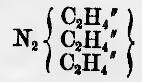
EXAMPLE.

Ethylenic diamine.


$$N_2\left\{\begin{array}{c}C_2H_4''\\H_2\\H_2\end{array}\right.$$

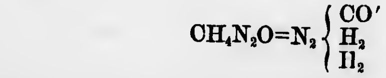
Diethylenic "


$$N_2\left\{\begin{array}{c}\left.\begin{array}{c}C_2H_4''\\C_2H_4''\end{array}\right\}\\H_2\end{array}\right.$$

Triethylenic "


$$N_2\left\{\begin{array}{c}C_2H_4''\\C_2H_4''\\C_2H_4''\end{array}\right\}$$

UREA.



$$CH_4N_2O=N_2\left\{\begin{array}{l}CO''\\H_2\\H_2\end{array}\right.$$

Rouelle, Jr., was the first to obtain this body in an impure state from urine.

Fourcroy and Vanquelin first obtained it pure.

Woehler, in 1828, prepared it artificially by a remarkable synthesis, the first attempt to form a body synthetically. Urea forms the chief constituent of the urine of mammalia, amounting to nearly one-half of the solid constituent; a small proportion of urea is found in all the fluids of the body.

It is an excretory product, as the hydrogen and carbon which have taken their part in the body, escape mainly in the form of water and carbon dioxide, so the nitrogen is eliminated from the system chiefly in the form of urea.

Urea may be extracted from urine by evaporating this liquid to one-tenth its volume and adding, after it has become cold, an excess of nitric acid. Brown crystals of nitrate of urea are formed: these are drained, expressed, re-dissolved in water and boiled with animal charcoal. This solution is filtered, and on evaporation it deposits crystals of nitrate of urea. This salt is then dissolved in as small a quantity of water as possible, and the solution treated first with barium carbonate, then with a strong solution of potassium carbonate; urea is set free and barium and potassium nitrates formed. The above mentioned salts are added as long as effervescence is produced; the liquid is then evaporated to dryness, and the residue treated with absolute alcohol, which dissolves only the urea. (J. E. Loughlin, 100-5-362.)

The synthetic method employed by Woehler, consists in preparing cyanate of ammonia, which body is isomeric with urea.

CYANATE OF AMMONIUM=$H_4CN_2O=NH_4-O-CN$.

This substance changes spontaneously into urea.

Heat, upon an earthen plate, 28 parts of potassium ferrocyanide and 14 parts of manganese dioxide, both finely pulverized, and dry until the mixture becomes pasty; when cold, the mass is pulverized and treated with water, and 20 parts of ammonium sulphide added to the liquid, which is now evaporated in a water bath, and the residue treated with boiling alcohol. On evaporating the alcoholic solution, crystals of urea are deposited. Urea is also obtained as a product of other reactions. It crystallizes in prisms of the tetragonal system; these crystals are colorless, without odor, and have a cooling taste.

It is soluble in its own weight of water at 15°, in an equal weight of boiling alcohol, and in 5 parts of cold 80 per cent. alcohol; it is difficultly soluble in ether. Its solutions are neutral.

Urea fuses at 120°; at about 150° it is decomposed, yielding ammonium carbonate, *ammelide*, $C_3OH_5N_5$, and *biuret*, $C_2O_2H_5N_3$.

Oxydizing agents decompose urea. Chlorine also decomposes solutions of urea in the following manner:

$$3Cl_2+H_2O+CH_4N_2O=6HCl+N_2+CO_2.$$

Urea heated to 140° with water in sealed tubes, is transformed into ammonia and carbon dioxide:

$$H_2O+CH_4N_2O=CO_2+2NH_3.$$

This transformation likewise occurs when urea is heated with strong sulphuric acid, or fused with potassa, also, spontaneously, in presence of the nitrogenous matters of the urine.

Urea does not appear to unite with all acids. It has not yet been combined with carbonic, chloric, lactic or uric acids. The nitrate, chloride and oxalate of urea are crystalline.

Urea forms combinations with mercury, silver, and sodium oxides, also with mercuric and silver nitrates, etc.

NATURAL FATS AND OILS.

The fatty bodies are very widely distributed throughout the vegetable and animal kingdoms. Some are liquid, others are more or less solid. Certain oils remain liquid exposed to the air, as olive oil; others oxydize and thicken, as linseed oil, poppy oil, and nut oils; the latter are called *siccative* oils, and are used in the manufacture of varnishes, printers' ink, oil cloth, also in paints.

Fats and oils are insoluble in water; they are among the very few bodies which are wholly insoluble in this menstrum; they are also, in general, difficultly soluble in alcohol. They generally dissolve in ether, and the liquid hydro-carbons. Their specific gravity is less than that of water.

Heat destroys them; acrolein is usually formed associated with other products.

Since oil and water repel each other, many other substances may be protected from moisture by simply coating them with oil. Shoe-leather may be rendered water-proof and iron protected from rusting by greasing. Wood, saturated with oil, will last for a long time when buried in moist ground.

Stearin or Stearine, (from στέαρ, suet) $C_{57}H_{110}O_6$, is prepared by melting suet in turpentine; the two other proximate principles present, are precipitated, while the stearine remains in solution. It is separated from the liquid by water, and purified by several recrystallizations in ether; it fuses at 71°, and solidifies at 50°.

Berthelot has reproduced stearine synthetically, by heating 3 parts of stearic acid with one part of glycerine, in a sealed tube.

This synthesis, as well as other researches, establishes the fact that the neutral fats are compound ethers of glyceryl, and the fatty acids.

On account of the heat generated by oxidizable oils when exposed to the air, frequent instances of spontaneous combustion occur when cotton rags, or waste soaked with oil, are allowed to remain in a heap.

Fats, especially if mixed with nitrogenous matter, become acid, *rancid*. The chemical nature of this change is not entirely understood.

Olein or oleine, is the chief constituent of olive oil and fish oil. Berthelot has shown, by the action of oleic acid on glycerine, that natural oleine is a mixture of monoleine, dioleine, and trioleine. Oleine heated with a small quantity of mercury nitrate, or any other body capable of furnishing nitric oxide, becomes solid, owing to the transformation of the oleine into an isomeric body, *elaidine*. Siccative oils contain, instead of oleine, another principle called *elaine*.

Neutral fatty bodies and other ethers of glycerine are decomposed by alkaline solutions; a combination with water takes place, glycerine and fatty acids are formed. We may take as an example, stearin.

$$3KHO+C_{57}H_{110}O_6=3(KC_{18}H_{35}O_2)+C_3H_8O_3.$$

Alkalies, therefore, react upon the ethers of glycerine in the same manner as do the ethers of glycol and ordinary alcohol. This reaction is called *saponification*, and soaps are salts formed by stearic, margaric, and oleic acids, with a metal.

SOAPS. STEARINE CANDLES.

The only soluble soaps are those whose base is potassa or soda. Soda soaps, those ordinarily in use, are hard, while potassa soaps are soft. On adding to an aqueous solution of soap a solution of a metal, a precipitate is formed which is the soap of the metal employed; thus the precipitate which common water produces in soap is a lime soap.

Ordinary soap is made by boiling fats of inferior quality with an alkaline solution. When the oil is completely decomposed the soap is precipitated by salt water, in which soap is insoluble.

Stearine candles have hitherto been made by saponifying suet or tallow with lime in the presence of boiling water. At present the amount of lime employed in the saponification is considerably diminished (amounting to only 4 per cent.) by operating at a temperature of 150°.

The saponification of fats of inferior quality is also effected by means of sulphuric acid instead of lime; this acid forms with the fatty acids, double or conjugate acids, which are decomposed by water. The decomposition of fats into their constituents, the fatty acids and glycerine, for the manufacture of candles, is at present effected on a large scale by simply heating the fats with steam under pressure, and at a temperature of 260°. This is the celebrated process of the American inventor, Tilghman, to whom the wonderful "sand blast" is also due.

This decomposition of fats is most remarkable, as, by the same process, only at a lower temperature, Berthelot obtained a result exactly the reverse, causing stearic acid and glycerine to reform stearine by simple direct synthesis.

STEARIC ACID, $C_{18}H_{36}O_2$, is crystalline, insoluble in water, soluble in alcohol and ether, and melts at 70°. It unites with the bases; its alkaline salts alone are soluble.

MARGARIC OR PALMITIC ACID, $C_{17}H_{34}O_2$, (from *μαργαρον*, a pearl, owing to its pearly lustre) is crystalline. It melts at 60° and forms salts with the metals.

OLEIC ACID, $C_{18}H_{34}O_2$, is an oil becoming colored in the air and converted into an acid called *elaidic acid*, which is fusible at 44°, in contact with a small quantity of hyponitric acid.

These three acids, stearic, margaric, and oleic, are those that, with glycerine, constitute most of the natural fats, or glyceryl ethers.

LEAD PLASTER is essentially a lead-soap compound of plumbic oleate.

CROTON OIL.

This oil is extracted from the seed of the *Croton tiglium* of the family of euphorbiaceæ.

The seeds are ground and expressed, or they are treated with ether, which is afterwards driven off by distillation.

This oil is yellowish, very bitter, and possesses a disagreeable odor. Alcohol and ether dissolve it. It produces blisters whenever it comes in contact with the skin, and is a drastic poison.

Pelletier and Caventou have extracted from this oil an acid body, $C_4H_6O_2$, denominated *crotonic acid.*

COD-LIVER OIL.

This oil is extracted from the liver of the cod, and several other species of the genus *Gadus.* Two processes are employed for its extraction; either the oil is obtained by putrefaction, in which case the oil separates out naturally, or the livers are cut into small pieces and heated in large pans, then placed in cloth sacks and pressed. It is of a brownish color. A white oil is sometimes sold, which has been bleached by treatment with weak lye and animal charcoal. The efficiency of this latter oil is much less than that of the natural oil.

There has been found in this oil 3 to 4 thousandths of iodine, and a small quantity of phosphorous; and its medical qualities are thought to be due to these two substances, but it is probable that its efficiency is more frequently due simply to its fatty character.

BUTTER.

Ordinary Butter. Butter contains stearic, margaric, oleic, and butyric acids, and several other proximate neutral principles. Its density is 0.82. It dissolves in 30 per cent. of boiling common alcohol. The odor which it emits on becoming rancid is due to the liberation of fatty acids.

"*Oleo-margarine*" is artificial butter, consisting mainly of oleine and margarine obtained from suet or lard.

SPERMACETI.

This substance which is formed in peculiar cavities in the head of the sperm whale, and is a neutral fatty body sometimes employed in pharmacy. It is an ether, which, on saponification, produces a fatty acid called *ethalic* acid, and a monatomic alcohol, *ethal.*

$$H_2O+\underbrace{C_{32}H_{64}O_2}_{\text{Spermaceti.}}=\underbrace{C_{16}H_{31}OHO}_{\text{Ethalic Acid.}}+\underbrace{C_{16}H_{34}O}_{\text{Ethal.}}$$

WAX.

Yellow bees-wax is obtained by submitting honeycomb to pressure, then fusing the same under boiling water. It is bleached by being cut into thin cakes and exposed to the air and sunlight. Thus prepared it fuses at 62°. Mixed with 3 per cent. of oil of sweet almonds it forms a *cerate*, used in pharmacy.

On being treated with alcohol it separates into two proximate principles: one, soluble in this liquid, is acid, and is called *cerotic acid*, having the formula $C_{27}H_{54}O$; the other, which is but slightly soluble, is called myricin. The latter is a compound ether, and is decomposed by bases into an acid, *ethalic acid*, and an alcohol, *melissic alcohol*, $C_{30}H_{62}O$.

CASTOR OIL.

This oil is extracted from the *Ricinus communis*, a plant of the family of Euphorbiaceæ.

The castor-oil beans are hulled, pulverized, and the pasty mass obtained subjected to strong pressure. This oil is slightly yellow. Its density is 0.926 at 12°, and it remains liquid at a temperature of −18°. It is very soluble in alcohol, a characteristic which distinguishes it from most other oils.

This oil is also an ether of glycerine; the acid which it contains is *ricinoleic acid*, $C_{18}H_{34}O_3$.

SUGARS.

The general name of *sugars*, by some regarded as polyatomic alcohols, is given to bodies which are capable of fermenting, that is, of decomposing directly or indirectly into different products, of which the principal ones are alcohol and carbon dioxide. Fermentation requires the presence of certain microscopic plants, and, according to Pasteur, is a phenomenon correlative with the vital development of these organisms. This, however, has been latterly disproved by Tyndall.

Sugars may be divided into three classes. In the first are those in which the proportion of hydrogen is more than sufficient to convert the whole of the oxygen into water. It contains:

Mannite, $C_6H_{14}O_6$, extracted from manna.

Dulcite or *melampyrite*, $C_6H_{14}O_6$, found in Madagascar.

Pinite, $C_6H_{12}O_5$, extracted from a Californian pine tree.

Quercite, $C_6H_{12}O_5$, extracted from acorns.

These bodies do not ferment with beer yeast alone; but in presence of certain ferments and calcium carbonate they furnish alcohol, carbon dioxide, and hydrogen.

Sugars of the second and third class contain hydrogen and oxygen in the proportions to form water.

The second class includes the glucoses, *isomeric* bodies, whose general formula is, $C_6H_{12}O_6$. Among these are:

Ordinary *Glucose* or *grape sugar*.

Levulose, associated with glucose in the form of inverted sugar.

Maltose, obtained from malt.

Galactose, obtained by treating sugar of milk, or gums, with dilute acids.

Eucalin, obtained by the action of maltose on beer yeast.

Sorbin exists in the berries of the mountain ash.

Inosite is found in the embryo of young plants and in the fluids of flesh.

Lactose or Sugar of Milk. The glucoses may be divided into two series. The first includes those bodies (ordinary glucose, levulose) which, on being oxydized, form saccharic acid, and on being hydrogenized by means of sodium amalgam, produce *mannite*. The second includes those substances (galactose, lactose) which, on oxydation produce mucic acid, and on hydrogenation furnish *dulcite*. The third class of sugars contains bodies whose general formula is $C_{12}H_{22}O_{11}$, and are called *saccharoses*, by Berthelot. It contains, besides cane sugar, three bodies called:

Melitose, an exudation of certain eucalypti.

Trehalose or *mycose*, extracted from the Turkish manna and certain mushrooms.

Melezitose, obtained from an exudation of the larch.

The sugars of the first two classes are placed by Berthelot among the polyatomic alcohols.

MANNITE.

$C_6H_{14}O_6$.

This body exists naturally in an exudation of various species of ash (*Fraxinus rotundifolia*), called manna, of which it forms the greater portion. It is also found in mushrooms, algæ, the sap of most fruit trees, onions, asparagus, celery, etc. It may be prepared by dissolving manna in one-half its weight of water, to which a small quantity of egg albumen is added, and the mixture brought to boiling and filtered. On cooling, colored crystals are deposited which are expressed and redissolved in hot water. This solution is mixed with animal charcoal, boiled and filtered while hot. The liquid deposits crystals on cooling. Mannite crystallizes in rhombic prisms and has a sweet taste. It dissolves in seven times its own weight of cold water, is slightly soluble in alcohol, and insoluble in ether. Its solutions are optically inactive.

Mannite fuses at about 165°; at about 200° it yields a certain quantity of a substance called *Mannitane*, $C_6H_{12}O_5$. It oxydizes in presence of platinum black, furnishing a non-crystallizable acid called *mannitic acid.* Boiling nitric acid converts it into saccharic and oxalic acids.

Mannite, treated with a small quantity of nitric acid, is changed into a body insoluble in water, called *nitro-mannite*, $\left.\begin{matrix}(C_6H_8)\\(NO_2)_6\end{matrix}\right\}O_6$, which may be regarded as a compound ether.

Dulcite.—Dulcite is very analogous to mannite, but differs from it, in that it furnishes, with nitric acid, mucic acid.

GLUCOSES.

$C_6H_{12}O_6$.

These compounds may be considered as representative carbohydrates. Ordinary glucose (from γλυκυς, sweet,) or grape sugar, is a crystalline substance, and is found in honey, figs, and various other fruits, together with another insoluble glucose. It has been found in small quantity in the liver and in most of the fluids of the body. It is obtained by the decomposition of salicine, tannin, and other substances, which, for this reason, have been named *glucosides.*

Vegetable cellulose, the envelope of many invertebrates (chitin and tunicin) and the glycogenous principle of the liver furnish glucose on treatment with dilute acids.

It is manufactured on a large scale by the action of starch upon dilute sulphuric acid. Water containing four to eight per cent. of sulphuric acid is placed in vats and heated to boiling by means of superheated steam. Before the water boils, starch mixed with water is added, and ebullition maintained as long as a small quantity of the mixture gives a blue reaction with iodine. The sulphuric acid is not changed during this transformation.

It is then saturated with chalk and the liquid allowed to become clear. It is decolored by passing through

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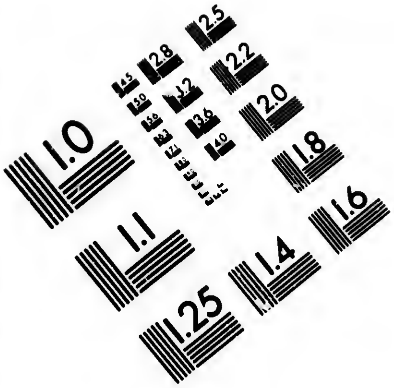

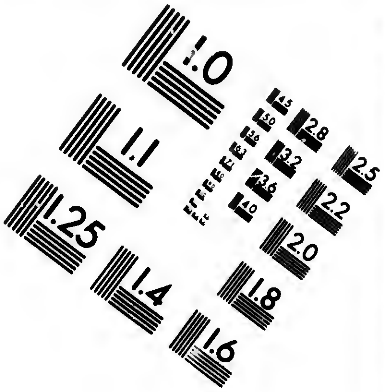

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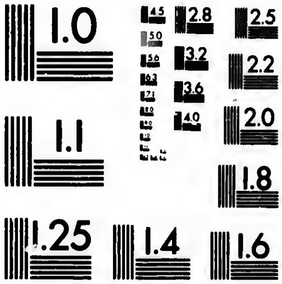

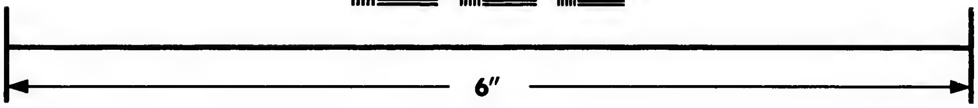

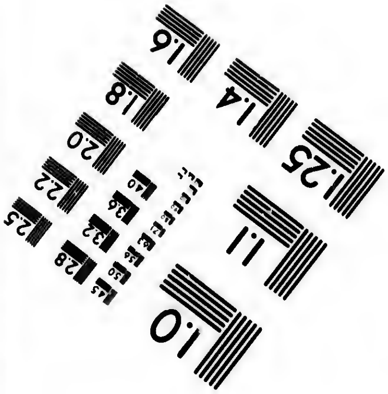

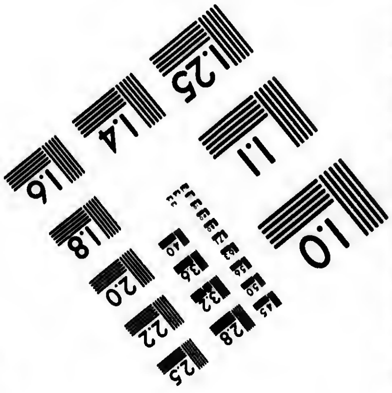

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filters containing animal charcoal and evaporated to a density of 41° Baumé. The glucose crystallizes in compact masses. Often the liquid is evaporated to only 3° B., when a syrup is obtained known as *starch syrup*. Honey treated with cold concentrated alcohol, also furnishes glucose. The crystals of glucose are small, opaque, and ill defined.

They are represented by the formula $C_6H_{12}O_6,2H_2O$, but they may be obtained having the composition $C_6H_{12}O_6$ by precipitating the glucose in boiling concentrated alcohol. The water may also be driven off by heating the glucose to about 100°.

Glucose is soluble in a little more than its own weight of water. Weak alcohol dissolves it readily. It is slightly soluble in cold concentrated alcohol.

Its solutions turn the plane of polarization to the right. This rotatory power is feeble in the cold.

Glucose, heated to about 170°, acts in the same manner as mannite. Gelis has demonstrated that it loses a molecule of water; the body formed $C_6H_{10}O_5$, is called *glucosane*, $C_6H_{12}O_6=C_6H_{10}O_5+H_2O$. It reproduces glucose on being boiled with acidulated water. If glucose is boiled with dilute nitric acid, saccharic and oxalic acids are formed. Fuming nitric acid forms with glucose a very explosive compound.

Hydrochloric acid turns it brown. With dilute sulphuric acid it furnishes a double acid (*sulphoglucic acid*); with strong sulphuric acid, carbon. Glucose oxydized with care, furnishes saccharic acid.

Heated to 100° with butyric, or various other acids, it loses water, and the glucosane formed reacts upon the acid, forming an ether, *saccharide*, or *dibutyric glucosane*,

$$\left.\begin{matrix}(C_6H_6)\\(C_4H_7O)H_2\end{matrix}\right\}O_5.$$

This body, as well as other *saccharides*, are decomposed under the action of boiling acidulated water, into an acid and glucose.

Glucose combines, with sodium chloride, forming several crystalline compounds; it also forms unstable compounds with the metallic bases,

$$\begin{matrix}CaC_6H_{10}O_6\\BaC_6H_{11}O_6, \text{etc.}\end{matrix}$$

Péligot has shown that the solutions of these glucosates are gradually changed into salts of a special acid called *glucic acid*, whose formula is

$$C_{12}H_{16}O_9.$$

Cupric acetate boiled with glucose is reduced to the state of suboxide.

This action, which is very slow with salts of copper with inorganic acids, becomes rapid and complete in presence of alkalies. On adding glucose to a solution of copper sulphate, this salt is not precipitated by potassa. If, however, the liquid is heated, it deposits cuprous oxide. (Trommer's test.) This reaction is more delicate with copper salts, whose acids are organic. A mixture is used of copper sulphate, Rochelle salt and soda (Fehling), or a solution of copper tartrate in potassa. (Barreswil.)

Prof. W. S. Haines has found in glycerine a very desirable substitute for the tartrate in Fehling's test. The proportions employed by him for qualitative examinations are: cupric sulphate, 30 grains; potassic hydrate, 1½ drachms; pure glycerine, 2 fluid drachms; distilled water, 6 ounces.

LEVULOSE, $C_6H_{12}O_6$.

This name is given to a variety of glucose, which is found in many fruits. It may be obtained by boiling inulin with water, or, better, it can be prepared from cane sugar by the action of dilute acids. It differs from the other sugars in that its rotary power diminishes on heating.

GALACTOSE,

$$C_6H_{12}O_6.$$

This body is produced by boiling, for two or three hours, sugar of milk with water acidulated with sulphuric acid. It is soluble in water and insoluble in alcohol; nitric acid transforms it into *mucic acid.*

INOSIN, INOSITE OR MUSCLE SUGAR.

$$C_6H_{12}O_6 + 2H_2O.$$

This substance is found in many animal organs, and is the chief constituent of the liquid which impregnates the muscles.

It may be prepared by first extracting the creatin from the muscles, then separating the inosic acid with baryta. To the liquid is then added a quantity of sulphuric acid sufficient to precipitate the whole of the baryta and the liquid treated with ether, which dissolves the foreign substances.

The aqueous solution is removed and alcohol added to it until a precipitate is formed. Crystals of potassium sulphate first separate out, then beautiful crystals of inosite. This substance has a sweet taste. At a temperature of 100° it loses two molecules of water. It dissolves in one-sixth of its weight of water while it is insoluble in ether and strong alcohol.

Inosite is without action upon polarized light. It is not converted into glucose by the action of dilute acids, and does not reduce copper salts. Mixed with milk and chalk it undergoes lactic fermentation. (Page 122.)

SACCHAROSES.

Ordinary Sugar,

$C_{12}H_{22}O_{11}$.

This body exists in a large number of plants, though it is almost exclusively extracted from the sugar-cane and beet-root.

The sugar-cane, *Arunde saccharifera*, contains 17 to 20 per cent. of sugar. To extract, the juice of the cane is first obtained by expressing. This juice represents 60 to 65 per cent. of the total weight of the cane, and would alter rapidly in the air if care were not taken to bring it rapidly to a temperature of 70°, and adding a quantity of lime. The juice soon becomes covered with foam and deposits different albuminoid and other matters, which are precipitated by the lime. It is decanted into pans and rapidly evaporated. The sugar crystallizes out, and the mother liquor is evaporated as long as it furnishes crystals. The thick liquid which remains is *molasses*. The sugar thus obtained is brown sugar, and is subsequently refined.

The beet-root most rich in sugar is that of Silesia. It contains about 10 per cent. of sugar. Sugar crystallizes in clinorhombic prisms. They may be readily obtained by slowly evaporating a solution of sugar.

The crystals of ordinary sugar are very small, as the syrup is made to crystallize quite rapidly. Cold water dissolves three times its weight of sugar; hot water dissolves it in all proportions, forming a syrupy liquid. It is not dissolved by cold alcohol or ether. Dilute alcohol dissolves it in proportion as it is more or less aqueous. Its solutions are dextrogyrate. Sugar melts at about 180°, and yields a liquid which solidifies to a vitreous, amorphous mass, called *barley sugar*, which becomes opaque and crystalline after some time.

If sugar is heated a little above this point, it is transformed into glucose and levulosane.

$$C_{12}H_{22}O_{11}=C_6H_{12}O_6+\underbrace{C_6H_{10}O_5.}_{\text{Levulosane.}}$$

At about 190° sugar loses water, becomes brown, and finally furnishes a substance which is commonly known as *caramel.* According to Gelis three products of dehydration are formed, *caramelane, caramelene* and *carameline.* At a temperature of 230° to 250° sugar is decomposed into carbon monoxide, carbon dioxide, carbohydrides and different empyreumatic products. Sugar is transformed slowly in the cold, and rapidly at 80°, in contact with dilute acids into *inverted sugar*, which is thus called on account of its inverted action upon polarized light. On prolonged ebullition the solution is rendered brown and ulmic products are formed. Sugar reacts with baryta water and lime water, forming different compounds called *sucrates* or *saccharates.*

The solutions of these sucrates are decomposed by carbon dioxide: sugar is reformed. Rousseau makes use of this fact in the manufacture of sugar on a very large scale.

Sugar does not ferment immediately in contact with beer yeast.

SUGAR OF MILK, LACTIN OR LACTOSE.

$$C_{12}H_{22}O_{11}+H_2O.$$

It is obtained from milk, by precipitating the casein with a few drops of dilute sulphuric acid, filtering and evaporating the liquid.

Crystals are deposited, which are purified by redissolving and treating with animal charcoal.

In Switzerland large quantities of sugar of milk are made by evaporating the whey which remains after the separation of the cheese.

The crystals of this body are rhombic prisms. This sugar is insoluble in ether and alcohol, and requires 2 parts of boiling and 6 parts of cold water for its solution.

Its solutions are dextrogyrate. At a temperature of about 140° it loses H_2O, and becomes brown at 160° to 180°.

In presence of sour milk and chalk it undergoes lactic fermentation.

Sugar has been found in a sample of a saccharine matter extracted from the sap of a sapodilla tree, the tree furnishing caoutchouc.

Reichardt has obtained (60-'75-807) from a sugar distinct from ordinary sugar, a body though having the same formula. He names it *para-arabin.*

HONEY.

Honey is produced by the domestic bee (Apis mellifica), an insect of the order Hymenoptera.

It is separated from the wax by exposing the honeycomb to the sun, on wire nets; very pure honey is thus obtained.

The mass which remains is expressed, and this product is a second quality of honey, more colored and of a less agreeable taste and odor than the first. The comb is then heated with water to remove the remainder of the honey. The wax thus isolated is melted and run into moulds. Honey owes its sweet taste to several sugars. There is found in it a dextroyrgate, crystallizable glucose, and on removing this sugar there remains a viscid uncrystallizable liquid, which contains levulose. In addition to these, small quantities of ordinary sugar have also been found in honey.

GLUCOSIDES.

This name is given to certain bodies which have the property of forming various products by combining with water, among which is glucose, or some other saccharine matter.

This change is produced by the action of acids, bases, or by the action of ferments. We cite the following, but shall only study the most important:

Salicin, $C_{13}H_{18}O_7$, extracted from the bark of the Willow.

Amygdalin, $C_{20}H_{27}NO_{11}$, extracted from the Bitter Almond, *Amygdalus communis.*

Orcin, $C_7H_8O_2$, extracted from various Lichens.

Tannin, $C_{27}H_{22}O_{17}$, extracted from the Oak.

Phlorizin, $C_{21}H_{24}O_{10}$, extracted from the Apple, Pear, or Cherry tree.

Populin, $C_{20}H_{22}O_8$, extracted from Aspen leaves.

Arbutin, $C_{13}H_{16}O_7$, extracted from the leaves of the Uva-Ursa.

Convolvulin, $C_{31}H_{50}O_{18}$, extracted from the *Convolvulus orizabensis* and *schiedeanus.*

Jalappin, $C_{34}H_{56}O_{16}$, extracted from *Convolvulus orizabensis* and *scammonia.*

Saponin, a white amorphous powder whose solution is very frothy and of which the powder is very sternutatory.

Daphnin, $C_{31}H_{32}O_{17}$, the crystalline matter extracted from the bark of the Ash (*Fraxinus excelsior*).

Cyclamin $C_{20}H_{24}O_{10}$, extracted from the tubercles of the *Cyclamen europæum.*

Quinovin, $C_{30}H_{48}O_8$, a resinous, bitter matter, soluble in alcohol, existing in the bark of the *Quina nova* and other cinchonas.

Solanin, $C_{43}H_{71}NO_{16}$. This has already been studied, (page 165).

Esculin, $C_{21}H_{24}O_{13}$, extracted from the bark of the Horse Chestnut.

Quercitrin, $C_{29}H_{30}O_{17}$, from the bark of the yellow oak (*Quercus tinctoria*).

Coniferin, $C_{16}H_{22}O_8$, from the *Larix europaea*, etc.

Vanillin, from the Vanilla bean, and recently obtained artificially (60–74–608).

SALICIN, $C_{13}H_{18}O_7+H_2O$.

This body crystallizes in white needles, fusible at 120°, insoluble in ether, soluble in alcohol and water. These solutions are levogyrate and very bitter. It is used as a febrifuge, but is of little value in well defined intermittent fevers.

It has as a distinguishing chemical character, the property of becoming red with sulphuric acid.

Under the action of dilute sulphuric, or hydrochloric acid, or even with emulsin, salicin is decomposed. With the latter the reaction is:

$$C_{13}H_{18}O_7+H_2O=\underbrace{C_6H_{12}O_6}_{\text{Glucose.}}+\underbrace{C_7H_8O_2}_{\text{Saligenin.}}$$

In contact with cold nitric acid it loses hydrogen, and a body is formed called *helicin*, $C_{13}H_{16}O_7$.

When treated with oxydizing agents, it gives off an odor which is identical with that of the essence of meadow sweet (*Spirea ulmaria*).

This body is produced especially when salicin is treated with a mixture of sulphuric acid and potassium bichromate, and is also known by the name of *hydride of salicyl*.

Its formula is identical with that of benzoic acid, $C_7H_{16}O_2$, but it has not the properties of this acid.

It is an aromatic liquid, boiling at 196°, and has the property of oxydizing spontaneously, giving rise to an acid called *salicylic acid*, $C_7H_6O_3$.

Salicin, treated with fused potassa, furnishes potassium oxalate and salicylate. Cahours has shown that essence of *Gaultheria procumbens*, a heath of New Jersey, contains, besides, an isomer of the essence of turpentine, a sweet-scented liquid, boiling at 220°, which is salicylic methyl ether, and is re-converted, in contact with alkalies, into methyl alcohol and salicylic acid : it may be produced artificially by treating wood spirit with a mixture of salicylic and sulphuric acids.

Salicylic or oxybenzoic acid has been lately produced by Kolbe (56 –'74 –22), by a remarkable synthesis in acting on carbolate of sodium with CO_2.

$$\underbrace{2C_6H_5ONa}_{\text{Sodium phenol.}}+CO_2=\underbrace{C_6H_6O+C_7H_4O_3}_{\text{Sodium salicylate}}\underbrace{Na_2}_{\text{of sodium.}}$$

It has now come to be a very important article in pharmacy and in the arts, on account of its efficiency as an antiseptic, equaling or surpassing carbolic acid (phenol), yet without the unpleasant odor of the latter body, or its toxical qualities. As of considerable importance theoretically, it should be stated that Herrmann has very lately (60–April, '77) obtained salicylic acid by the action of sodium upon succinic ether.

TANNINS.

This is the name given to different principles existing in plants, which are characterized by the following properties:

1st. They give, with ferric salts, a black coloration approaching blue or green.

2d. They precipitate solutions of albuminoid substances, particularly those of gelatine.

The principal ones are:

Tannin of oak, $C_{27}H_{22}O_{17}$.
" " cachou (catechin or catechic acid).
" " quinquinia (quinotannic acid).
" " coffee (caffetannic acid).
" " fustic (morintannic acid).

Oak tannin is best prepared from gall-nuts which contain much more than does the bark. The nuts are pulverized and submitted to the action of commercial sulphuric ether, which is made aqueous. This ether may be replaced with advantage by a mixture of 600 grams of pure ether, 30 grams of 90 per cent. alcohol, and 10 grams of distilled water for every 100 grams of gall-nuts. After twenty-four hours the apparatus contains two layers of liquid; the upper one is ether, containing but little tannin, while the lower one is a very strong aqueous solution of tannin.

The lower layer is removed and evaporated in an

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oven on shallow plates. There remains an amorphous spongy substance, very soluble in water, less soluble in alcohol, and almost insoluble in ether. This residue is very astringent and slightly acid.

Solutions of tannin give a white precipitate with tartar emetic.

It precipitates solutions of the alkaloids, and coagulates blood.

With solutions of gelatin it gives a voluminous precipitate, soluble on heating in an excess of gelatin.

Tannin forms, with fresh hide, an imputrescible compound, which is *leather*. The art of tanning is based on the action of oak-bark tannin on hides from which the hair has been removed, usually by lime.

GALLIC ACID. In solution, tannin is gradually decomposed, the liquid becoming covered with mould.

Carbon dioxide is disengaged and an acid, called *gallic acid*, is formed.

This transformation does not take place if all air is excluded; and the air *alone* is not sufficient. It requires the presence of a mycelium of a mucedin conveyed to the liquid either by the air or in some other manner.

This transformation is, like alcoholic fermentation, a phenomenon correlative with the development and growth of an organism. On boiling tannin with water acidulated with hydrochloric or sulphuric acid, it is decomposed into glucose and gallic acid:

$$C_{27}H_{22}O_{17}+4H_2O=3\underbrace{(C_7H_6O_5)}_{\text{Gallic acid.}}+\underbrace{C_6H_{12}O_6}_{\text{Glucose.}}$$

Gallic acid is deposited as the liquid becomes cool. It is purified by redissolving and treating with animal charcoal, and recrystallizing.

Gallic acid, $C_7H_6O_5=\left.\begin{matrix}C_7H_2O\\H,H_3\end{matrix}\right\}O_4$, crystallizes in silky needles, soluble in three parts of boiling water, but little soluble in cold water. This solution, on standing in the air, becomes altered after a long time, carbon dioxide is disengaged and the solution turns brown; alkalies accelerate this change.

Gallic acid produces a blue color with ferric salts, and precipitates tartar emetic, but does not precipitate gelatin when pure, nor the alkaloids.

Mixed with pumice-stone and heated to 210° it produces a beautiful sublimate of *pyrogallic acid*, carbon dioxide being liberated at the same time.

$$C_7H_6O_5=C_6H_6O_3+CO_2.$$

This body occurs in colorless, acicular crystals, fusible at about 115°, and soluble in 2.5 parts of water. Its solution absorbs oxygen from the air, in presence of alkalies, and becomes quite brown.

It reduces gold and silver salts, and forms unstable compounds with certain acids. It may properly be placed among the phenols. This body is employed in photography, and in the laboratory. Mercadante (47–'74–484) finds that gallic acid is injurious to vegetation, inasmuch as it combines with the mineral food of the plant rendering it insoluble.

Grimaux was the first to consider gallic acid as tetratomic and monobasic (77–620).

VEGETABLE CHEMISTRY.

At the moment when the radicle of a plant appears above the ground, its vital phenomena undergo a marked change.

The plant decomposes carbon dioxide, water and certain nitrogenous compounds furnished by the soil, and grows by retaining carbon, hydrogen, nitrogen and a little oxygen, and returns to the air the greater part of the oxygen derived from the carbon dioxide, water and nitrogenous compounds.

Bonnet observed, in the last century, that leaves, exposed to the sun in areated water, disengage a gas, which Priestly showed is oxygen. Sennebier discovered that this oxygen is derived from carbon dioxide. De Saussure verified these facts, and demonstrated that this decomposition of carbon dioxide does not take place in the dark, and that the green portions of the plant alone are capable of effecting the change.

J. Belluci (9–78–362) has lately shown that, contrary to former belief, none of the oxygen exhaled by plants is in the form of ozone.

Experiment.—Place a few leaves in a flask half full of water containing carbon dioxide, "soda water," invert the flask over a glass of water, and expose it to the sunlight, after having covered it, if the sun is very hot, with a sheet of transparent paper; minute bubbles will soon be seen to form on the leaves, as small as the point of a pin, will increase in size, unite and mount to the upper part of the flask. Transfer this gas to a test-tube, and, on examination, it will be found to be oxygen. Substitute for this flask an opaque vessel, or perform the experiment in the dark, and the carbon dioxide will not be altered in the least.

Where do the plants find this carbon dioxide? Chiefly in the air. Boussingault, in order to demonstrate this, placed under a bell-glass some peas planted in calcined sand; he watered them with pure distilled water, and passed air into the glass; the peas grew, flowered and bore fruit.

Now the substance of these peas contained carbon hydrogen and nitrogen, in much greater quantity than the seed from which they grew, consequently these constituents were taken from the air and water.

If, however, the air be made to pass through an alkaline solution before escaping from the vessel, no carbon dioxide is absorbed, which also proves that the carbon dioxide existing in the air has been removed by the plant. The plant takes up, in the same manner, carbon dioxide from the water which passes from the soil into its roots.

Plants are also capable of decomposing water, in fact, Collin and W. Edwards have proved that the submerged stems of the *Polygonum tinctorium* and certain mushrooms, exhale hydrogen.

On the other hand, Payen has proved that the hydrogen exceeds the oxygen in the woody parts of plants, and, indeed, many substances produced by plants, as oils and resins, are very rich in hydrogen. In short, the oxygen contained in the plant would not be sufficient to oxydize or transform into water the whole of the hydrogen it contains, consequently it must be admitted that water is decomposed by plants. The conditions under which this change takes place have not as yet been determined.

The experiment of Boussingault proves, as Ingenhousz has claimed, that the air furnishes the plant with nitrogen; but where does this nitrogen come from? Is it taken by the plant from the free nitrogen of the atmosphere? or is it derived from the nitric or nitrous acids, or from the ammonia contained in the atmosphere, or, in one word, from the nitrogenous compounds existing in the air?

Boussingault has shown that while certain families of plants, principally the common vegetables, derive from the air a large quantity of nitrogen, even taking up free nitrogen, others, the cereals for instance, derive nitrogen chiefly from the soil; for, on causing clover and wheat to grow in calcined sand in presence of air deprived of its nitrogenous compounds, and distilled water, he observed that the clover took up carbon, hydrogen, water and nitrogen, while it appears that the wheat obtained from the air carbon and water only.

Nitrogen, which is present in the air in the form of ammonium nitrate, is absorbed by all plants. Direct experiments have shown that the salts of ammonium, especially ammonium nitrate, constitute an excellent compost, and consequently this nitrate can lose its oxygen, or become reduced in the plant.

Now, it is known that urea and animal excreta are transformed into ammoniacal compounds on exposure to the air; therefore, in order to obtain a good crop, even with plants which take up the nitrogen of the air, it is necessary to employ manures which furnish not only easily assimilated nitrogen, but those which, besides, furnish the plant with soluble organic compounds and the mineral substances necessary for its development and growth. Of these latter there is required for the plant, potassium and calcium chlorides, sulphates, phosphates, etc.

With the four elements, carbon, hydrogen, nitrogen, and oxygen, nature forms an infinite variety of compounds by mysterious methods, to which we have not, as yet, the key, but of which synthetical research gives us some idea. Thus, with carbon dioxide and water, Berthelot produces formic acid; with formic acid he obtains alcohol, and subsequently acetic acid. Pasteur also has shown that glycerine, one of the principles of fat, is produced in the process of fermentation and that a complex acid, succinic acid, is also formed under the same circumstances. However, we are far from knowing how to produce those substances which nature forms at ordinary temperatures, and *with only four elements*. What wondrous chemistry is that of the plant, fitted by an all-wise Creator to elaborate with such simple materials, the beauteous violet, the fragrant rose, or the luscious fruit!

By combining six atoms of carbon with five atoms of water, nature forms either the woody principle, *cellulose*, or the essential constituent of the potato, *starch*. By uniting ten atoms of carbon with sixteen atoms of hydrogen, she produces, in the orange and in the pine, two essences or oils very different in character. By associating the four organic elements she forms the most different substances, the nourishing cereal as well as the most deadly strychnia; and often products as unlike as these are found side by side in the same plant.

Thus the plant is a structure which decomposes carbon dioxide, water, and compounds of nitrogen; which forms its substance out of carbon, hydrogen, nitrogen, and a part of the oxygen of these compounds, and which exhales oxygen. Hence, chemically, it would be proper to call the plant *a reducing apparatus.*

We should add that the flowers and portions of plants not green, also the buds in developing, produce an exhalation of carbon dioxide, and that during germination, and especially during the time of flowering, a sensible amount of heat is disengaged. As a result of this elevation of temperature, there is produced in plants some slight oxydation or combustion, as in the respiration of animals.

Hence, we must conclude that plants and animals, in many circumstances at least, deport themselves in a similar manner.

Many experimenters, and especially Dutrochet and Garreau, go further, and say that plants and animals respire in an identical manner, and according to their theories all living creatures take up oxygen and exhale carbon dioxide.

The experiments of Garreau especially deserve attention. He placed branches, detached or affixed to the plant, in vessels full of air, and exposed them to a diffused light. The volume of the air was known and the oxygen absorbed was determined by a special contrivance; the carbon dioxide produced was removed by placing in the vessel an alkaline solution of known weight. Thus the variations of these gases were carefully studied.

As a result of his experiments Garreau claimed to have established that both in the dark and in the light, there is an absorption of oxygen and an exhalation of carbon dioxide, but the amount of carbon dioxide collected does not represent the amount really exhaled, as the greater part is reduced at the moment of liberation. From these facts it would appear that in all living creatures the same phenomenon of respiration takes place, which consists in a consumption of oxygen and an exhalation of carbon dioxide.

This phenomenon is associated with another; viz., assimilation or nutrition. It is here that the difference, indeed a complete opposition, between the two kingdoms is established. The plant grows by reducing, under the influence of heat and sunlight, carbon dioxide, water and nitric acid, by accumulating carbon, hydrogen, nitrogen and by exhaling the greater part of the oxygen. The animal, on the other hand, forms its substance from that of the plant, oxydizing, or consuming, the vegetable products with the oxygen of the air exhaled by the plants; it reduces the complex products formed in the vegetable to the state of carbon dioxide, water and ammonia; thus the animals supply the plants with food, receiving in turn nourishment from them. Those desirous of further studying this and other interesting topics relating to Vegetable Chemistry, will find very valuable the works of Prof. S. W. Johnson, "How Crops Grow," and "How Crops Feed"; also Prof. John C. Draper's article in Am. Jour. Sci. and Arts, Nov. 1872, entitled "Growth of Seedling Plants."

ORGANIZED SUBSTANCES.

Among the chemical substances of which we have spoken certain ones participate more in vital phenomena, and have more definite physical structure than do others.

These are designated as *organized or organizable substances*, the term *organic* being reserved for the definite compounds studied in organic chemistry. All these substances play an important part in the vegetable kingdom, forming the network of vegetable tissue, as cellulose or as starch, etc.

CELLULOSE OR CELLULIN, $(C_6H_{10}O_5)_n$.

On examining a young plant under the microscope, we observe that it is built up of little cells and minute, diaphanous ducts or vessels filled with sap and air. The material of which these tissues are composed is called *cellulose*. The pith of the elder, cotton fibre, and paper are almost exclusively composed of this substance.

Cellulose is a carbo-hydrate; $C_6H_{10}O_5$, is the formula, ordinarily given to it, although a multiple formula at least three times as large, or $C_{18}H_{30}O_{15}$ is necessary to explain certain reactions with nitric acid.

EXPERIMENT. Pure cellulose may be obtained in the following manner: cotton, linen or paper is treated with dilute alkaline solutions, washed and immersed in weak chlorine water; finally it is submitted to the action of various solvents, as water, alcohol, ether and acetic acid until nothing more is dissolved.

This substance is solid, white and insoluble. It is destroyed at a red heat, producing carbon and numerous carbohydrides, gaseous and liquid, which distil over. With monohydrated sulphuric acid it produces a colorless, viscid liquid, which contains, at first, an insoluble substance having the properties of starch and yielding a blue color with iodine. If the action of the acid is continued, the whole is dissolved and the same products are obtained as in the case of starch when brought in contact with sulphuric acid, i. e. dextrin and glucose. To separate the latter substance, it is simply necessary to saturate the acid with chalk and evaporate the liquid.

Concentrated hydrochloric acid produces the same effect. If paper be immersed for *an instant* only in sulphuric acid, diluted with half its volume of water, and carefully washed, it acquires the toughness of parchment. Paper thus prepared is frequently employed in experiments on dialysis; it is also much used by pharmacists to cover the stoppers of bottles. It is known in commerce as *vegetable parchment.*

GUN COTTON OR PYROXYLIN.

Gun cotton was first made by Schoenbein, in 1846.

To prepare it cotton is plunged for two or three minutes into fuming nitric acid, or, better, into a mixture of 1 vol. nitric acid (of a density of 1.5), and 2 vols. of strong sulphuric acid; it is then thoroughly washed and dried at a low temperature.

The cotton is not changed in appearance other than becoming somewhat wrinkled. When well prepared it burns completely, leaving no residue. The temperature at which it takes fire varies from 100° to 180° according to the manner in which it has been prepared. It is cellulose in which from six to nine atoms hydrogen have been replaced by an equivalent quantity of the monad radicle NO_2 that, having the formula $C_{18}H_{21}O_{15}9NO_2$, has the greatest explosive energy. Pyroxylin regenerates cellulose in contact with ferrous chloride. If cellulose be considered a sort of alcohol, as claimed by some, pyroxylin would be a nitric ether of this alcohol.

Pyroxylin has the advantage over gunpowder of being more easily prepared, and of remaining unaffected by moisture, but its cost is relatively greater, and its shattering power renders its employment dangerous.

The term *collodion* (from κολλα, glue) is given to a preparation obtained by dissolved gun-cotton in a mixture of 1 part of alcohol and 4 parts of ether.

Chas. H. Mitchell has made (52–74–235) a number of experiments, with the view of ascertaining the relative proportions of cotton and acid, together with the proper time of maceration necessary to produce a cotton which should combine the largest yield with the highest explosive power and solubility.

The following formula was at length adopted:

Raw cotton, - - - -	2 parts.
Potassium carbonate, - - - -	1 "
Distilled water, - - -	100 "

Boil for several hours, adding water to keep up the measure; then wash until free from any alkali, and dry. Then take of—

Purified cotton, - - - - -	7 oz. av.
Nitrous acid (nitric, saturated with nitrous acid), s. g. 1.42, - - - - -	4 pints.
Sulphuric acid, s. g. 1.84, - - -	4 "

Mix the acids in a stone jar capable of holding 2 gals., and when cooled to about 80° Fahr., immerse the cotton in small portions at a time; cover the jar and allow to stand 4 days in a moderately cool place (temp. 50° to 70° Fahr.) then wash the cotton in small portions, in hot water, to remove the principal part of the acid; pack in a conical glass percolator, and pour on distilled water until the washings are not affected by solution of barium chloride.

Collodion, on spontaneously evaporating, forms a transparent and impermeable membraneous coating, and is much employed in photography, also somewhat in surgery.

Cellulose is attacked by chlorine; the use of solutions of chloride of lime, and of chlorine, in large quantities in washing, or bleaching, will cause a rapid deterioration of linen or cotton goods.

Schweizer has shown that cotton, paper, etc., is very easily dissolved by an ammoniacal solution of copper. Attempts by the author to employ this solution for a "water-proof" coating of fabrics, as has been suggested, failed to yield a satisfactory result, on account of the liability of the coating to crack and peel off.

Péligot has found in the skin of silk worms, and Schmidt has discovered in the envelopes of the Tunicates, a substance, *tunicine*, which has the composition and properties of cellulose.

Linen, hemp, cotton, wood and paper are all essentially cellulose.

AMYLACEOUS SUBSTANCES.

These substances are almost universally present in plants; particularly that known as *starch* or *fecula*.

The potato yields about 20 per cent. of starch. In order to obtain it, this root is grated and the pulp placed upon sieves, arranged one above the other, and through which a stream of water flows.

The grains of starch being extremely minute pass through the meshes of the sieve, while the walls of the cells remain behind. The starch is washed, drained, and dried, first at ordinary temperature, afterwards by the application of a moderate heat.

STARCH. $x(C_6H_{10}O_5)$ probably $C_{18}H_{30}O_{15}$. Flour contains, besides starch, nitrogenous substances, denominated gluten; this gluten is capable of fermenting, whereupon it becomes soluble, while the starch remains unaltered and insoluble. Under these conditions the gluten gradually dissolves, disengaging ammoniacal compounds, hydrogen sulphide and other products of putrefaction.

At the end of twenty or thirty days, the gluten having become dissolved, the liquid is removed, and the starch, washed and dried, shrinks into columnar fragments, which are readily pulverized by gentle pressure.

A more modern method is that employed in France, which is essentially the same as the process cited above, as that used in making potato starch here. The water carries away the starch while the gluten remains behind in the form of an elastic mass, which is also utilized. For this purpose it is incorporated with flour poor in gluten, to be made into macaroni, and for the manufacture of a very nutritive preparation, "granulated gluten;" it is also employed, according to the recommendation of Bouchardat, in making bread for persons afflicted with diabetes.

Starch, examined with a microscope, exhibits flattened ovate granules of different size in various plants, but always very small. Those of the Rohan potato have a length of 0.185 mm.; the smallest are those of the *Chenopodium quinoa* whose length is 0.002 mm.

When starch is heated with water to 70°, the granules increase from 20 to 30 times their original volume, and become converted into a tenacious paste. A small quantity of the starch passes into solution, and to this the name *amidin* has been given. Starch paste and the solutions of starch have the characteristic property of becoming blue in contact with small quantities of iodine. The liquid becomes colorless at about 70°, but regains its color on cooling. If to this blue liquid a solution of a salt, sodium sulphate for instance, be added, we obtain a dark-blue floculent precipitate. This substance, called starch iodide, is not a chemical compound, but a sort of lake, containing variable quantities of iodine diffused throughout the starch and solvent. This reaction with iodine is a very valuable test for starch, but is open to several fallacies, and apt to mislead in inexperienced hands.

Until lately, it has been claimed that starch is insoluble in water, and that if water in which starch has been boiled gives with iodine the characteristic reaction of this substance, it is due to particles of starch sufficiently minute to pass through the pores of the filter. But the results of the experiments of Maschke and Thenard, show that if starch is heated for some time at 100°, it is partially transformed into a variety soluble in water. This substance is colored by iodine; it furnishes, on evaporation, a gummy solid which is precipitated by alcohol as an amorphous powder.

If we boil starch for a long time with water it is converted into a substance called *dextrin.* The presence of a small per centage of sulphuric acid facilitates this change, which is soon followed by the transformation of the dextrin into glucose. The sulphuric acid is not at all altered during the reaction.

The change of starch into glucose also takes place when water containing starch, and to which germinated barley has been added, is heated to about 70°.

This transformation is due to a substance called *diastase* (from δίαστασις, separation), which is formed in the seed during germination. The production of diastase on the formation of the young shoot, explains how starch becomes soluble and serves as nutriment to the young plant.

The *ptyalin* of the saliva, the pancreatic juice, the soluble parts of beer yeast, gluten, and many other substances, are capable of producing this transformation of starch into dextrin and glucose.

It has generally been considered that the molecule of starch, in being transformed into glucose, simply united with one molecule of water directly, thus:

$$C_6H_{10}O_5+H_2O=C_6H_{12}O_6.$$

Musculus, however, claims to have established that the starch is first transformed into a soluble metamer, and this, thereupon, splits up into dextrin and glucose:

$$C_{18}H_{30}O_{15}+H_2O=\underbrace{2C_6H_{10}O_5}_{\text{Dextrin.}}+\underbrace{C_6H_{12}O_6.}_{\text{Glucose.}}$$

By further action, the whole of the dextrine becomes converted into glucose, (2–[3]60–203).

Starch, heated simply to about 160°, is also changed into dextrin.

It is attacked by dilute nitric acid, nitrous vapors are given off and different substances are produced, chiefly, however, oxalic acid.

If starch is agitated with fuming nitric acid, it is dissolved and water precipitates from the solution a nitrous compound which is explosive.

The alkalies, in concentrated solutions, when heated with starch disorganize and dissolve it. Solutions containing two to three per cent. of alkali, accelerate the formation of starch paste.

Starch is employed in the laundry and therapeutically in poultices, injections and baths.

Tapioca is the starch of the root of the *Jatropa manihot*, called cassava or manioc.

Sago is obtained from the pith of various sago palms.

Arrow-root is the starch of the *Maranta arundinaceæ*, and one or two other tropical plants.

Salep is obtained from the *Orchis mascula*.

INULIN. There has been found in the roots of the Jerusalem artichoke, of the chicory, and the bulbs of the dahlia, a substance isomeric with starch, called *inulin*.

LICHENIN. There is extracted from certain lichens and mosses a substance called *lichenin*, which has the property of swelling in cold water and of being dissolved in boiling water. It is prepared by treating Iceland moss with ether, alcohol, a weak solution of potassa, and finally with dilute hydrochloric acid.

There exists in the animal organism a variety of starch designated by the name of *glycogen*.

DEXTRIN, OR DEXTRINE.

$C_6H_{10}O_5$.

To prepare dextrin, starch may be heated with water containing a small quantity of sulphuric or oxalic acid; the operation should be arrested when the liquid gives with iodine only a wine-colored reaction.

For the acids, a small quantity of germinated barley may be substituted, placed in a bag immersed in the liquid. Dextrin thus prepared always contains glucose. It may be obtained free from this substance by heating starch with $\frac{1}{3}$ its weight of water and $\frac{2}{1000}$ of nitric acid.

Dextrin is amorphous, slightly yellow, very soluble in water, insoluble in alcohol and concentrated ether.

It is used somewhat in preparing bandages in case of fracture, and very extensively as a paste for calico-printers.

Dextrin, forms viscid adhesive solutions which are used for the same purposes as gum-arabic. The mucilage used by the U. S. government for postage stamps is composed of dextrin two ounces, acetic acid one ounce, water five ounces, alcohol one ounce. Dextrin may be distinguished from gum-arabic by not being precipitated on adding a dilute solution of lead acetate, and by furnishing with nitric acid a solution of oxalic acid and not a precipitate of mucic acid.

FLOUR.

Amylaceous substances are of great importance as food. Wheat and other cereals are the most important sources of these aliments.

Starch, as also sugar and the neutral carbohydrates, are respiratory foods whose principal effect is the production of heat by being oxidized, or burned, in the body.

The composition of four of the leading cereals is herewith given:

	Water.	Starch.	Dextrin and Glucose.	Cellulose.	Nitrogenous Substances.	Fat.	Mineral Substances.
Wheat,	14.0	59.5	7	1.7	14	1.2	1.5
Rye,	16.0	57.5	10	3.0	9	2.0	2.0
Oats,	14.0	53.5	8	4.0	12	5.5	4.0
Rice,	14.5	77.0		0.5	7	0.5	0.7

The sticky, elastic substance found with starch in flour is *gluten* (called also *glutin*), and is a mixture of various proximate compounds but chiefly of three; legumin, or vegetable casein, fibrin and gelatine.

Flour of good quality is dry and soft to the touch; it forms with water an elastic, non-adhesive dough.

The value of flour depends largely upon the gluten it contains, though not as stated in most authors upon the percentage of this substance, but upon the quality rather, as shown by recent investigations of R. W. Kunis (26–74–1487).

The modern "patent process," originating in Minnesota, is mainly a method of grinding which introduces into the flour more gluten than in older processes.

GUM.

$C_6H_{10}O_5$.

This substance is very widely distributed in the vegetable kingdom. Gums either swell in water or are dissolved, imparting to it a mucilaginous consistency.

From a chemical standpoint they are essentially characterized by giving a precipitate of *mucic acid* on being boiled with nitric acid, and by precipitating lead subacetate.

GUM-ARABIC, ARABIN. This gum exudes from different species of acacias, as *Acacia arabica*, *A. senegalensis*, *A. vera;* it is obtained from Arabia and Senegal.

According to Fremy, gum-arabic is a salt formed by the combination of an acid, *gummic* or *arabic acid*, with lime and potassa. This acid may be isolated by pouring hydrochloric acid into a solution of gum, and adding alcohol; an amphorous deposit is formed which, dried at 120°, has the formula $C_6H_{10}O_5$. This acid is very soluble in water. Its solution is levogyrate, like that of gum-arabic. On being heated to 150° it is transformed into a substance insoluble in water called *meta-gummic acid*, whose salts are likewise insoluble. Gum-arabic gives with ferric salts an orange-colored, floculent precipitate soluble in acids.

CERASIN. The gum which exudes from cherry and plum trees is a mixture of soluble gummates and insoluble meta-gummates; hence it is only partially soluble in water.

Cerasin becomes soluble on being boiled with water, as the meta-gummates are transformed into gummates by the action of boiling water.

These gums heated with dilute sulphuric acid furnish a dextrogyrate sugar.

Gum-tragacanth often contains starch.

Mucilage or Bassorin. There exists in the seeds of the quince and flax, in the roots of the marsh-mallow and in portions of many other plants, a substance or substances, which, exposed to the action of boiling water, furnish a thick mucilage, which appears to consist of a soluble, together with an insoluble substance. Nitric acid converts this mucilage into mucic and oxalic acids. Gum and mucilage are frequently employed as emollients, and in syrups, also extensively in confectionery.

Pectin Group. Many roots, as the carrot, beet, etc., also green fruits, contain a neutral gelatinous substance, insoluble in water, alcohol and ether, called *pectose.* It is that which gives to green fruits their harshness. This substance is modified during the ripening of the fruit and becomes soluble, vegetable jelly, or *pectin* (from πηκτίς, a jelly), to which Fremy assigns the formula $C_{32}H_{48}O_{32}$.

Pectin, submitted to the action of a ferment found in the cellular tissues of vegetables, called *pectase*, or of cold, very dilute, alkaline solutions, is changed into a gelatinous acid called *pectosic acid*, then into another substance likewise gelatinous, which is known by the name of *pectic acid.* All these substances are amorphous, and non-nitrogenous. Their formulæ are not yet definitely determined.

According to Fremy, to whom we are indebted for the foregoing facts, the jelly obtained from the current and other fruits is due to the action of the pectase on the pectin of these fruits.

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These substances resemble gums in producing, on boiling with nitric acid, a precipitate of mucic acid.

Much doubt still exists respecting the composition of the pectin group.

LEGUMIN OR VEGETABLE CASEIN.

Legumin is found in most leguminous seeds, such as sweet and bitter almonds, also in beans, peas, etc., the latter containing about 25 per cent. It is considered to be identical with casein by Liebig and Woehler.

It may be obtained by digesting coarsely powdered peas in cold or tepid water for two hours, allowing the starch and fibrous matter to subside, and then filtering the liquid. It forms a clear, viscid solution, which is not coagulated by heat unless albumen is also present, but, like emulsin and unlike albumen, it is precipitated by acetic acid. It is coagulated by lactic acid, also by alcohol; in the latter case the precipitate is redissolved by water.

Acetic acid, diluted with 8 to 10 parts of water, is carefully dropped into the filtered solution obtained above, and the legumin is precipitated; an excess of the acid should be avoided, as this would dissolve the precipitate. It falls in the shape of white flakes, and after having been washed on a filter should be dried, pulverized and freed from adhering fat by digestion in ether. Legumin may be obtained from lentils with the same facility as from peas; but it is less easily procured from beans (haricots), in consequence of their containing a gummy matter which interferes with its precipitation and with the filtration of the liquids.

The chemical properties of legumin are identical with those of casein.

Liebig supposes that grape-juice and other vegetable juices which are deficient in albumen, derive their fermentation power from soluble legumin. This principle is soluble in tartaric acid, and to its presence he ascribes the tendency of sugar to form alcohol and carbon dioxide instead of mucilage and lactic acid.

VEGETABLE ALBUMEN.

Vegetable albumen is contained in many plant-juices and is deposited in flocculi on applying heat to such liquids. It can also be precipitated by nitric acid, tannin and mercuric chloride precisely like animal albumen. Vegetable albumen is composed of carbon, hydrogen, nitrogen, oxygen and sulphur. There is no trustworthy formula for this substance.

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INDEX.