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ELEMENTARY
HOUSEHOLD CHEMISTRY



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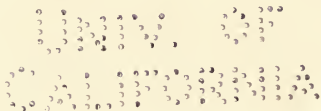
ELEMENTARY HOUSEHOLD CHEMISTRY

AN INTRODUCTORY TEXTBOOK FOR
STUDENTS OF HOME ECONOMICS

BY

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New York
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Set up and electrotyped. Published June, 1914. Reprinted
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Norwood Press
J. S. Cushing Co. — Berwick & Smith Co.
Norwood, Mass., U.S.A.

PREFACE

THE recent development of courses of instruction in Home Economics in America has created a field for textbooks prepared to meet the special needs of this new class of students. The course in chemistry presented in this book is the outcome of several years' experience with a class of students, the majority of whom have had no previous instruction in the science. The text has been written with the needs of such students primarily in mind, but the hope is entertained that, with suitable omissions, it may also be found useful in the many institutions in which the student of household chemistry approaches the subject after a preliminary training in general chemistry. The principle which has been kept constantly in mind is to introduce the applications of chemistry to household affairs as early and as often as possible and to present only such portions of the subject matter of theoretical chemistry as is essential to the comprehension of these applications. In this way the student's interest is enlisted and maintained — a most important consideration in the teaching of an applied science.

The author's thanks are due to the many friends who have taken an interest in the preparation of this volume and more particularly to Professor John Bonsall Porter of McGill University; Mr. F. O. Farey, of the Robert W. Hunt Company, Montreal; and Mr. Peter H. Walsh, Chemist of the Dominion Textile Company, Magog, Quebec, for suggestions in regard to the chapters on fuels, soaps, and textiles, respectively; to Miss Katharine A. Fisher, Head of the Household Science Department, Macdonald College, for the table of weights of one cupful of various food materials; and to Professor H. C. Sherman, of Columbia University, for numerous suggestions.

For permission to use illustrations the author desires to make acknowledgments to Misses Kinne and Cooley, authors of "Shelter and Clothing"; to Sir William Ramsay; to Professor R. H. Richards, and Mrs. W. O. Atwater; to Messrs. Eimer and Amend, New York; to the Niagara Electrochemical Company; and to the publishers.

J. F. SNELL.

MACDONALD COLLEGE,

January 1, 1914.

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ELLEN HENRIETTA SWALLOW.

MRS. ROBERT HALLOWELL RICHARDS.—1842-1911.

Trained as a chemist, and engaged up to the time of her death in the teaching of chemistry, Mrs. Ellen H. Richards became one of the foremost leaders in the application of scientific principles to the management of the household.



ELEMENTARY HOUSEHOLD CHEMISTRY

CHAPTER I

THE SUBJECT MATTER OF CHEMISTRY

CHEMISTRY is a science. The word **science** is derived from a Latin word, *scire*, meaning "to know." Science and knowledge are therefore closely related words. Science *is* knowledge. But the term science is applied only to *such* knowledge as is based upon careful and accurate observations and correct reasoning thereupon. A man might gain a rough knowledge of the distance between Montreal and New York by recalling that his grandfather had walked from the one city to the other in two weeks' time, and observing that he himself could walk twenty-five miles a day. Such knowledge would be unscientific. In contrast with it we have represented in our maps and geographical books the *scientific* statement of the distance between the two cities, based upon painstaking measurements or "surveys."

In building up science we make much use of **experiment**; that is, we arrange that the conditions under which we make our observations shall be as favorable as possible to accuracy and to the drawing of correct conclusions. The man who wished to know the distance from New York to Montreal could obtain a more accurate estimate by making the journey himself on foot, taking care to maintain a uniform pace and to walk the same number of hours each day, than by relying upon his recollection of his grandfather's account of the time

required for the journey. The former would be an *experimental* determination of the distance. The professional surveyor's measurement is also an experimental one, but the conditions of observation are much more carefully controlled, and the correctness of the measurements is checked in many different ways, *all depending upon experiments*.

Chemistry is only a *branch* of science. That is to say, it is the body of knowledge of a particular *class of phenomena* which the human race has been able to acquire by such carefully conducted experimental observations and such logical deductions as we have referred to above. To understand what chemistry is, it is, therefore, necessary that we should get a clear conception of the kind of phenomena (changes) to which this science relates. And it is fitting that this clear conception should be gained through the use of experiments. In making experiments the student should bear in mind that the basis of all science is *careful observation*. She should therefore examine closely every material used and every stage of the experiment, so as to get as clear and full a knowledge as possible of what is going on under her eyes.

A written record should be made of every experiment, and this record should always be in the following order :

1. What I did.
2. What I observed (*i.e.* saw, smelled, tasted, heard, or felt).
3. What I concluded from my observations.

The knowledge that one *has* to record an experiment always of itself conduces to more careful observation and reasoning.



FIG. 1.—*Bunsen burner.* Ordinary form for use with coal gas.

Experiment 1. The Bunsen Burner.—Unscrew and examine your gas burner. Make a sketch of the burner and indicate upon it where the gas enters and where the air enters. Learn how the supply of each is in-

creased and diminished. Close the air holes. Turn on and light the gas and note the appearance of the flame. Hold a cold porcelain dish in the flame. Is soot deposited? Gradually open the air holes and note the effect on the flame. Practice lighting the burner with the air holes closed, and then regulating the supply of air and gas until you can readily obtain a good non-luminous (blue) flame. Determine whether such a flame deposits soot on the cold porcelain.

Experiment 2.

Materials:

Magnesium ribbon in $\frac{1}{2}$ -inch pieces.

Platinum wire.

Iron nail.

Asbestos paper or light asbestos board, 2 inches \times $\frac{1}{2}$ inch, previously ignited to destroy organic matter.

Paper in pieces 2 inches \times $\frac{1}{2}$ inch.

File.

Crucible tongs or forceps.

(1) Bring into the Bunsen (non-luminous)

flame a piece of magnesium ribbon, held in a pair of forceps or crucible tongs. Describe what occurs. Examine the

product. Is it magnesium? In what respects does it differ from magnesium?

(2) Bring a piece of platinum into the flame. Note the changes of color as it becomes hot. Allow to cool. Is it still platinum?

In the same manner heat (3) an iron nail, (4) a piece of asbestos, (5) a piece of paper.

Note appearance of each, (a) while it is in the flame, (b) after it has cooled again.

Write in one column the names of those substances which are the same at the end of your experiment as at the beginning, and in another column those which have been changed into something different. The former suffered *physical changes* during the heat-



FIG. 2.—Tirrill burner. A modification of the Bunsen burner suitable for gasoline gas, as well as for coal gas.



FIG. 3.—Breaking a piece of glass tubing. Make a scratch on one side of the tubing with a single stroke of the file. Place the thumbs on the other side of the tubing, directly opposite the file mark. Grasp the tubing with the thumbs and press backwards towards the thumbs.

ing, the latter *chemical changes*. Note that iron will be classed differently, according as you consider (a) the outer surface or (b) the interior as disclosed by filing off the surface.

Experiment 3.*

Materials:

An accumulator or any type of primary cell.

A wire resistance.

A mounted magnetic needle.

Connect the two poles of a voltaic cell through a resistance. Bring a magnetic needle near the connecting wire. What occurs? Break and remake the connection. Does the needle undergo a *physical* or a *chemical* change when brought near the wires?

Experiment 4.

Materials:

Glass tubing, about 6 mm. diameter.¹

File.

Cut off a piece of glass tubing about 15 cm. (6 in.) long. Heat the middle of the piece of tubing in the Bunsen flame, rotating it constantly.

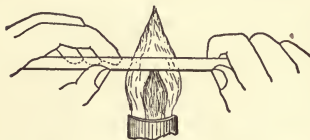


FIG. 4.—Drawing out glass tubing.

The glass is held above the inner cone of the flame and is constantly rotated until soft. Just before drawing, it is removed from the flame.

When it is quite soft, remove from flame, draw out to a small thread, and fuse off the thread in the flame, forming two small tubes closed at one end. Heat the closed end of each of these tubes in the flame, rotating constantly, and when quite soft, remove from flame and blow into the open end of the tube, so as to round out the glass. It may

either be rounded off, forming simply a closed tube (Fig. 6), or blown into a bulb, forming a matras (Fig. 7).

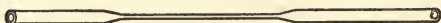


FIG. 5.—Glass tubing drawn out.

In what respects does the sealed tube differ from the original? Is it still glass? In what respects does hot glass differ from cold?

* All experiments marked by the asterisk are recommended for demonstration by the teacher rather than for performance by the individual student.

¹ See Tables of Metric System, p. 294.

Are hot glass and cold glass different substances? Does glass suffer a physical or a chemical change during heating? Does hot glass suffer physical or chemical changes when drawn out, and when blown?

Keep the matrass or sealed tube for use in a later experiment.

Experiment 5.

Materials:

Compressed yeast, $\frac{1}{4}$ cake.
Solid commercial grape sugar ("glucose" or "dextrose"), 2.5 grams.

Dissolve 2.5 grams glucose in 20 cc. water. Rub up a little yeast ($\frac{1}{4}$ cake or less) with 5 cc. water. Add it to the glucose solution, and allow to stand two or three hours in a test tube in a warm part of the laboratory. The effervescence (bubbling) observed is caused by the formation of a gas (carbonic acid gas) which has the property of turning limewater milky. To test for the gas, dip a glass loop (Fig. 9) into limewater (calcium hydroxide) solution, and hold the film of liquid in the test tube above the glucose solution for about half a minute. Then look through the film towards the light. The test is obtained more promptly if the test tube has been loosely covered for a few minutes.

The chemical change illustrated in this experiment occurs in the common *fermentation* of fruit juices (which contain *glucose*). Besides the *carbonic acid*, *alcohol* is formed. While the carbonic acid gas escapes, the alcohol remains in the liquid and the fruit juices become *wines*, *cidars*, etc.



FIG. 7. — A matrass.



FIG. 6. — Glass tube closed at one end. The narrow thread of glass (Fig. 5) is melted and drawn off. The end of the tube is then softened in the flame, and, by blowing, either rounded off or expanded into the bulb of a matrass (Fig. 7).

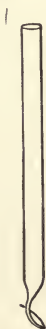


FIG. 9. — Glass loop for limewater films.

This can be made from a piece of small (2 to 4 millimeter) glass tubing by softening in the flame, drawing out, and quickly turning the soft glass thread back upon itself. The loop should be about 5 to 7 millimeters long and 2 to 3 millimeters wide.



FIG. 8. — A test tube.

Experiment 6.*Materials:*

Common salt.

Silver nitrate — a solution and also a specimen of the solid substance.

Dissolve the salt in water in a test tube. The silver nitrate reagent has been made similarly by dissolving solid silver nitrate in water. Note that both solutions are clear. Pour a little of the silver nitrate solution into the salt solution. The clouding which appears is due to the separation of innumerable minute particles of a substance (silver chloride) which does not dissolve in water. These particles are in the solid state. To verify this close the test tube with the thumb and shake vigorously, so as to combine the particles into larger ones. A solid forming in, and separating out from, a liquid is called a *precipitate*. In this experiment the substance *silver chloride* is formed as a precipitate when salt (sodium chloride) and silver nitrate solutions are mixed. At the same time a substance, called sodium nitrate, is also produced, but this substance being soluble in water, like the original substances, does not make itself visible in the experiment.

Experiment 7.*Materials:*

Milk.

Fold a filter and fit it in a glass funnel. Pour milk upon the filter. Does it pass through the filter unchanged? Add a few

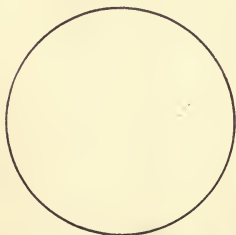


FIG. 10. — *Folding a filter.*
First stage.

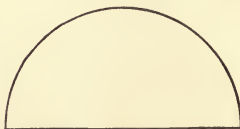


FIG. 11. — *Folding a filter.*
Second stage.



FIG. 12. — *Folding a filter.*
Third stage.

drops of acetic acid to the milk, and again pour upon the filter. Has the acid caused a chemical change in the milk?

Experiment 8.*Materials :*

Milk.

Junket tablets or rennin solution.

In a test tube surrounded by a beaker of water, heat milk to the temperature of the hand. Add a few drops of rennin solution or of an aqueous solution of junket tablets (which contain rennin) and mix. Allow to stand for 15 minutes. Shake the test tube and pour the contents on a filter. Has a chemical change occurred in the milk?

Experiment 9.**Materials :*

Potassium iodide crystals.

Mercuric chloride crystals
(Poison!).*Apparatus :*

Mortar and pestle.

Rub together in the mortar a crystal of potassium iodide with one of mercuric chloride. What evidence appears that a new substance is formed? Actually two new substances are formed, but one of these is white like the potassium iodide and mercuric chloride.



FIG. 14.—Mortar and pestle.

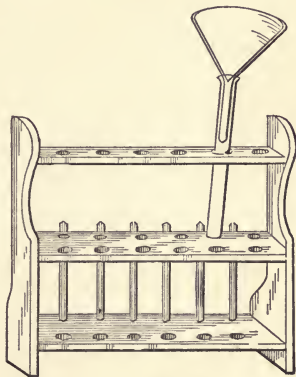


FIG. 13.—A filter ready for use.

Experiment 10.*

Dissolve a crystal of potassium iodide in water in a test tube. In another tube dissolve about an equal quantity of mercuric chloride. Shaking and warming will hasten solution. Pour a little of the potassium iodide solution into a third

test tube, and gradually add mercuric chloride solution to it. The red precipitate is the same red substance that was formed in Experiment 9. The white substance, referred to above as being formed at the same time, is in solution in the water.

NOTE. Directions for making reagents called for in some of the experiments in this and other chapters will be found in Appendix B.

Experiment 11.*

Add the remainder of the potassium iodide solution to the test tube containing the red precipitate (Expt. 10). Does a chemical change occur? What is the evidence?

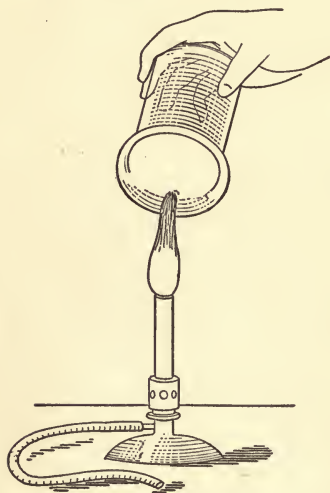


FIG. 15. — Collecting the products of the burning of gas.

Experiment 12.

Hold a cold, *dry* beaker, mouth downward, above a Bunsen flame for an instant. Note the deposition of dew — composed of minute droplets of water. Close the beaker with a watch glass, invert it, pour in a little limewater and shake. What gas was present in the beaker? (See Expt. 5.)

Repeat this experiment, using an *unlighted* burner with the gas flowing. Is any dew deposited? Is the gas which affects lime water present? What kind of change do you infer to be involved in the burning of gas?

EXERCISES

1. Make a tabular summary of the results of Experiments 3-12, putting the chemical changes into one column, the physical into another.

2. Arrange the following changes in their proper columns as (a) chemical or (b) physical:

- (a) Breaking stone.
- (b) Passing an electric current through a copper wire.
- (c) Making horseshoes from bar iron.
- (d) Making wine from fruit juice.
- (e) Burning wood.
- (f) Milling wheat, *i.e.* grinding it and separating the flour from the bran.
- (g) Ironing linen.
- (h) Scorching linen.

- (i) Manufacturing glass from sand, soda, and lime.
- (j) The rusting of iron.
- (k) The growing of a tree.
- (l) The assimilation of food by an animal.

All the changes which substances undergo in the processes of nature and of the arts may be divided into the two classes illustrated by the above experiments, viz. :

1. **Physical changes**, in which no new substance is formed. Changes in state of motion, such as that involved in throwing or catching a ball, are purely physical. So also are changes in form, such as are produced by cutting, grinding, or hammering. Changes in temperature and changes in electrical condition may bring about chemical changes, but they are not in themselves chemical.

2. **Chemical changes**, in which one or more new substances are formed. We recognize new substances by observing such physical properties as color, physical state (solid, liquid, or gaseous), density (weight of a given volume, "heaviness"), solubility in water or in other solvents, etc. In some instances it is difficult to decide whether a new substance has been formed or not. But in many others, as we have seen in the experiments, the product of the change is readily recognized as a new substance.

Chemistry is the science which treats of those changes or "reactions" in which new substances are formed.

Chemical changes seldom, if ever, occur without the accompaniment of physical changes. In Experiment 2, for example, not only is a new substance formed in place of the magnesium, but heat and light are given out. Again, the heat evolved produces an upward current in the air, and some of the white, solid product of the chemical change is carried up as a smoke. There are thus a number of physical changes occurring concomitantly with the chemical change. In studying chemical changes we cannot ignore these concomitant physical changes, but we direct our attention partic-

ularly to the question whether new substances have been produced, and, if so, what those new substances are.

It must not be thought, however, that chemical changes are the only objects of study in the science of Chemistry. The science includes also the study of the *properties* of substances and of their "composition," a term which will be understood when the next three chapters have been read.

CHAPTER II

DECOMPOSITION AND COMBINATION

THE following experiments illustrate chemical changes of two classes. The chief point to be studied in each experiment is the alteration in the *number* of substances present.

Experiment 13.

Materials :

Mercuric oxide (best the red modification prepared by ignition).

Matrass or glass tube closed at one end, prepared in Experiment 4.

Splints of pine or other soft wood.

Heat mercuric oxide in a matrass or glass tube closed at one end. Test the escaping gas with a glowing splint. Note what collects on the inner surface of the tube. How many substances were put into the matrass? How many new substances were formed? Is this a chemical or a physical change?

The gas which affects the splint is called *oxygen*.

Experiment 14.

Materials :

Potassium chlorate.

Splints.

Heat potassium chlorate in a test tube until bubbling ceases. Apply a glowing splint to the gas escaping during the bubbling. Determine whether the substance left in the tube is potassium chlorate or not. For this purpose not only may the effect of heat on this residual substance be compared with that on the original potassium chlorate, but also a portion of each may be dissolved separately in water and treated with silver nitrate solution.



FIG. 16. — A test tube holder.

In the main experiment how many substances were put into the tube to be heated? How many new substances were found to be formed?

Experiment 15.

Heat a little sugar (about 0.5 gram) in a test tube. Note what escapes from the tube and what is left in it. Test the escaping gas with blue litmus paper. How many substances were put into the tube? Were new substances formed? How many were detected?

Experiment 16.*

Materials:

Sulphuric acid solution,
about 10 per cent.

Apparatus:

Hofmann's electrolysis apparatus (Fig. 18) or the simpler apparatus represented in Figure 17.

3 accumulators in series (or other appropriate source of direct current).

With the Hofmann apparatus full of the dilute sulphuric acid solution up to the bottom of the reservoir (or with the test tubes of the simplified apparatus full of the acid and inverted in the beaker of acid) connect the battery to the binding posts and allow the current to pass until a considerable quantity of gas has collected in each branch of the apparatus. Note that about twice as much gas collects in one branch of the apparatus as in the other. Invert a small test tube over one of the outlet

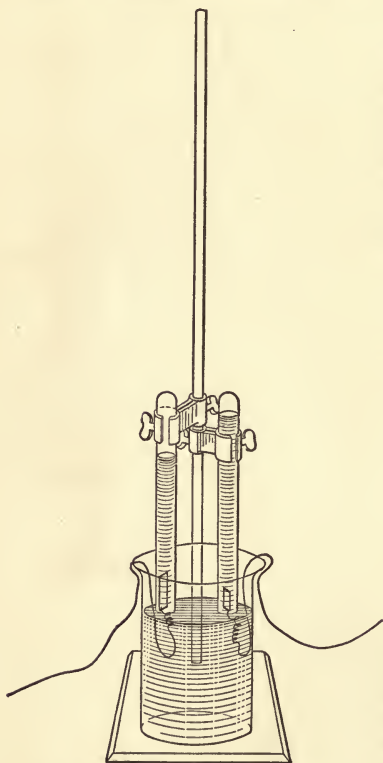


FIG. 17.— A simple apparatus for the electrolysis of water.

posts and allow the current to pass until a considerable quantity of gas has collected in each branch of the apparatus. Note that about twice as much gas collects in one branch of the apparatus as in the other. Invert a small test tube over one of the outlet

tips, open the cock, and allow the gas to escape into the test tube. Cover the tube with the thumb, invert, and immediately apply a flaming splint. Make the same test upon the gas from the other limb of the apparatus. Also test each with a splint with a *glowing*, but not flaming, end. Compare the behavior of the two gases. One of these gases is the substance already met with in Experiments 13 and 14. What is its name? The other is *hydrogen*. Which of the gases is obtained in the larger quantity? Careful experiments have shown that none of the sulphuric acid is used up in this experiment. Indeed, several other substances can be substituted for the sulphuric acid without altering the result. The amount of *water* in the apparatus is, however, a little less after the experiment than before. The diminution of the quantity of water is not *visible*, unless the current has been passed for some hours. But it has been found by accurate measurement that the water lost weighs exactly the same as the sum of the weights of the hydrogen and oxygen produced. The use of the sulphuric acid is to make the water a better conductor of electricity. Pure water conducts electricity so badly that, using it, we should require years to obtain as much gas as we do in a few minutes with the mixture of sulphuric acid and water.

If the hydrogen and oxygen produced in the electrolysis of water are both collected and mixed and set on fire, an explosion takes place, and if the experiment is conducted in a closed apparatus strong enough to stand the shock of the explosion, there is found in the apparatus after the explosion a quantity of water weighing just the same as the hydrogen and oxygen, and therefore just the same as the water which was destroyed by the electrolysis that produced the hydrogen and oxygen.

Experiment 17.*

In a hard-glass test tube fitted with a cork and bent delivery tube and supported in a clamp on a ring stand heat a piece of



FIG. 18.—Hofmann's apparatus for the electrolysis of water.

marble weighing from 2 to 5 grams. A large Bunsen or a Teclu or Meker burner should be used. Immerse the lower end of the delivery tube in limewater, contained in a small test tube. Continue to heat for several minutes and note the continued slow evolution of gas and the effect of the gas on limewater.

To hasten the action transfer to a porcelain crucible the marble remaining in the test tube and heat in the flame of a blast lamp for 15 to 30 minutes. Allow to cool and examine the residue. Add to it as much warm water as it will absorb and allow it to stand a few minutes. Add more water to the product and test the water with litmus paper.

The material of which marble consists is known in chemistry as *calcium carbonate*. The gas, which it evolves on heating and which affects the limewater, is called *carbon dioxide*, and the residue left in the crucible after all the carbon dioxide has been driven out is quicklime or *calcium oxide*. Quicklime is commonly made from limestone, a less pure calcium carbonate than marble. Quicklime and water react to form *slaked* (or *slacked*) *lime*, and slaked lime dissolves slightly in water, yielding *limewater*.

The student will have observed that in each of the above experiments (Nos. 13-17) *one* substance is converted into *two or more* new substances. Chemical change of this type is called **decomposition**. Thus we say that the red solid, mercuric oxide, is *decomposed* by heating into the metallic liquid, *mercury*, and the colorless gas, *oxygen*; and that water under the influence of an electric current decomposes into the two gases, hydrogen and oxygen. A great many substances are decomposed by heating, and some of them, like the sugar in Experiment 15, give a large number of decomposition products. A great many also are decomposed by the electric current, and a special name, *electrolysis*, is applied to decomposition so effected. The decomposition products, we say, are *simpler* substances than those from which they are made. Thus, mercury and oxygen are simpler substances than mercuric oxide; and potassium chloride (the white residue in Expt. 14) and oxygen are simpler substances than potassium chlorate.

In many instances the decomposition products can be readily *recombined* into the original substance. For instance, the hydrogen and oxygen obtained from water in Experiment 16 can be recombined into water by simply mixing the gases and setting the mixture on fire. We are therefore justified in regarding the more complex substances as **compounds** of the simpler. Thus we say that mercuric oxide is *composed* of mercury and oxygen, or that it is a *compound* of the simpler substances, mercury and oxygen — although it does not in the least resemble either of these simpler substances; and that water is a compound of hydrogen and oxygen (p. 13). When water is put upon hard lumps of quicklime the two substances combine, forming the powdery substance which we call slaked lime. (See Expt. 50, p. 96.)

We commonly speak of the *decay* of dead animal and vegetable matter as “decomposition.” The chemical changes involved in such decay are much more complex than any of those we have studied in our experiments. Every animal or vegetable organism comprises a great many different substances. Even the parts our eyes readily recognize as different — such as bone, blood, muscular tissue (flesh), and fat — are generally mixtures of a number of different substances. And very commonly substances outside of the organisms, particularly water and air, are involved in the process of decay. Nevertheless, since such decay does result for the most part in the production of simpler substances than those originally present in the decaying organism, the word *decomposition* as applied to decay has a signification closely allied to our definition of the term.

Chemical change which results in the formation of *one* substance from two or more is called **combination**. Combination has already been illustrated in the instance of hydrogen and oxygen. The following experiments furnish further illustrations of this class of chemical action.

Experiment 18.*Materials:*

Roll sulphur.

Copper foil, 1 inch \times $\frac{1}{4}$ inch.

Heat a little roll sulphur to boiling in a test tube. While the sulphur is actively boiling, drop in a piece of copper foil. Note what occurs. The great majority of chemical changes are accompanied by the evolution of more or less heat. In some, the heat is so great as to make the solid substances involved in the change give out light. Many of the chemical reactions which produce great quantities of heat belong to the class we are now considering, viz. combinations. (See Expt. 19.)

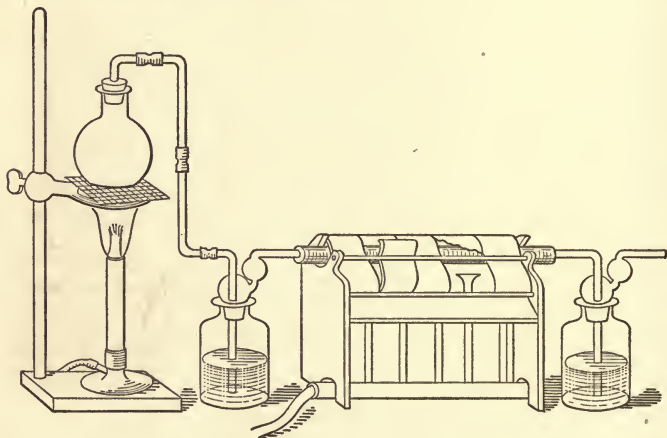


FIG. 19. — *Burning carbon (charcoal) in a current of oxygen.* The oxygen is generated in the flask by heating potassium chlorate. By bubbling through 30 per cent potassium hydroxide in the first wash bottle, it is freed from any carbon dioxide it may contain. It then passes through the heated glass tube containing the charcoal, and finally through the second wash bottle, which contains limewater. (*Experiment 19.*)

Examine the product formed from the copper, comparing it with the original copper and sulphur as regards color, cohesion, etc. (Ordinarily there will be a considerable quantity of unchanged sulphur left in the test tube, but this is readily distinguished from the new substance, which takes more or less nearly the form of the piece of copper used.) In this experiment how many substances entered into action and how many new ones were formed?

Experiment 19.**Materials:*

Lumps of charcoal, thoroughly dried by heating.

Apparatus:

Oxygen generator, or cylinder of compressed oxygen provided with a soda-lime tube or with a wash bottle containing a 30 per cent solution of potassium hydroxide.

Small combustion furnace (with 4-10 burners).

Hard-glass tubing.

Glass and rubber tubing for connections.

Place a few lumps of dried charcoal in a hard-glass tube in a small combustion furnace. Provide the tubes with corks and connect one end with the oxygen generator, the other with a delivery tube. Pass oxygen through the apparatus to expel the air. Immerse the end of the delivery tube in limewater and continue to pass pure oxygen through the apparatus. Is the limewater affected by the pure oxygen?

Heat the hard-glass tube gently at first, then gradually raise the heat to redness. Pass a very slow current of oxygen over the heated carbon into the limewater. What occurs? What gas has been formed?

If the experiment is continued long enough, the charcoal will disappear, leaving only a small quantity of white or gray ash. Except for this ash, charcoal consists entirely of a substance called *carbon*. This substance, when raised to a sufficiently high temperature, *combines* with oxygen. What substance is the product of this combination?

Air contains oxygen, and exactly the same chemical action takes place when charcoal burns in a draft of air as when it burns in pure oxygen. Is any heat produced in this combination? What practical use is made of this chemical change?

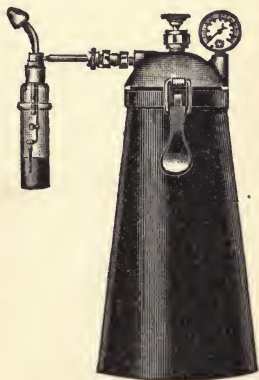


FIG. 20.—Oxygen generator using fused sodium peroxide and water. Oxygen prepared in this way contains no carbon dioxide. When this style of generator is employed limewater may be used in both the wash bottles, or the first wash bottle may be omitted entirely.

CHAPTER III

ELEMENTS

WATER, which is one of the decomposition products of sugar (see Expt. 15), may, as we have seen in Experiment 16, be itself decomposed into hydrogen and oxygen. In Experiment 14 one of the products obtained in the decomposition of potassium chlorate is *potassium chloride*, a white solid. If this substance is highly heated, it melts, and if an electric current is passed through the molten mass, decomposition occurs, the products being a soft metal, called *potassium*, and a greenish yellow gas, called *chlorine*.

While, therefore, water is a simpler substance than sugar, it is less simple than hydrogen and oxygen; and while potassium chloride is a simpler substance than potassium chlorate, it is evidently less simple than potassium and chlorine.

When limestone is heated in a limekiln, quicklime and carbon dioxide (carbonic acid gas) are produced. (See Expt. 17.) But carbon dioxide, as we have seen (Expt. 19), is composed of the simpler substances, *carbon* and *oxygen*. Similarly, quicklime is a compound of a metal called *calcium* and the gas *oxygen*.

We see, then, that the products of some decompositions can in their turn undergo decomposition. However, there are a number of substances which it has not been found possible to decompose. Among these are hydrogen, oxygen, potassium, chlorine, calcium, mercury, and carbon.

Substances which we cannot decompose are known as elements. This is the *only* sense in which the word **element** is used in chemistry. When we speak, as we commonly do, of wind



THE HON. ROBERT BOYLE.—1626-1691.

The great English chemist who originated the modern conception of elements. Born in Ireland, a son of the first Earl of Cork, Boyle was educated in England and spent most of his life at Stalbrige, Dorsetshire. He was a member of the "Invisible College," an association of men devoted to the new experimental philosophy, and of the Royal Society, into which the Invisible College developed (1663). Boyle's predecessors had studied chemistry with a view to its applications to medicine or to the transformation of the baser metals into gold. He studied it with the single purpose of discovering the truth.

and rain as "the elements," or, as the ancients did, of fire, air, water, and earth as the elements, we are not speaking *scientifically*, but rather poetically. It is not even permissible to speak of quicklime and carbon dioxide as elements of limestone, though we may call them the *constituents* of limestone. The *elements* of limestone are calcium, carbon, and oxygen. In science every word has a very definite meaning, and words of slightly different signification may not be interchanged, as they frequently are in common speech.

Recent investigation growing out of the discovery of radioactivity has shown that some of the elements, such as uranium, thorium, and radium, gradually change into other elements. No means has yet been found to cause, or prevent, or in any way to control, such changes, which are nevertheless going on at an entirely definite rate. The distinction between this kind of change and decomposition proper can scarcely be made clear without reference to the atomic theory, which will be outlined later. (See Chapter VI.)

At present (1913) eighty-three substances are officially recognized as elements by an international committee of the leading chemical societies of the world. Some of these are familiar substances like *iron, gold, silver, copper, carbon* (charcoal), and *sulphur*; others are substances rarely heard of in ordinary speech. A list of these eighty-three substances will be found at the end of Chapter VI. In addition to these there are a few other rare substances which in all probability are also elements, but which have not been investigated thoroughly enough to secure official recognition.

Eleven of the recognized elements are *gases*. Of these the most important are *oxygen, hydrogen, nitrogen, and chlorine*. Two elements are *liquids*, one of which, *mercury*, is familiar from its use in thermometers and barometers, while the other, *bromine*, is a disagreeable-smelling, red, fuming substance. Of the seventy *solid* elements several examples are given in the preceding paragraph.

Gas, liquid, and solid are the three *physical states* of *matter* (a general term for all substances). The elements which under ordinary conditions are gases can be changed into liquids and solids by more or less intense cooling and compression. Many of those which under ordinary conditions are solids can easily be melted by heating, *e.g. tin, lead, sulphur*. They thus become liquids. By further heating many of them have been converted into gases, *e.g. sodium, sulphur, mercury, bromine*. There can be little doubt, then, that under suitable conditions every element can be made to exist in all three physical states, and when we speak of oxygen as a gas or of sulphur as a solid, it is understood that we are referring to the ordinary temperature of a room, about 20° C. (68° F.).

Metals and Non-Metals

The great majority of the solid elements, and one of the two liquids (mercury), are classed as **metals**. Metals have certain chemical, and the following physical, characteristics: (1) *A bright luster*, when polished; (2) *good conducting power for heat*; (3) *good conducting power for electricity*. Among the elements of this class are the familiar metals, *iron, tin, zinc, copper, silver, gold, etc.*, and other important but less familiar substances, such as *sodium, potassium, calcium, and radium*. Among the **non-metals** are such solids as *carbon* (which exists in the three forms of charcoal, graphite, and diamond), *sulphur, phosphorus, and iodine*; the evil-smelling red liquid, *bromine*; and all the gaseous elements.

Experiment 20.

Examine samples of the following elements and classify them as metals and non-metals: iron, platinum, sulphur, phosphorus, gold, silver, copper, carbon (charcoal), iodine, zinc, calcium, magnesium, sodium, potassium, mercury, bromine.

Experiment 21.*Materials :*

Covered jars of chlorine, oxygen, hydrogen, and nitrogen.

Examine specimens of the four common gaseous elements. Remove the cover of each jar slightly, and waft a very little of the gas towards the nose. *Be especially careful not to take a full breath of the chlorine.* Which of these four gases is readily distinguished by its color and odor? Note the different effects of the other three upon a burning splint of wood.

CHAPTER IV

COMPOUNDS

THE products of chemical combination of the elements are called **compounds**. Thus, water is a *compound of oxygen and hydrogen*; salt is a *compound of sodium* (a metal) and *chlorine* (a yellow gas); saltpeter is a *compound of the metal potassium* with the gaseous elements *nitrogen and oxygen*; and sugar is a *compound of carbon* with *hydrogen and oxygen*.

A *compound* is to be clearly distinguished from a *mixture*. Sulphur and iron can be *mixed* by grinding the two together in a mortar. In the mixture each of the two elements retains its individual characteristics. The iron is still attracted by a magnet. Carbon disulphide dissolves out the sulphur, leaving the iron undissolved; hydrochloric acid dissolves the iron, leaving the sulphur untouched. But when iron and sulphur are heated together, a new substance, *iron sulphide*, is formed, which is entirely different from either of its elements. It is not attracted by the magnet; carbon disulphide dissolves out nothing from it, while it dissolves completely in hydrochloric acid, liberating a gas different from that produced by the action of the acid on iron.

Experiment 22.*

Materials :

Iron powder or fine filings.

Sulphur.

Carbon disulphide.

Iron sulphide.

Apparatus :

Mortar and pestle.

Magnet.

Grind together in a mortar about 2 grams each of sulphur and iron. Divide the mixture into two portions. Place one portion in a test tube and heat to redness. Do you observe any evidence of chemical action? Allow the test tube to cool, break it, and examine the contents. Grind these and compare with the unheated portion. Make the following tests upon *each* of these two powders, comparing the results:

(a) Pass a magnet through the powder. If both powders are attracted by the magnet, shake the magnet and see whether there is in either case any evidence of a separation of the iron and sulphur from each other; also which powder is more strongly attracted.

(b) Shake a little of the powder in a test tube with carbon disulphide. Pour off the carbon disulphide through a filter on to a watch glass and set aside in a warm place but not near a flame.

When the carbon disulphide has evaporated, is a residue left in either watch glass? What is this residue?

(c) Treat a portion of the powder in a test tube with dilute hydrochloric acid. Note the odors. Also treat a portion of the iron powder with dilute hydrochloric acid. In this test, which powder gives an odor identical with that given by the iron itself? If the differences between the mixture of iron and sulphur and the compound prepared in this experiment are not sufficiently marked

(as may happen if some of the iron and sulphur have not reacted together), the above comparisons may also be made between the mixture and a portion of the sample of iron sulphide supplied.

Refer to your notes on Experiment 18 (p. 16) and describe the compound of copper and sulphur, noting differences between that compound and its elements.

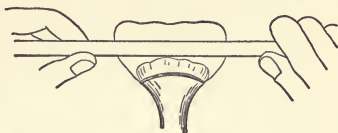


FIG. 21. — *Softening glass tubing in order to bend it.* To produce a long, narrow, yellow flame, provide the Bunsen burner with a "wing top," and close the air holes at the base of the burner. Hold the glass above the dark inner cone of the flame (which is cool) and keep it rotating until soft enough to bend.

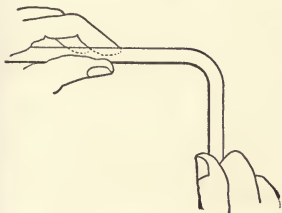


FIG. 22. — *Bending glass tubing.* Remove the softened glass from the flame and immediately bend it to the desired angle.

Air is a *mixture* of the two gases, *nitrogen* and *oxygen*. A similar mixture can be made of hydrogen and oxygen. This latter mixture is, of course, not air, but it is a clear, colorless gas looking exactly like air, and also like the unmixed elements — hydrogen and oxygen. But when oxygen and hydrogen *combine*, the resulting *compound*, *water*, is a liquid, entirely unlike the elements from which and of which it is formed. The compound (water) can be produced by setting fire to the gaseous mixture of oxygen and hydrogen.

Further Discussion of the Subject Matter of Chemistry

Having learned that all substances can be resolved into a limited number of elements, we are prepared to add something to the definition of the subject matter of chemistry made in Chapter I. In studying chemistry we examine bodies or objects with special reference to their *composition*. We endeavor to find out what *substances* the objects under consideration are made of, what *elements* they contain, and whether these elements are present in the *free state* or *combined* into compounds. *Chemical analysis* is the *art* of finding out the composition of bodies. *Chemistry* is the *science* which treats of the composition of bodies. This is, of course, not intended as a complete definition of chemistry, for the science investigates not only what substances are present in a given body, but also under what *conditions* these substances are transformed into other substances by rearrangement of the elements.

Nomenclature of Compounds

The number of chemical compounds of the eighty-odd elements is enormous. To provide systematic names for them all many devices are required, but only two of the fundamental principles of nomenclature require consideration at this point.

1. The suffix *-ide* implies that no elements are present, other than those mentioned in the name of the compound. Thus, *sodium chloride* (common salt) contains no elements but *sodium* and *chlorine*; *ferrous sulphide*, none but *iron* and *sulphur*; *calcium oxide*, none but *calcium* and *oxygen*, etc.

2. The suffix *-ate* (also the less common one *-ite*) implies that, in addition to the elements named, the compound contains oxygen. Thus, *potassium nitrate* (saltpeter) contains *potassium*, *nitrogen*, and *oxygen*; *potassium chlorate* is a compound of *potassium*, *chlorine*, and *oxygen*; and *magnesium sulphate* (Epsom salt) is composed of *magnesium*, *sulphur*, and *oxygen*.

EXERCISE

What elements do the following compounds contain: (1) Calcium oxide, (2) Magnesium nitrate, (3) Silver chloride, (4) Hydrogen sulphide, (5) Sodium sulphate, (6) Gold chloride, (7) Potassium iodide, (8) Magnesium iodate, (9) Sodium sulphite, (10) Calcium phosphate?

CHAPTER V

CHEMICAL NOTATION

CHEMISTS represent each element by a **symbol**, usually the initial letter of the Latin name, which in most cases is identical with the initial letter of the English name. Examples:

Oxygen, O	Nitrogen, N
Hydrogen, H	Carbon, C
Iron (Ferrum), Fe	Potassium (Kalium), K
Tin (Stannum), Sn	

Where the names of two or more elements have the same initial the symbols of all but one have a second characteristic letter added to the initial. Thus:

Boron, B	Sulphur, S
Barium, Ba	Silicon, Si
Bromine, Br	Strontium, Sr
Carbon, C	Silver (Argentum), Ag
Chlorine, Cl	Sodium (Natrium), Na
Cobalt, Co	
Chromium, Cr	
Copper (Cuprum), Cu	

Compounds are represented by **formulas** made up of the symbols of the composing elements. Thus: Ferrous sulphide, FeS ; Calcium oxide, CaO . To the chemist the formula signifies not merely the *qualitative* but also the *quantitative* composition of the compound — not only *what* elements it contains, but *in what proportions* they are present. For this purpose the formulas of most compounds contain some figures in addition to the symbols of their elements. Thus: Water, H_2O ; Sulphuric acid, H_2SO_4 ; Potassium



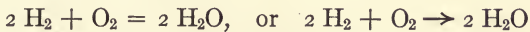
BARON JÖNS JAKOB BERZELIUS. — 1779-1848.

The Swedish chemist who originated our modern system of chemical notation. Berzelius, the most influential chemist of the early part of the nineteenth century, excelled as an experimenter, as a philosopher, and as a teacher. He discovered several of the elements and determined the atomic (or "combining") weights of those previously known.

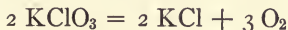


chlorate, KClO_3 ; Carbon monoxide, CO , but Carbon dioxide, CO_2 ; Cane sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; etc.

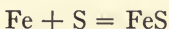
Chemical changes or *reactions*, as they are often called, are represented by **equations**, one side of which is made up of the formulas of the *reacting substances* (together with certain figures), the other side of the formulas of the *products* of the reaction. Thus:



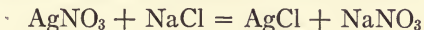
signifies that *hydrogen* and *oxygen* unite, forming water;



that *potassium chlorate* decomposes into *potassium chloride* and *oxygen*;



that *iron* and *sulphur* combine to form *ferrous sulphide*; and



that *silver nitrate* and *sodium chloride* (common salt) react, forming *silver chloride* and *sodium nitrate*.

The table on p. 33 gives the names and symbols of all the eighty-three substances accepted as elements in the year 1913 by the International Committee of Chemists referred to above (p. 19).

The twenty-six elements of chief interest to the house-keeper are given also in the table on inside of back cover.

EXERCISE

Referring to the table at the end of Chapter VI for the interpretation of the symbols, write names for the compounds represented by the following formulas:

(1) FeS , (2) K_2S , (3) Na_2CO_3 , (4) KNO_3 , (5) $\text{Ca}(\text{NO}_3)_2$, (6) CaSO_4 , (7) MgCl_2 , (8) FePO_4 , (9) KClO_3 , (10) HgO .

Write formulas, omitting figures, for the compounds whose names follow:

(1) Silver iodide, (2) Sodium nitrate, (3) Potassium iodate, (4) Magnesium nitride, (5) Calcium sulphate.

CHAPTER VI

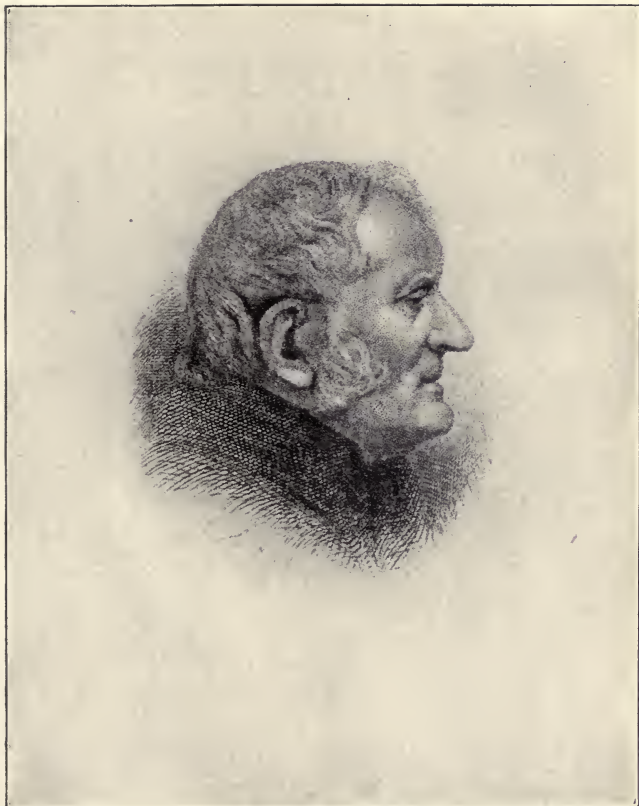
THE ATOMIC THEORY

OUR chemical formulas are an outgrowth of the atomic theory, originated by John Dalton, an English teacher and chemist, about 1803. According to Dalton's theory all substances are made up of minute particles, which (in the modern terminology of the theory) are called **molecules** (diminutive from Latin, *moles*, mass). The smallest visible particle of any substance contains millions of such molecules.

Lord Kelvin estimated that if a drop of water were magnified to the size of the earth, the molecules would appear larger than small shot but smaller than cricket balls. Even invisible gases are regarded as composed of molecules, and it has been estimated that one cubic centimeter of gas (measured at ordinary temperature and pressure) contains approximately thirty million million molecules.

The molecules of each pure substance (whether element or compound) are conceived of as being exactly like one another but different from those of every other substance. The difference recognized is a difference of mass, and weighing is our most familiar way of comparing masses. All the molecules of any given substance, such as *water*, are equal in weight, but the weight of a water molecule is different from that of an *alcohol* molecule.

The molecules of a substance cannot be in any way subdivided without destroying the substance — *not annihilating* it, but converting it into *other* substances. In chemical *decompositions* the molecules of the original substance are split up into the *smaller* molecules of the decomposition



JOHN DALTON. — 1766-1844.

Dalton originated the modern atomic theory and roughly determined the atomic weights of several elements.

products. Thus, when calcium carbonate (limestone or chalk) decomposes into calcium oxide (quicklime) and carbon dioxide (see Expt. 17, p. 13), we conceive that each *molecule* of the calcium carbonate has split up into two smaller molecules — one *the molecule of calcium oxide*, the other *the molecule of carbon dioxide*.

The molecules of compounds are conceived to be made up of particles of the constituent *elements* of the compounds. Such particles of the *elements* are known as *atoms*. Thus, the *molecule* of calcium oxide would contain at least one *atom* of calcium and one *atom* of oxygen.

The *symbols* of the elements are used to represent the *atoms*. The *formula*, CaO, stands for a *molecule* of calcium oxide, composed of one *atom* of the *element calcium* and one *atom* of the *element oxygen*. Similarly, the formula, KCl, stands for a *molecule* of the compound potassium chloride, consisting of one *atom* of the element potassium (K) and one *atom* of the element chlorine (Cl).

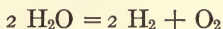
The formula, CO₂, represents a molecule of carbon dioxide, consisting of one atom of carbon united to two atoms of oxygen; the formula, H₂O, a molecule of water, composed of two atoms of hydrogen united to one atom of oxygen; and the formula, KClO₃, a molecule of potassium chlorate containing one atom each of potassium and chlorine and three atoms of oxygen. The chemists' reasons for regarding a molecule of carbon dioxide as containing *two* atoms of oxygen rather than *one* need not concern us here — though we may note that there is another compound of carbon and oxygen, called *carbon monoxide*, whose molecule is regarded as composed of one atom of each of the two elements. This substance, carbon monoxide, is represented by the formula, CO.

The molecules of any substance — for instance the calcium carbonate molecules in a piece of limestone — are conceived to be in motion. *Physical changes* may often be

accounted for by changes in the arrangement of the molecules with respect to one another or in the rate or manner of motion of the molecules. Heating, for example, is believed to make the molecules move faster. But any change which results in a disruption of the molecule or a rearrangement of the atoms so as to form new molecules is a *chemical change*. In calcium carbonate such a disruption takes place when the temperature has become sufficiently high. According to the theory, the molecules have then acquired so rapid a motion that they break asunder into molecules of calcium oxide and molecules of carbon dioxide.

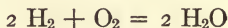
In the electrolysis of water the atoms of hydrogen and oxygen composing the molecule of water separate from one another. The hydrogen atoms set free at the one electrode unite in pairs to form hydrogen molecules, H_2 ; and the oxygen atoms set free at the other electrode likewise unite in pairs, forming oxygen molecules, O_2 . Two molecules of water thus yield two molecules of hydrogen and one molecule of oxygen.

This is represented by the equation:



The reasons for regarding the oxygen (and hydrogen) molecules as consisting of two atoms need not be considered here.

Conversely, when hydrogen burns in oxygen, the atomic theory regards the atoms of hydrogen and oxygen as uniting, two of the former with one of the latter, into molecules of water:



Before the reaction the atoms of hydrogen are united with each other in pairs, forming hydrogen molecules; and the atoms of oxygen are united in pairs, forming oxygen molecules. After the reaction the atoms are combined in groups of three — two hydrogen and one oxygen — into molecules of water, thus, $H-O-H$. We commonly abbreviate the formula $H-O-H$ into H_2O .

In such reactions as that of silver nitrate with sodium chloride (Expt. 6, p. 6) there is an exchange of partners among the atoms. Thus, the silver atoms separate from the nitrogen and oxygen atoms, with which they are originally united, and combine with the chlorine atoms of the sodium chloride, forming molecules of silver chloride; and the sodium atoms, originally united with the chlorine atoms, transfer their allegiance from chlorine to nitrogen and oxygen.



By measuring the proportions in which the elements combine with one another and reasoning from the results, chemists have arrived at definite conclusions regarding the *relative* weights of the various kinds of atoms. *Hydrogen*, it is concluded, has the lightest atom. The *oxygen* atom is about sixteen (more accurately 15.87) times as heavy as the hydrogen atom. The *carbon* atom is three-fourths as heavy as the oxygen atom or about twelve times as heavy as the hydrogen atom. The heaviest atom known is that of *uranium*, which weighs about 237 times as much as the hydrogen atom.

The relative weights of the atoms are given in the table on p. 33. A table of atomic weights might be made in which the weight of a hydrogen atom was taken as the unit. In such a table the atomic weight of oxygen would be 15.87, meaning that one atom of oxygen weighs 15.87 times as much as one atom of hydrogen, and the atomic weight of carbon would be 11.9, meaning that a carbon atom weighs 11.9 times as much as a hydrogen atom. This was actually the basis upon which the first tables of atomic weights were made out. But the present international committee prefers to take the atomic weight of oxygen as exactly 16 and that of hydrogen as 1.008 ($16 \div 15.87 = 1.008$). The ratio between any two atomic weights is the same on the one basis as on the other, and it is *only the ratios* which chemists profess

to know, the atoms themselves being immeasurably small, and therefore of unknown absolute weight.

As already stated, the atomic theory in its modern form dates from the beginning of the nineteenth century. However, the view that matter is not infinitely divisible but is made up of minute indivisible particles (atoms) had been held by many philosophers of ancient times and by some of the great modern scientists who lived before Dalton's day, for instance, by Robert Boyle (1626-1691) and by Sir Isaac Newton (1642-1727). But the idea that each element has an atom of a *definite weight*, and that the smallest particles (molecules) of every compound are made up of atoms of the elements of that compound, originated with Dalton.

The word **atom** (Greek, *atomos*, from *a*, not, and *temno*, cut) implies indivisibility. Until recently the atoms of the chemical elements were regarded as absolutely indivisible. The investigations arising out of the discovery of *radioactivity* have shown that some of the elements (especially some of those having very heavy atoms) are gradually undergoing a spontaneous transmutation into other elements of lower atomic weight. In undergoing such transmutation these elements emit certain radiations, some of which are believed to consist of particles much smaller than atoms. These particles are called *electrons*. Accordingly, it appears not improbable that the atomic theory will receive an extension, according to which the various kinds of atoms will be regarded as aggregations of various numbers of electrons.

Up to the present no means have been found of controlling the transmutations of the radioactive elements. Accordingly, while it is no longer permissible to define an element as a substance which *cannot* be decomposed, it is still permissible for us to apply the term *element* to those substances which *we* cannot decompose, and the term *atom* to the theoretical particle which remains intact in all chemical changes that are not accompanied by radioactivity.

INTERNATIONAL ATOMIC WEIGHTS, 1913

<i>Element</i>	<i>Symbol</i>	<i>Atomic Weight</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic Weight</i>
Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.07
Cadmium	Cd	112.40	Phosphorus	P	31.04
Cæsium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Holmium	Ho	163.5	Thorium	Th	232.4
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	119.0
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.5
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.10	Ytterbium (Neoytterbium)	Yb	172.0
Lithium	Li	6.94	Yttrium	Yt	89.0
Lutecium	Lu	174.0	Zinc	Zn	65.37
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Manganese	Mn	54.93			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

CHAPTER VII

THE LAW OF DEFINITE PROPORTIONS

IF Dalton's atomic theory be correct, every compound must contain its elements in *certain definite proportions by weight*. Thus a water molecule, made up of two atoms of hydrogen, weighing 2 (or more precisely 2.016), and one atom of oxygen weighing 16, has evidently 8 times as much of oxygen by weight as of hydrogen. And since a cupful (or a barrellful) of water is made up of individual molecules, every one of which contains 8 times as much oxygen as hydrogen, the cupful (or barrellful) of water if decomposed would yield 8 times the weight of oxygen as of hydrogen. Experiment shows that this is true no matter what the quantity of water used. The same principle applies to every compound.

A chemical compound always contains the same elements in the same proportions by weight. This is known as the **Law of Definite Proportions**.

This principle of Definite Proportions is not confined to reactions of combination. It governs chemical reactions of all kinds.

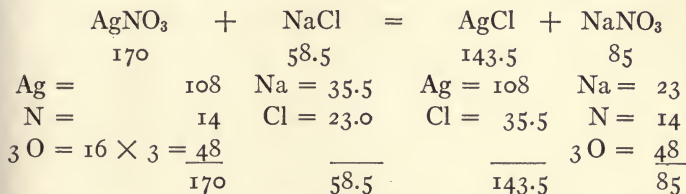
The molecule of *calcium carbonate*, CaCO_3 , being made up of one atom of *calcium*, weighing 40, one atom of *carbon*, weighing 12, and three atoms of *oxygen*, each weighing 16, has a total weight of $40 + 12 + 48 = 100$. Similarly, the *molecular weight* of calcium oxide, CaO , is 56 ($40 + 16$) and that of carbon dioxide, CO_2 , is 44 ($12 + \text{twice } 16$). According, then, to the equation



100 parts of calcium carbonate decompose into 56 parts of calcium oxide and 44 parts of carbon dioxide. And this is

true, whatever the units in which we express the weight. Thus 100 *grains* of calcium carbonate give 56 *grains* of calcium oxide and 44 *grains* of carbon dioxide; 100 *ounces* of calcium carbonate give 56 *ounces* of calcium oxide and 44 *ounces* of carbon dioxide; and so on for *pounds, tons, grams, kilograms*, and all other units of weight.

So also 170 parts of silver nitrate by weight react with 58.5 parts of salt (sodium chloride), no more and no less:

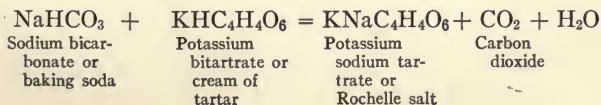


Every pound of silver nitrate takes $58.5 \div 170 = 0.344$ pound of salt, and every *ton* of silver nitrate 0.344 *ton* of salt. If more salt is used, the excess will be left unchanged. If, for instance, one pound of silver nitrate and one pound of salt are brought together in solution, 0.344 pound of the salt will be used up in precipitating the silver nitrate and the remaining 0.656 pound of salt will be left in the water unchanged.

This principle is of some importance in the household applications of chemistry. Baking powders, for instance, should be so made as to contain exactly the right quantity of soda to react with all the cream of tartar. If too much of either constituent is used, the excess will remain in the cake or biscuit, making it sour or bitter as the case may be.

EXERCISES

1. The reaction between baking soda and cream of tartar is represented by the equation:



Using the atomic weights of the table on the inside of the back cover of the book, calculate how many pounds of pure cream of tartar are required for every pound of baking soda.

2. How many ounces of carbon dioxide are obtainable from a pound (16 ounces) of baking soda by the reaction with cream of tartar?

3. 100 pounds of cream of tartar 90 per cent pure are to be made up into baking powder. How many pounds of pure baking soda should be used?

4. When baking soda is heated, washing soda (Na_2CO_3) is formed according to the following equation :



This equation signifies that two molecules of sodium bicarbonate are converted into one each of sodium carbonate, water, and carbon dioxide.

How many pounds of washing soda would 100 pounds of baking soda make?

5. 100 grams each of baking soda and pure cream of tartar are mixed and used as a baking powder in making a batch of biscuits. How much baking soda will be left over when the cream of tartar has all been acted upon?

6. Assuming that the baking soda left over in Example 5 is all converted into washing soda in the baking, how many grams of washing soda will the batch of biscuits contain?

Experiment 23.

Materials:

Potassium bitartrate.

Sodium bicarbonate.

Litmus solution.

25 cc. graduated cylinders.

Dissolve 1.88 grams potassium bitartrate in 50 cc. of hot water in a beaker. Keep the liquid hot, but not boiling, and stir with a glass rod until all the solid is dissolved. Dissolve 0.84 gram sodium bicarbonate in 20 cc. of cold water. Divide each solution into two exactly equal portions. To one portion of each add enough litmus solution to color it distinctly. Observe the color the litmus takes in the two liquids. Put the colored bicarbonate solution into a beaker or dish and gradually pour the colored bitartrate solution (still hot) into it. What do you observe? Hold a film of limewater (calcium hydroxide) in the escaping gas.

What is this gas? If the color of the bicarbonate solution is not changed, add some of the second portion of bitartrate solution little by little, until the color does change. Then add the uncolored portion of bicarbonate solution, and finally the remainder of the bitartrate solution. If necessary, dissolve a little more bitartrate and add it. If the materials are perfectly pure (which they often are not) and the weighings exact, the color changes will occur when the half portion of the two solutions are mixed and again when the whole of the bitartrate solution has been added.

CHAPTER VIII

COMPOUNDS OF THE SAME ELEMENTS IN DIFFERENT PROPORTIONS

IF different numbers of atoms of two elements combine, the molecules formed are different. Thus, there is a liquid substance, similar in appearance to water, which yields by decomposition 16 times as much oxygen by weight as hydrogen, *i.e.* equal *volumes* of the two gases. This substance is known as *hydrogen peroxide*. A mixture of 3 parts of it with 97 parts of water (a 3 *per cent* solution) is a common article of commerce, being used as a bleaching agent and as an antiseptic. Now, the molecule of hydrogen peroxide must contain 16 times as much oxygen as hydrogen; that is to say, one atom of oxygen to every atom of hydrogen. It is believed to contain two atoms of each element and is therefore given the formula H_2O_2 .

Similarly, we have two compounds of oxygen and carbon, both gases, (1) carbon monoxide, CO , and (2) carbon dioxide, CO_2 ; two oxides of copper, *viz.* (1) cuprous oxide, Cu_2O , a red solid, and (2) cupric oxide, CuO , a black solid; and two chlorides of iron, *viz.* (1) ferrous chloride, $FeCl_2$, a greenish solid, and (2) ferric chloride, $FeCl_3$, a reddish solid; and there are many other instances of the existence of more than one compound of the same elements. Indeed, there are several hundred compounds of the elements carbon and hydrogen (hydrocarbons) and thousands of compounds of the three elements carbon, hydrogen, and oxygen.

Nomenclature of Such Compounds

Where the number of different compounds of the same elements is limited to two, the two are often distinguished by using the suffixes *-ous* and *-ic* on the adjective part of the name. The suffix *-ous* — signifying “full of”¹ — is applied to the compound containing the larger proportion of the element to whose name the suffix is attached. Thus:—

Cuprous oxide, Cu_2O ; Cupric oxide, CuO .

Ferrous chloride, FeCl_2 ; Ferric chloride, FeCl_3 .

Sulphurous acid, H_2SO_3 ; Sulphuric acid, H_2SO_4 .

Mercurous chloride, HgCl ; Mercuric chloride, HgCl_2 .

Ferrous sulphate, FeSO_4 ; Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$.

Ferrous chloride has one atom of iron to every two atoms of chlorine, while ferric chloride has only one atom to every *three*; sulphurous acid has one of sulphur to every three of oxygen, while sulphuric acid has only one to every four, etc.

EXERCISES

Name the following compounds on the above principle :

- | | |
|--|--|
| (1) CuCl and CuCl_2 . | (2) AuCl and AuCl_3 . |
| (3) HgNO_3 and $\text{Hg}(\text{NO}_3)_2$. | (4) SnCl_2 and SnCl_4 . |
| (5) HClO_2 and HClO_3 (acids). | (6) H_3PO_3 and H_3PO_4 (acids). |

Another means of distinguishing compounds of the same elements in different proportions is to modify the substantive part of the name with a prefix indicating the number of atoms of the element, whose name is thus modified, contained in the molecule of the compound. The prefixes used are derived from the Greek numerals:

Mono- or *mon-*, one; *di-*, two; *tri-*, three; *tetra-* or *tetr-*, four; *penta-* or *pent-*, five; *hexa-* or *hex-*, six; *hepta-* or *hept-*, seven; *octo-* or *oct-*, eight; etc.

Carbon monoxide, CO ; Carbon dioxide, CO_2 .

Nitrogen trioxide, N_2O_3 ; Nitrogen pentoxide, N_2O_5 .

The prefix *per-*, signifying “thorough,” is sometimes used to denote that the compound named has more of a certain element

¹ Compare such words as *dangerous*, *beauteous*, *mysterious*, and *tyrannous*.

(usually oxygen) than some other compound. Thus: hydrogen peroxide, H_2O_2 , has more oxygen than water, H_2O ; and barium peroxide, BaO_2 , more oxygen than barium oxide, BaO . Also perchloric acid, HClO_4 , has more oxygen than chloric acid, HClO_3 , and perboric acid, HBO_3 , a larger proportion of oxygen (*e.g.* to one atom of hydrogen) than boric acid, H_3BO_3 .

EXERCISES

Name the following:

- (1) PCl_3 , (2) PCl_5 , (3) P_2O_3 , (4) P_2O_5 , (5) SO_2 , (6) SO_3 , (7) PbO ,
(8) PbO_2 .

CHAPTER IX

COMBUSTION

ONE of the most familiar, as well as one of the most useful, of chemical phenomena is **combustion** or burning. Fire has been known to mankind from time immemorial, and advance in its control and utilization has kept pace with the progress of civilization. Even to-day, when electrical energy is so much made use of, practically our only source of artificial heat is combustion. Our rural homes, for the most part, depend upon combustion, not merely for heat but also for light, and even the electricity which lights our towns and cities comes largely from power generated by the burning of coal.

Combustion can take place either with or without the phenomenon of **flame**. Flame appears in the burning of paper, wood, coal, candles, oils, alcohol, and gas. Charcoal and coke, however, burn without flame. As charcoal is made by heating wood, and coke by heating coal, we have flameless combustion in the later stages of wood and coal fires.

Experiment 24.

Materials :

Test tube.

Pieces of hard wood.

Cork and cork borer, or one-holed rubber stopper.

Glass tube drawn to a tip at one end.

Provide a test tube with a tightly fitting, single-hole cork or rubber stopper, through which passes a short piece of glass tubing drawn to a tip at the upper end. Place a piece of dry, hard wood in the test tube, and apply heat. Apply a match to the smoke which issues from the glass tip. The visible part of the smoke

consists of small particles of solid matter and minute drops of liquid. But these solid particles and liquid droplets are suspended in invisible *gases*, which are themselves combustible.

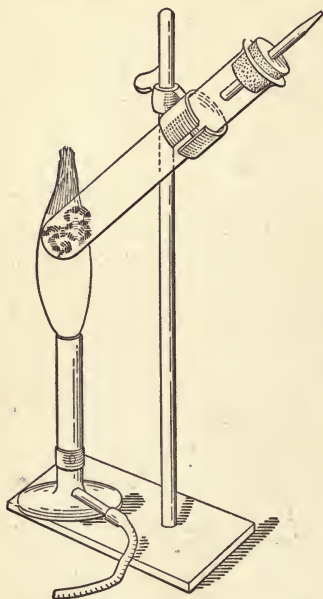


FIG. 23. — A apparatus for destructive distillation of wood or coal.

When the gas ceases to burn and will not relight, open the test tube and examine the residue left from the wood. What is it? Heat one end of it in the Bunsen flame for a minute or two. On withdrawing it from the flame note whether it is burning, and if so, whether with or without flame.

In the light of this experiment, how do you account for the fact that a wood fire shows flame in its early stages, but later no flame but only glowing coals?

Experiment 25.

Materials :

Hard-glass test tube.

Soft coal in small pieces.

Repeat Experiment 24 in a hard-glass test tube, using soft coal instead of hard wood. The

residue left in the test tube in this instance is *coke*.

Experiment 25 illustrates the process of manufacture of the illuminating gas known as “coal gas.” Before the gas is delivered into the mains to be distributed it is purified by the removal of the solid and liquid particles which constitute the cloud. In the purification processes some of the gaseous products also are eliminated—for instance, sulphur compounds, the burning of which would yield products injurious to health.

Flame occurs only in the combustion of gases. Solid and liquid fuels which burn with flame do so because they are converted, wholly or partially, into gases by the heat pro-



JOHN MAYOW.

JOHN MAYOW.—1645-1679.

Mayow, an English physician, recognized that air contained a constituent concerned in combustion, in respiration, and in the rusting of metals. He estimated that this active constituent made up about one fourth of the air and found that it was present in saltpeter. Mayow called the active substance "fire-air" and "nitre-air." We call it oxygen.

duced by the combustion. The reason that charcoal and coke burn without flame is that (except for the ash which they contain) these fuels consist wholly of the element carbon, which is not converted into gas by the heat of its own combustion. The *solid* carbon combining with the gas oxygen yields much heat — so much that it is heated to incandescence — but no flame.

We have next to consider the part the gases of the air play in the process of combustion.

Experiment 26.

Materials :

Supply of nitrogen from a generator or gasometer.

Supply of oxygen from a generator or gasometer.

Splint.

Candle.

Labels.

Plunge a flaming splint into (1) a bottle of air, (2) a bottle of oxygen, (3) a bottle of nitrogen. Do the same with a lighted candle.

Experiment 27.*

Apparatus :

A bell glass with open narrow neck. Rubber stopper to fit.

A basin or stoppered sink, or pneumatic trough.

A porcelain crucible.

A wire stand for the crucible about $\frac{1}{3}$ the height of the bell.

A straight, stiff, iron wire, longer than the height of the bell.

A candle on a bent wire.

Materials :

Phosphorus under water. (Dangerous! Handle only with tongs.)

Support a crucible on a wire stand in a basin, glass trough, or sink containing water. Dry a small piece of phosphorus on filter paper and transfer to the crucible with tongs. Invert the open

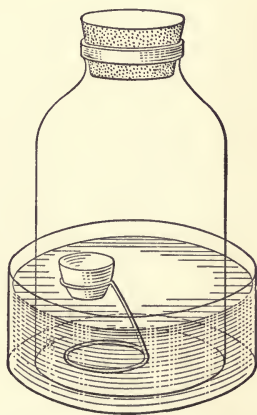


FIG. 24.—Apparatus for Experiment 27. Removing the oxygen from the air by burning phosphorus.

bell glass over the crucible. Heat the iron wire in a flame, touch it to the phosphorus, immediately withdraw the wire from the bell and insert the stopper. The water in the basin should be deep enough to prevent the escape of any air on account of the expansion due to the burning. Allow to stand until the fumes have settled and the glass has cooled to the room temperature (10 or 15 minutes), pouring sufficient water into the basin from time to time to keep the inner and outer levels equal. Remove the stopper and lower into the bell (*a*) a lighted candle, (*b*) a flaming splint.

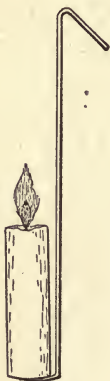


FIG. 25. — *Candle on bent wire.*

Compare the results with those obtained with air and with nitrogen in Experiment 26.

Experiment 28.

Fill a wide-mouthed bottle with water and pour out the water into a graduated cylinder. Note the quantity of water (number of cubic centimeters) and pour it back into the bottle in five equal portions, marking the level of each fifth with a label. Cover the full bottle tightly with a glass plate, and invert it into a trough of water. Deliver oxygen into the bottle until one-fifth of the water is displaced. Displace the remaining four-fifths similarly with nitrogen. Again cover the mouth of the bottle with the glass plate, and turn the bottle over several times to mix the gases. Test this mixture with a lighted splint or a lighted candle, comparing the result with those obtained in Experiment 26.

Experiment 29.

Apparatus :

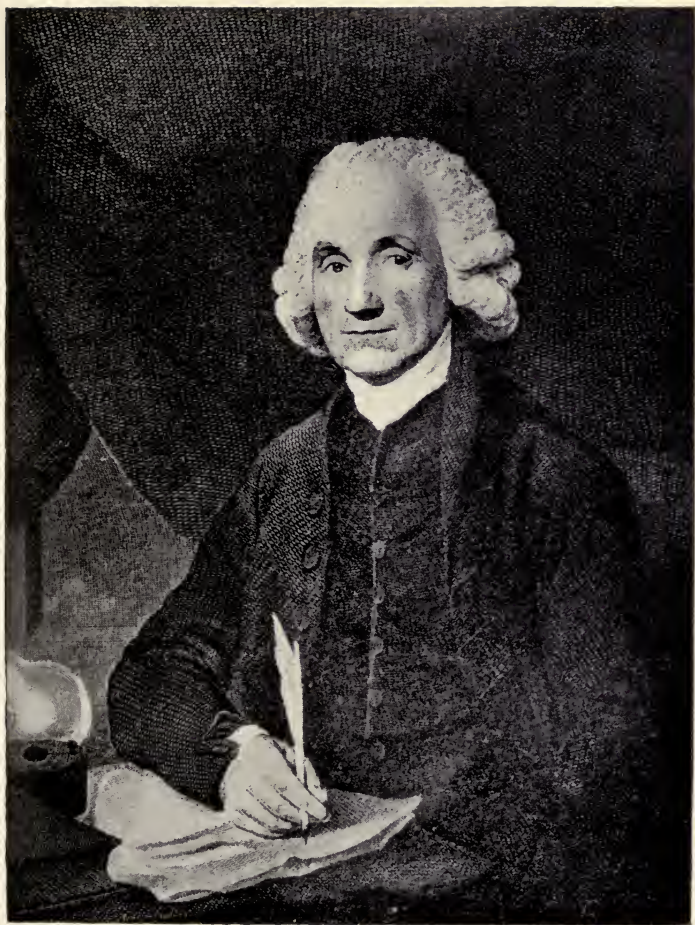
Pan.

Candle.

Wide-mouthed bottle.

Attach a candle to the bottom of a pan, and cover the bottom of the pan with water. Light the candle, and invert over it the wide-mouthed bottle divided into fifths (Expt. 28). Is the flame extinguished immediately? After a time? Allow to stand until cool. How much has the air decreased in volume?

Invert pan and bottle over a sink, allowing the water in the pan to fall out. Remove the pan and immediately test the gas in



JOSEPH PRIESTLEY.— 1733-1804.

An English Unitarian minister, accredited with the discovery of oxygen (1774), because he was the first to describe the pure substance. Persecuted in England for his religious and political views, Priestley emigrated to the United States, settling in Northumberland, Pennsylvania, where he spent the last ten years of his life.

the bottle with a flaming splint or candle. Which of the two air gases was left in the bottle?

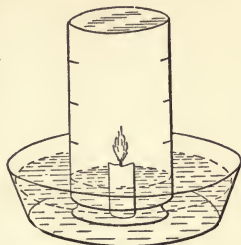


FIG. 26. — *Experiment 29.*
Burning a candle in a
bottle of air.

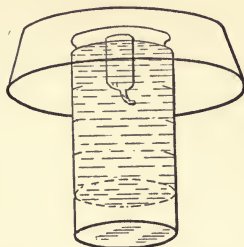


FIG. 27. — *Experiment 29.*
Inverting the bottle to ex-
amine the residual gas.

When a splint or candle or any fuel substance is burned in air, the oxygen of the air disappears and the nitrogen remains. We must next inquire what becomes of the oxygen.

Experiment 30.

Materials :

Candle.

Wide-mouthed bottle.

Over a lighted candle invert a dry, cold, wide-mouthed bottle. Note the mist which gathers on the inside of the bottle. This consists of droplets of water. Cover the bottle, turn it right side up, pour in a little limewater, and shake. What gas must have been formed in the combustion of the candle?

What products are formed in the combustion of illuminating gas? (See Expt. 12.)

When a candle burns, it obviously loses weight. But we have just seen that the gases, steam and carbon dioxide, are products of the combustion. In open-air combustion these gases are constantly being swept away from the burning substance by the air currents. It will be interesting to examine whether, when these gases are retained and weighed along with the diminished candle, there has been any loss of weight. The following experiment determines this point.

Experiment 31.**Apparatus:*

Balance.

Sodium hydroxide in sticks.

Two lamp chimneys or open glass cylinders.

Candle.

Wire gauze.

Close the lower ends of the lamp chimneys with wire gauze, and fill them with approximately equal quantities of sodium hydroxide, a substance which will take up both the water and the carbon dioxide. Attach the candle to a card or flat cork, and fix it beneath one of the cylinders of caustic soda. Suspend the

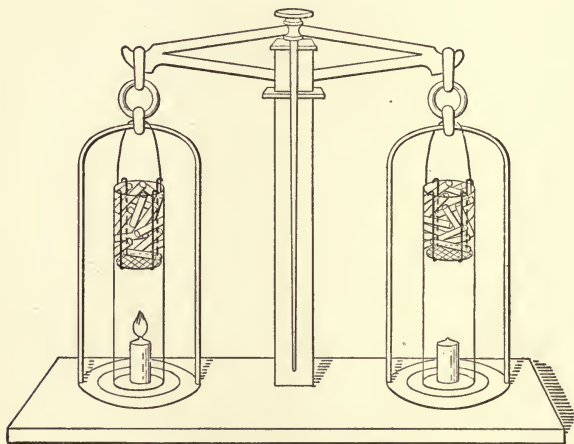


FIG. 28. — *Experiment 31. Comparing the weight of an unburned candle with that of a burning candle and the products of its combustion.*

chimneys from the hooks of the balance and counterpoise the balance, *e.g.* with sand. Light the candle, and note whether the system becomes lighter or heavier when the products of the combustion are not allowed to escape. Account for the fact that the weight does not remain *unchanged*.

Burning in an abundant supply of oxygen, the elements carbon and hydrogen, respectively, combine with oxygen, forming carbon dioxide and water. These same products

are formed in the combustion of all compounds of carbon and hydrogen, and of all compounds of carbon, hydrogen, and oxygen. No other products than carbon dioxide and water are formed unless (1) other elements are present, or (2) the conditions are such that the combustion is not complete. Carbon dioxide and water vapor are not poisonous. They are present in small quantities, even in the purest of outdoor air. On the other hand, the products of combustion of some of the other elements, *e.g.* sulphur and arsenic, are injurious to the health, and so also are some of the products of *incomplete* combustion of carbon and of compounds of carbon and hydrogen, or of carbon, hydrogen, and oxygen. The most dangerous of these poisons is the colorless gas, carbon monoxide, CO, which has the property of combining with that constituent of the blood (hemoglobin) whose function it is to take up oxygen in the lungs and convey it to other parts of the body. Hemoglobin which has combined with carbon monoxide cannot combine with oxygen. Hence, carbon monoxide poisoning completely deranges the respiration and quickly produces fatal results. It is important that the student of household science should have some knowledge of this poisonous gas.

Experiment 32.*

Apparatus:

Carbon dioxide generator.

Iron tube.

Furnace (see Fig. 29).

3 Woulff bottles.

Pneumatic trough.

Glass cylinder.

Connections.

Materials:

Charcoal in lumps.

Potassium hydroxide, 30 per cent solution.

Pass a slow current of carbon dioxide into a train of apparatus comprising (1) a Woulff bottle containing concentrated sulphuric

acid, (2) an iron tube packed with charcoal and heated to redness

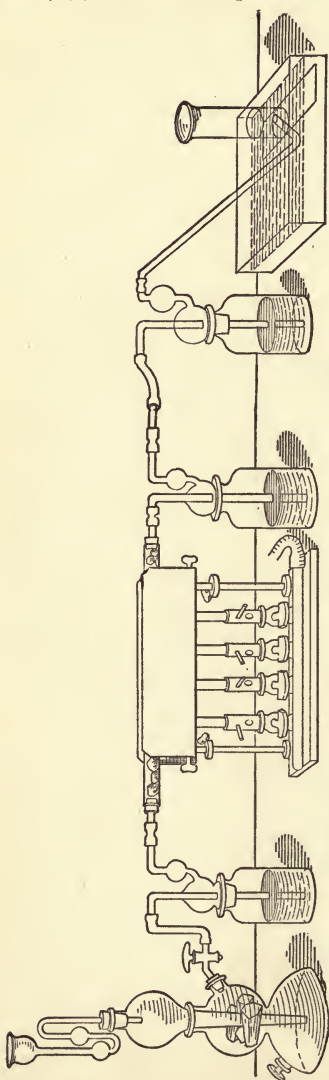
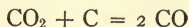


FIG. 29. — Apparatus for the generation of carbon monoxide from carbon dioxide and carbon.

in a furnace, (3) 2 Woulff bottles containing 30 per cent potassium hydroxide, (4) a delivery tube leading to a cylinder of water inverted in a pneumatic trough. (See Figure 29.) The carbon dioxide gas from the generator is dried by bubbling through the sulphuric acid. That part of the gas which is not acted upon by the red-hot carbon in the iron tube is absorbed by the potassium hydroxide solution in the two Woulff bottles. The carbon monoxide gas is formed by the action of the carbon on the carbon dioxide, thus:



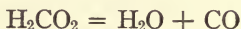
and this gas passes over into the pneumatic trough, where it is collected by displacement of water.

Reject the first two or three cylinders of the collected gas, this being in part the air originally present in the apparatus. Test the gas subsequently collected by applying a burning splint. Note the color of the flame. When the gas is all burnt, pour a little calcium hydroxide solution (limewater) into the cylinder, and shake. What gas is formed in the combustion of carbon monoxide?

Carbon monoxide is formed in coal stoves and furnaces, and burns with a blue flame at the top or back of the fire, where it meets with more air. Some of the carbon dioxide formed at the bottom of the fire is "reduced" (the word **reduced** is used in chemistry in the sense of "deprived of oxygen") to carbon monoxide, by the red hot carbon of the fire, just as carbon dioxide was reduced to carbon monoxide in our experiment. If the draft is poor, some of this poisonous gas may escape from the stove and contaminate the air of the house. It requires only $\frac{1}{4}$ to $\frac{1}{2}$ per cent of carbon monoxide in the air of a room to have a fatal effect upon the human occupants if they remain exposed to it for any considerable length of time, and even $\frac{1}{10}$ per cent is decidedly injurious. Inhaled in small quantities, carbon monoxide causes dullness, sleepiness, and headache. Being odorless and stupefying, it is a very insidious poison. Fortunately, odorous gases usually escape with it, and these may suggest its possible presence to one on the lookout for it. Persons poisoned with the gas should be immediately taken into the open air and made to breathe deeply. In the event of unconsciousness or stupefaction artificial respiration should be established, as in the treatment for drowning. This consists in alternately extending the arms above the head and pressing them firmly against the chest.

An easier but less instructive way of preparing carbon monoxide depends upon the so-called dehydrating action of concentrated sulphuric acid. In Experiment 32 concentrated sulphuric acid was used to dry the carbon dioxide, *i.e.* to take up the water vapor mixed with the gas. Now, concentrated sulphuric acid not only takes up free water molecules, as in the above instance, but actually breaks up many molecules by withdrawing the elements of water from them. Formic acid, H_2CO_2 , is one of the substances which is decomposed in this way by sulphuric acid. If we examine the formula of formic acid, we see that the removal

of a molecule of water from a molecule of formic acid leaves a molecule of carbon monoxide.



Carbon monoxide may, therefore, be prepared as follows:

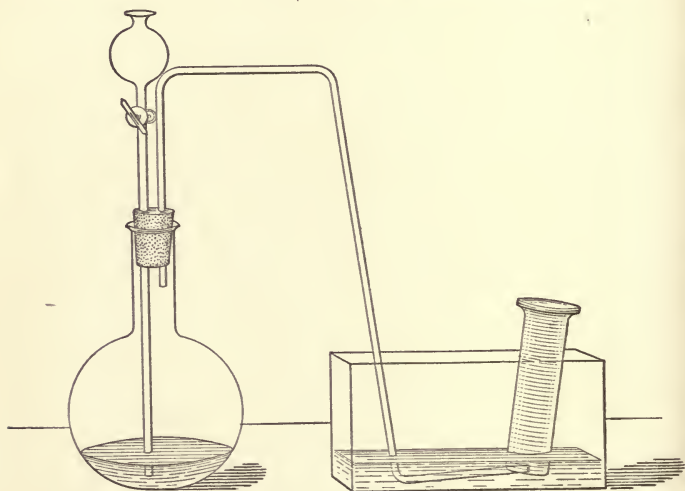


FIG. 30.—*Experiment 33. Apparatus for the generation of carbon monoxide from formic acid.*

Experiment 33.*

Materials :

Formic acid solution (or a strong solution of sodium formate).
Crude sulphuric acid.

Apparatus :

Flask provided with a dropping funnel and a delivery tube.
Pneumatic trough.
Cylinders or bottles.
Connections.

Allow the formic acid or sodium formate solution to drop slowly upon the concentrated sulphuric acid, and collect the gas by displacement of water.

CHAPTER X

THE RELATION OF COMBUSTION TO HEAT

HEAT is not a substance in the sense in which the word *substance* is used in chemistry. If we weigh a body cold (say a platinum crucible), then heat it and weigh it again, we find that in spite of the addition of heat there is no increase of weight. Had we added any *substance* to the platinum, the weight would have increased. There is no molecule of heat. On the contrary, heat is regarded as consisting in molecular motion, the molecules of hot bodies vibrating back and forth more rapidly than those of cold bodies. (See Chapter VI.) That mechanical work or energy can be converted into heat is illustrated by the primitive methods of obtaining fire practiced by savage races, such as the rubbing together of two sticks of wood, or the twirling of one stick upon a hollowed part of a second stick. The same principle was demonstrated on a larger scale in 1798 by Count Rumford, who, by an experiment performed publicly before the Elector of Bavaria, showed that in boring a cannon with a blunt borer it is possible to heat over 25 pounds of water to the boiling point in about two hours and a half.

That, conversely, work can be obtained from heat is illustrated by the steam engine, which is a machine devised for that very purpose.

Heat is therefore a form of energy, and the study of heat belongs to the domain of physics. On account of its relation to combustion, however, it is desirable that we have clear conceptions of the meanings of some words relating to heat.

Temperature is a familiar term. A hot body is said to have a high, and a cold one, a low temperature. Instruments

used to measure temperature are called *thermometers*. Two styles of thermometers are in common use in America — the Fahrenheit and the Centigrade, or Celsius. Placed in melting ice or in freezing water the Fahrenheit thermometer registers 32 degrees; the Centigrade thermometer, zero. Placed in the vapor of boiling water the Fahrenheit thermometer registers 212 degrees; the Centigrade, 100 degrees. Thus the interval between the freezing and boiling points of water is divided on the Fahrenheit thermometer into 180 degrees, and on the Centigrade thermometer into 100 degrees. In other words, 100 Centigrade degrees = 180 Fahrenheit degrees, or 1 Centigrade degree = 1.8 Fahrenheit degrees.

The *quantity of heat* in a body depends not only on its temperature, but also on its mass and on the substance of which it is composed. Thus, while a cupful of boiling water and a barrellful of boiling water have exactly the same temperature they contain very different quantities of heat. Instruments used to measure quantity of heat are known as *calorimeters*. (See p. 55.)

Various units of quantity of heat have been proposed. We shall define two — the *Calorie* (“large calorie” or “kilogram calorie”¹) and the *British Thermal Unit* (B. T. U.).

A Calorie is the quantity of heat that will raise the temperature of one kilogram of water one degree Centigrade.

A British Thermal Unit is the quantity of heat that will raise the temperature of one pound of water one degree Fahrenheit.

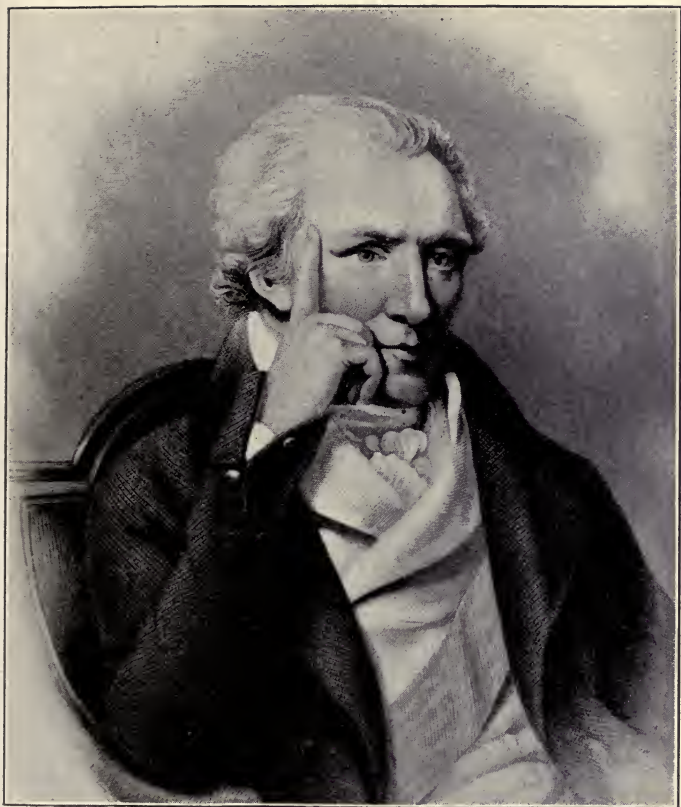
A Calorie is approximately equal to 4 British Thermal Units.²

¹ A “small” or “gram” calorie is the quantity of heat that will raise the temperature of one gram of water one degree Centigrade. One Calorie (spelled with a capital) is therefore equal to 1000 calories (spelled with a small *c*). It should be noted, however, that in books in which there is no reference to small calories the large calorie may be found spelled without the capital.

² 1 Kilogram = 2.2 lb.

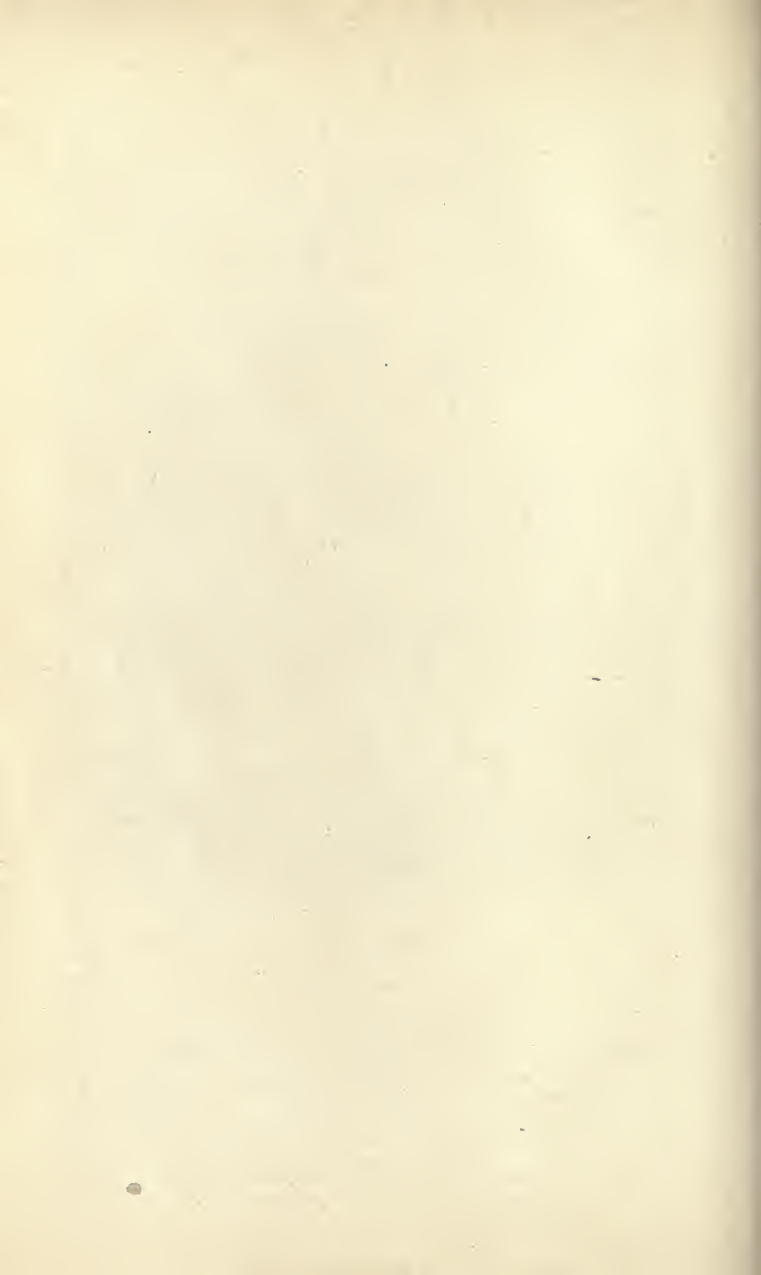
1 Centigrade degree = 1.8 Fahrenheit degrees.

∴ 1 Calorie = 2.2 × 1.8 = 3.96 B. T. U.



SIR BENJAMIN THOMPSON, COUNT RUMFORD.—1753-1814.

Who demonstrated the production of heat by friction. Born at Woburn, Massachusetts, Thompson removed to England early in the War of Independence and later returned in command of British troops, which did not see active service. In 1783 he entered the service of the Elector of Bavaria, becoming a minister of state. For his services to Bavaria he was created a Count of the Holy Roman Empire, his title of Rumford being derived from the New Hampshire town (now Concord), where he had taught school. Returning to England in 1795, he projected the Royal Institution and selected Sir Humphry Davy as its first scientific lecturer. The last ten years of his life were spent in France, where he married the widow of the great French chemist, Lavoisier. Amongst his numerous interests Rumford devoted much attention to problems of cooking, clothing, and fuel economy.



Ignition Temperature

Experiment 34.

Materials:

Disks of sheet iron or tinned iron 4 inches in diameter.

Coke, charcoal, yellow phosphorus (under water), red phosphorus, sulphur, pine, and soft coal.

Forceps to handle the yellow phosphorus.

Filter paper to dry the yellow phosphorus.

At equal distances from the center of a circular piece of metal, *e.g.* the cover of a tin, supported on a tripod or an iron ring, place small portions of coke, charcoal, red phosphorus, yellow phosphorus, sulphur, pine, and soft coal. Place a Bunsen flame exactly under the center of the metal, and note the order in which the materials take fire.

It is a familiar fact that most substances must be heated before they will burn, and that some substances must be made much hotter than others. Everybody knows, for instance, that anthracite coal (hard coal) cannot be ignited as easily as pine wood. Every substance may be said to have its ignition temperature. Thus, while some kinds of dry peat will ignite at 200° C., and charcoal in pure oxygen ignites at 345° C., graphite will not take fire below 690° C. in pure oxygen, nor diamond below 800° C. (Charcoal, graphite, and diamond are three modifications of the element *carbon*.) A few substances will ignite at ordinary atmospheric temperatures, but such are rare and unimportant.

Matches are tipped with substances of ignition temperatures sufficiently low to be attained by friction. Yellow phosphorus, covered with a protective coating, has been much used for this purpose, but is now prohibited in most civilized countries, on account of its injurious effects upon the health of the factory operatives. Red phosphorus is free from this objection, and so is the compound phosphorus pentasulphide, P_2S_5 . Matches can also be made without any phosphorus. Indeed, the earliest friction matches (known as

lucifer matches or "Congreves"¹) were tipped with a phosphorus-free mixture, consisting of antimony sulphide, potassium chlorate, starch, and gum.

Safety matches are tipped with a mixture that is difficult to ignite by simple friction, but which ignites when rubbed upon a second mixture (containing red phosphorus) which is applied to the surface of the match box.

Heat of Combustion

The heat of combustion of a substance is the quantity of heat produced when a given quantity (one pound or one gram) of the substance is completely oxidized. The heat of combustion of any substance is always the same whether the substance burns rapidly, *e.g.* in compressed pure oxygen, or more slowly, as in air; or even oxidizes slowly without the phenomena of combustion. The *temperature* attained during the oxidation is, however, greater the more rapidly the substance burns.

Experiment 35.*

Materials:

Bottle of oxygen.

Small pieces of yellow phosphorus in a dish of water.

Deflagrating spoon.

Forceps.

Porcelain dish.

With the forceps remove one piece of phosphorus from the water, place it on filter paper for a moment to dry, then leave it in the dry porcelain dish exposed to the air. Dry a second piece, transfer it to the deflagrating spoon, and ignite it by warming.

Dry a third piece, ignite it in the deflagrating spoon, and immediately plunge it into the oxygen.

¹ So named by the inventor, John Walker, in 1827, in honor of Sir William Congréve.



FIG. 31. — *A*
deflagrating
spoon.

In the experiment just performed the higher temperature attained in the more rapid combustion is made apparent by the greater brilliance and smaller volume of the flame. Careful experiment with a calorimeter shows that the *quantity of heat* set free in the oxidation of a given amount of phosphorus is identical in the three instances. But the same quantity of heat, set free in a smaller space and at a more rapid rate, produces a higher temperature.

To measure heats of combustion accurately the combustion is caused to take place as rapidly as possible, and the heat produced is used to heat water. To this end a weighed quantity of the substance, whose heat of combustion is to be determined, is burned in compressed oxygen in a steel bomb. (See Fig. 32.) The bomb is immersed in a vessel of water, into which a thermometer dips. The heat produced in the combustion heats the water surrounding the bomb.

Knowing the weight of this water, and how much its temperature is

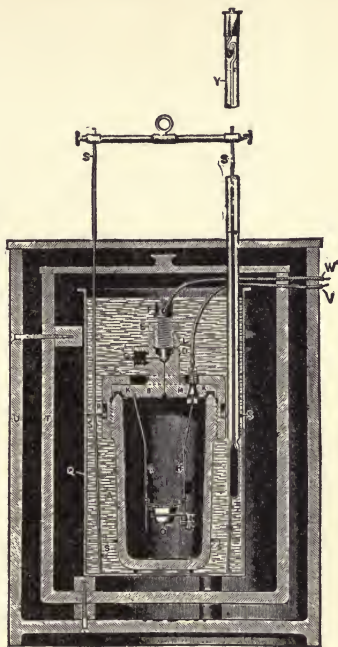


FIG. 32.—A bomb calorimeter. The substance in the bomb is ignited by an electrical device. The platinum wires, *H* and *I*, the former of which is insulated from the steel of the bomb, are connected inside the bomb by a little coil of iron wire just above the capsule, *O*, which contains the substance to be burned. An electric current, passed through these wires for a few seconds, heats the iron wire to redness, when it burns, and, falling on the substance in the capsule, sets it on fire. *S* in the figure is a stirrer, which is kept in constant motion to keep the water well mixed.

raised, we can easily calculate the number of calories or British Thermal Units of heat that have gone into it. If, for instance, 2 pounds of water have been heated 2 Fahrenheit degrees, we know that $2 \times 2 = 4$ B. T. U. must have gone into the water.

When 12 pounds of carbon (one atomic weight in pounds) are burned to carbon dioxide, 174,500 B. T. U. are set free. When the quantity of carbon monoxide containing 12 pounds of carbon (viz. 28 pounds) is burned, 122,400 B. T. U. are set free. From this we infer that when 12 pounds of carbon are burned to carbon monoxide, only 52,100 B. T. U. are liberated. In other words, any carbon monoxide allowed to escape up the chimney unburned involves a loss of more than two-thirds of the heat the carbon contained in it was capable of yielding. It is, therefore, bad economy to have the upper part of a coal stove or furnace so tightly closed that air cannot enter to burn the carbon monoxide. Moreover, if the carbon monoxide is not burned, there is danger that some of this extremely poisonous gas may escape into the room. A blue flame on the top of a coal fire is evidence that the carbon monoxide is burning.

Propagation of Combustion

Fire once started has a tendency to spread. This is because, once a portion of the combustible substance is in active combustion, the heat set free raises neighboring portions to the kindling point. In solid and liquid fuels burning with a flame, a part of the heat produced by the combustion is used in converting the solid or liquid into the gaseous condition. In gases all the heat is available for the ignition of new portions of the gas. If the combustible gas is mixed with sufficient air to provide all or nearly all the oxygen necessary to burn it, an explosion takes place. This is because the combustion spreads almost instantaneously.

An enormous quantity of heat is consequently liberated in an instant. Gases tend to expand when heated. If they are confined within an inclosed space (such as a bottle or even a room), they exert a pressure on the walls of the space in consequence of this tendency to expand. If the pressure is sufficiently great, the walls of the inclosing vessel or room may be shattered.

When gas has been escaping into a room or oven, there is always a possibility that it may be mixed with the air in explosive proportions. It is, therefore, extremely dangerous to bring a light into the room or near the oven until the gas has been shut off and the room or oven well ventilated. Vessels containing volatile¹ liquids such as gasoline and benzine are apt to have explosive mixtures in the space above the liquid. Such liquids should not be used for cleaning purposes in a room in which a lamp or fire is burning. Explosions have been known to occur when benzine was used many feet from a flame.

Finely divided solid or liquid combustibles may also form explosive mixtures with air. Explosions of coal dust and of flour dust are not uncommon in the air of mines and mills.

Gas and gasoline engines derive their power from the explosive combustion of mixtures of air with combustible gases and minute droplets of combustible liquids.

Spontaneous Combustion

Oxidation of many substances occurs slowly at temperatures below their ignition points. Phosphorus, for example, oxidizes slowly but completely at ordinary room temperature, although its ignition point is considerably higher. Iron oxidizes slowly in moist air, and, curiously enough, combines with more oxygen than when it is burned in pure

¹ A *volatile* liquid is one which is readily converted into vapor or gas.

or even in compressed oxygen. Linseed oil, exposed to the air in thin layers, as when used in paint, oxidizes partially, yielding a solid film. The "drying" of paint is due to this reaction rather than to the evaporation of any liquid.

We have learned that when *slow oxidations* such as these occur the quantity of heat set free is the same as if they occurred rapidly. Now if the oxidation goes on at such a rate that heat is produced a little more rapidly than it is conveyed away from the oxidizing body, it is evident that the latter will gradually become warmer. This will cause the rate of oxidation to become greater; heat will therefore be liberated more rapidly than before; and the temperature of the oxidizing body will continue to go up, until finally the ignition temperature is attained and the substance bursts into active combustion. Spontaneous combustion has been observed in stored coal, in cotton waste wet with oil, in hay, and in other materials.

CHAPTER XI

FUELS

FUELS are conveniently classified according to their *physical state*, thus :

1. **Solid Fuels.** — Wood, peat, the several varieties of coal, charcoal, coke.

2. **Liquid Fuels.** — Alcohol, wood alcohol, gasoline, kerosene (coal oil), “fuel oil,” crude petroleum.

3. **Gaseous Fuels.** — Natural gas, coal gas, water gas, producer gas, air gas (or gasoline gas), oil gas, acetylene.

These all contain *carbon*, and all but charcoal and coke contain *hydrogen*. Most of them are mixtures of different substances, *e.g.* coal gas of free hydrogen, carbon monoxide, and methane (CH_4); water gas of free hydrogen, carbon monoxide, and nitrogen; etc. The solids and most of the gases contain more or less incombustible matter. In the gases this consists usually of free nitrogen, free oxygen, argon, and carbon dioxide; in the solids, of oxides and salt-like compounds of the metals. The incombustible *gases*, of course, pass up the chimney with the carbon dioxide and steam produced in the combustion. The incombustible *solids*, for the most part, remain as *ashes*, though the smaller particles may be swept away into the chimney with the gases.

As the hot gases from a fire cool, the water and some of the products of incomplete combustion *condense*, *i.e.*, change from the gaseous to the liquid form, and the minute droplets so formed, together with the particles of ash, constitute the white matter of smoke. Some of the oily products of incomplete combustion which are most easily condensed,

and some of the carbon and ash lodge in the chimney or pipes, and the mixture constitutes *soot*. The oily matter of soot, sometimes spoken of as "oil of smoke," is a complex mixture of compounds analogous to carbolic acid.

Solid Fuels

Wood. — The *hard* woods are most valued for fuel purposes. These all come from deciduous trees — trees which shed their foliage annually. Those most used as fuel may be placed in the following approximate order of merit, though it must be remembered that there are many varieties of each species and that these have unequal merit: hickory, oak, ash, sugar maple, black maple, beech, birch.

The evergreen conifers and some of the deciduous trees yield *soft* woods, which ignite readily and are therefore particularly useful as kindling for harder wood and for coal. Soft woods may also be used for fuel proper. The most valuable soft-wood fuels are those from the conifers: pine, spruce, hemlock, cedar, sequoia, and redwood.

Wood consists, in the main, of compounds of carbon, hydrogen, and oxygen — largely cellulose and closely related substances, having an average composition roughly represented by the formula, $C_6H_{10}O_5$, *i.e.* C, 44.4 per cent; H, 6.2 per cent; O, 49.4 per cent.

Mixed with these compounds there is always a considerable quantity of water and some incombustible "mineral" matter, *i.e.* ash. The conifer woods also contain turpentine and resins, consisting of compounds of carbon and hydrogen, some of them without any oxygen, some with much less oxygen than is contained in the cellulose-like compounds. These substances have high heats of combustion, and it is their presence which renders the *conifer* woods more valuable for fuel than the *soft deciduous* woods such as poplar, willow, and basswood.

The amount of water in the wood has a great effect on

its practical calorific value, for if much water is present, a large proportion of the heat is used in vaporizing (boiling) this water.

The amount of water in the wood depends upon the variety, upon the season at which the wood is cut, and upon the seasoning. Wood cut in midwinter contains less water than that cut at other seasons. No wood is water-free unless it has been kiln-dried. But while seasoned wood has only 20 per cent or less of water, green wood or wet wood may have as much as 50 per cent. Green ash contains about 30 per cent, green poplar about 50 per cent, of water. It is at least partly due to the water contained even in air-dried wood that it is impossible to get a very hot fire with wood, except in the later stages of the combustion. At that time the water and the gases produced by the decomposition have been driven off and the fire has become essentially a charcoal fire.

Weight for weight, there is little difference in the calorific value (*i.e.* heat of combustion) of perfectly dry soft woods and perfectly dry hard woods. But wood is bought and sold by measure, not by weight. A cord of dry pine — a pile 8 feet long, 4 feet wide, and 4 feet high — is said to weigh 3000 pounds, and a cord of dry maple from 4500 to 5000 pounds. Cord for cord, then, dry hard wood has a much higher calorific power than soft wood. A cord of hard wood yields about the same quantity of heat as a ton of coal, *viz.* 20 to 30 million B. T. U.

Soft woods, particularly those which are light and porous, not only ignite more readily, but also burn more rapidly than hard woods. They thus give a hot fire, but one which requires constant attention. Hard woods produce more charcoal than soft woods, and of a better quality. This is another reason why a hard-wood fire is steadier and more persistent than one of soft wood.

The ash from hard wood contains potassium carbonate, which in former days was commonly leached out and used

for soap-making and other purposes. Hard-wood ashes have considerable value as agricultural fertilizers. This is due to the compounds of potassium, phosphorus, and calcium contained in them. The potassium compounds are the most important in this respect, and since these are soluble in water, ashes which have been leached, either intentionally, as in the making of lye, or through carelessness, *e.g.* by exposure to rain, have but little fertilizing value. Soft-wood ashes, even if protected from leaching, have, as a rule, very little value as fertilizers.

Peat is a substance produced by the decay under water of certain swamp plants, particularly mosses. In its natural state it contains more water than even green wood. It is very difficult to dry below a moisture content of 30 to 50 per cent, and in this condition its calorific value is little, if any, above that of wood. Better drying can, however, be accomplished if the fiber is broken up by mechanical treatment. Peat improved by such processes of manufacture is now an important fuel in some European countries and is beginning to be of importance in Canada. It is admirably adapted to domestic use.

Coal is a general name given to the solid fuels found as minerals. There is good evidence that for the most part these have been formed by the decay of plants of the conifer, fern, and palm families. Under varying conditions there have been formed coals showing very material differences in composition and physical properties.

Lignite or **brown coal** owes its name (from the Latin *lignum*, wood) to the fact that it often shows more or less clearly the structure of wood. On account of its propensity to break up into powder as it dries, lignite has little commercial value except in the immediate neighborhood of its mines, where it can be used comparatively soon after being brought to the surface. There are large deposits of lignite in the western regions of the United States and Canada,

but the larger part of the western coals and practically the whole of the eastern fuels fall in the following groups.

Lignitic coal resembles lignite in structure, but is darker in color, contains less water, and is more stable. In composition and fuel value it is intermediate between true lignite and bituminous coal. Most of the coals found in the great plains and a considerable part of those found in the far West belong to this class. They range from the true lignites, containing say 20 per cent of water, down to the lighter grades of bituminous coal which contain little or no combined water. Lignitic coals are valuable fuels.

Lignitic coal with 18 per cent of water contains about 50 per cent of carbon, a little less than 5 per cent of hydrogen, and 16 per cent of oxygen and nitrogen. It burns with a smoky flame and yields from 8000 to 11,000 B. T. U. per pound.

Bituminous or soft coal contains more carbon and much less oxygen than lignitic coal, and has, therefore, a higher calorific value. Some varieties (*e.g.* Connellsville) melt slightly and cake in burning; others burn without caking. Some burn with little, others (*e.g.* Nova Scotia) with much flame and smoke. It is from bituminous coal of medium grades that coke and coal gas are best manufactured. Bituminous coal contains from 55 to 80 per cent of carbon, and from 15 to 50 per cent of volatile matter (matter driven off as gas in the manufacture of coke). The caking coals have usually less oxygen and more volatile matter than the non-caking. The surface of a caking coal fire requires breaking up occasionally, so as to allow free draft through the fire. Bituminous coal is by far the most important fuel in North America, if not in the whole world.

Semi-bituminous or semi-anthracitic coal is intermediate between bituminous coal and anthracite. It has over 80 per cent of carbon and 15 to 20 per cent of volatile matter. It burns with a shorter flame than bituminous coal, but may

be either harder or softer. An example of this kind of coal is Pocahontas.

Anthracite or **hard coal** is the densest and hardest variety of coal and contains the most carbon and the least hydrogen, oxygen, and volatile matter. It is hard to kindle, burns with a steady, intense heat, produces little or no smoke, and requires less frequent attention than any of the other varieties. Anthracite has from 84 to over 96 per cent of carbon and but 3 to 10 per cent of volatile matter.

Good grades of semi-bituminous and anthracite coal yield from 13,500 to 15,500 B. T. U. per pound.

The figures given above for the composition of coals of the various classes refer to pure air-dried coals with a minimum of ash. Commercially, all coals contain considerable quantities of dirt and mineral impurity; and coal as mined and shipped always carries some moisture, as distinguished from chemically combined water. Perhaps the average of all coals sold would contain 10 to 12 per cent of ash and 1.5 to 2 per cent of moisture. The amount and character of the ash in coal is an important practical consideration. In amount it ranges from 3 to 20 per cent, with extremes above and below. Coals containing sulphur are more likely to give clinkery ashes than sulphur-free coals. Clinkers, accumulating upon the grate of a furnace or stove, are objectionable, not only because they are apt to clog the shaking mechanism, but also because they interfere with the draft.

Coal ashes have much the same composition as clay. They have practically no fertilizing value.

Charcoal is made by the destructive distillation of wood; **coke** by that of bituminous coal. (See Expts. 24 and 25.) They both consist of free carbon mixed with the ash constituents of the wood or coal from which they are made. Both burn without flame (or with a carbon monoxide flame if the fire is deep), and both yield about 13,000 B. T. U. per pound. Coke is of two kinds: (1) *Furnace or metallurgical coke*, made

in so-called "coke ovens" as a primary product, the gas, tar, etc., being secondary products or in all too many cases wasted; (2) *Gas coke*, a much softer material left in the retorts used in the manufacture of illuminating gas from coal. Gas coke is a valuable domestic fuel, igniting almost as easily as bituminous coal and burning with a very intense flameless fire. Furnace coke, on the other hand, is a very hard substance and is more difficult to ignite than anthracite. While of great industrial importance, this kind of coke is unsuitable for domestic use.

In all solid fuel fires, and especially in coal fires, it is important to keep the grate and the surface of the fuel free from an accumulation of ashes. Ashes not only impede the draft but, covering the surface of the fuel, they prevent the oxygen from coming in contact with the combustible solid. The shaking of the fire not only clears the grate of the ashes which tend to clog it, but also shakes off the covering of ashes from the face of the coals and exposes the latter to the action of the oxygen.

For further information about solid fuels the reader is referred to Chapter V of Benson's "Industrial Chemistry" (New York, 1913) and to the numerous references there cited.

CHAPTER XII

FUELS (*Continued*)

Liquid Fuels

THE most important liquid fuels are the petroleum products — especially kerosene. The alcohols are at present fuels of secondary importance.

Petroleum is an oil obtained from underground sources. It is a mixture of a great many compounds of carbon and hydrogen. In the refining process the more volatile compounds are separated from those less volatile. A large number of products are thus obtained.

Benzine and **gasoline** are two of the most useful of the light or volatile products; **kerosene** is heavier and less volatile; the still less volatile constituents of the crude petroleum make up such products as lubricating oils, axle greases, vaseline (or petrolatum), and paraffin wax.

The vapor of benzine and gasoline is given off in sufficient abundance at ordinary temperatures to form explosive mixtures with air. On account of this danger benzine and gasoline should not be used as household fuels.

Kerosene (called "paraffin" in England and "coal oil" in some parts of America), if well made, gives off very little vapor at ordinary temperatures — enough to affect the sense of smell, but not nearly enough to form an explosive mixture with air. The momentary application of a flame, either above or directly to the surface of the cold oil, will cause no ignition. The flame or "flash" test commonly applied to kerosene is a test to determine to what temperature the oil must be heated in order that it may give off sufficient

vapor to form a combustible mixture with air. The laws of most countries prescribe a minimum flash point for oils offered for sale for illuminating purposes.

Kerosene stoves are of two types. One type is constructed like a large kerosene lamp and gives a yellow, sooty flame. The other type gives a blue flame like a Bunsen burner. In the lamp-like stove the oil rises from the reservoir to the burner through a wick, and is converted into gas in the flame itself. In the blue-flame stoves the oil is vaporized and mixed with air before it reaches the flame. The latter type is practically a combined gas factory and Bunsen burner. Figure 33 shows such a stove.

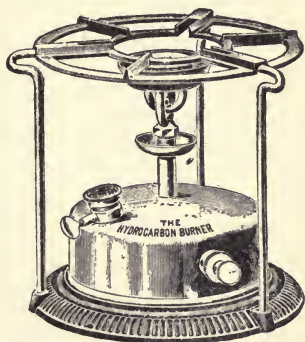


FIG. 33. — A blue flame kerosene stove.

Wood alcohol and “denatured” grain alcohol are convenient household fuels for small fires, such as those of chafing dishes, table kettles, and coffee percolators. *Wood alcohol* (methyl alcohol) is a product of the destructive distillation of wood (see Expt. 24, p. 41), and therefore a by-product of the charcoal industry. *Grain alcohol* (ethyl alcohol) is produced by the fermentation of sugars. The reason it is called “grain” alcohol is that it is so often made by converting the starch of grain, such as corn or rye, into sugar, by the action of malt, and fermenting the sugar so obtained. But it is also made from molasses and from potatoes. Ethyl alcohol is the active, intoxicating principle of all fermented and distilled beverages. *Denatured* alcohol is ethyl alcohol to which some substance has been added to render it unpalatable. *Methylated spirits* is a common variety of denatured alcohol. It is grain alcohol to which a small proportion (about 10 per cent) of wood alcohol and

usually a small proportion of some other substance, such as benzine, has been added.

Both wood alcohol and grain alcohol contain the three elements, carbon, hydrogen, and oxygen. Both liquids are readily ignited and burn with smokeless flames.

Three quarts of grain alcohol, or of methylated spirits, will give nearly as much heat as four quarts of wood alcohol.

The present importance of the alcohols as fuels is, as already stated, a secondary one. This is due to their relatively high price as compared with the petroleum products. The quantity of these two alcohols which could be produced from agricultural products is practically unlimited, and it is possible that some day these substances may find more use as fuels than they do at present.

Gaseous Fuels

The gases most used in the household for fuel purposes are *natural gas*, *coal gas*, *water gas*, and *gasoline* or "*air*" gas.

Natural gas exists underground in certain localities, usually in porous strata, whence it is obtained by boring wells. It consists of the compound methane, CH_4 , mixed with small quantities of other gases. Used with suitable burners it is the most convenient and most efficient of all the natural fuels. It yields about 1000 B. T. U. per cubic foot. Natural gas is supplied to many of the cities of Pennsylvania, Ohio, Indiana, and western New York. In Canada it occurs in New Brunswick, Alberta, and other places.

Coal gas, made by the destructive distillation of bituminous coal, constitutes the gas supply of most European and of many American cities. The coal is heated in closed retorts, the gases produced being conducted off through pipes. The gases are purified by cooling, washing with water, and passing through lime or iron oxide. The by-products are *gas coke*, which remains in the retort; *coal tar*, which con-

denses from the gases on cooling, and from which numerous useful compounds are manufactured — antiseptics (such as carbolic acid), dyes (see Chapter XLIII), etc.; and *ammonia*, which remains in the wash water (see Chapter XXIII). The lime and iron oxide remove the sulphur compounds from the gas.

The chief constituents of coal gas are *free hydrogen* and *methane*, each of these being present to the extent of about

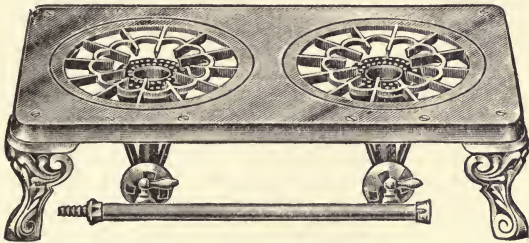


FIG. 34. — A gas stove.

40 per cent. In addition to these two main constituents there are *carbon monoxide* (usually 6 to 8 per cent) and some compounds of carbon and hydrogen, other than methane. It is these latter hydrocarbons which make the gas burn with a luminous flame. To obtain a flame which will not deposit soot, burners on the principle of the Bunsen burner are used. In such burners the gas is mixed with air before ignition. Coal gas yields 600–625 B. T. U. per cubic foot. A ton of coal yields about 10,000 cubic feet of gas, which contain only about one fifth of the original fuel value of the ton of coal.

Water gas is used in many American cities. It is prepared by passing steam through white-hot coke or anthracite coal. The chief constituents of water gas are carbon monoxide and hydrogen. Gas made from coke contains about 45 per cent of each of these two gases, the remaining 10 per cent being methane, carbon dioxide, free nitrogen, and free oxygen.

Gas made from anthracite has a higher proportion of these minor constituents — about 20 per cent instead of 10.

Consisting largely of carbon monoxide, water gas is extremely poisonous — much more so than coal gas. The smallest leakage of water gas from pipes or cocks is therefore a serious matter. Water gas has from 40 to 60 per cent of the fuel value of the coal or coke from which it is made. It yields about 350 B. T. U. per cubic foot, but the fuel value is frequently increased by *enrichment*. (See below.)

Water gas burns with a blue flame, which has very low illuminating power. In order to make it into an illuminating gas for use with old-style burners, it is common to mix with it a gas made by heating petroleum oils to a high temperature. (See "Oil gas," p. 77.) This process is called *enriching* the gas. *Enriched water gas* may have a fuel value as high as 700 B. T. U. per cubic foot. In many cities a mixture of coal gas and water gas is used.

Gasoline gas ("air" gas) is made chiefly in private plants for the supply of rural homes or of institutions situated at a distance from a city supply. It is a mixture of gasoline vapor and air. Gasoline consists of the more volatile hydrocarbons of petroleum. The gas is made from it by exposing the liquid on folds of canvas to a current of air. The gasoline evaporates, the vapors mixing with the air, the supply of which is so regulated that the hydrocarbons will not become liquid again in the pipes. The gasoline gas burns with a luminous (and therefore sooty) flame, but a blue flame is obtained by admitting additional air at the burner, which must be of the Bunsen type.

Compressed and Liquefied Gas. — When the gas mixtures used for fuel purposes, such as coal gas or oil gas, are subjected to great pressure, some of the constituents (hydrocarbons containing a large proportion of carbon) liquefy. This liquefied portion of the gas may be separated from the portion which remains in the gaseous condition, and the latter

may be stored in cylinders in its compressed state and shipped to houses or institutions which are not supplied with gas through pipes.

A German chemist, named Hermann Blau, has patented a process in which some of the constituents of oil gas are liquefied and removed, then the remaining gases are compressed to a liquid condition. *Blau gas* is used more for lighting than for cooking purposes.

Surface Combustion

Gas burners have recently been designed which render it possible to mix the gas with exactly sufficient air for its complete combustion and to cause the mixture to burn flamelessly in a pile of granular incombustible material, such as pieces of silica, SiO_2 , or alumina, Al_2O_3 . Combustion of gas so conducted is termed *surface combustion*. Surface combustion is very economical because (1) it avoids the heating of air not used in the combustion, and (2) heat radiated from the incandescent pile of refractory material is more penetrative than heat from a gas flame. It is claimed that surface combustion gas stoves, doing the same work as stoves of the ordinary Bunsen type, will use 35 to 45 per cent less gas than the Bunsens.

Further information on liquid and gaseous fuels, including numerous references to the literature of the subject, will be found in Chapter VI of Benson's "Industrial Chemistry" (New York, 1913). For a practical method of comparing the values of the common household fuels, the reader is referred to Lynde's "Physics of the Household" (New York, 1914), pages 152-153.

CHAPTER XIII

LIGHT AND ILLUMINANTS

Experiment 36.*

Materials :

Platinum wire, 2 or 3 inches.

Iron wire, same gauge and length.

Magnesium ribbon, $\frac{1}{2}$ inch.

Quicklime, small lump, say, $\frac{1}{2}$ -inch cube.

Crucible tongs or forceps.

Blowpipe.

(a) With the tongs hold in a Bunsen flame side by side a piece of iron wire and a piece of platinum wire. Note the gradual changes of color as the temperature of the wires rises.

(b) Hold a piece of magnesium wire in the tongs, and ignite it with the Bunsen flame. Note the white light emitted as the magnesium burns. (This is the light used in making flashlight photographs.)

The ash, which remains after the combustion of the magnesium and which retains something of the form of the original ribbon, is magnesium oxide (sometimes called magnesia). Bring this ash again into the flame and note the change of color it undergoes as it is heated. Blow into the flame with the blowpipe, directing a gentle current of the flowing gases towards the magnesia. Does it become brighter? Is its color altered? (c) Hold a piece of lime in the flame a little above the inner cone. Note its color. Blow the flame upon it with the blowpipe. Does the color change? If an oxyhydrogen blowpipe is available, direct its flame against the lime. Is more light now emitted? What is its color?

When substances are heated to a sufficiently high temperature, they give out light. They are then said to be in an *incandescent* condition. Like heat, light is a form of energy, and incandescence is due to a transformation of some of the heat into light.

Gases can be heated to incandescence, and the colors of the light they then give out are characteristic of the various substances. Each gaseous compound yields its own color, unless when heated to incandescence it is decomposed, in which event it gives the colors of its decomposition products.



FIG. 35. — A form of tube in which gases are electrically heated to incandescence.

To obtain the characteristic colors of gases, a glass tube provided with metal electrodes (see Fig. 35) is first filled with the gas. Then most of the gas is pumped out and the tube is sealed by melting the glass. On passing the electric discharge (spark) from an induction coil through the gas from

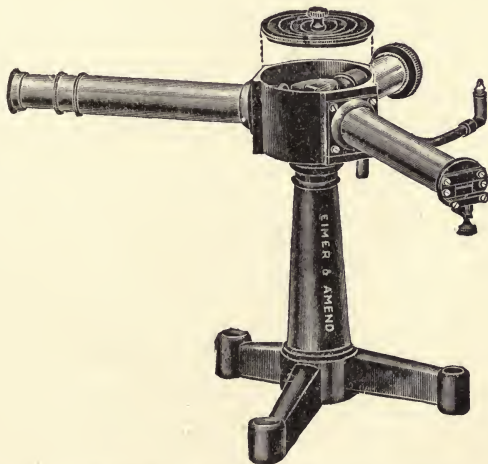


FIG. 36. — *Bunsen and Kirchhoff's Spectroscope.* An instrument used in the analysis of light.

electrode to electrode the characteristic light appears. The color of the light may be analyzed by means of an instrument called a spectroscope.

It was by the color of its light that the element helium was

discovered in the sun's atmosphere many years before it was found upon our planet; and it was from observations of light color that astronomers inferred that the tail of Halley's comet (visible in 1910) contained cyanogen gas (C_2N_2). Incandescent sodium vapor emits yellow light; potassium, violet; calcium, red; barium and copper, green, etc.; and most compounds of these metals when heated in a Bunsen flame impart to it these characteristic colors.

Experiment 37.*

Materials:

Small portions of the chlorides of sodium, potassium, calcium, strontium, and barium.

Platinum wires sealed in glass handles and carefully cleaned by alternate heating in Bunsen flame and dipping in pure concentrated hydrochloric acid until they do not color the flame.

Heat a clean platinum wire and dip it while hot into one of the salts, then bring again into the Bunsen flame and note the color imparted to it. Repeat with the other salts, using a thoroughly clean wire in each instance.

In practical illumination, however, the incandescence of solids is of much more importance than that of gases. The color of the light emitted by an incandescent solid depends not only on what substance the solid is, but also on the temperature to which it is heated. As the temperature of any solid is gradually raised, red light is first emitted, then the other colors of the rainbow are successively combined with the red until finally white light (which is composed of all the rainbow colors) is given out. The terms commonly used to distinguish high temperatures are said to correspond roughly to the following points on the Centigrade and Fahrenheit scales:

Incipient red heat	525° C. or 1000° F.
Dull red heat	700° C. or 1300° F.
Bright red heat	950° C. or 1750° F.
Yellow heat	1100° C. or 2000° F.
White heat	1500° C. or 2700° F.

Substances which radiate heat badly are more readily heated to high temperatures than good heat radiators. This fact is taken advantage of in "gas mantle" lighting (see p. 78).

Experiment 38.

Materials:

Candle.

Kerosene lamp.

Porcelain dish or piece of broken porcelain.

Hold a cold piece of porcelain in the flame of (1) a candle, (2) a kerosene lamp, (3) a luminous gas flame.

Candles and Lamps

In the more primitive methods of lighting — the candle, the gas light, and the oil lamp — the light is given off by the particles of *carbon* which are formed by the decomposition of some of the hydrocarbon gases of the flame. For the heat of the flame not only changes the liquid oil or the solid candle into gases, but decomposes these gases into simpler constituents, one of which is carbon. *Lampblack* is manufactured by cooling the luminous flame of pine knots, crude petroleum, or natural gas, by means of a metal plate or revolving drum, or by burning such substances in a limited draft of air and conducting the smoke into settling chambers. Where such flames are used for lighting purposes the supply of air must be sufficient to cause the carbon to burn completely in the outer layers of the flame. One great advantage of a lamp over an open flame is that the chimney promotes an upward draft of air around the flame and thus permits the fuel to be supplied to the flame at a rate which would cause smoking in an open flame. As air is supplied more rapidly to the flame the fuel gases can also be more rapidly supplied. The result is a brighter, more intense light. It is possible, however, as every one knows, to supply fuel too rapidly to a lamp flame — by turning up too much

of the wick. This causes smoking in the lamp, with consequent deposition of soot on the chimney.

Candles were formerly made of tallow. The materials now commonly used for the cheaper kinds of candles are (1) *paraffin* and (2) a mixture of solid acids made from animal or vegetable fats and known commercially as "*stearin*." *Wax* and *spermaceti* candles are more expensive. The wax most used is beeswax bleached by sunlight; spermaceti is a wax obtained from the sperm whale. Mixtures of these various materials are sometimes used, — spermaceti and stearin, etc.

The earliest **lamps** burned vegetable and animal fatty oils, such as olive oil, lard oil, and whale oil. Lamps for petroleum oils were first made about 1853, and after the discovery of petroleum in Pennsylvania (1859) they quickly replaced the older forms. To-day *kerosene* is the universal lamp fuel in America. Its one disadvantage, as compared with the fatty oils previously used, lies in the possibility of explosions. Much ingenuity has been expended upon the construction of lamps, and the best types now on the market can be used with little risk, provided they are kept in good condition. Explosions can only occur when the bowl of the lamp contains a mixture of oil vapor and air in explosive proportions, and when that mixture is ignited. Ignition of the mixture may occur either through the wick being turned down so far that the lighted portion comes in contact with the gas in the bowl, or through a portion of the explosive mixture reaching the flame, or *vice versa*.

The danger of explosion may be lessened by (1) keeping the lamp clean — free from charred wick, oil, and dirt of all kinds; (2) keeping the bowl well filled, so as to lessen the space available for the accumulation of explosive gas; (3) using only a loosely plaited, soft, long-staple cotton wick, and soaking it in oil before lighting it the first time; (4) avoiding moving the lamp, and (in case it must be moved) carrying

it steadily so as not to shake up the oil; (5) putting out the light by means of an extinguisher, or, if the lamp be not provided with one, turning down the wick until the flame flickers, and then blowing a sharp puff of breath across the top of the chimney, but *not down* it.

Lamps with side fillers should not be purchased. If they are in use, the side fillers should be kept well closed. Of course, oil should never be poured into the bowl of a lighted lamp. Lamps with the wick tube well extended down into the bowl, or prolonged into a wire-gauze wick mantle, are safer than those without such an appliance. Lamps with metal bowls are much safer than those with glass bowls. It is only rarely that a glass bowl is shattered by an explosion, but the alarm caused by the explosion is apt to result in the lamp being dropped, in which case the glass bowl is apt to be broken and the oil ignited. Wicks should be long enough to trail on the bottom of the bowl for about two inches. When this two inches is burned off, the wick should be renewed.

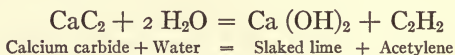
Gas Lights

The older methods of gas lighting depend on the same principle as the candle and kerosene lights. Carbon is liberated within the flame and heated to incandescence. The amount of light obtained depends on (1) the number of carbon particles liberated and (2) the temperature to which they are heated. Coal gas and gasoline gas (see p. 70) contain sufficient of the so-called higher hydrocarbons — those containing a higher proportion of carbon than does methane — to give luminous flames. So also do "oil" gas and acetylene gas.

Oil gas is made from certain heavy oils; for instance, some of the heavier petroleum products. The oils are vaporized by heating and the vapors then subjected to a still higher temperature (1800° F.). The heavy molecules of the oils

are thus decomposed into the smaller molecules of substances which remain gaseous at ordinary temperatures. The process is known technically as "cracking." Oil gas is often compressed into cylinders for transportation. It has been and is still much used for lighting railway cars. It requires a special form of burner.

Acetylene gas differs from other illuminating gases in consisting, not of a mixture, but of a single chemical compound, C_2H_2 . It is formed by the action of water on calcium carbide, CaC_2 , a substance made in the electric furnace from lime and coke. The reaction occurring in an acetylene generator is the following:



It requires a special form of burner, but gives a brilliant white light. Its great disadvantage is its explosiveness. Not only does it form explosive mixtures with air, but in a compressed state it is itself explosive. Although acetylene was at first used exclusively for lighting purposes, it is now used also for cooking and heating.

Natural gas and **water gas** do not burn with sufficiently luminous flames for illuminating purposes. They are, however, rendered suitable for such purposes by adding to them a suitable quantity of the "higher hydrocarbons." This may be added in the form of light petroleum oils, such as benzine, or in the form of oil gas. (See p. 70.)

Gas Mantles

Another device much used to obtain light from flames which otherwise are non-luminous is to suspend in them an incombustible solid capable of converting a part of the heat of the flame into light. The first substance used successfully for this purpose was lime. To obtain light from lime a very high temperature is necessary, as the light obtained

is white. A small quantity of fine lime powder can be heated to the requisite temperature by the heat of an alcohol burner (spirit lamp). To heat a large pencil of lime, however, it is necessary to supply undiluted oxygen to a flame of hydrogen or of one of the commercial illuminating gases. The oxyhydrogen limelight has been much used in projecting lanterns, and we owe the familiar phrase "to stand in the limelight" to the use of such lanterns in the theater. At the present time the limelight has been largely superseded for such purposes by the electric arc light.

The success of the limelight prompted many attempts to find other incombustible and infusible substances which could be used to convert some of the heat of non-luminous flames into light. The "mantle" invented by Auer von Welsbach represents the result of the most successful of these attempts. This mantle consists of a mixture of the oxides of two of the rarer metals — thorium and cerium. The mixture which gives the best results is composed of 1 part of cerium oxide to 99 parts of thorium oxide. A fabric of ramie or mercerized cotton is made into the form of the desired mantle, and is sewed with asbestos thread. This mantle of textile fabric is then soaked in a solution of the nitrates of the metals. When the mantle is "burned off," the organic matter is oxidized and passes off. At the same time the nitrates are decomposed, yielding gases (which pass off) and the *oxides*, which remain as an ash, retaining the form of the original fabric. The flame used to heat these mantles is a Bunsen flame. For the same amount of gas burned these incandescent burners give 6 to 8 times as much light as the best of the old flat-flame burners, and 5 to 6 times as much light as the round flame (Argand) burners, which depended for their luminosity on the incandescence of liberated carbon.

Electric Lighting

There are two processes of electric lighting, viz. the arc and the incandescent electric light. As the former is used only for lighting streets and large buildings it need not be considered here.

In the most common forms of **incandescent electric light** a filament of *carbon* or a wire of some metal, such as *tungsten* or *tantalum*, is heated to incandescence by means of an electric current. As the filament or wire is enclosed in a glass bulb from which the air has been pumped out, no combustion occurs. The light and heat produced come directly from the electric energy of the current. Incandescent electric lights, therefore, neither use up the oxygen of the house air nor give off any products of combustion nor any leakage products to contaminate the air.

Electric lights are more conveniently lighted and extinguished, and are less dangerous than any of the other forms of light. They require less attention than incandescent gas lights and much less than lamps or candles.

Filament lamps, particularly those of carbon, deteriorate in use. Some of the material of the filament vaporizes and condenses on the inner surface of the glass. This both darkens the glass and weakens the filament. The "burning-out" of lamps is due to the breaking of the filament. It is usually economical to discard a lamp before the filament becomes thin enough to break, because, as the filament deteriorates, the light-giving power of the lamp is greatly diminished. When the light becomes reddish in color, the lamp should be replaced by a new one.

The metallic filament lamps commonly made at the present time use only about one third the current used by carbon lamps of the same *candle power*, that is to say, of the same light-giving power. The earlier tungsten filaments were very fragile, and the lamps had to be handled much more

carefully than carbon lamps. But means have been found of making stronger tungsten filaments, and the best modern ones are sufficiently strong for most purposes. Metallic filaments are stronger when hot than when cold. In dusting or cleaning lamps of this type the current should be turned on during the operation.

Carbon filaments and tungsten filaments last about the same length of time. They average about 1000 hours of actual lighting, or about one year's ordinary household service.

For discussion of the physical properties of light with special reference to the household the reader is referred to pages 246-273 of Lynde's "Physics of the Household" (New York, 1914).

CHAPTER XIV

ACIDS AND SALTS

THE following experiments are designed to show what common characteristics the substances called **acids** have, and to illustrate the relations existing among *acids*, *metals*, and the substances called *salts*.

Experiment 39.

Materials :

Tartaric acid, a few crystals.

Citric acid, a few crystals.

Magnesium ribbon, 6 or 8 pieces, $\frac{1}{2}$ inch long.

Copper foil, 2 pieces, $\frac{1}{2}$ inch \times $\frac{1}{4}$ inch.

Zinc foil, half a dozen pieces, 1 inch \times $\frac{1}{2}$ inch.

1. Label six test tubes and fill them with distilled water. Into them put respectively :

- (1) One or two drops concentrated sulphuric acid.
- (2) One or two drops concentrated hydrochloric acid.
- (3) Five to ten drops reagent acetic acid.
- (4) A few crystals tartaric acid.
- (5) A few crystals citric acid.
- (6) Nothing.

2. Shake each tube to mix the contents. Use them for the following experiments :

(a) Taste each. What similarity of taste do you observe in the tubes to which acid was added?

(b) Test each with blue litmus paper.

(c) Pour out a small portion of each into another test tube and add a piece of magnesium ribbon. Describe and explain what occurs. What three characteristics are common to the acids tested?

Experiment 40.

Materials :

Acid solutions prepared for Experiment 39.

Copper foil, 2 pieces, $\frac{1}{2}$ inch \times $\frac{1}{4}$ inch.

Zinc foil, 4 pieces, 1 inch \times $\frac{1}{2}$ inch.

Iron fillings.

To what class of elements do the four substances, magnesium, zinc, iron, and copper, of which you have specimens, belong? What properties are common to the four?

To discover whether zinc and iron are acted upon by acids as the magnesium was, place two portions of each in separate test tubes and add a little of any two of the acid solutions prepared for Experiment 39.

Test copper in the same way. Also heat concentrated hydrochloric acid till it just begins to boil, remove from flame, and when boiling ceases, add a piece of copper foil.

From your experiments infer whether *every* acid acts on *every* metal.

Experiment 41.

Materials :

Magnesium ribbon in pieces of about 0.25 gram.

Zinc foil, 1 inch \times $\frac{1}{2}$ inch.

To discover what products are formed by the action of acids on metals make the following experiments :

(a) Place a piece of magnesium ribbon in a test tube and pour in enough dilute sulphuric acid to cover it. Keep the mouth of the tube covered with the thumb for a minute or two; then, bringing the flame of a burner or match to the mouth of the tube, remove the thumb. If no effect is noted, keep the tube closed for a longer time and then apply the flame again. Add a little more magnesium and set the tube aside for Experiment (d).

(b) Treat magnesium with dilute hydrochloric acid, testing the gas evolved as in (a).

(c) Treat zinc with dilute sulphuric or dilute hydrochloric acid and test the gas evolved as in (a).

(d) Filter off any magnesium left undissolved in (a), collecting the filtrate (liquid which runs through the filter) in a dish. Evaporate this filtrate to dryness under the hood. Examine what remains in the dish.

What gas is produced by the action of an acid on a metal? Is this gas an element? From which of the reagents (substances entering into the chemical change) is this gas derived? Can it be from the metal? From the water? Recall experiment with magnesium and water without acid. What element is common to all acids?

Experiment 42.*

Materials :

Sodium in small pieces under oil.

Alcohol.

Ether.

Apparatus :

Forceps to handle the sodium.

Filter paper.

(Where this experiment is made for demonstration purposes the use of a filter pump is recommended.)

In an evaporating dish under the hood place a little concentrated hydrochloric acid. Cut sodium into pieces smaller than a pea, dry them with filter paper, and add one by one to the hydrochloric acid. What gas is given off? (See Expt. 41.) Note what forms in the acid. Filter, wash with alcohol, then with ether, allow to dry, and taste. What familiar substance is the product of the action of hydrochloric acid on sodium? This substance lends its name to the class of solid substances produced by the interaction of metals and acids.

There is a large class of compounds of hydrogen having the following characteristics in common :

- (1) They taste sour.
- (2) Their aqueous solutions turn blue litmus¹ red.
- (3) They react with many metals, setting hydrogen free.

Compounds of this class are known as acids. A few of the acids contain only one other element combined with their hydrogen. Thus, *hydrochloric acid* (called also *muratic acid*) is simply *hydrogen chloride*, HCl; and *hydrofluoric acid*, simply *hydrogen fluoride*, HF.

The majority contain some oxygen. Thus, *sulphuric acid*, H₂SO₄, contains hydrogen, sulphur, and oxygen; *nitric acid*, HNO₃, contains hydrogen, nitrogen, and oxygen. The **organic acids**, of which there are a great many, always contain carbon, hydrogen, and oxygen. The sour taste of fruits

¹ Litmus is a coloring matter derived from lichens found on trees and cliffs on the sea coasts of Europe.

is due to organic acids. The chief acid of grapes is *tartaric*, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$; of apples, pears, and mountain ash berries, *malic*, $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$; of lemons, oranges, gooseberries, cranberries, and currants, *citric*, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$. Vinegar owes its sourness to *acetic acid*, $\text{HC}_2\text{H}_3\text{O}_2$. Sour milk contains *lactic acid*, $\text{HC}_3\text{H}_5\text{O}_3$, and rancid butter, *butyric acid*, $\text{HC}_4\text{H}_7\text{O}_2$.

Salts

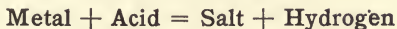
Whenever an acid acts upon a metal, not only is hydrogen set free, but there is produced also a compound belonging to the class known as *salts*. In the majority of cases, if water is present, the salt is left in solution in the water. Thus:

Sodium with hydrochloric acid yields hydrogen and *common salt* (*sodium chloride*).

Zinc with sulphuric acid yield hydrogen and *zinc sulphate*.

Magnesium with acetic acid yields hydrogen and *magnesium acetate*.

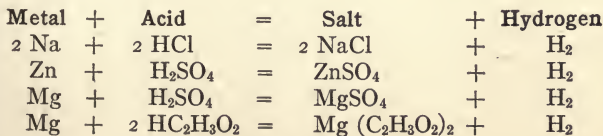
In general terms, then, we may write:



The salt is composed of the metal and the elements of the acid other than the hydrogen set free.

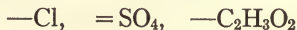
Thus, common salt is a compound of sodium with the chlorine of the hydrochloric acid; zinc sulphate, a compound of zinc with the sulphur and oxygen of the sulphuric acid; and magnesium acetate a compound of magnesium with the carbon, oxygen, and three fourths of the hydrogen of acetic acid.

This may perhaps be made clearer by writing the equations for the above reactions:



Acid Radicles

The common constituent of the acid and salt — the Cl, the SO_4 , and the $\text{C}_2\text{H}_3\text{O}_2$ — is known as the **acid radicle**.¹ It does not exist as a separate substance, but is present in the acid and all its salts. Thus, the acid may be regarded as a compound of the radicle with hydrogen, and the salts as compounds of the radicle with metals. The formulas of radicles customarily include one or more dashes representing the bonds that join the radicles to the hydrogen or metal. Thus:



Definitions of Acid and Salt

An acid may be defined as a substance containing hydrogen, replaceable by a metal, and a salt as a compound derived from an acid by the replacement of hydrogen by a metal.

Nomenclature of Salts

It will be noted that, as a rule, the name of the salt is obtained from that of the acid by substituting the suffix *-ate* for the suffix *-ic*. Thus, the salts of *nitric acid* are *nitrates*, those of *acetic acid*, *acetates*, etc. An important exception is *hydrochloric acid*, whose salts, being compounds of metals and chlorine, are called *chlorides*. Thus, NaCl , Sodium chloride; FeCl_3 , Iron chloride; etc.

Notation

The formulas of acids and salts are always so written as to indicate clearly what acid radicle they contain. For example, the formulas of all nitrates have the nitrate radical, $-\text{NO}_3$. We therefore write the formula of calcium nitrate

¹ Also spelled *radical*.

$\text{Ca}(\text{NO}_3)_2$, rather than CaN_2O_6 ; and that of aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$, rather than $\text{Al}_2\text{S}_3\text{O}_{12}$. For the same reason, in writing the formulas of the organic acids, the replaceable hydrogen atoms are written separately from the hydrogen atoms which form a part of the radicles. Thus, tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, not $\text{H}_6\text{C}_4\text{O}_6$; and acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, not $\text{H}_4\text{C}_2\text{O}_2$.

Valence

When sodium or potassium or silver replaces the hydrogen of an acid, one atom of the metal is regarded as having replaced each atom of hydrogen driven out of the molecule. Thus nitric acid, HNO_3 , yields the salts NaNO_3 , KNO_3 , and AgNO_3 ; sulphuric acid, H_2SO_4 , the salts Na_2SO_4 , K_2SO_4 , and Ag_2SO_4 ; and phosphoric acid, H_3PO_4 , the salts Na_3PO_4 , K_3PO_4 , and Ag_3PO_4 . But the magnesium and calcium atoms are regarded as having each the power of replacing *two* atoms of hydrogen. We have therefore for the nitrates of these metals the formulas $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$; for the sulphates MgSO_4 and CaSO_4 ; and for the phosphates $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2$. In the magnesium nitrate the atom of magnesium has replaced the hydrogen atoms in two molecules of the acid; in the sulphate it has replaced the two atoms of the sulphuric acid molecule, H_2SO_4 ; in the phosphate three atoms of magnesium have replaced the six atoms of hydrogen in two molecules of phosphoric acid.

The aluminium atom replaces *three* atoms of hydrogen. The formulas of aluminium nitrate, sulphate, and phosphate are, therefore, $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, and AlPO_4 .

The valence of a metal is the number of atoms of hydrogen which its atom will replace.

Thus, *sodium, potassium, and silver* have a valence of *one*. These metals are said to be *univalent*.

Magnesium and calcium have a valence of *two*. They are, therefore, called *bivalent* metals.

Aluminium has a valence of *three*. It is *trivalent*.

Some metals have one valence in one set of compounds and another valence in another set. Thus, iron in ferrous oxide, FeO , ferrous chloride, FeCl_2 , and ferrous sulphate, FeSO_4 , is bivalent; but in ferric oxide, Fe_2O_3 , ferric chloride, FeCl_3 , and ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, it is trivalent. Mercury in mercurous chloride (calomel), HgCl , is univalent; in mercuric chloride (corrosive sublimate), HgCl_2 , it is bivalent.

The term valence is also used with reference to the non-metallic elements. Thus *oxygen* is said to be *bivalent* because its atom combines with two atoms of hydrogen, forming H_2O ; and *chlorine* is *univalent* in many of its compounds, such as HCl and its salts, KCl , NaCl , CaCl_2 , etc.

The acid radicles, $-\text{Cl}$, $-\text{NO}_3$, and $-\text{C}_2\text{H}_3\text{O}_2$, may also be said to be univalent; $=\text{SO}_4$, $=\text{CO}_3$, $=\text{C}_2\text{O}_4$, etc. to be bivalent; and $\equiv\text{PO}_4$, to be trivalent.

Acid Salts

Acids whose molecules have more than one atom of replaceable hydrogen may form compounds in which only a part of the replaceable hydrogen is actually replaced by a metal. Thus if half the hydrogen of sulphuric acid is replaced by sodium, we have NaHSO_4 ; when one third of the hydrogen of phosphoric acid is replaced by potassium, we have KH_2PO_4 ; and when two thirds of the hydrogen of phosphoric acid is replaced by potassium, we have K_2HPO_4 .

These compounds come within our definition of salts because they are formed from acids by replacement of hydrogen by metals. But they also come within our definition of *acids* because they contain *hydrogen replaceable by metals*. They are therefore called *acid salts*. Among the important acid salts we have:

Acid sodium carbonate, more commonly called sodium bicarbonate, or baking soda, NaHCO_3 .

Acid sodium sulphate or sodium bisulphate, NaHSO_4 .

Acid potassium sulphate or potassium bisulphate, KHSO_4 .

Acid potassium oxalate, potassium binoxalate, "salt of sorrel" or "salt of lemons," KHC_2O_4 .

Acid potassium tartrate, potassium bitartrate or "cream of tartar," $\text{KHC}_4\text{H}_4\text{O}_6$.

Disodium phosphate, Na_2HPO_4 . This is the most common phosphate of sodium and is often called simply sodium phosphate.

Monocalcium phosphate, acid phosphate of lime, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or $\text{CaH}_4(\text{PO}_4)_2$.

EXERCISES

1. Write the formulas and names of the acids corresponding to the salts whose formulas follow :

- | | | | |
|---------------------|-------------------------------|-----------------------------------|----------------------|
| (1) NaNO_3 | (2) KNO_2 | (3) MgSO_3 | (4) MgSO_4 |
| (5) HgCl_2 | (6) HgCl | (7) FeCl_2 | (8) FeCl_3 |
| (9) AgCl | (10) Ag_2SO_4 | (11) $\text{Al}_2(\text{SO}_4)_3$ | (12) AlPO_4 |

2. Give the valences of the metals in Exercise 1.

3. Write the names of :

- (1) The sodium salt of nitric acid.
- (2) The calcium salt of sulphuric acid.
- (3) The silver salt of hydrochloric acid.
- (4) The magnesium salt of malic acid.
- (5) The potassium salt of nitrous acid.
- (6) The sodium salt of carbonic acid.
- (7) The two iron salts of hydrochloric acid.
- (8) The calcium salt of sulphurous acid.
- (9) The two iron salts of sulphuric acid.
- (10) The two mercury salts of hydrochloric acid.

4. Write the formulas of the salts of Exercise 3.

5. Write the names of the compounds represented by the following formulas :

- | | | | |
|--------------------------------|----------------------------------|---------------------------------|---|
| (1) H_2SO_4 | (2) HCl | (3) HNO_3 | (4) $\text{HC}_2\text{H}_3\text{O}_2$ |
| (5) CaSO_4 | (6) $\text{Fe}_2(\text{SO}_4)_3$ | (7) Ag_2SO_4 | (8) HgNO_3 |
| (9) $\text{Hg}(\text{NO}_3)_2$ | (10) AuCl_3 | (11) FeSO_4 | (12) KI |
| (13) PbS | (14) PbSO_4 | (15) Na_2SO_3 | (16) KNO_3 |
| (17) KNO_2 | (18) $\text{Mg}(\text{NO}_2)_2$ | (19) $\text{Mg}(\text{NO}_3)_2$ | (20) $\text{CaC}_4\text{H}_4\text{O}_5$ |

6. Write formulas of :

- | | |
|------------------------|----------------------------|
| (1) Oxalic acid | (2) Sodium oxalate |
| (3) Calcium oxalate | (4) Hydrochloric acid |
| (5) Silver chloride | (6) Magnesium chloride |
| (7) Nitric acid | (8) Potassium nitrate |
| (9) Calcium nitrate | (10) Acetic acid |
| (11) Magnesium acetate | (12) Sodium acetate |
| (13) Sulphuric acid | (14) Sodium sulphate |
| (15) Ferrous sulphate | (16) Potassium bicarbonate |

CHAPTER XV

ALKALIES

CONTRASTED with acids in their effects upon litmus are the alkalis.

Experiment 43.

Materials :

Salt	Baking soda	Lemon, slice
Sugar	Washing soda	Apple, slice
Vinegar	Cream of tartar	Slaked lime
Alum	Ammonia water	Saltpeter
Borax	Epsom salt	Ferric chloride

Taste each of the above-named materials and note which of them are sour. Dissolve the solids in water. Squeeze out the juice of the lemon and apple. Test all the liquids thus obtained with red and with blue litmus paper. Record results in tabular form as follows :

TASTE		REACTION TO LITMUS		
Sour	Not Sour	Acid	Alkaline	Neutral
Lemon, etc.	Salt, etc.			

Alkalies

Some *salts* affect litmus in the same way as acids — turning *blue to red*. These are said to have an *acid reaction*. Examples are alum, zinc sulphate, and cream of tartar. A considerable number have no action on either red or blue litmus. These are said to have a *neutral* reaction. Salt, saltpeter, and Epsom salt are neutral. Still others have an effect directly the opposite of that of the acids; that is, they *turn red litmus blue*. Such are said to have an **alkaline** re-

action. Examples are baking soda (sodium bicarbonate), washing soda (sodium carbonate), and borax (sodium borate).

Experiment 44.

Materials:

Sodium under oil, cut in pieces large enough to yield a test tube of gas in the experiment. (Cubes of 3 mm. or $\frac{1}{8}$ inch are suitable for a 30 cc. test tube.)

Lead foil (tea lead) or oiled paper in pieces $\frac{3}{4}$ inch square.

Caustic soda sticks $\frac{1}{4}$ inch long.

Red litmus paper.

Apparatus:

Forceps.

Dish.

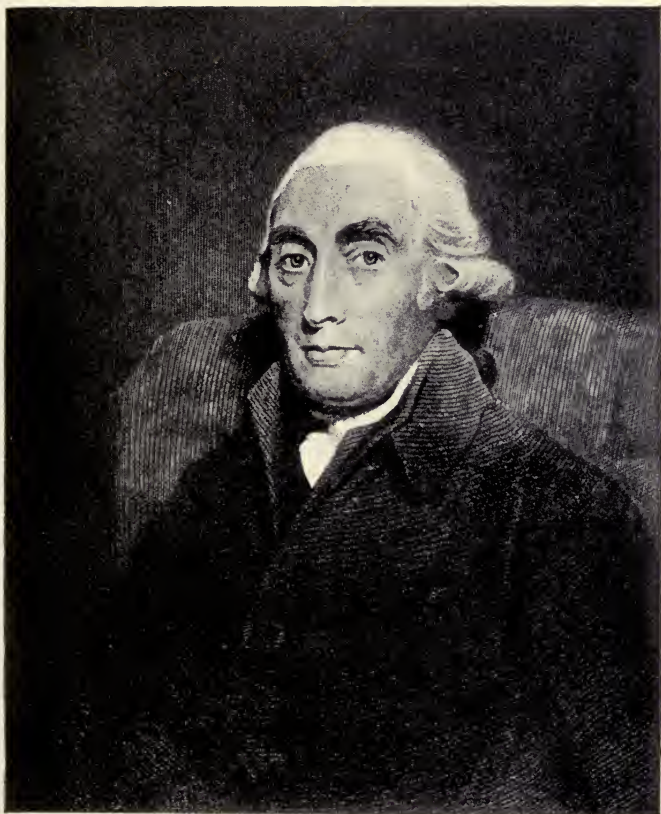
Handle the sodium with forceps, being careful not to allow it to touch the hands or clothing. Examine a freshly cut surface of sodium and compare it with the lead and aluminium. To what class do all three of these substances belong? Lay the sodium on filter paper for a few seconds to free it from oil, then wrap it in the lead foil (or oiled paper) leaving a small opening at one end. Fill a test tube with water, cover it with the thumb, and invert it in a dish of water. Seizing the wrapped piece of sodium, open end up, with the forceps, bring it quickly underneath the mouth of the inverted test tube. As the water enters the wrapping and comes in contact with the sodium, gas is evolved and collects in the test tube, displacing the water. When the action ceases, again cover the mouth of the test tube and invert the tube. Remove the thumb and *immediately* apply a lighted match or splint to the mouth of the test tube. What gas do you infer to have been formed by the reaction of the sodium and water?

Examine the liquid left in the dish, comparing it with the water originally used. Note its feel and its effect on red litmus paper.

Dissolve the piece of caustic soda in half a test tube of water. Compare this solution with the liquid in the dish.

To determine what elements caustic soda contains, answer the following questions and make Experiment 45.

Can the gas collected in the present experiment have been produced by decomposition of the sodium? Why? Where must the sodium be at the end of the experiment? What are the elements of water? Which of these two elements must be a constituent of the caustic soda? What two elements does caustic



JOSEPH BLACK.—1728-1799.

A Scottish chemist and physicist, noted for his researches upon heat and for his discovery of carbon dioxide, which he called "fixed air." Black explained the difference between the mild and the caustic alkalies, the relation of lime to limestone, and the distinction between lime and magnesia.

soda therefore contain? Is it possible it may also contain a third element? If so, what?

Experiment 45.

Materials :

Solutions prepared in Experiment 44.

Aluminium foil $\frac{1}{2}$ inch \times $\frac{3}{4}$ inch, two or three pieces.

(a) Put a piece of aluminium foil in a test tube of hot water.

(b) Heat the liquid left in the dish in Experiment 44, and put in a piece of aluminium foil. What difference do you observe in the behavior of this liquid and water?

(c) Heat the strong solution of caustic soda prepared in Experiment 44, drop in aluminium foil, and cover the mouth of the test tube loosely with the thumb for a few moments to allow the evolved gas to collect. Test this gas with a flame, *immediately after removing the thumb*.

What gas is produced by the action of aluminium on caustic soda? Does aluminium act on water under the conditions of these experiments. (See (a).) What element must caustic soda, therefore, contain? Name the elements of caustic soda discovered in this experiment and the preceding one.

The experiments just performed have illustrated the fact that in addition to the alkaline salts there are some other substances which have an alkaline reaction. These are the hydroxides (compounds with oxygen and hydrogen) of the most active metals — sodium hydroxide (caustic soda), potassium hydroxide (caustic potash), and calcium hydroxide (slaked lime, the aqueous solution of which is limewater).

These hydroxides are designated the *strong* or *caustic* alkalies in contradistinction to the salts of alkaline reaction, which are called *weak* or *mild* alkalies — the former being more vigorous than the latter in such actions as characterize alkalies in general; for example, in their effects upon fats, of which we shall learn more later.

Experiment 46.

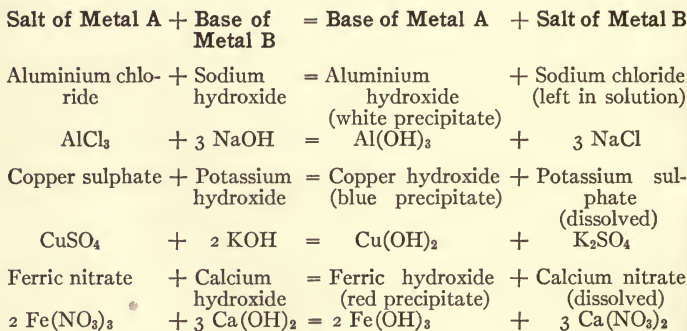
Test solutions of potassium hydroxide and calcium hydroxide with red litmus paper. Give the common names of these two substances.

CHAPTER XVI

BASES AND BASIC OXIDES

THE *hydroxides of metals* are called **bases**. The strong alkalis are therefore bases. These are rather exceptional among bases in being soluble in water. The majority of the bases are insoluble; for example, *ferric hydroxide, cupric hydroxide, aluminium hydroxide*.

The insoluble base of a given metal (*e.g.* aluminium) can be obtained as a precipitate by adding one of the soluble bases (sodium hydroxide or potassium hydroxide) to the solution of a salt of the metal (such as aluminium chloride or sulphate).



Experiment 47.

Materials:

Small portions of the following solids:

- Aluminium nitrate.
- Aluminium sulphate.
- Copper sulphate.
- Ferric nitrate.
- Ferric chloride.

Dissolve the salts in water in separate test tubes, labeling the tubes. Test a portion of each solution with potassium hydroxide solution and another portion of each with sodium hydroxide. Compare the precipitates obtained where the two soluble bases are added to the same salt. Also compare the precipitates obtained on adding the one soluble base to two salts of the same metal. Save the precipitates for use in Experiment 48.

Experiment 48.

Treat a very small portion of one or two of the solutions with calcium hydroxide solution, using a much larger quantity of this solution than of the sodium or potassium hydroxide.

EXERCISE

1. Write verbal equations for the reactions involved in Experiments 47 and 48, underscoring the names of the precipitates.
2. Rewrite the above equations in symbols, underscoring the formulas of the precipitates.

Basic Oxides

Most of the bases on drying or heating are decomposed into *basic oxides* and water. Thus:

Base	=	Basic oxide	+ Water
Cupric hydroxide (blue)	=	Cupric oxide (black)	+ Water
Ferric hydroxide	=	Ferric oxide	+ Water
Magnesium hydroxide	=	Magnesium oxide	+ Water
Calcium hydroxide (slaked lime)	=	Calcium oxide (quicklime)	+ Water

With cupric hydroxide this decomposition occurs even in the presence of water, as is evident from the change of color which occurs when the blue precipitate is heated.

Experiment 49.

Materials :

Copper sulphate solution.

Specimen of cupric oxide.

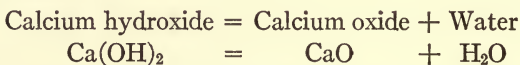
To copper sulphate solution in a test tube add sodium hydroxide

solution. Note the color of the precipitate. What substance is it? Heat to boiling. What change occurs? When this substance is dried, it is found to be identical with that obtained by burning copper in oxygen, viz. cupric oxide, CuO . Compare the color of the heated precipitate with that of a specimen of cupric oxide.

The hydroxides of most metals, however, do not show such a color change when they are converted into oxides by the removal of water from their molecules.

In a few instances the basic oxide in the cold readily recombines with water to form the base. A striking instance is that of calcium oxide (quicklime) which takes up water with evolution of great heat in the familiar process of lime slaking (or slacking).

The reaction :



is thus seen to be a reversible one, running in one direction at high, but in the opposite direction at lower, temperature.

Experiment 50.

Materials :

Quicklime.

Red litmus paper.

Place a small lump of good quicklime (say 10 grams) in a porcelain dish and add as much warm water as the lime will absorb. Allow to stand for a few minutes. What change occurs in the lime? Treat a little of the slaked lime with water in a test tube and test the water with red litmus paper.

Experiment 51.

Materials :

Magnesium ribbon, $\frac{1}{2}$ inch.

Red litmus paper.

Burn a piece of magnesium ribbon. What is the product? Place this product in a dish, add water, and stir for some time. Test the liquid with red litmus paper. Account for the result.

EXERCISE

1. Write equations for the reactions of Experiments 49, 50, and 51.
2. Write equations representing the dehydration of, that is, removal of water from:
 - (1) Cupric hydroxide
 - (2) Ferric hydroxide
 - (3) Ferrous hydroxide
 - (4) Magnesium hydroxide
 - (5) Calcium hydroxide
 - (6) Aluminium hydroxide

CHAPTER XVII

REACTIONS OF ACIDS WITH BASES AND WITH BASIC OXIDES. IONIZATION

Experiment 52.

Put into a clean evaporating dish about 10 cc. ($\frac{1}{3}$ test tube) sodium hydroxide solution and a piece of litmus paper. Slowly add dilute hydrochloric acid, stirring constantly, until the color of the paper is permanently changed. Now add a few drops more of the sodium hydroxide solution, then a few more of the hydrochloric acid solution, noting the effect on the color of the paper.

Leaving the mixture finally just acid, take out the paper, place the dish on a wire gauze over a burner, and evaporate to dryness. Taste the product. What is it? Write an equation for the reaction involved in this experiment.

Experiment 53.

In test tubes place small portions of solutions of (a) sodium hydroxide, (b) potassium hydroxide, (c) calcium hydroxide. Add litmus solution or litmus paper and treat portions of each solution with (1) dilute hydrochloric acid, (2) dilute nitric acid, (3) dilute sulphuric acid. Note the effect on the litmus. What is the effect of adding more of the base? Write equations for the reactions of this experiment.

In the above experiments the acid and base are said to *neutralize* each other. In every case a salt is formed and also water. The formation of water is not evident because the reaction takes place in presence of much water. The formation of the salt could be demonstrated in each instance by driving off the water by evaporation, as was done in Experiment 52.

The action of acids on *insoluble* bases is illustrated in the following experiments.



SVANTE AUGUST ARRHENIUS.—1859.

The Swedish scientist who in 1887 originated the modern theory of ionization of electrolytes.



Experiment 54.

Prepare the hydroxides of magnesium, copper, and iron (ferric hydroxide) as in Experiment 47. Treat one of these precipitated hydroxides with dilute hydrochloric acid, another with dilute nitric acid, and the third with dilute sulphuric acid, shaking each test tube well and allowing time for the reaction to complete itself. How are the insoluble bases affected by acids? What compounds are in solution at the end of the experiments? Write equations for the reactions of the acids on the bases.

Bases, both soluble and insoluble, then, readily react with acids, yielding salts and water. Thus:

Base	+	Acid	=	Salt	+ Water
Sodium hydroxide (caustic soda)	+	Hydrochloric acid	=	Sodium chloride (common salt)	+ Water
Potassium hydroxide (caustic potash)	+	Nitric acid	=	Potassium nitrate (saltpeter)	+ Water
Cupric hydroxide	+	Sulphuric acid	=	Copper sulphate (bluestone)	+ Water
Ferric hydroxide	+	Oxalic acid	=	Ferric oxalate	+ Water
Magnesium hydroxide	+	Sulphuric acid	=	Magnesium sulphate (Epsom salt)	+ Water

If, as in the last three of the above examples, the base is insoluble but the salt soluble, the effect of the acid is to *dissolve* the base (by converting it into salt).

Experiment 55.

Materials:

Quicklime.

Cupric oxide, powder.

Magnesium oxide (magnesia).

Place small portions ($\frac{1}{2}$ gram or less) of the above solids in test tubes. To the quicklime add dilute hydrochloric acid, to the cupric oxide dilute nitric acid, and to the magnesia dilute sulphuric acid. Warm gently.

Experiment 56.

Make cupric oxide by adding sodium hydroxide to boiling copper sulphate solution as in Experiment 49. Acidify with dilute sulphuric acid, and warm.

We see from these experiments that basic oxides, whether made from the hydroxides by heating or from the metals by direct combination with oxygen, react with acids, yielding salts and water. Thus :

Basic oxide	+	Acid	=	Salt	+ Water
Calcium oxide	+	Hydrochloric acid	=	Calcium chloride	+ Water
Cupric oxide	+	Sulphuric acid	=	Copper sulphate	+ Water
Ferric oxide	+	Oxalic acid	=	Ferric oxalate	+ Water
Magnesium oxide	+	Sulphuric acid	=	Magnesium sulphate	+ Water

Whenever the salt formed is soluble in water, the acid dissolves the oxide. This, however, is not simple solution like that of salt or sugar in water. It is solution on account of chemical action producing a soluble product.

EXERCISE

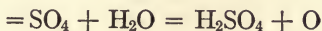
Rewrite the above equations, using symbols.

Ionization

Solutions of acids, bases, and salts in water have a number of characteristics distinguishing them from other solutions, whether those others be aqueous solutions of substances of other classes (such as sugar, alcohol, glycerin, or hydrogen peroxide), or whether they be solutions in other solvents than water.

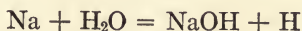
1. Water is practically a non-conductor of electricity. Solutions of so-called "indifferent" substances (alcohol, sugar, hydrogen peroxide, etc.) are also non-conductors. But aqueous solutions of acids, bases, and salts conduct the electric current. In acting as conductors these substances do not remain unchanged as do metallic conductors such as copper wire. On the contrary, they undergo continuous decomposition as the current passes. For this reason

they are called *electrolytic conductors* or more briefly *electrolytes* (from a Greek verb, *luo*, I loose). When an electric current is passed through a solution of hydrochloric acid, for example, *chlorine* is set free at one electrode and *hydrogen* at the other. Again, when the current is passed through sodium chloride solution, *chlorine* is set free at the same electrode as in the case of hydrochloric acid; at the other electrode *sodium* is, no doubt, set free, but it immediately reacts with the water, producing *hydrogen* and *sodium hydroxide*. What we observe at the latter electrode, therefore, is that hydrogen gas is given off and that the water becomes alkaline, due to the production of sodium hydroxide. When a current is passed through an aqueous solution of sulphuric acid, the products obtained are hydrogen at one electrode, oxygen at the other. (See Expt. 16, p. 12.) This is quite consistent with the supposition that the primary products are hydrogen and the sulphuric acid (or *sulphate*) radicle =SO₄, and that the latter, being incapable of independent existence, reacts with water:

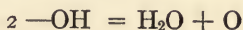


Thus, oxygen is liberated and the sulphuric acid is regenerated. The net result is, therefore, the decomposition of water, and we ordinarily speak of the process as the "electrolysis of water."

The passage of a current through sodium hydroxide solution likewise yields hydrogen and oxygen as final products. The primary products are (a) *sodium*, which reacts with water, liberating hydrogen and regenerating the sodium hydroxide:



(b) the *hydroxyl* radicle, —OH, which is immediately converted into water and oxygen:



2. Reactions between dissolved acids and bases (neutralization) are instantaneous. So, also, are reactions between two salts (precipitation reactions), e.g.:

Silver nitrate + Sodium chloride = *Silver chloride* + Sodium nitrate

Reactions between *non-electrolytes* in solution are usually much slower.

3. All the electrolyte chlorides give the same precipitate (silver chloride) with all silver salts. All sulphates (including sulphuric acid) give the same precipitate (barium sulphate) with all barium salts.

Experiment 57.

Materials:

Solutions of sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminium chloride.

Solutions of silver nitrate and silver sulphate.

Solutions of sodium sulphate, potassium sulphate, magnesium sulphate.

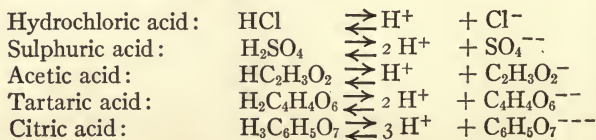
Solutions of barium chloride, barium nitrate, and barium acetate.

Mix a little of each chloride solution with a little of each silver solution (10 experiments in all) and compare the precipitates produced. Also mix dilute hydrochloric acid with a little of each of the silver solutions.

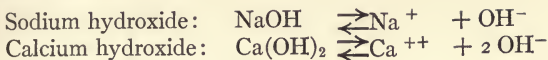
Mix a little of each sulphate solution with a little of each barium solution (9 experiments) and compare the precipitates. Also mix dilute sulphuric acid with a little of each of the barium solutions.

These and other peculiarities of electrolyte solutions are explained by assuming that when an electrolyte dissolves in water, some of its molecules immediately undergo a reversible decomposition into what are called **ions**.

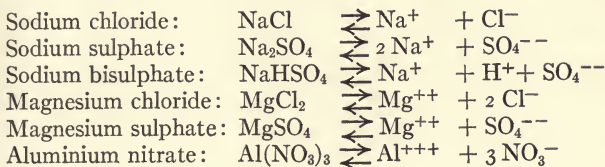
The mode of ionization of a few acids, bases, and salts is illustrated by the following equations:



Ionization of bases :



Ionization of salts :

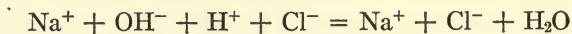


The double arrows, used in place of the usual equality sign, signify that the reaction is a reversible one. There are always present in the solution some un-ionized molecules of the acid, base, or salt. In some instances, *e.g.* acetic acid, most of the molecules are un-ionized; in others, *e.g.* sodium chloride, there are only a few un-ionized molecules. When a solution is diluted (by adding more water), more of the molecules ionize. When the solution is concentrated (by evaporating off some of the water), some of the ions recombine into molecules; when it is evaporated to dryness, all of the ions recombine into molecules.

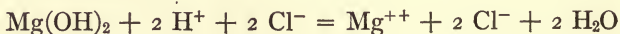
All *acids* yield the *hydrogen ion*, H^+ , as their positive ion (*cation*). The effects of acids on litmus may, therefore, be regarded as an action of the hydrogen ion. When an acid acts on a metal, the hydrogen ions are converted into molecules of hydrogen gas and the molecules of metal are converted into metal ions.

All *bases* yield the *hydroxyl ion*, —OH , as their negative ion (*anion*). The action of bases on litmus or other indicators is, accordingly, a reaction of the hydroxyl ion. The neutralization of an acid by a base involves the combining of the hydrogen ions with the hydroxyl ions to form water molecules. Thus, when hydrochloric acid and sodium hydroxide

solutions are mixed, the hydrogen and hydroxyl ions disappear, but the sodium and chloride ions remain :



When the insoluble base magnesium hydroxide, $\text{Mg}(\text{OH})_2$ is acted upon by hydrochloric acid, the magnesium is converted into ions :



CHAPTER XVIII

METAL TARNISHES

Most metals, when heated in oxygen or air, readily combine with the oxygen. The following are examples of oxides formed from metals in this way :

Magnesium oxide or magnesia, MgO . (See Expt. 51, p. 96.)

Calcium oxide or quicklime, CaO .

Aluminium oxide or alumina, Al_2O_3 .

Cupric oxide (black), CuO .

Magnetic iron oxide (black), Fe_3O_4 .

Sodium peroxide, Na_2O_2 .

In the presence of moisture such combination of metal with oxygen occurs also at ordinary temperatures, though at a much slower rate than when the metal is heated. In case the oxide formed upon the surface adheres closely to the metal, the oxidation soon comes to a stop, because the film of oxide prevents the air coming in contact with any more of the metal. Magnesium, zinc, and aluminium form light-colored tarnishes of this kind, and consequently retain their whitish color, although losing something of their metallic luster. Lead also tarnishes rapidly by oxidation, but the oxide formed is darker in color than the metal itself.

Experiment 58.

Materials:

Magnesium ribbon.

Zinc sheet or rod.

Aluminium.

Lead.

Emery cloth.

Polish a little of each of the metals and compare the freshly polished with the tarnished surface.

Platinum, gold, and tin do not tarnish. Nickel tarnishes very slowly, the tarnish being yellowish.

Silver is not acted upon by oxygen, or by any other constituent of pure air, but takes a black tarnish of silver sulphide, Ag_2S , when exposed to the action of the element sulphur. It is also tarnished in the same way by many compounds of sulphur. Small quantities of sulphur compounds are sometimes present in the air, particularly where coal is burnt or coal gas used and in the neighborhood of smelting works.

Silver is also tarnished by contact with organic materials containing sulphur; for example, vulcanized rubber and the proteins of foods (such as eggs) and of wool. Silverware should not be wrapped in any fabric containing wool nor in bleached or dyed cotton goods in the manufacture of which sulphur may have been used. Soft unbleached cotton goods and tissue paper make suitable wrappings for silver.

In the tarnishing of copper the carbon dioxide present in the air plays a part as well as the oxygen and moisture. The product is a carbonate of copper. This is soluble in dilute acids such as are present in fruits. Bright copper is not acted upon by such acids. A bright copper kettle may therefore be safely used in preserving or other cooking operations, but not a tarnished one. Brass and bronze are *alloys* of copper, *i.e.* materials made by combining copper with other metals — *zinc* for *brass*, *tin* (sometimes together with other metals) for *bronze*. The tarnish of brass and bronze is similar to that of copper.

Removal of Tarnish

The basic oxides which constitute the tarnish of most metals are, of course, soluble in suitable acids. But the use of acids for the removal of tarnish from metals is seldom resorted to. In some instances it would be difficult to find a suitable acid — one that would dissolve the oxide without

attacking the metal. It has also to be remembered that there is usually other dirt to be removed in addition to the tarnish compound and also that the surface of the metal, which has been roughened by the formation of the oxide, must be polished smooth in order that it may appear bright.

The polishing of metals is usually done with a cloth or piece of soft leather, such as chamois, and a fine powder as whiting, rottenstone, or rouge. When polished metals are examined under the microscope, they are found to be covered with a thin film, in which the metal behaves more like a liquid than a solid. The smooth, level film reflects light just as the surface of mercury does. This film is produced by the pressure of the cloth and polishing powder, both of which are softer than the solid metal. The presence of hard particles in the polishing powder, and especially that of *large* hard particles, is to be avoided. Suitable materials for polishing copper, brass, bronze and nickel are rouge, Venetian red, whiting, putty powder, and rottenstone (called also tripoli). For silver and aluminium, which are softer metals, whiting, rouge, or putty powder should be used.

The polishing powder may advantageously be mixed into a paste with an oil or grease, or it may be made up in paste or semi-liquid form with a suitable liquid — either one that will dissolve grease or one that will dissolve the tarnish compound. Ammonia, which dissolves the oxides of copper and nickel, may be used in polishes for these metals and for brass and bronze. Acids, such as oxalic, citric, cream of tartar, lemon juice, buttermilk, and vinegar (or vinegar and salt) are sometimes recommended for silver, copper, and brass. Their efficacy doubtless depends upon their action on the oxide films. When any of these tarnish solvents, or polishes containing them, are used, care must be taken to leave none of the active agents on the metal, for the reason that they would promote the oxidation of the metal.

Experiment 59.

Material :

Copper oxide, powder.

Shake a very little powdered copper oxide with ammonia in a test tube. Allow to settle and note the color of the liquid.

Experiment 60.

Materials :

Copper foil.

Whiting.

Moisten a little whiting with a few drops of ammonia. Dip a rag in this paste and polish both sides of the copper foil. Cut the foil into three pieces. Wash two of these thoroughly. Place one of the washed pieces in a test tube, partly cover with ammonia water, and leave standing for a few minutes, shaking occasionally.

Leave the unwashed piece of foil standing for a few hours. Then compare it with the washed piece. Explain the results.

Among the liquids used in metal polishes on account of their action upon grease are *alkalies*, such as aqueous solutions of soda, ammonia, ammonium carbonate, borax, and soap; and *hydrocarbons*, such as kerosene (coal oil), gasoline, benzine, and turpentine. Sometimes both a hydrocarbon and an alkali is used, *e.g.* soft soap and turpentine.¹ A mixture of whiting with alcohol and a few drops of ammonia makes a good polish for aluminium as well as for silver.

Brass may be prevented from tarnishing by covering with a lacquer which prevents the air coming in contact with the metal. Lacquers are solutions of shellac in alcohol (1 to 4 ounces shellac to 1 pint of alcohol). To the simple lacquer various red and yellow coloring matters are added. The metal to be lacquered is scrupulously cleaned, and the lacquer is very evenly applied with a camel's-hair brush or by dipping, and is allowed to dry without being touched.

¹ Many recipes for polishing powders may be found in such books as "The Scientific American Cyclopaedia of Receipts, Notes, and Queries" or Seaman's "Expert Cleaner."

CHAPTER XIX

IRON RUST

IRON is at the present day the most useful of all the metals. So large a part does it play in modern life that ours has been called the "Iron Age." By modifying the processes by which iron ores (which are chiefly oxides of iron) are converted into the commercial forms of the metal we obtain products differing considerably in strength and hardness and therefore suitable for different uses. We have, for instance, the soft, tough *wrought iron* and *mild steel* used in wire, horseshoes, andirons, and all other products shaped on the anvil; the *hard steel*, capable of being tempered to various degrees of hardness and elasticity for use in razors, penknives, scissors, tableknives, and watch springs, and the brittle *cast iron*, more easily melted than the other kinds of iron and used in making objects that have to be molded to a definite shape, for example, the frames and treadles of sewing machines.

As compared with most of the common metals, iron has one serious defect, the consequences of which have always to be carefully guarded against. It tarnishes readily, and the tarnish, called *rust*, does not adhere closely to the surface of the metal, as do the tarnishes of magnesium, aluminium, zinc, and copper. Iron rust scales off and thus continually exposes new surface of metal to the corroding effect of the air. The prevention of the corrosion of iron and steel goods is, therefore, an important economic problem.

Iron rust is a red, powdery substance, consisting of ferric

oxide, Fe_2O_3 , or, strictly speaking, of a substance intermediate in composition between ferric oxide and ferric hydroxide, $\text{Fe}(\text{OH})_3$. It is therefore a substance similar to the oxides and hydroxides of other metals.

There are two general methods of preventing rusting of iron. One is to *keep the metal dry and brightly polished*. A rust-free surface rusts much less readily than one already spotted, and a polished surface is less liable to rust than a rough one. Water and carbon dioxide promote rust formation. Indeed, rust cannot form in absence of water. If, therefore, the iron is brightly polished and kept dry, it will not corrode. This is the method commonly used to keep household cutlery bright. The more promptly knives and forks are scoured and dried after use, the less labor will be involved in keeping them in prime condition.

The *second* method of preventing rusting is to cover the iron with some material which will protect it from the air. A great variety of coverings are used for different purposes. A covering of *oil* or of vaseline is sufficient for some purposes, *e.g.* for tools, knives, etc., which are to be laid away for some time. Melted paraffin wax may be used for the same purpose as well as for smoothing irons before they are put away on ironing day.

Stoves and stovepipes which are to be temporarily stored may also be oiled. But it is perhaps better to varnish them with a thin solution of asphalt in turpentine, which will burn off when they are put into use again. Common stove polish is made of *graphite*, a mineral form of the element carbon, which burns very slowly, and without odor. Other names for graphite are *plumbago* and *black lead*.¹

¹The word "graphite" is derived from the Greek *grapho*, I write, and the word "plumbago" from the Latin, *plumbum*, lead. All three names — graphite, plumbago, and black lead — are derived from the circumstance that this form of carbon is so soft that, like lead, it will mark on paper. "Lead" pencils are made of a mixture of graphite with clay.

More permanent coatings for iron are *paint, japan, enamel*, and *less corrodible metals*. **Paint** is used on the structural steel of bridges, as well as on wagons, agricultural machinery, and other outdoor hardware; also on water-pipes and some other indoor articles. Carriage hardware, tea trays, the handles of scissors, and many other small articles are **japanned**, *i.e.* covered with a lacquer, which is then baked on, polished, and varnished.

Enamelware is now very commonly used in the kitchen. This is iron covered with a glaze similar to that used on porcelain and chinaware. It is put on in a molten condition, and solidifies on cooling. Enamelware is particularly satisfactory for culinary vessels, as it resists the action of the acids contained in foods, as well as that of the oxygen of the air. In using enamelware care should be taken not to crack the enamel by shock or by too rapid heating or cooling of the dry vessel.

Among the *metals* used to cover iron to protect it from the air are :

(a) **Zinc**. Iron covered with zinc is said to be “galvanized.” The word is derived from the name of Galvani, the discoverer of the electric current, but the modern processes of galvanizing iron consist simply in immersing the cleaned iron in molten zinc, passing the sheet between rollers, and allowing to cool.

(b) **Tin**. Ordinary tinware is made of “tinplate,” which is sheet iron covered with tin by a process similar to that used with zinc.

(c) **Nickel**. Iron is sometimes nickel-plated, the nickel being welded to the iron.

The magnetic oxide of iron, Fe_3O_4 , formed by the action of atmospheric oxygen, or by that of very hot steam, on hot iron, adheres closely to the iron. In this respect it differs from rust, but it resembles the oxides of other metals. This fact has been utilized to prevent rusting. The iron is heated

in a furnace and superheated steam is blown in upon it. Iron with a blue finish has been so treated.

When once the covering layer is broken at a single point, tinware and nickelware will rust more rapidly than iron which has not received a protective coating. The same is true of iron covered with magnetic oxide, and probably also of enamelware. Galvanized iron, however, when similarly injured, does not corrode as fast as unprotected iron. The zinc appears to exert a protective action, even upon the exposed parts of the iron. This is one reason why galvanized iron is preferred to tinware for outdoor use. On the other hand, zinc is acted upon by vegetable acids. Hence galvanized iron is not suitable for culinary vessels or for receptacles for soft fruits, milk, or any acid food.

Rust Stains on Fabrics

Linen, cotton, and other textiles not infrequently become soiled with iron rust. Iron-rust stains are sometimes called "iron mold," possibly on account of some confusion with mildew, which is really a mold. Being composed of ferric oxide, which is insoluble in water and in alkalies, such stains are not removed by the ordinary washing processes. Like other basic oxides, however, iron oxide is converted into soluble salts by the action of suitable acids.

Experiment 61.

Materials:

Oxalic acid.

Acid potassium oxalate.

Heat about 10 cc. ($\frac{1}{3}$ test tube) of ferric chloride solution to boiling and add sodium hydroxide solution. What is the precipitate? Write equation for the reaction by which it was produced.

Allow the precipitate to settle, pour off the supernatant liquid, add water, shake, allow to settle, and again pour off. (This is called *washing by decantation*.) Finally add a half test tube of water, shake thoroughly, and divide into five equal portions in test

tubes. To these add respectively: (1) dilute hydrochloric acid, (2) dilute sulphuric acid, (3) acetic acid, (4) oxalic acid, dissolved in hot water, (5) acid potassium oxalate, dissolved in hot water. Which of these acids dissolve the precipitate? Write equations for reactions. (In the last reaction potassium oxalate is formed as well as ferric oxalate.)

The acid chosen for the removal of rust stains from textile fabrics must be one that will do the work quickly and thoroughly but without injury to the textile itself.

Those most commonly employed are *oxalic acid*, $H_2C_2O_4$, and *its acid potassium salt*, KHC_2O_4 . This acid salt is commonly known as "salt of lemon" or "salts of lemon," although actually oxalic acid does not occur in lemons. *Salt of sorrel* is a more appropriate name. The action of this salt is less vigorous — both on the rust and on the fabric — than that of free oxalic acid.

Any of the acids used to remove rust stains may injure the fabric if not thoroughly washed out. As the fabric dries, the acid solution becomes more and more concentrated until it reaches a concentration at which it acts upon the textile fibers and weakens them. This may occur even with the volatile acid, hydrochloric, which may reach the concentration of 20 per cent hydrochloric acid before drying off completely. Goods which have been treated with acid for the removal of rust stains should be washed immediately in pure water, and afterwards in water containing a little ammonia.

CHAPTER XX

STRONG AND WEAK ACIDS AND BASES

Experiment 62.*

Materials :

3 equal pieces of magnesium ribbon, each weighing about 0.04 gram.

Lead foil, *e.g.* tea lead.

3 eudiometer tubes, 50 cc.

3 dishes, *e.g.* glass evaporating dishes.

Stands and clamps.

Normal (or approximately normal) solutions of hydrochloric, acetic, and formic acids.¹

Fill one eudiometer tube with each acid solution, invert it in a dish of the same acid, and clamp it with the mouth a little below the surface of the liquid in the dish. Attach each of the pieces of magnesium ribbon to a piece of lead foil (*e.g.* by passing it through a slit in the latter) so that the magnesium cannot rise in the liquid. Bring the anchored pieces of ribbon quickly beneath the mouths of the eudiometers and compare the rates at which the hydrogen gas collects in the eudiometers.

Experiment 63.

Materials :

The normal acid solutions used in Experiment 62.

3 pieces of marble of about equal size and form.

¹ If the laboratory reagents are on the normal system, the two former can be made by diluting the reagent dilute hydrochloric and acetic acids. A normal solution of formic acid may be made from pure formic acid (specific gravity 1.22) by diluting 37.7 cc. to 1 liter; and from acid of specific gravity 1.06 by diluting 173.6 cc. to 1 liter. Normal acetic acid may be made by diluting 57.1 cc. of glacial acetic acid to 1 liter. Normal hydrochloric acid may be made as follows: Dilute 105 cc. concentrated acid or 165 cc. of acid of specific gravity 1.10 to 1 liter. Compare the solution so obtained with a normal solution of sodium carbonate — 53 grams of the pure, dry salt to 1 liter — by adding to the latter two or three drops of methyl orange solution and running in the acid from a burette until the well-mixed solution is just red. Then dilute the acid solution to such a strength that 10 cc. of it will exactly neutralize 10 cc. of the normal sodium carbonate solution.

Put the three pieces of marble in separate test tubes and pour one acid on each. Compare the rates at which gas (carbon dioxide) is evolved, and also the rates at which the marble is dissolved. Do the three acids arrange themselves in the same order with respect to their activity in dissolving marble as they did with respect to their activity in dissolving magnesium?

Some acids are much more active than others. If we take two quarts of water and dissolve in one enough hydrochloric acid, in the other enough acetic acid, to yield one cubic foot of hydrogen gas by their action on zinc or magnesium, the hydrochloric acid will produce the gas much more rapidly than the acetic, although ultimately the same quantity will be set free from both. Hydrochloric acid also excels acetic in the speed of its action upon metallic oxides (such as magnesia, cupric oxide, etc.) and upon marble.

Compared in these and many other ways, hydrochloric acid is always found to be more active than acetic. For this reason it is designated a *strong* acid, whereas acetic acid is classed as *weak*. The relative strengths of other acids may be similarly compared, and by methods not very different the relative strengths of bases may be compared. The results of such comparison lead to the following classification:

Acids:

Strong: Hydrochloric, Nitric, Sulphuric.

Moderately strong: Oxalic, Tartaric, Citric.

Weak: Acetic, Palmitic, Stearic, Oleic.

Very weak: Carbonic, Boric (or Boracic).

Bases:

Strong: Sodium hydroxide (caustic soda), Potassium hydroxide (caustic potash), Calcium hydroxide (slacked lime — in aqueous solution, limewater).

Moderately strong: Magnesium hydroxide.

Weak: Ammonium hydroxide.

Very weak: The hydroxides of copper, iron, aluminium, and most other metals.

The student should memorize the above classification.

Ionization Theory of the Strength of Acids and Bases

According to the theory of ionization, as we have seen (p. 103), the characteristics common to all acids in aqueous solution are due to the hydrogen ion contained in all these solutions. Accordingly, the more ionized hydrogen there is in a given volume of water the more marked will these characteristics be. The "normal" solutions of hydrochloric, formic, and acetic acid used in Experiments 62 and 63 contain equal quantities of *ionizable* hydrogen in a given volume, viz. 1 gram per liter. But the hydrochloric acid solution had more of this hydrogen actually *ionized* than either of the others. This is evidenced not only by the greater activity of the hydrochloric acid, but also by the fact that a normal solution of hydrochloric acid is a very much better conductor of electricity than a normal solution of formic or of acetic acid. It is the ions which, traveling through the solution, conduct the electric current. The un-ionized molecules play no part in conduction. The superior conducting power of the hydrochloric acid solution is largely due to the great proportion of ionized molecules present in its solution as compared with those in normal solutions of the formic and acetic acids. It is estimated that in a normal solution of hydrochloric acid 780 out of every thousand molecules are ionized, while in formic acid only 14 and in acetic acid only 4 in a thousand are ionized.

Strong acids are, therefore, highly ionized acids, weak acids slightly ionized acids. Similarly, strong bases are highly ionized and weak bases only slightly ionized, and the superior activity of the strong bases is due to the greater quantity of hydroxyl ions, OH^- , present in a given volume of solution.

CHAPTER XXI

HYDROLYSIS OF SALTS

Experiment 64.

Materials :

Litmus paper, red and blue.

Distilled water.

Small quantities of the following salts: Sodium chloride (salt); sodium sulphate (Glauber's salt); potassium nitrate (saltpeter); sodium carbonate (washing soda); sodium borate (borax); ammonium carbonate (smelling salt); ferric chloride (perchloride of iron); ferrous sulphate (copperas); aluminium sulphate; soap (contains sodium palmitate, sodium stearate, and sodium oleate); copper sulphate (blue stone); sodium bicarbonate (baking soda).

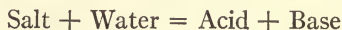
In distilled water in clean test tubes dissolve the salts named above, and test the solutions with red and with blue litmus paper. Tabulate, as illustrated below, the salts, their reactions to litmus, the acids and bases to which they correspond, and the relative strengths of these latter :

SALT		ACID		BASE	
Name	Reaction	Name	Strength	Name	Strength
Stannous chloride	Acid	Hydrochloric	Strong	Stannous hydroxide	Weak

Look over your results and state what general relations there are between the reactions of salts and the relative strengths of the acids and bases to which they correspond.

When the salt of a weak acid or the salt of a weak base is dissolved in water, the water acts upon the salt, partially reversing the action by which the salt and water are formed

from acid and base. That is to say, the following reaction takes place upon a part of the dissolved salt :



This, it will be noticed, is the reverse of the reaction of acid with base which we studied in Chapter XVII.

Whenever a compound is acted upon by water with the production of two new compounds, it is said to be *hydrolyzed* (literally, split up by the action of water). Thus, in the above reaction, the salt is said to undergo *hydrolysis*.

Now, if the salt is one of a *weak base* with a *weak acid* (e.g. aluminium carbonate), it may be completely decomposed by the action of water.

Experiment 65.

To ferric chloride solution add sodium carbonate solution. Note the immediate formation of a precipitate, and watch for subsequent action. Test the gas evolved with a film of limewater in the glass loop. (See Expt. 5, p. 5.)

Carbonic acid, when it is formed, soon breaks up into water and carbon dioxide :



If the precipitate is examined after this action ceases, it is found to be the base, ferric hydroxide, $\text{Fe}(\text{OH})_3$.

Make the same experiment with aluminium sulphate instead of ferric chloride. The white precipitate remaining in the test tube after the action ceases is the base, aluminium hydroxide. Write equations representing the hydrolysis of: (a) ferric carbonate, (b) aluminium carbonate.

If the salt treated with water is one of a *weak base* with a *strong acid*, it is not completely, but only partially, hydrolyzed, but the water acquires an *acid reaction* from the strong acid produced. Examples are aluminium sulphate, ferric chloride, and copper nitrate. Solutions of these salts turn blue litmus red.

If the salt corresponds to a *strong base* and a *weak acid*,

it is partially hydrolyzed and imparts an *alkaline* reaction to the water. Examples are sodium carbonate (washing soda) and sodium borate (borax). Solutions of these turn red litmus blue. These are the mild alkalies previously referred to (p. 93).

Salts of strong acids with strong bases are not hydrolyzed. Their solutions are quite neutral, like water itself. Examples are sodium chloride (common salt), sodium sulphate (Glauber's salt), and potassium nitrate (saltpeter).

The effect of water on the salt of a weak base and a strong acid is well illustrated in the following experiments with a substance much used in the household, viz. soap. *Hard soap* is a mixture of the *sodium* salts of the three weak acids, *palmitic*, *stearic*, and *oleic*. *Soft soap* is a mixture of the *potassium* salts of these same acids.

EXERCISE

1. Write the names of these sodium and potassium salts.
2. Write equations for the hydrolytic reactions studied in Experiment 64.

Experiment 66.

Materials:

Soap, good quality, in shavings.

Phenolphthalein solution.

Phenolphthalein is an indicator, *i.e.* a substance which, like litmus, has a different color in acid solution from what it has in alkaline solution. It is used in this experiment in preference to litmus because it is soluble in alcohol, whereas the active constituent of litmus is not. To discover what color the phenolphthalein takes in acid, neutral, and alkaline solutions, add a drop or two of the solution of this indicator to (a) a little dilute acid, (b) a little distilled water, (c) a little dilute alkali.

Dissolve a little of the soap in warm water and a little in alcohol. Add a drop or two of phenolphthalein to each solution. What difference is observed? Now add water to the alcoholic solution. What change occurs? What do you infer as to the action of water on the soap salts?

Poorly made soap may contain some "free alkali", *i.e.* sodium hydroxide. This can be determined by dissolving the soap in alcohol and adding a drop or two of phenolphthalein solution. Good soap will not give a color. Soap containing free alkali will yield a pink color.

Experiment 67.

Materials :

Samples of commercial and homemade soaps.

Test these soaps for free alkali by dissolving them in alcohol in clean water-free test tubes and adding a drop or two of phenolphthalein solution.

CHAPTER XXII

HARD WATER

SOME natural waters are called *hard* on account of the difficulty experienced in washing with them. Soap added to such waters causes the separation of a curdy precipitate.

Experiment 68.

Materials :

A solution of soap in water.

Hard water.

Solutions of calcium chloride and calcium sulphate.

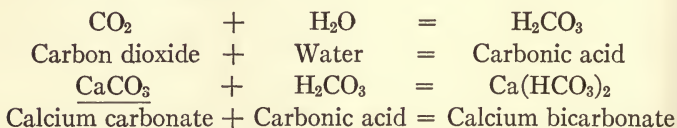
To separate portions of the soap solution add (1) calcium chloride solution, (2) calcium sulphate solution, (3) hard water. Note the curdy precipitate which rises to the top of the liquid.

The precipitate produced when soap solution is mixed with the hard water is identical with that produced when it is mixed with a solution of calcium chloride, calcium sulphate, calcium nitrate, or any other calcium salt. The reaction by which this precipitate is formed is one between the calcium ion and the anions of the soap — the palmitate, stearate, and oleate ions. The precipitate consists of calcium palmitate, calcium stearate, and calcium oleate and may appropriately be termed *calcium soap*. Just as the silver ion, contained in solutions of silver salts, precipitates the chloride ion of potassium chloride, sodium chloride, etc., forming silver chloride (see p. 102), so the calcium ion, contained in all solutions of calcium salts, precipitates the palmitate, stearate, and oleate ions of soap solutions, forming the insoluble calcium soap.

Hard water, then, is water containing the calcium ion.¹

¹ Some hard waters contain the magnesium ion, which also produces precipitates with the palmitate, stearate, and oleate ions.

The calcium ion is present in such waters because they have dissolved some of the calcium salts present in the soil and rocks with which they have come into contact. The mineral called *gypsum* is a crystal compound of *calcium sulphate* with water. Its formula is $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Water kept in contact with this mineral for a sufficiently long time will dissolve about $\frac{1}{500}$ of its own weight of calcium sulphate. If the contact is less prolonged, a smaller quantity of the calcium sulphate will be dissolved. Another compound of very common occurrence as a mineral is *calcium carbonate*. This occurs well crystallized as *calcite* and in less pure or less clearly crystallized forms as *marble*, *limestone*, *chalk*, and *marl*. Small particles of calcium carbonate are also commonly found in the soil. Pure water does not dissolve calcium carbonate appreciably.¹ But water which percolates through soil takes up carbon dioxide from the soil air and, combining with it, forms *carbonic acid*, which in turn combines with the calcium carbonate, forming a soluble compound called *calcium bicarbonate*. These reactions are represented by the following equations:



The following experiment illustrates (1) the formation of the insoluble calcium carbonate from carbonic acid and calcium hydroxide, (2) the formation of the soluble calcium bicarbonate by the action of carbonic acid upon the carbonate.

Experiment 69.

Materials:

Limewater.

Carbon dioxide gas from generator or from cylinder of liquid carbon dioxide.

¹ It takes 100,000 parts of water to dissolve 1 part of calcium carbonate.

Graduated cylinders, 25 cc.

Soap solution.

Dilute 25 cc. limewater with an equal volume of distilled water. Pass in carbon dioxide. Note the precipitate of calcium carbonate. Continue to pass in carbon dioxide for some time. What happens to the precipitate?

If the solution does not become perfectly clear, filter it. Mix a little of this artificial hard water with soap solution. Reserve the remainder for Experiment 70.

Temporary and Permanent Hardness

Some hard waters can be softened or partially softened by simply boiling them. Hardness that can be thus removed is termed temporary hardness. Temporary hardness is due to calcium bicarbonate. The effect of boiling is to decompose the bicarbonate into calcium carbonate (which precipitates), carbon dioxide, and water. Thus:



Experiment 70.

Measure into a test tube 5 cc. of the temporarily hard water obtained in Experiment 69. Add a solution of soap, little by little, from a burette or graduate, covering the test tube with the thumb and shaking vigorously after each addition. Note the quantity of soap solution required to give a lather which persists for one minute.

Measure out a second 5 cc. of the temporarily hard water, and boil it for a few minutes. What separates from the liquid? Add soap solution from the burette or graduate as before, and note how the quantity of soap required differs from that required by the unboiled hard water.

Hardness due to calcium sulphate cannot be removed by boiling. Such hardness is termed *permanent* hardness.¹

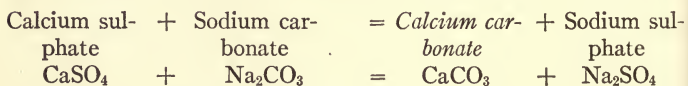
Of course, the hardness of the water of a given well, lake, or river may be partly temporary and partly permanent.

¹ Magnesium bicarbonate also produces temporary hardness and magnesium chloride and sulphate permanent hardness.

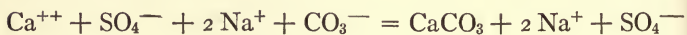
That is to say, the same water may contain both calcium bicarbonate and other calcium salts, such as the sulphate.

The Softening of Water

The softening of water consists in the precipitation of the calcium (and magnesium) which it contains. Water may be softened by adding to it a salt having an anion which combines with the calcium ion to form an insoluble compound. The carbonate of calcium is insoluble. So if we add to hard water a soluble carbonate, the calcium will be precipitated in the form of its carbonate. Since washing soda is the cheapest soluble carbonate, it is the material most commonly used. If the hard water contains calcium sulphate, the reaction is:



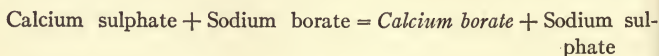
or in ionic notation:



The calcium being thus removed from solution by conversion into the insoluble carbonate, the water is no longer hard, and can therefore no longer act upon soap. In other words, the water now acts as a soft water.

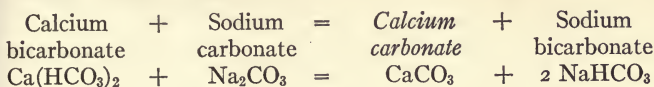
It is, however, not quite as satisfactory a laundry water as naturally soft water, because the sodium sulphate left in solution has a slight effect in precipitating soap. (See Expt. 84, Chapter XXVI.)

The action of borax (sodium borate) in softening water is similar to that of soda. Calcium borate is precipitated:



The calcium is thus removed from the water, which thereafter acts as a soft water.

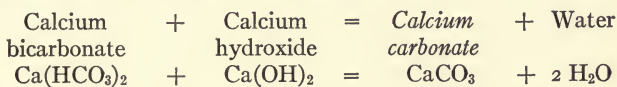
Temporarily hard water also can be softened by the use of soda. The reaction is:



Experiment 71.

To 5 cc. of the temporarily hard water add sodium carbonate solution. Then add soap solution from a burette or graduate, comparing the quantity required with that used with the untreated hard water in Experiment 70.

A method sometimes used in softening municipal water supplies is to add lime. The reaction is:



This method, however, is not well adapted for household use, since it is necessary to measure the degree of hardness of the water to determine just how much lime should be used.

Degrees of Hardness

There are of course *degrees* of hardness of water, and the term is sometimes given a strict quantitative signification. A water is said to have one degree of hardness when it has in every gallon the same quantity of calcium as is contained in one grain of calcium carbonate; two degrees of hardness, when it has twice this quantity of calcium per gallon, and so on.

It has been estimated that each degree of hardness involves an increased consumption of 2 to 2½ ounces of soap for every 100 gallons of water. This quantity of soap is used up in softening 100 gallons of water, and it is wasted, so far as any useful effect towards the washing of clothes is concerned. Indeed, it is worse than wasted, since the precipitate of lime soap forms an objectionable stain upon white fabrics. Al-

lowing 10 gallons of water per person per day, the soap used in softening hard water for a family of five would amount to over 21 pounds per year *for each degree of hardness*. Many hard waters have 10 to 20 degrees of hardness. It is therefore obvious that the waste may amount to something quite serious.

A hundred gallons of hard water can be softened by the use of about two thirds of an ounce of washing soda crystals for each degree of hardness. Water for a family of five persons estimated as above ($50 \times 365 = 18,250$ gallons) could be softened by the use of $7\frac{1}{2}$ pounds of soda per annum, for each degree of hardness. The $7\frac{1}{2}$ pounds of soda would cost about one ninth as much as the 21 pounds of soap.

With a water of a hardness of 10 degrees the comparison would be between 210 pounds of soap and 75 pounds of soda. Adopting the wholesale prices of 6 cents per pound for soap and 2 cents per pound for soda, we have :

Cost of softening with soap, 210 pounds at 6 cents	. .	\$ 12.60
Cost of softening with soda, 75 pounds at 2 cents	. .	<u>1.50</u>
Saving when soda is used		\$ 11.10

In softening water with soda, the use of too much soda should be avoided. What is not used up in the reaction with the calcium compounds is left in the water. If a great excess is used, the water may be rendered so strongly alkaline as to injure delicate fabrics.

CHAPTER XXIII

AMMONIA AND THE AMMONIUM RADICLE

Experiment 72.

Materials :

Red litmus paper.

Turmeric paper.

Pour a little ammonia water into a test tube. Note the odor and the effect produced on pieces of red litmus paper and yellow turmeric paper held at the mouth of the tube. Bring an open bottle of concentrated hydrochloric acid near the mouth of the test tube. What forms?

Experiment 73.

Materials :

Solid specimens of :

Ammonium carbonate.

Ammonium chloride.

Ammonium nitrate.

Ammonium oxalate.

Ammonium sulphate.

Note whether these salts have the odor of ammonia. Is there an exception among them? Of the others, mix one with slaked lime and heat gently, heat one with sodium hydroxide solution, and one with potassium hydroxide solution. Note odor in each experiment.

Ammonia is the name of the gas of pungent odor which escapes from ammonia water (*aqua ammoniæ, liquor ammoniæ*). Ammonia gas is formed in nature in the putrefactive decomposition of animal and vegetable matter containing nitrogen. The odor is often distinctly perceptible in horse stables in which manure has been allowed to accumulate.

Ammonia was formerly obtained, for medicinal use, by destructive distillation of nitrogenous animal wastes, such

as bones, hoofs, and horns; hence the name, "spirit of harts-horn," sometimes applied to aqua ammoniæ. The compound is now manufactured as a by-product of the coal-gas industry. In the process of destructive distillation (heating the coal in closed retorts) much of the nitrogen of the coal escapes with the gas as ammonia, which is afterwards separated from the other constituents of coal gas and obtained pure. (See Chapter XII.)

The gas can be converted into a liquid by cold and pressure, and in this form is used in the refrigerating machines of cold-storage plants and ice factories. This *anhydrous* liquid ammonia is not to be confounded with the more commonly used *liquor ammoniæ*—the solution of this gas in water. Ammonia contains the elements nitrogen and hydrogen and has the formula NH_3 .

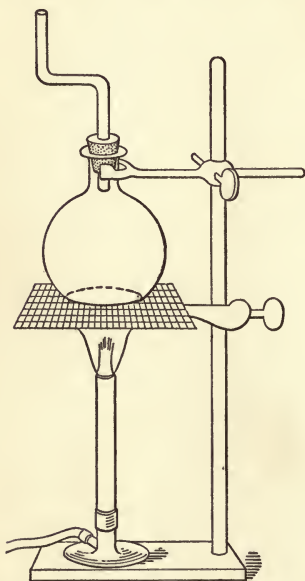


FIG. 37. — Experiment 74. Apparatus for generating ammonia.

Experiment 74.*

Materials:

Ammonium chloride.
Slaked lime.
Red litmus solution.

Apparatus:

Figure 37. Small round-bottomed flask connected through drying tube containing quicklime to upward delivery tube.

Figure 38. Fountain apparatus, consisting of (a) $\frac{1}{2}$ -liter round-bottomed flask, fitted with tightly fitting two-holed stopper, carrying (1) a glass tube reaching nearly to bottom of flask, (2) a medicine dropper; (b) a retort stand with ring to hold this flask in inverted position; (c) glass dish or beaker.

Mix ammonium chloride and slaked lime and heat gently in the generating flask in the hood, collecting the gas in the flask of the fountain apparatus.

Fill the medicine dropper with water, and the glass dish with the red litmus solution.

From time to time hold an open bottle of concentrated hydrochloric acid near the mouth of the inverted flask, and when a heavy cloud of white fumes is observed, insert the rubber stopper and transfer the flask to its position in the retort stand of the fountain apparatus. Press the bulb of the medicine dropper so as to force a few drops of water into the apparatus. These few drops dissolve practically all the ammonia in the flask, thus creating a vacuum, into which the water is then forced by the pressure of the air on the water in the dish. Note also the effect of the ammonia on the litmus. What does this indicate?

Ammonia gas is enormously soluble in water. One gallon of water will absorb about 700 gallons of ammonia, or about one half its own

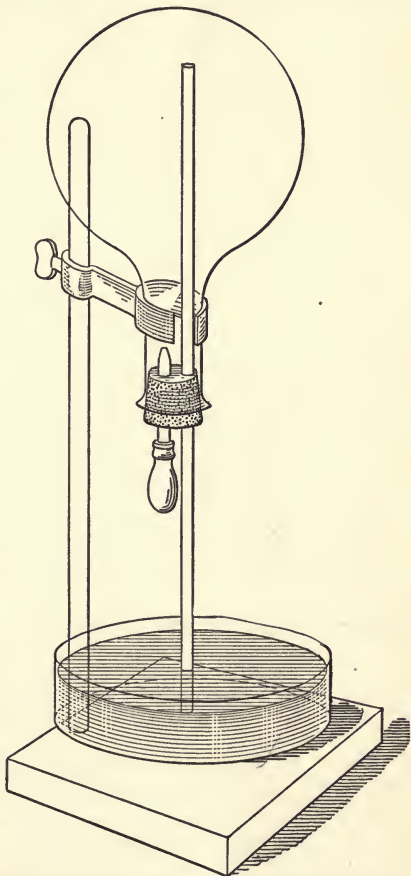


FIG. 38. — Experiment 74. Fountain apparatus.

weight of the gas. Thus about one third of the weight of the strongest ammonia water consists of the gas, and the

water constitutes the other two thirds. For ordinary household use much weaker solutions than this are sold. Commercial "household ammonia" sometimes contains impurities which fade colors or cause white materials to turn yellow. It will be found safer and more economical to buy concentrated ammonia from a druggist, dilute it with its own volume of water, and keep it in bottles carefully closed with glass or rubber stoppers. This solution can be further diluted with three times its own volume of water for most household uses. In pouring ammonia water from bottle to bottle discomfort can be avoided by holding the bottles above the level of the eyes. The escaping gas, being lighter than air, ascends.

The Ammonium Radicle

Ammonia water has an alkaline reaction, and, like the hydroxides of metals, neutralizes acids, producing salts. These facts lead us to infer that when ammonia gas dissolves in water, it combines with the water, forming a hydroxide.



The base would thus be the hydroxide of a radicle, NH_4- , made up of nitrogen and hydrogen. To this radicle the name "ammonium" is applied. The same radicle is present in all ammonium salts, e.g. ammonium chloride (sal ammoniac) NH_4Cl , ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, and ammonium carbonate (smelling salts) $(\text{NH}_4)_2\text{CO}_3$. In their solubilities the ammonium salts are very similar to the corresponding salts of potassium.

To include ammonium hydroxide among the bases we may expand our definition of a base (see p. 94) into the following:

A base is the hydroxide of a metal or of a radicle which plays the part of a metal.

Ammonium hydroxide is said to be a "volatile" alkali, because it evaporates without leaving a residue. This property gives it an advantage over "fixed" alkalies, such as sodium hydroxide or sodium carbonate, for many purposes, such as the washing of window panes and the neutralization of acid stains on fabrics.

Ammonium carbonate gradually liberates ammonia and carbonic acid gases at ordinary temperatures and, therefore, smells strongly of ammonia. It is the basis of "smelling salts," which, as a rule, contain also some other fragrant substance, such as lavender. Ammonium carbonate is popularly known as "crystal ammonia." Mixtures of soda with just enough ammonium carbonate to impart an odor are sometimes fraudulently sold as "solid household ammonia."

Experiment 75.

Heat a small quantity ($\frac{1}{4}$ gram) ammonium carbonate in a porcelain dish. What becomes of the substance? How could one detect soda as an adulterant of crystal ammonia?

EXERCISES

1. Write equations for the reactions obtained in Experiment 73.
2. Write equations for the reaction of ammonia gas with (a) hydrochloric acid, (b) nitric acid, (c) sulphuric acid, (d) acetic acid, (e) carbonic acid.
3. Write equations representing the neutralization of ammonium hydroxide by (a) hydrochloric acid, (b) sulphuric acid, (c) nitric acid, (d) acetic acid.

CHAPTER XXIV

ORGANIC RADICLES. HYDROCARBONS AND ALCOHOLS

THE compounds of the element *carbon* (with the exception of carbon monoxide, carbon dioxide, and the carbonates) are called **organic compounds**. Many of them are found in, or made from, animal and vegetable organisms, and it was formerly believed that they could not be made without the agency of life. This is now known to be untrue for many of them, but the term "organic" is still applied to the branch of chemistry which treats of the very numerous compounds of this one element, carbon.

Among the compounds of carbon there are many instances of radicles existing as the common constituents of a number of compounds, much in the same way as the ammonium radicle, $\text{NH}_4\text{—}$, exists in all the ammonium salts (see p. 130), or as an acid radicle exists in an acid and all its salts (see p. 86). These organic radicles may consist of carbon and hydrogen in various proportions; of carbon, hydrogen, and oxygen; of carbon, hydrogen, and nitrogen; etc.

Among the simplest and most frequently occurring organic radicles are the *hydrocarbon* radicles, consisting of carbon and hydrogen only. Many of these can be arranged in classes or *series* in which each member differs in formula from the preceding one by one atom of carbon and two atoms of hydrogen.

Thus we have as one important series :

- The *methyl* radicle, $\text{CH}_3\text{—}$
- The *ethyl* radicle, $\text{C}_2\text{H}_5\text{—}$
- The *propyl* radicle, $\text{C}_3\text{H}_7\text{—}$
- The *butyl* radicle, $\text{C}_4\text{H}_9\text{—}$
- The *amyl* radicle, $\text{C}_5\text{H}_{11}\text{—}$
- etc., etc.

The compounds of the radicles of such a series with any element, or with any other radicle, have certain points of similarity, and there is a gradual variation in properties from the compounds at one end of the series to those at the other end. For example, the compounds of the above radicles with hydrogen are substances which resist the action of many of the reagents (such as chlorine, nitric acid, and sulphuric acid) which act readily on other compounds of carbon and hydrogen. For this reason they are called the *paraffins* (Latin, *parum affinis*, possessing little affinity). Petroleum and its commercial products — benzine, gasoline, kerosene, and paraffin wax — are mixtures of the higher compounds of this series. Natural gas (see Chapter XII) consists chiefly of the first member of the series, — methane, CH_4 , — but also contains a little ethane, C_2H_6 , and smaller quantities of a few of the other members of the series. The following table of the densities and boiling points of a few members of this series will illustrate how the properties of the compounds gradually change from one end of the series to the other.

NAME	FORMULA	DENSITY AS A LIQUID	BOILING POINT
Methane	CH_4	.42	-164°
Ethane	C_2H_6	.45	- 93
Propane	C_3H_8	.54	- 38
Butane	C_4H_{10}	.60	+ 1
Pentane	C_5H_{12}	.63	+ 37
Hexane	C_6H_{14}	.66	+ 69

At ordinary room temperature (20° C.) the first four members of this series are gases, those with 5 to 10 carbon atoms to the molecule are liquids, and the higher members of the series solids. One has been made with 60 carbon atoms to the molecule, *i.e.* $\text{C}_{60}\text{H}_{122}$. It is a solid, melting at about the boiling point of water.

Alcohols

When yeast is allowed to grow in grape juice or in the "wort" obtained by extracting malt with water, the substance called *alcohol* (or grain alcohol) is produced. This substance is the characteristic intoxicating constituent of all liquors. When obtained pure, it is exactly the same substance whether it comes from cider, wine, beer, or whisky.

A similar but distinct substance is obtained as one of the products of the "dry" distillation of wood (heating the wood in closed retorts and cooling the vapors evolved). This substance is known as *wood alcohol* in contradistinction to *grain alcohol*. (Cf. pp. 41 and 67.)

Still other allied substances are produced in very small quantities along with grain alcohol in the fermentation of the sugar of fruit juices or malt wort. These constitute the *fusel oil* which is separated from grain alcohol in the process of distillation (which consists in boiling the liquid and recondensing the vapors to liquid by cooling).

To all the compounds of this class the general term **alcohols** is applied. They are all found to be *hydroxides of hydrocarbon radicles*. The alcohols of the radicles given above constitute the following series:

FORMULA	NAME	DENSITY	BOILING POINT
CH ₃ OH	Methyl alcohol (wood alcohol)	.812	66° C.
C ₂ H ₅ OH	Ethyl alcohol (grain alcohol)	.806	78
C ₃ H ₇ OH	Propyl alcohol	.817	97
C ₄ H ₉ OH	Butyl alcohol	.823	117
C ₅ H ₁₁ OH	Amyl alcohol	.829	138

As in the case of the hydrocarbon series, the density and boiling point of each member of the series are higher than

those of the preceding compound. There is, however, an exception in the density of ethyl alcohol, as compared with that of methyl alcohol.

In that they are hydroxides, the alcohols resemble the bases. In most respects, however, there is a marked difference between the alcohols — the hydroxides of hydrocarbon radicles — on the one hand, and the bases — the hydroxides of metals or metal-like radicles — on the other hand. All the alcohols are neutral in reaction; while all soluble bases are alkaline. The simpler alcohols, *e.g.* all those listed above, are liquids, and so are some of the more complex compounds of this class; while the simpler bases, *i.e.* the hydroxides of the metals, are solids, and only the more complex bases, *e.g.* hydroxides of metal-like radicles such as ammonium NH_4 —, aniline $\text{C}_6\text{H}_5\text{NH}_3$ —, etc., are liquids, or exist in the dissolved form in water. Alcohols do not ionize when dissolved in water; bases do.

Experiment 76.

Examine specimens of pure methyl alcohol, pure ethyl alcohol, and amyl alcohol. Note odor of each and effect on litmus paper, red and blue. Determine for each whether it is completely miscible with water.

Glycerol

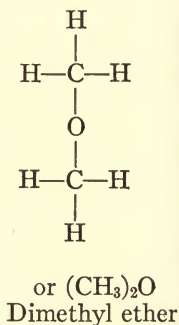
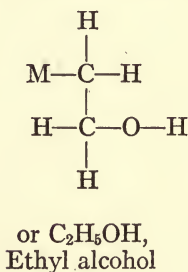
Just as there are *bases* with more than one hydroxyl group, —OH, in the molecule, *e.g.* $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, so also there are *alcohols* with more than one hydroxyl group. The most important of these, in relation to household chemistry, is **glycerol**, known commercially as *glycerin* or *glycerine*. Glycerol is the hydroxide of the trivalent radicle glyceryl, $\text{C}_3\text{H}_5 \equiv$. Its formula is $\text{C}_3\text{H}_5(\text{OH})_3$.

Experiment 77.

Examine a specimen of glycerin (commercial glycerol). Note its viscosity, miscibility with water, taste, and effect on red and blue litmus paper.

Structural Formulas

In organic chemistry it is a common thing for several compounds to contain the same elements in the same proportions. Thus we have three different sugars with the formula $C_{12}H_{22}O_{11}$ — cane sugar, milk sugar, and malt sugar. Such compounds are said to be *isomers*, or *isomeric compounds*. In many instances we are able to distinguish isomers from one another by representing their atoms as differently joined in the molecule. Thus the formula, C_2H_6O , represents two compounds, viz. ethyl alcohol and dimethyl ether. These are distinguished as follows :

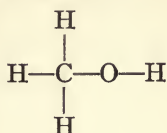


Ethyl alcohol is the *hydroxide* of the *ethyl* radicle, while dimethyl ether is the *oxide* of the *methyl* radicle. In the former the two carbon atoms are represented as joined directly together and the oxygen atom as connecting one of the hydrogen atoms to a carbon atom. In the latter all six hydrogen atoms are joined directly to carbon, and the oxygen atom unites the two carbon atoms.

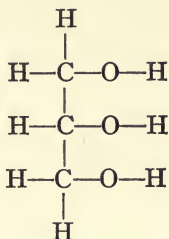
Formulas of this kind are called *structural* or *graphic* formulas.

The structural formulas of all alcohols have the hydroxyl group, $-\text{OH}$, joined to a carbon atom to which no other oxygen atom is attached.

The following are the structural formulas of methyl alcohol and glycerol.

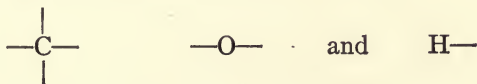


or CH_3OH ,
Methyl alcohol



or $\text{C}_3\text{H}_5(\text{OH})_3$,
Glycerol

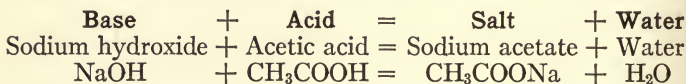
It will be noted that in all these formulas the carbon atom is represented as having four valence bonds, the oxygen atom two, and the hydrogen atom one; thus:



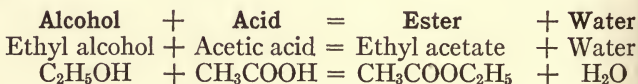
CHAPTER XXV

ESTERS. FATS

IN their behavior towards acids, alcohols resemble, but differ from, bases. It will be remembered that a base reacts with an acid to give water and a product called a salt. Similarly, an alcohol reacts with an acid to give water and a product analogous to a salt. For instance



So also



Thus the esters bear the same relation to acids and alcohols that salts bear to acids and bases. The ester is obtained from the acid by the replacement of the hydrogen of the acid by the radicle of the alcohol. In their physical properties, however, esters are no more like salts than alcohols are like bases. Ethyl acetate and other esters of the simpler alcohols with the simpler organic acids are neutral, volatile liquors, with pleasant fruity odors. They are nearly insoluble in water and do not ionize when dissolved. The flavors and odors of fruits and wines are in part due to the esters they contain. Some esters are manufactured and sold as flavoring matters or perfumes. Amyl acetate, for example, is sold as pear oil, methyl butyrate as pineapple oil, etc. Esters of more complex alcohols and acids are important constituents of the waxes — beeswax, Carnauba wax, etc.

Experiment 78.

Examine specimens of methyl acetate, ethyl acetate, propyl acetate, amyl acetate (pear oil), methyl butyrate (pineapple oil), ethyl citrate, methyl salicylate (oil of wintergreen).

The reactions between alcohols and acids are much slower than those between bases and acids. When ethyl alcohol and acetic acid are mixed and kept at ordinary room temperature, the formation of ethyl acetate goes on slowly for several months. If the mixture is kept hot, the reaction goes on more rapidly. There are also certain substances, such as sulphuric acid, which will accelerate the action. A common method of preparing esters is to mix the alcohol with sulphuric acid, add the acid whose ester is wanted, and distill out the ester.

Experiment 79.

Mix equal volumes of alcohol and concentrated sulphuric acid. Add acetic acid and boil. Note the odor and compare with those of alcohol, acetic acid, and ethyl acetate. Has ethyl acetate been formed? Write equations for the reaction (omitting the sulphuric acid from the equation).

Fats

The esters of the alcohol, glycerol, with certain organic acids, constitute the *fats*. Natural fats and animal and vegetable oils — lard, tallow, butter, lard oil, olive oil, cottonseed oil, linseed oil, castor oil, etc. — are mixtures of the glycerol esters of a number of different acids.

The most common of these acids are *palmitic*, $\text{HC}_{16}\text{H}_{31}\text{O}_2$, a soft solid; *stearic*, $\text{HC}_{18}\text{H}_{35}\text{O}_2$, a soft solid; and *oleic*, $\text{HC}_{18}\text{H}_{33}\text{O}_2$, a liquid.

The most common simple fats are therefore:

Glyceryl palmitate, $\text{C}_3\text{H}_5(\text{C}_{16}\text{H}_{31}\text{O}_2)_3$ known as *palmitin* or *tripalmitin*. This, like palmitic acid, is a solid.

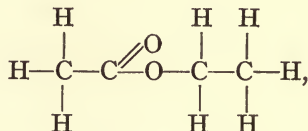
Glyceryl stearate, $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$, *stearin* or *tristearin* — also a solid.

And *glyceryl oleate*, $C_3H_5(C_{18}H_{33}O_2)_3$, *olein* or *triolein* — a liquid.

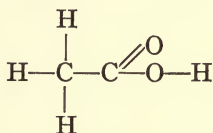
Experiment 80.

Examine specimens of palmitic, stearic, and oleic acids, and of the three simple fats, tripalmitin, triolein, and tristearin.

The structural formula of *ethyl acetate* is $CH_3COOC_2H_5$, or

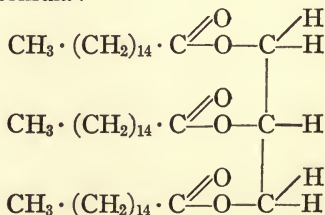


that of *acetic acid* being CH_3COOH , or



Palmitic and stearic acids belong to the same series of acids as acetic acid. In structure they differ from acetic acid in having a long chain of carbon atoms (each carrying two hydrogen atoms) between the carbon atom of the CH_3 —radicle and that of the $-COOH$ radicle.¹ Palmitic acid has 14, stearic acid 16, of these intermediate carbon atoms in its chain.

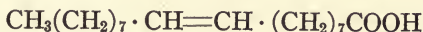
Tripalmitin may, therefore, be represented by the following structural formula :



¹ The $-COOH$ radicle, called *carboxyl*, is the characteristic radicle of organic acids.

and *tristearin* by a formula differing from this in having 16 CH_2 's instead of 14.

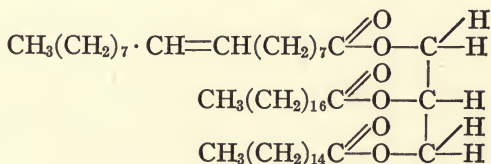
The structural formula of *oleic acid*, which contains two hydrogen atoms less than stearic acid, is:



that is to say, the middle carbon atoms of the molecule are joined by two bonds instead of one.

The structural formula of *triolein*, therefore, resembles that of tripalmitin given above, except that two $-\text{CH}=\text{s}$ are inserted between the seventh and eighth of the chain of CH_2 's.

It will be readily understood that fats may also be derived from the reaction of two or three acids with glycerol. Thus we might have an *oleo-stearo-palmitin*, derived from three fatty acids. Its formula would be:



“Mixed” esters of this type are actually found in natural fats. Butter, for instance, has been shown to contain a fat which is an ester of palmitic, oleic, and butyric acids, the last-mentioned being an acid of the same series as acetic, palmitic, and stearic, viz. $\text{CH}_3(\text{CH}_2)_2\text{COOH}$.

The natural fats are mixtures of these various compounds, and owe their physical differences to differences in the proportions of the individual glycerides which they contain. The oils and more liquid fats (*e.g.* lard) contain larger proportions of olein, the more solid fats (*e.g.* tallow) smaller proportions of olein and larger proportions of stearin and palmitin. Some of them, such as butter, castor oil, linseed

oil, etc., also contain material quantities of the glycerol esters of other acids than palmitic, stearic, and oleic.

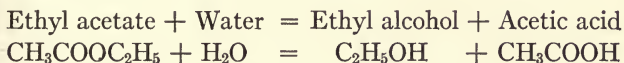
Even the fat of two animals of the same species may differ if the two have been on different diets. The bacon from hogs fed on oats, peas, and barley is firmer than that from hogs fed on Indian corn and beans. When the fat of the firm bacon and that of the soft bacon are analyzed, it is found that the former contains a larger proportion of stearin and palmitin than the latter. In one investigation the fat from soft bacon was found to contain four times as much olein as stearin and palmitin together, while the fat of firm bacon had only about twice as much olein as stearin and palmitin.

CHAPTER XXVI

HYDROLYSIS OF ESTERS. SAPONIFICATION

Hydrolysis of Esters. — We have seen (Chapter XXI) that the reaction by which salts and water are formed from weak acids and bases is to some extent reversible — the salts reacting with water to form acids and bases. This reaction of salts with water we have called the *hydrolysis* of the salt.

Esters are subject to hydrolysis to even a greater extent than salts. The products of such hydrolysis are, of course, acids and alcohols, *e.g.*:



The *rate* at which esters react with water is, however, small, unless there is present some substance which has the power of accelerating the reaction. The acids are one class of substances possessing this accelerating power, particularly the strong acids, such as hydrochloric and sulphuric. In accelerating hydrolysis these acids are not themselves changed, and we do not understand why they influence the rate of hydrolysis of esters. But the fact that they do so is well established.

Another class of substances having a similar effect — particularly upon the hydrolysis of fats — is the class known as *lipases*, a special division of a more general class of substances, known as *ferments* or *enzymes*. Ferments are organic substances possessed of the power of promoting reactions between other substances without being themselves destroyed.

Ferments are secreted, some of them by microorganisms, others by plants, and still others by special organs (glands) of the bodies of the higher animals. A ferment of the lipase class (sometimes called *steapsin*) is present in the digestive juices which act upon foods in the small intestine. It has the power of "splitting" fats; that is to say, of causing them to react with water to yield fatty acids and glycerol. Though the digestion of fats is not thoroughly understood, it is believed that they are thus hydrolyzed in the intestine, and that the acids and glycerol, after passing into the intestinal wall, are recombined to build up the fat of the body. In this recombination, the proportions of olein, palmitin, stearin, and "mixed" esters formed are not always the same as those originally present in the fat of the food, since the animal may take apart the fats of its food and reconstruct them into the fats peculiar to its own species. On the other hand, when an animal is fattened rapidly on fatty food, the food fat may be deposited in the adipose tissues without loss of its chemical characteristics.

Saponification

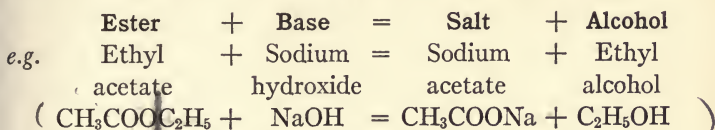
Experiment 81.

Materials:

Ethyl acetate.

Dissolve a few drops of ethyl acetate in half a test-tubeful of water. If not all the ethyl acetate added mixes with the water on shaking, add more water until a clear solution is obtained. Divide the solution into three exactly equal parts in three test tubes of equal diameter. Into the test tubes put respectively, (1) $\frac{1}{2}$ cc. dilute sulphuric acid, (2) exactly the same volume of the reagent sodium hydroxide solution, (3) exactly the same volume of water. Label the three test tubes and place them, side by side, in a beaker of water which feels just warm to the hand. Allow to stand, comparing the odors of the three every five minutes. From which tube does the odor of ethyl acetate disappear first? What do you infer as to the effect of sodium hydroxide in promoting the hydrolysis of ethyl acetate? How does it compare with sulphuric acid in this respect?

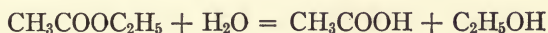
When an ester is treated with a strong base (alkali), it reacts with the base, forming a salt and a free alcohol.



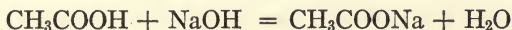
This reaction may be compared with that of a strong base on an ammonium salt, e.g. that of sodium hydroxide with ammonium chloride:



the sodium salt of the acid being formed and the weak base liberated. It may also be regarded as a combination of hydrolysis and neutralization. As fast as any free acetic acid is formed by the hydrolysis of the ester

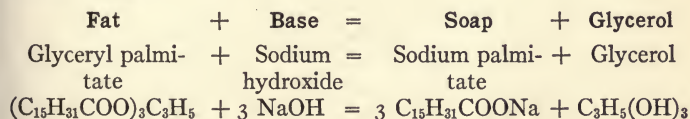


it is neutralized by the alkali,



The effect of thus immediately removing the acid by neutralization is to accelerate the hydrolysis greatly and also to allow the hydrolysis to become complete, the whole of the ethyl acetate being used up, which is not the case when the ester is hydrolyzed alone.

When the ester is a fat, the salt formed by action of the base is a soap. Thus



This is *saponification* (soap making) proper, but the term has been extended in meaning so as to include the reaction of any ester with a base. Hence we speak of the saponification of ethyl acetate as well as that of lard or tallow.

Soaps

Experiment 82.

Materials :

Lard.

10 per cent solution of potassium hydroxide in alcohol.

Flask, 150 cc.

Evaporating dish, 6 inch.

Water bath.

Weigh out 25 grams lard and introduce it into the flask. Add 75 cc. alcoholic potash. Heat on a water bath until a drop let fall into water dissolves clear, *i.e.* without leaving any globules of fat. Place 100 cc. water in the evaporating dish and pour the contents of the flask into the dish. Place on the water bath and evaporate until the odor of alcohol is gone and a pasty residue remains. Redissolve this residue in hot water. Note the feel of this solution. To a small portion add calcium chloride solution. Save the main portion for Expt. 83, and a small one for Expt. 84.

Experiment 83.

Materials :

Sodium carbonate, powdered.

Potassium bisulphate, powdered.

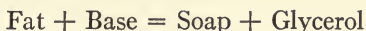
Place a piece of litmus paper in the solution saved from Experiment 82 and acidify with dilute hydrochloric acid. Note what rises to the surface. This precipitate consists of a mixture of the fatty acids, the salts of which constitute the soap. Write equations for the reaction of hydrochloric acid with potassium palmitate.

Boil the liquid and filter through a wet filter. The fatty acids do not pass through the wet filter. To the filtrate add powdered sodium carbonate, little by little, stirring, until the acid is neutralized. Evaporate to dryness. Allow to cool. Stir up the residue with alcohol, filter, and evaporate the alcohol on the water bath.

Examine the sirupy residue. Mix a drop or two with powdered potassium bisulphate and heat in a test tube, noting odor. Make the same test on glycerol, comparing results with those obtained with the residue. The odor produced by heating glycerol with potassium bisulphate is that of a substance called *acrolein*, C_3H_4O . This is one of the products of a decomposition of glycerol, the other being water :



The chemical reaction involved in the manufacture of soap is that given above (p. 145), viz.:



For the preparation of soft soaps the base used is potassium hydroxide; for the hard soaps, sodium hydroxide.

The fat may be boiled with an aqueous solution of the base, or the two may be put together and either left standing for several days or subjected to pressure for a shorter space of time.

Soaps made by the latter method (the "cold process") contain the glycerol produced in the reaction. Glycerol, being an emollient, healing substance, is an unobjectionable constituent of toilet soap. In the boiling process it is more common to separate the soap and glycerol by "salting out" the former. When the saponification is complete, common salt is added to the pot. The soap, being insoluble in salt solutions, is precipitated and collects on the surface of the water. Soap made in this way is known as "curd" soap.

Experiment 84.

Heat a soap solution until it is quite clear. Add solid sodium chloride. Note what separates from the liquid. Allow this precipitate to collect at the surface of the liquid. Pour or skim off into a test tube, add distilled water, and warm. Does it dissolve?

In what respect does the effect of sodium chloride on a soap solution differ from that of calcium chloride? Sodium sulphate has an effect similar to that of sodium chloride. Explain why permanently hard water softened with soda is not quite as satisfactory for laundry purposes as naturally soft water.

The glycerol, which is left in solution in the brine in this "boiling process" of soap making, is subsequently refined and sold as "glycerin" for medicinal use or for the manufacture of explosives, — nitroglycerin, dynamite, etc.

In the manufacture of soft soap it is customary to leave the glycerol in the soap.

CHAPTER XXVII

COMMERCIAL SOAPS

THE chemical reactions involved in the manufacture of soap conform, of course, to the law of definite proportions. (See Chapter VII.) To saponify a given weight of a pure fat, *e.g.* glyceryl palmitate, a definite weight of a pure base, *e.g.* sodium hydroxide, is required. If too much fat is used, the excess will be left in the soap as "unsaponified fat." If too much base is used, the excess will remain in the soap as "free alkali." Moreover, since saponification is a rather slow process, it is quite possible for a soap to contain *both* free alkali and unsaponified fat, if time has not been allowed for the reaction to run to completion. Since all natural fats are mixtures and the commercial alkalies used in soap manufacture are not chemically pure substances, it requires great skill and care to manufacture soap which is free from both unsaponified fat and free alkali. For rough cleaning purposes, such as scrubbing, an excess of free alkali can be tolerated, and soap suitable for such purposes may be made at home. On painted or varnished surfaces soaps should be used with extreme care, if at all. If used, they should contain no free alkali. Scouring powders and soaps containing much free alkali are injurious to aluminium ware. For laundry purposes, except for woolens or silks, a little free alkali is permissible, but the amount should not be as much as one per cent of the weight of the dry soap. Toilet soaps and wool soaps should not contain any free alkali. Laundry soaps should not contain any unsaponified fat.

Experiment 85. — Test for Unsaponified Fat.*Materials:*

A number of samples of commercial and home-made soaps.

Benzine.

An alcoholic solution of the dye Sudan III.

Finely slice about 5 grams of the soap. Spread on a watch glass and dry in a water oven. Place half the dried residue in a test tube, cover with benzine, and shake for some time. Filter off the benzine through a dry filter on to a clean watch glass and allow it to evaporate. Evaporation may be hastened by placing the watch glass on a steam radiator or on a steam bath. A smeary residue is an indication of fat. To confirm, add a little of the Sudan III solution, and stir with the smeary residue. Pour off the Sudan III from the watch glass, wash once with alcohol, and add hot water. Globules of fat, colored pink with the dye, will float on the water.

Experiment 86. — Test for Free Alkali*Materials:*

Soaps used in Experiment 85.

Phenolphthalein solution.

Shake a portion of the fresh soap with alcohol and add a drop or two of the phenolphthalein solution. A pink color shows the presence of free alkali.

Why may not the soap be dissolved in *water* for this test? (See Chapter XXI.)

All commercial soaps contain more or less water. A well-made soap should not contain over 25 per cent. Low-grade soaps sometimes contain 35 per cent or even more; good toilet soaps sometimes as low as 13 to 15 per cent.

Experiment 87. — Determination of Water Content.*Materials:*

Soap.

100 cc. beaker.

Sand.

Water bath.

Air bath with thermometer.

In an evaporating dish heat enough of the sand to cover the bottom of the beaker to the depth of half an inch. Allow to cool.

Shave all the soap finely, mix well, and weigh out 5 grams. Place the sand and a glass stirring rod in the beaker and determine the weight. Add the soap and 25 cc. or more alcohol. Heat on the water bath, stirring well to dissolve the soap in the alcohol. Evaporate to dryness on the water bath, then place in the air bath and regulate the flame so as to keep the temperature constant at 110° C. After one hour remove the beaker from the air bath, allow to cool, and weigh. Return the beaker to the air bath for half an hour. Cool again and weigh. Repeat until constant or nearly constant weight is attained. Calculate what percentage of water the soap contained.

Not only is the quantity of water contained in a soap of interest in relation to the price, but it is also of importance with reference to the lasting quality of the cake or bar. Moist soap is soft and tends to waste in use. The drying of soap is, therefore, a good household practice. The bars should be cut into pieces of convenient size for use and kept in a warm place, piled loosely, so as to allow a free circulation of air.

Although soda soaps are all classed as "hard," there is actually a great deal of variation in the hardness of different samples. The hardness depends to some extent, as we have just seen, on the proportion of water in the soap. It also depends on the materials from which the soap was made. Soaps containing too much oleate will be soft and soluble. Thus, soaps made from olive or cottonseed oil lather better, but waste away more rapidly than those made from the solid fats, palm oil and tallow, which contain a larger proportion of stearate and palmitate.

CHAPTER XXVIII

FOREIGN INGREDIENTS OF COMMERCIAL SOAPS

WE have seen that in addition to the soaps proper — *i.e.* the salts of fatty acids — commercial soaps always contain water and may contain glycerol, unsaponified fat, and free alkali. But in practice other substances are frequently added, either to lower the cost of production or to render the soap more attractive. The substances added to lower the cost of production are of two classes: (1) other detergents; (2) fillers.

Detergents

Among the detergents added to soaps are:

Sodium and Potassium Carbonates. — These are cheap and harsh alkalies and are to be regarded as adulterants, except in soaps to be used for rough cleaning. Even for such purposes the soda or potash can be more economically purchased separately, as soda ash or washing soda, and as pearl ash, respectively. Sodium carbonate cannot be added to soap in greater quantity than 5 per cent without causing a white incrustation on the surface of the soap. Potassium carbonate can be added in larger quantity, and has the property of making the soap look finer in texture and therefore more attractive.

Experiment 88. — Test for Carbonates

Materials:

Soda ash (sodium carbonate).

Pearl ash (potassium carbonate).

Commercial soaps and washing powders.

Add a little dilute sulphuric acid to (1) soda ash, (2) pearl ash. Note and account for the effervescence. Write equations for the reactions.

Test the commercial soaps and washing powders for carbonates in the same way.

Sodium silicate is known as "water glass." This substance gives firmness to soap, and enables it to hold more water and still remain hard. In small quantities it is a legitimate addition to soaps for some purposes. Soaps containing more than a very little silicate, when used in the laundry, leave a deposit of silica (an insoluble substance of the same composition as sand) in the clothes.

Experiment 89. — Test for Silicate.

Treat the finely shaved soap with hot alcohol until nothing further dissolves; filter and wash with hot alcohol. Now wash the residue with hot water, collecting the solution obtained. Acidify this solution with hydrochloric acid, evaporate to dryness, and gently heat the residue for some time. If it chars, heat more strongly until it is completely burned. Allow to cool, add water and a little hydrochloric acid, and warm. Silica will be left as an insoluble, gritty residue.

Sodium Resinate. — Rosin (also termed *colophony*) consists of acids which react with alkalis to form salts called resinates, which, like soaps, have detergent properties. These resinates cannot be used separately for cleansing purposes. In dilute hot solutions they hydrolyze to so great an extent as to precipitate the rosin acids. These are deposited on the goods, causing a yellow stain having the odor of rosin. Resinates are often contained in laundry soaps, particularly yellow soaps, and are objectionable constituents, unless present in only small quantities. Yellow soaps have been analyzed which contain up to 40 per cent of resinates. Soaps containing resinates are sometimes called "rosin soaps" and are spoken of as containing rosin.

Experiment 90. — Test for Rosin.

Materials:

Soaps with and without rosin.

Acetic anhydride.

Compare the odors of the soaps containing rosin with the odors of the non-rosin soaps. Dissolve the soaps in water. Acidify with sulphuric acid. Filter. Dissolve the precipitate in acetic anhydride. What is this precipitate (1) if the soap is pure? (2) if the soap contains rosin?

To 5 cc. water add 5 cc. concentrated sulphuric acid. Cool the mixture. Place about 2 cc. in a test tube and add a few drops of the acetic anhydride solution of the fatty acids. A violet coloration shows that rosin is present.

Petroleum Products. — Petroleum products, such as paraffin wax, kerosene, and naphtha (a volatile product resembling benzine) are sometimes added to soap. These, being fat solvents, have value as detergents. Kerosene itself is sometimes used in the clothes boiler, both in the household and in commercial laundries. The naphtha soap, however, cannot be used with *hot* water.

Borax is a sodium borate, whose detergent property is well known. It is an excellent ingredient of soaps.

Fillers

Among the "fillers," *i.e.* cheap, weight-making substances of little or no detergent value, used as ingredients of commercial soaps, are the sulphates of sodium, potassium, calcium, and barium, infusorial earth (a fine form of silica, SiO_2 , left from the decay of minute marine organisms called infusoria), fine clay, chalk, or whiting (calcium carbonate), French chalk (a soft, powdery magnesium silicate), starch, and impure vaseline. In the detection of these substances advantage is taken of the circumstances that none of them is soluble in alcohol and only the sodium sulphate and potassium sulphate are soluble in water.

Experiment 91. — Tests for Fillers.

Dissolve the finely shaved soap in alcohol. Filter and wash the insoluble residue with alcohol, rejecting the alcoholic solution. Boil the residue insoluble in alcohol with water. Treat the residue insoluble in water and the water solution as follows:

Residue

Acidify with dilute hydrochloric acid. Effervescence indicates a carbonate such as chalk or whiting.

Residue insoluble in dilute acid may be calcium sulphate, barium sulphate, silica, clay, French chalk, etc.

Solution

Acidify with dilute hydrochloric acid. Effervescence shows presence of sodium or potassium carbonate.

To a portion of the acidified solution add barium chloride. A white precipitate, insoluble in acids, shows the presence of sodium or potassium sulphate.

Cool a portion of the acidified solution and add iodine. A blue color shows starch.

CHAPTER XXIX

SPECIAL SOAPS AND SCOURING POWDERS

Perfumed and Colored Soaps. — The perfumes and coloring matters ordinarily added to toilet soaps are harmless, but sometimes excessive quantities of perfume are used to conceal disagreeable odors due to the use of decomposing fats. Strongly perfumed soaps are, therefore, to be regarded with suspicion.

Transparent Soaps. — The best transparent soaps are made by dissolving the soap in alcohol, filtering off the undissolved residue, then removing the alcohol by evaporation. Glycerin is often added to give a pleasant emollient feel. Cheaper transparent soaps are made by the cold process from tallow, castor oil, palm oil, or coconut oil. These usually contain free alkali. Some contain sugar, an undesirable adulterant, because, being so soluble, it causes rapid wasting of the soap.

Experiment 92. — Test for Sugar.

Dissolve the soap in water, acidify with dilute sulphuric acid, filter off the precipitated fatty acids. Boil the filtrate for about half an hour, neutralize with sodium hydroxide, add a little of the neutralized solution to Fehling-Benedict solution, and boil for a minute. A red or yellow precipitate (cuprous oxide, Cu_2O) shows sugar.

Floating Soaps. — Floating soaps are made by beating the molten soap to incorporate air bubbles.

Marine Soap. — Marine soap is a soap made from palm-nut or coconut oil, and takes its name from the fact that it will form a lather with sea water. Marine soap has been known to contain as much as 70 per cent of water.

Mottled Soaps. — Soap with a faint gray mottle has been known for a very long time. The mottling was originally due to the use of rather impure fats and alkalies. When melted soap is solidifying, the more solid of its ingredients, sodium stearate and sodium palmitate, become solid before the sodium oleate. Some of the impurities, such as iron salts, tend to accumulate in the liquid sodium oleate. When the soap has all solidified, the dark-colored impurities are left in the places where the sodium oleate had accumulated. This gives a mottled appearance.

Modern mottling, which is often much more pronounced than the older kind, is accomplished by the intentional addition of coloring matters — ultramarine for blue, boneblack (carbon) or manganese dioxide for gray, etc. The mottling has no effect on the quality of the soap and has no bearing upon its real value.

Medicated Soaps. — A great variety of medicinal substances are added to soaps. Carbolic acid, tar, and oatmeal are among the commoner ones.

Soap Powders. — Soap powders are made by melting soda crystals (crystallized sodium carbonate) and adding soap. They may have as little as 1 or 2 per cent or as much as 20 per cent of soap and from 10 to 60 per cent of water.

Scouring Soaps. — Scouring soaps and scouring powders usually contain 10 to 20 per cent of soap, with 80 to 90 per cent of abrasive material — such as fine sand, ground pumice, whiting, or ground slate. Many also contain washing soda. The quality of such powders depends greatly on the fineness of the abrasive. Even a small proportion of coarse particles may do much damage by scratching. It is usually much more economical for the housekeeper to buy soap, soda, and abrasives, such as powdered bath brick, whiting, etc., separately, and to mix them for immediate use. It is much easier to judge of the fineness of an abrasive separately than when it is mixed with soap.

Experiment 93. — Test for Soda or Pearl Ash and Coarse Abrasives.*Apparatus:*

Bolting cloth sieves.

Dissolve as much of the powdered material as possible in alcohol. Treat the residue with hot water. Filter. Acidify the filtrate. Effervescence shows the presence of water-soluble carbonates — sodium or potassium carbonate.

Dry the residue from the treatment with water, and sift it successively through bolting cloths Nos. 4, 8, 12, and 16. The coarse particles of abrasive materials will be left on the sieves. By using a weighed quantity of soap (*e.g.* 100 grams) and weighing these coarse particles left on the sieves, we may estimate the proportion of coarse abrasive in the soap.

CHAPTER XXX

SOLUTION AND EMULSIFICATION OF FATS. THE CLEANING OF FABRICS

Experiment 94.

Materials :

Cottonseed oil or olive oil, lard, and the liquids enumerated below.

Caution.—Perform this experiment in a room in which no flames are burning.

Put the oil into 8 test tubes, to the depth of $\frac{1}{4}$ inch. Cover, respectively, to the depth of 1 inch, with the following liquids, shake, and allow to settle: (1) Ether, (2) Benzene (from coal tar), (3) Benzine (from petroleum. Note the difference in spelling), (4) Gasoline, (5) Kerosene, (6) Chloroform, (7) Carbon tetrachloride, (8) Turpentine.

Put a little lard into a beaker or evaporating dish, add one of the more volatile of the above liquids, *e.g.* benzine or benzene, and stir for a minute or two. If the lard does not all dissolve, filter through a dry filter on to a watch glass, allow to evaporate in a warm place, and test the residue either by putting it in a cool place to see if it will solidify, or by stirring it with a little Sudan III solution, washing off with alcohol and adding hot water. (See Experiment 85, p. 149.)

Experiment 95.

Materials :

Cottonseed or olive oil.

Lard.

Soap solution.

Wood alcohol.

Albumin solution (made either by mixing white of egg with an equal volume of water and beating with an egg beater, or by dissolving dry egg albumin in water).

Put the oil into 7 test tubes to the depth of $\frac{1}{4}$ inch. Cover with the following liquids to the depth of 1 inch, shake, and allow to settle: (1) Water, (2) Alcohol, (3) Wood alcohol, (4) Soap solu-

tion, (5) Sodium carbonate solution, (6) Albumin solution, (7) Albumin solution to which a few drops of sodium carbonate have been added.

What general difference do you observe between the behavior of these liquids towards the oil and that of the liquids used in Experiment 94? What differences do you observe between the behavior of liquids 1, 2, and 3, and that of liquids 4, 5, and 7 of the present experiment?

Shake lard with cold soap solution and with hot soap solution. In which instance does it behave like the oil?

When a fat or oil dissolves in ether, gasoline, benzine (a petroleum product) or benzene (a coal-tar product), the product is a clear, homogeneous liquid, similar to that obtained by dissolving salt, sugar, or alcohol in water. This clear liquid is a solution. Liquid fats (oils) shaken with water, in which they are insoluble, break up into fine globules which are distributed through the water and impart to it a turbid appearance. This turbid suspension of oil in water rapidly separates into two clear layers, the lower one being water, the upper one oil. There are, however, certain substances which when dissolved in water render it capable of holding the minute droplets of oil in more permanent suspension. Such a permanent or persistent suspension of oil in water is termed an **emulsion**. Soap is one of the best emulsifying agents. Washing soda and caustic soda have a similar effect — due to the formation of a certain amount of soap by their action upon the fatty acids always present in small quantities in natural oils.

The detergent effect of soap is due to its emulsifying properties. Those constituents of the dirt on soiled or spotted clothing which are not soluble in water are, as a rule, of a fatty nature. The addition of soap or soda to the water renders it capable of emulsifying the fats into fine droplets, which are then carried out of the fabric. The removal of the fat loosens any other dirt (earthy matter, etc.) which was held in position by the fat.

A number of plant and animal substances are known which have decided emulsifying power, and some of these have found use in household practice. Examples are *ox gall* (*i.e.* bile), *soapbark*, and *soapwort*.

The Cleaning of Fabrics

Stains on clothing commonly consist of a solid or sirupy substance holding miscellaneous particles of dirt.

Numerous devices are used practically for the removal of such stains, but all of these are directed towards the removal of the dirt-retaining agent. If this is of the nature of a sugar, starch, or gum, hot water will remove the stain. Stains based on fats are, however, more troublesome. A fat may be removed: (1) By melting and absorption, (2) by solution, and (3) by emulsification. Blotting paper, Fuller's earth, French chalk, and pipe clay are among the best substances used to absorb fats. A hot iron is used with the blotting paper or other absorbent to melt solid fats and to make liquid ones flow more readily. They flow away from the hot iron into the absorbent, which is placed *beneath* the cloth.

Dry cleaning practice depends upon the *solvent* action of the liquids used. Of the solvents enumerated in the directions for Experiment 94, only those can be used which evaporate quickly, so as to leave the cloth dry and free from disagreeable odor. Kerosene and turpentine are not sufficiently volatile for the purpose. Of the more volatile solvents, ether, benzene, benzine, and gasoline form explosive mixtures with air, and are therefore not suitable for use in the same room with a stove, lamp, or flame of any kind. Ether and chloroform are objectionable on account of their anæsthetic action. Carbon tetrachloride is the safest solvent to use, being non-inflammable and having only slight physiological effect. But the petroleum products, benzine and

gasoline, are much cheaper, and are therefore frequently used. The disagreeable odor of benzine can be partially removed by shaking it with charcoal and then filtering—a process easily carried on in the household. A more effective method is to shake it with sodium plumbite (Na_2PbO_2) and redistill it. The odor is also sometimes masked by the addition of oil of sassafras.

Since grease spots frequently contain other substances than fats, a mixture of solvents may be more efficient than a single liquid. Mixtures of alcohol with one or more of the fat solvents are sometimes used, *e.g.* 1 drachm each of ether, chloroform, and alcohol are mixed with 1 quart of deodorized benzine.

Common laundry practice is based largely upon the principle of emulsification, soap being the emulsifying agent. The use of hot water not only melts the fats, but assists the emulsification. Sometimes the action of the soap is supplemented by that of a fat solvent, such as carbon tetrachloride, paraffin wax, kerosene, naphtha. (See Chapter XXVIII.) These liquids, although not miscible with water, are emulsified by the soap solution. A very good combination of emulsifying and solvent agents for fats is a mixture of carbon tetrachloride with "Turkey-red oil." The latter is a substance, made by the action of sulphuric acid on castor oil, which dissolves in water, yielding a solution somewhat similar to that of soap. The mixture of Turkey-red oil and carbon tetrachloride is a clear liquid, which is readily miscible with water and which, like soap, renders the water capable of emulsifying fats. It may be used as a partial or total substitute for soap in the laundry, and also for the removal of stains by the use of cold water. In cold water it is also excellent for the removal of grease from the hands.

CHAPTER XXXI

THE GENERAL COMPOSITION OF FOODS

HUMAN foods — and the foods of animals in general — are complex mixtures of a large number of substances. The most important of these substances may be divided into two great classes, viz. :

I. The Inorganic Foodstuffs.

1. Water.
2. "Mineral matter" or "ash."

II. The Organic Foodstuffs.

1. Fats.
2. Carbohydrates.
3. Proteins.

The organic foodstuffs are compounds which contain the element carbon; the inorganic foodstuffs are those which do not contain carbon. The organic foodstuffs can be burned; the inorganic are incombustible.

The Inorganic Foodstuffs

Water is not only taken as a separate article of diet, and as the chief constituent of all beverages, but is also present in great abundance in some classes of solid foods, especially in fresh fruits, fresh vegetables, and fresh meats. Even many foods which are apparently dry contain very material quantities of water. Wheat flour, for example, contains about 12 per cent of water, and bread about 35 per cent. The amount of water in a food is determined (*i.e.* measured) by weighing the food, heating it to the boiling point of water until it ceases to lose weight, and then weighing the dried residue. The loss in weight represents the water which has been driven off. The weight of the residue represents the

combined weight of the organic foodstuffs and the mineral matter.

Experiment 96.

Materials :

Potato, turnip, or apple.

Apparatus :

Scales and weights.

Water bath.

Cut a slice of potato, turnip, or apple weighing about 25 grams. Immediately weigh it accurately. Cut up into fine, very thin pieces, place in a weighed dish, and dry on the water bath for several hours. Allow to cool in a dry atmosphere, and weigh the residue. Heat again on the water bath for an hour, allow to cool, and weigh. If the weight has not changed in the second weighing, the drying is completed. Deduct the weight of the dish, and calculate the percentage of moisture the vegetable or fruit contains.

EXERCISE

Consult the tables of food composition in Appendix A, and arrange the following foods in order of their water content, beginning with the driest.

- | | |
|--------------------|-----------------------|
| 1. Bananas | 12. Walnuts |
| 2. Apples | 13. Beef, hindquarter |
| 3. Grapes | 14. Salmon |
| 4. Watermelons | 15. Whole milk |
| 5. Green cucumbers | 16. Cream |
| 6. Tomatoes | 17. Butter |
| 7. Potatoes | 18. White of eggs |
| 8. Cabbage | 19. Yolk of eggs |
| 9. Oatmeal | 20. Oysters |
| 10. Flour | 21. Apple pie |
| 11. Bread | 22. Doughnuts |

When a food is thoroughly dried, the water all passes off as water vapor (steam). When the dried residue is strongly heated in the air, the organic foodstuffs are burned and pass off as gases and the inorganic salts remain behind in the ash. It must not be thought, however, that the ash consists entirely of salts which were present as such in the food. The

sulphur, phosphorus, and chlorine, and the potassium, sodium, calcium, and magnesium, which exist in the ash as sulphates, phosphates, and chlorides, may have been constituents of organic compounds in the unburned material. And the carbon which exists in the ash as a constituent of carbonates must have come either from the salts of organic acids or from more complex organic compounds, such as fats, carbohydrates, and proteins.

Nevertheless, the weight of the ash is regarded as a rough measure of the quantity of mineral matter in the food. The ash contains all the potassium, sodium, calcium, and magnesium and iron of the food. Part of the chlorine, sulphur, and phosphorus, however, may pass off as gases during the combustion of the food.

Except in foods which have been salted, the ash seldom amounts to five per cent of the weight of the food. In many foods it amounts to less than one per cent.

The Organic Foodstuffs

The nature of *fats* has already been discussed in connection with the manufacture of soaps and the removal of dirt from fabrics (Chapters XXV, XXVI, and XXX). Sugar and starch are typical *carbohydrates*. The white of egg, the lean of meat (muscle fibers), and the gluten of flour are examples of *proteins*.

It should be noted that while both fats and carbohydrates are composed of carbon, hydrogen, and oxygen, the proportion of carbon is much greater, and the proportion of oxygen much smaller in the former class of substances than in the latter.

Proteins differ from fats and carbohydrates in containing a fairly large proportion of nitrogen and a small proportion of sulphur, in addition to carbon, hydrogen, and oxygen. Besides these five elements a number of proteins contain a

small proportion of phosphorus. A few also contain iron or other elements.

The average composition of the three great classes of organic nutrients is given in the following table:

AVERAGE ELEMENTARY COMPOSITION OF NUTRIENTS

	FATS	CARBOHYDRATES	PROTEINS
	Per Cent	Per Cent	Per Cent
Carbon	76.5	44.4	53
Hydrogen	12.0	6.2	7
Oxygen	11.5	49.4	23
Nitrogen	—	—	16
Sulphur	—	—	1

The percentage of hydrogen in proteins does not differ greatly from that in carbohydrates. In carbon and in oxygen content, the proteins are intermediate between the fats and the carbohydrates.

CHAPTER XXXII

THE CARBOHYDRATES. I

BEFORE taking up the consideration of the functions of the various classes of foodstuffs it is desirable that we should learn something about the chemical constitution and behavior of the carbohydrates and proteins, similar to what we have already learned about the fats.

Carbohydrates (literally, *hydrates of carbon*) take their class name from the circumstance that in combination with carbon they contain the elements of water in the same proportion as water itself. Examples are *glucose*, $C_6H_{12}O_6$; *cane sugar*, $C_{12}H_{22}O_{11}$; *starch*, $(C_6H_{10}O_5)_n$. But the name does not adequately describe the class; for, on the one hand, many compounds which are not carbohydrates (*e.g.* formaldehyde, CH_2O ; acetic acid, $C_2H_4O_2$; lactic acid, $C_3H_6O_3$) contain hydrogen and oxygen in this proportion combined with carbon; and on the other hand there are a few rare carbohydrates whose molecules have more than twice as many hydrogen atoms as oxygen atoms.

The simplest carbohydrates are called *monosaccharides*. These are sweet-tasting substances, which are so abundantly soluble in water as to form sirups with it. In short, they are *sugars*. Honey is a sirup of two monosaccharides, called *glucose* (or *dextrose*) and *fructose* (or *levulose*), together with a small proportion (less than 10 per cent) of that sugar (cane sugar) which is most familiar to us — and which is not a monosaccharide. (See beyond.)

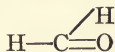
Now, the term **carbohydrates** embraces *the monosaccharides and all substances which by hydrolysis are converted into monosaccharides*.

Monosaccharides are divided into two classes — *aldoses* and *ketoses* — according to their structural formulas, and into several

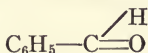
classes — *pentoses*, *hexoses*, etc. — according to the number of carbon atoms they contain. Glucose and fructose are both *hexoses*, having the molecular formula, $C_6H_{12}O_6$. Structurally, glucose is an *aldose*, fructose a *ketose*. Aldoses contain the radicle or "group" of atoms:



which is common to a class of compounds called *aldehydes*, of which the disinfectant, *formaldehyde*,

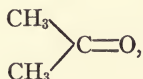


and the flavoring matter, *benzaldehyde* (oil of bitter almonds),



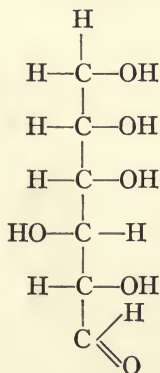
are familiar examples.

Ketoses contain the group =C=O , joined to two other carbon atoms, and belong to a class of compounds called *ketones*. *Acetone*,

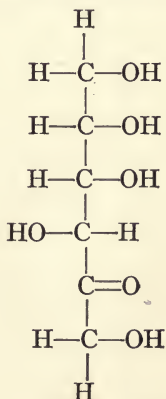


a product of the dry distillation of wood, is the simplest representative of the ketones.

The structural formulas of glucose and fructose are:



Glucose (Dextrose)



Fructose (Levulose)

It is clear from these formulas that these monosaccharides, in addition to being aldehydes or ketones, are also alcohols containing several —OH groups. And this alcoholic constitution appears to be true of all the carbohydrates, however complex their molecules.

Carbohydrates may be classified as follows:

I. **Sugars.** — These form crystals and dissolve in water. In solution they will pass through membranes of parchment paper. They have a sweet taste.

The most important sugars are:

(1) The monosaccharides — *glucose*, *fructose* and *galactose*.

(2) The disaccharides — *maltose*, *lactose*, and *sucrose*.

II. **Polysaccharides.** — This class includes *dextrin* and some other gums, *pectin*, *starch*, *glycogen*, and *cellulose*. Dextrin, pectin, and glycogen are soluble in water, but do not pass through parchment paper with the water. Starch is insoluble in cold water and cellulose insoluble even in hot water.

Experiment 97.

Materials:

Monosaccharides:

Glucose (dextrose, grape sugar).

Fructose (levulose, fruit sugar).

Disaccharides:

Maltose (malt sugar).

Lactose (milk sugar).

Sucrose (saccharose, cane sugar).

Polysaccharides:

Dextrin.

Starch.

Cellulose (absorbent cotton or filter paper).

Taste the carbohydrates. The sweet ones are *sugars*. Which of the above classes are included under this term?

Test the solubility of the carbohydrates in cold water by shaking about $\frac{1}{2}$ gram of each with half a test tube of water. Which of them are insoluble in cold water? Which one of the *sugars* is

much less soluble than the others? How does this one compare with the others in sweetness? Keep the solutions for subsequent experiments.

Find out whether any of the carbohydrates insoluble in cold water is soluble in hot water. Keep the solutions.

Experiment 98. — Fehling's Solution, Fehling-Benedict Solution, and the Meaning of "Reduction."

Materials :

Cuprous oxide, Cu_2O , and Cupric oxide, CuO .

Solutions of :

Copper sulphate, 17.3 grams to 1 liter.

Sodium potassium tartrate (Rochelle salt), 346 grams to 1 liter.

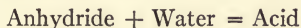
Sodium citrate, 173 grams to 1 liter.

(a) Note the colors of the two oxides of copper. Which of the two contains the larger proportion of oxygen? (See p. 39.)

To "reduce" a compound is to take away oxygen from it. Which of the oxides of copper can be changed into the other by reduction?

(b) Dissolve a little of the cupric oxide in dilute sulphuric acid. What salt is present in the solution so prepared? Write equation for its formation. We may regard this salt as containing cupric oxide, CuO , combined with SO_3 , the *anhydride* of sulphuric acid.

Acid anhydrides are the oxides which bear to acids the same relation that the basic oxides bear to the bases; *i.e.* :



Thus, carbon dioxide, CO_2 , is the anhydride of carbonic acid, H_2CO_3 ; sulphur dioxide, SO_2 , the anhydride of sulphurous acid, H_2SO_3 , etc.

(c) Add to a little of the solution prepared in (b) a little more than enough sodium hydroxide solution to neutralize the acid. What is the precipitate? Add more sodium hydroxide and boil. What is formed? (Compare Expt. 49.)

(d) To copper sulphate solution add, first, Rochelle salt solution, and then sodium hydroxide. What effect has the Rochelle salt on the reaction between sodium hydroxide and copper sulphate? We may regard the resulting solution (Fehling's solution) as containing cupric oxide, CuO .

(e) Make the same experiment as (d), using sodium citrate instead of Rochelle salt.

(f) To copper sulphate solution add sodium carbonate solution. What is the precipitate? Can it be regarded as containing cupric oxide?

(g) To copper sulphate solution add, first, sodium citrate, then sodium carbonate. The product is Fehling-Benedict solution which keeps better than Fehling's solution. Can Fehling-Benedict solution also be regarded as containing cupric oxide?

When Fehling's or Fehling-Benedict solution is reduced, *cuprous oxide* is formed. This oxide is not capable of forming soluble compounds with tartrates and citrates similar to those formed by *cupric* oxide, and is therefore precipitated. The precipitate obtained is, however, not always red, but often, especially with the Fehling-Benedict reagent, yellow or green, probably due to the presence of more or less *cuprous hydroxide*.

Experiment 99.

Materials:

The solutions of sugars prepared in Experiment 97.

To separate 5 cc. portions of Fehling-Benedict solution add a few drops of the sugar solutions. Boil for a minute or two. What is the precipitate? Which of the sugars produce it? These are called "reducing sugars." What sugar is *not* a reducing sugar?

Experiment 100.

Materials:

Sucrose solution prepared in Experiment 97.

To the sucrose solution add a little concentrated hydrochloric acid. Boil for a minute or two. Cool. Put in a small piece of litmus paper and add sodium hydroxide little by little until the acid is neutralized. Add a little of the neutralized solution to about 5 cc. Fehling-Benedict solution, and boil.

Does unchanged sucrose affect Fehling-Benedict solution? What change must have been caused by boiling the sucrose with the hydrochloric acid?

Experiment 101.

Material:

Starch.

Absorbent cotton (cellulose).

Sodium carbonate powdered (soda ash).

(a) In a beaker or dish mix a little starch ($\frac{1}{4}$ to $\frac{1}{2}$ gram) with a teaspoonful of water. Heat about 50 cc. of water in a dish to boiling, and add the mixture of starch and cold water. Boil for a minute or two, stirring constantly.

(b) Pour off some of the solution into a test tube and cool it under the tap. To a small portion of the cold solution add a little iodine solution. Warm the solution and cool it again. Does iodine color hot starch solution?

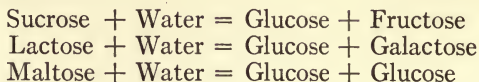
(c) To another portion of the cold solution add a few drops of concentrated sulphuric acid. Boil until a drop of the liquid poured off into cold iodine solution no longer colors the latter. This is evidence that starch is no longer present. Pour off the main portion of the boiled solution into a beaker and add powdered sodium carbonate, little by little, until the acid is neutralized. Add a little of this neutralized solution to Fehling-Benedict solution in a test tube, and boil for a minute.

What do you infer as to the effect of boiling the starch with the acid?

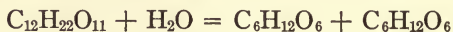
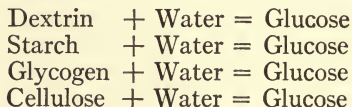
(d) Put a little absorbent cotton into a test tube, cover it with concentrated sulphuric acid, and allow to stand a minute or two. Note whether the cellulose dissolves in the sulphuric acid. Pour off into five or six times its volume of cold water and boil for two or three minutes. Neutralize the acid (in a beaker) with sodium carbonate as in (c), add to Fehling-Benedict solution, and boil.

It is evident from the above experiments that reducing sugars can be formed from cane sugar, starch, and cellulose by boiling with acids. The acid is, however, not used up in the reaction, which is really one between the carbohydrates and water — in other words, a *hydrolysis*. The acid is merely a catalytic agent, promoting the hydrolysis.

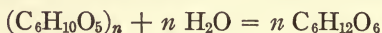
The final products of hydrolysis of all the higher carbohydrates (disaccharides and polysaccharides) are monosaccharides. Each *disaccharide* molecule hydrolyzes into *two* monosaccharide molecules, and each *polysaccharide* molecule into *several* monosaccharide molecules. The relations of the more familiar higher carbohydrates to the monosaccharides are as follows:

1. Disaccharides:

All three of these reactions are expressed by the equation:

**2. Polysaccharides:**

All of these reactions correspond to the equation:



in which n stands for an unknown number.

CHAPTER XXXIII

THE CARBOHYDRATES. II

Description of the Monosaccharides, $C_6H_{12}O_6$

Glucose, also called *dextrose* and *grape sugar*, occurs very widely distributed in plant juices, and also in smaller proportions in the blood of animals. It is a prominent constituent of honey and of raisins, and sometimes separates from these in the solid form. It does not crystallize nearly as readily as sucrose (cane sugar), however, and in the processes used to separate the latter from the juice of the sugar cane and from the juice of the sugar beet, the glucose remains in the molasses. It is less sweet than sucrose.

Commercial glucose, which appears on the market both in solid form and in a sirup, is manufactured by hydrolysis of starch by an acid. In addition to glucose proper, commercial glucose contains the polysaccharide dextrin, and the disaccharide maltose, — these being also formed by the hydrolysis of starch. Commercial glucose is cheaper than cane sugar, and is sometimes used as a substitute for, or as an adulterant of, the latter. It is also "compounded" (*i.e.* mixed) with cane sirup to form a table sirup known as "corn sirup."

Fructose, also called *levulose* (or *lævulose*) and *fruit sugar*, is found associated with glucose in fruit juices and in honey. A mixture of equal quantities of glucose and fructose is produced when cane sugar is hydrolyzed.

In the preparation of jams and preserves much of the cane sugar put in is hydrolyzed by the acids of the fruit, and the jam and preserves contain this mixture of glucose

and fructose. The hydrolysis of sucrose is technically spoken of as the *inversion* of sugar, and the mixture of equal quantities of glucose and fructose as *invert sugar*.

The term "inversion" refers to an effect which sugar solutions have upon so-called "plane-polarized" light. In terms of the wave theory of light, plane-polarized light has all its vibrations in *one* plane at right angles to the direction of the ray, while ordinary light has vibrations in *all* directions at right angles to the direction of the ray. The instrument used to measure the effect of substances upon polarized light is called a *polariscope* or *polarimeter*. It consists essentially of two prisms of calcite (crystallized calcium carbonate) at opposite ends of a tube. One prism is fixed in position; the other can be rotated about the axis of the tube. When light admitted through the fixed prism is allowed to pass through air or water to the second prism, it only passes completely in case this second prism is in a similar position to the first. If the second is rotated into a position at right angles to the first, the light is shut out entirely. In intermediate positions it is partially transmitted. Now, if in passing from prism to prism the light passes through a sugar solution, the second prism being in a similar position to the first, the light is no longer fully transmitted through the second prism. If, however, this second prism be rotated — it may be to the right or it may be to the left — through a certain angle, the light will be fully transmitted. The angle through which the prism has to be rotated is equal to the angle through which the "plane of polarization" is rotated by the sugar solution.

Now, sucrose and glucose rotate the plane of polarization to the right, while fructose ("levulose") rotates it to the left. At room temperature fructose rotates the plane more to the left than an equal quantity of glucose rotates it to the right. Hence, invert sugar is levorotatory,¹ and the hydrolysis of the sucrose changes a dextrorotatory solution into a levorotatory one.

Galactose does not occur as such, but is produced by hydrolysis of lactose and of certain higher carbohydrates, *galactans*, which bear to it a similar relation to that which starch bears to glucose.

¹ Latin, *laevus* = left, *dexter* = right.

Alcoholic Fermentation

The ferment, *zymase*, contained in yeast, causes the monosaccharides to decompose into alcohol and carbon dioxide :



This is the reaction which characterizes the fermentation of fruit juices. It is made use of in the manufacture of wines and sometimes occurs in jars of fruit which have not been thoroughly sterilized. The same reaction is involved in the final stage of fermentation of grains in the manufacture of beer and whisky, and in the raising of bread.

Description of the Disaccharides, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Sucrose, also called *saccharose* and *cane sugar*, is of very common occurrence in the vegetable world, being found in considerable quantity in the fruits and juices of many plants — usually mixed with more or less glucose and fructose. The most important sources of sucrose are the sugar beet, sugar cane, sorghum cane, and sugar maple.

Pure sucrose obtained from any of these sources does not differ from that obtained from any of the others. Rock candy is chemically pure sucrose, and commercial white sugar contains very little impurity.

The hydrolysis (inversion) of cane sugar can be brought about by boiling the aqueous solution with an acid. Hence this reaction takes place in the preserving of fruits. (See above.) It can also be accomplished by one or more ferments commonly called *invertases* or *invertins*, but more correctly termed *sucrases*. There is a ferment of this class in the yeast plant (which assists in alcoholic fermentation by converting sucrose into glucose and fructose) and another in the intestinal juice (which effects the same change as a step in the digestion of sugar).

Experiment 102.*Materials :*

Yeast.

Cane sugar.

Sand.

Mortar and pestle.

Grind a yeast cake with sand and a little water. Dilute to 50 cc., add 5 cc. ether, and filter. To the filtrate add 100 cc. alcohol. This precipitates the *sucrase* (invertase). Filter. Change the receiver and dissolve the precipitate by pouring about 20 cc. water through the filter.

Dissolve about $\frac{1}{3}$ gram sugar in a half test tube of water. Add a little of the *sucrase* solution just prepared, and allow to stand about half an hour. Then add a little of the solution to Fehling-Benedict solution, and boil for a minute or two. If no precipitate is formed, allow the sugar solution to stand another half hour and repeat the test.

Cane sugar has no action on Fehling's solution, but invert sugar, of course, has. In other words, cane sugar is non-reducing, but yields reducing sugars upon hydrolysis.

Maltose, or *malt sugar*, yields only a single kind of monosaccharide — one molecule of maltose hydrolyzing to two molecules of glucose. This hydrolysis is readily effected by boiling the maltose with dilute strong acids. It is also brought about by the action of ferments, called *maltases*, one of which is a constituent of the intestinal juice. Maltose is formed from starch by the action of amylolytic (*i.e.* starch-hydrolyzing) ferments, *amylases*. An amylase known as *diastase* is developed in germinating grain and hence is present in malt, malt extract, and beerwort. Two amylases are concerned in digestion of starch. These are the *ptyalin* of the saliva and the *amyllopsin* of the pancreatic juice. Maltose is also formed as an intermediate product when starch is hydrolyzed by boiling with acid, as in the manufacture of commercial glucose.

Lactose — *milk sugar* or *sugar of milk* — hydrolyzes to glucose and galactose. It occurs in the milk of mammals.

Fresh cow's milk contains about five per cent. Lactose is much less soluble in water than the other sugars, and has only a slightly sweet taste. It is commonly used in pharmacy as a "base" (or diluent) for pills and tablets. In digestion lactose is hydrolyzed in the intestine under the influence of a ferment known as *lactase*. Lactose is converted into lactic acid by a certain class of bacteria which are normally present in fresh milk and are very abundant in buttermilk. The souring of milk is due to this fermentation. Maltose and lactose reduce Fehling's solution.

The Polysaccharides ($C_6H_{10}O_5$)_n

Starch is the principal form of digestible carbohydrate in cereal grains and their products and in potatoes. It constitutes more than half the solid matter of all the common cereals and about three fourths of that of the potato. Being the principal storage form of carbohydrates in most green plants, starch is found in more or less abundance in almost all vegetable foods. For commercial purposes starch is isolated from wheat, maize (corn), rice, and potatoes. Arrowroot, tapioca, and sago are also almost pure starch. All these commercial forms of starch contain water, about eighteen per cent as an average. Starch granules of different plants vary in size and structure; so the source of a starch which has not been altered by heat, fermentation, or the action of chemical reagents can be determined by microscopic examination.

Experiment 103.

Materials :

- Cornstarch.
- Potato starch.
- Wheat starch.

Apparatus :

- Compound microscope.
- Slides.
- Cover glasses.
- Medicine dropper.

Prepare the three starches for microscopic examination by first sifting through a 60- or 80-mesh sieve, then placing a small portion on a slide by means of a knife point, adding a drop of distilled water, putting on the cover glass obliquely (so as to avoid inclosing air bubbles) and then rubbing out the material under the cover glass between the thumb and finger to separate the particles and distribute them evenly.

Examine the starches under the microscope, using a magnification of about 250. Note the general form and comparative size of the granules, and the presence or absence of concentric ring markings and of the little depression called the *hilum*.

The granules of these three starches are typical of the three general forms—the circular, the irregularly oval, and the polygonal. Note, however, that wheat starch consists of two kinds of granules—the larger having one form, the smaller another. In the form of their granules rye and barley starches resemble wheat starch; arrowroot, pea, and bean starches resemble potato; and oats, buckwheat, and rice resemble corn.

The most characteristic chemical test for starch is the reaction with iodine in the cold. (See Expt. 101 (b) above.)

When starch is treated with hot water, the granules swell and burst, and the starch apparently dissolves in the water, forming an opalescent liquid or paste. In many respects this liquid differs from the solutions of such substances as salts, acids, bases, and sugars. These latter substances, which separate from their solutions in crystalline form, are known as *crystalloids*, while starch is a *colloid* (literally, glue-like substance). When a starch solution evaporates, no crystals form, but the starch gradually dries to a hard, horn-like or glue-like mass, from which it is very difficult to drive off the last traces of water. An important difference between colloids and crystalloids in solution will be referred to later. (Chapter XXXVII.)

The hydrolysis of starch by acids and by amylases has been referred to in connection with glucose and maltose. On standing in the cold with a dilute strong acid, starch is converted into a soluble substance which gives a blue color

with iodine, and does not reduce Fehling's solution. This is known as *soluble starch*. Similar products are formed by the action of organic acids, dilute alkalies, and other reagents.

Further hydrolysis (by longer standing or by heating with acid) produces soluble substances known as **dextrins**, some of which give a red coloration with iodine, while others give no coloration at all. Commercial dextrin is prepared by heating starch for some time to about 200° C. about (400° F.) or by moistening with dilute nitric or hydrochloric acid and heating to a lower temperature (100–120° C.). In breadmaking some dextrin (together with maltose) is formed during the rising by the action of diastase on the starch of the flour. In the baking a further portion of the starch in the crust is converted into dextrin by the heat. The effect of toasting bread is to convert some of its starch into dextrin. It is present in considerable abundance in some of the malted breakfast foods.

Dextrin is white when pure, but commonly yellow in commercial samples. It is soluble in water, giving a strongly dextrorotatory solution (whence the name). The solution is colloidal, and on drying behaves like that of a starch. Dextrin is used as a substitute for natural gums (some of which are analogous carbohydrates) in the manufacture of mucilage, label gums, and "sizes" for giving a glazed finish to textiles, cardboard, and paper. Dextrin is precipitated from its aqueous solution by the addition of alcohol.

Glycogen, sometimes called *animal starch*, is similar to dextrin in properties. It plays a part in animal organisms similar to that played by starch in the vegetable world,—the part of a "reserve" or "storage" carbohydrate. It is found in the muscles and more abundantly in the liver, the amount present varying greatly with the condition of nutrition of the animal. Stored glycogen is rapidly used up under conditions of starvation and of hard muscular work. Glycogen is a white powder, soluble in water to an opalescent

colloidal solution. With iodine it gives a reddish coloration, somewhat similar to that given by dextrin.

The **celluloses** constitute the walls of the cells of plants, thus acting as a sort of plant skeleton. Celluloses are insoluble in water and in dilute acids and alkalies. The "crude fiber" which the analyst determines in foods, by successively treating with dilute acid and alkali, and weighing the undissolved residue, consists mainly of cellulose. By heating with strong acid, ordinary cellulose — such as that of cotton and linen — is hydrolyzed, yielding glucose. Cotton and linen are comparatively pure cellulose, and straw, wood, and paper contain large proportions of this class of carbohydrates.

The proportion of cellulose in different parts of a plant vary widely. It is usually most abundant in the stem, with less in the foliage and least in the fruit. Such vegetables as celery, beets, and turnips contain much more cellulose than do potatoes, flour, and fruits. As a plant matures, its cell walls thicken. Consequently the proportion of cellulose in its stem, branches, and roots increases, and some of the cellulose is converted into a harder form called *lignocellulose* or woody tissue. This accounts for the toughness of over-mature vegetables.

Cellulose is digested to only a slight extent. The foods rich in cellulose, *e.g.* turnips and green vegetables, do not contribute much to the fuel value of the diet. As regulators of physiological processes, however, they are of importance, both on account of the salts and other ash constituents which they contain and on account of the cellulose which mechanically stimulates the intestines, inducing peristaltic action.

Pectin is a polysaccharide contained in the juices of some fruits, *e.g.* red currants, and obtained from the pulp of many fruits and vegetables, and from the inner peel of oranges and lemons upon boiling with water. The addition of alcohol to such juices or extracts precipitates the pectin as a jelly. If the solutions are rich enough in pectin, or if they are boiled

down until they are rich enough in pectin, either an acid or a sugar will also precipitate the pectin. In the making of fruit jellies and marmalades the acid naturally present in the fruit juices and the added sugar serve to precipitate the pectin, and the secret of successful jelly making is to have the proportions of pectin, water, acid, and sugar so adjusted that the pectin is precipitated as a continuous network, filling the whole mold or glass into which it is poured. By boiling with strong acid, pectin can be hydrolyzed to reducing sugars, but the products obtained are probably not identical with any of the familiar sugars described above.

Caramel. — When cane sugar is heated, it melts at about 160°C . (320°F .), and at a little higher temperature begins to decompose. Effervescence occurs due to the evolution of water, and the melted sugar acquires a dark color and a peculiar flavor. Sugar which has suffered this change is said to be caramelized, the color and flavor being attributed to *caramel* (from the Latin, *calamellus*, sugar cane). In addition to caramel the caramelized sugar may contain glucose. When caramelized sugar is dissolved in water and fermented with yeast, the glucose and unchanged sucrose are destroyed and the caramel is left unaffected. Caramel has a dark brown color and a bitter taste. It is sometimes used to color milk and cream. Caramel is not a single substance, but a mixture of several compounds, all of which differ from cane sugar in that they reduce Fehling's solution and are not fermented by yeasts. Glucose, melted and heated, also loses water and yields caramel, and lactose yields a similar product known as *lacto-caramel*. The color and flavor of taffy are due to caramel, and it is produced in many cooking operations. Sugar which has been melted and only slightly yellowed by heating to 160°C . (320°F .), as in making taffy, is called *barley sugar*.

CHAPTER XXXIV

THE PROTEINS. I

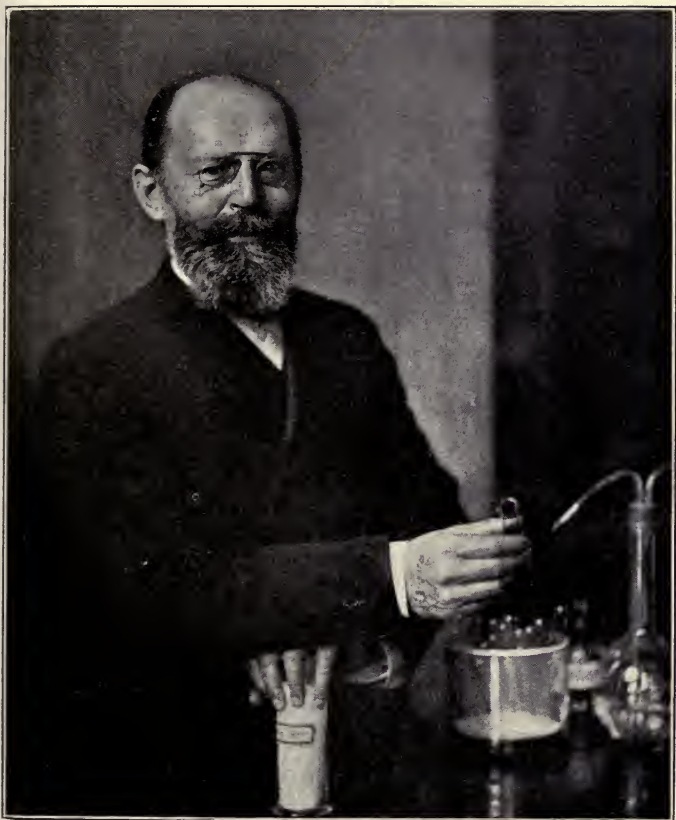
THE most important plant and animal substances containing the element nitrogen are the **proteins**. Being indispensable constituents of the cells of which all vegetable and animal organisms are made up, proteins are essential to life. Other nitrogen compounds than proteins exist in plants and animals. Among such are ammonium salts; the *alkaloids*, such as the caffeine of tea and coffee, the nicotine of tobacco, and the quinine of Peruvian bark; the *amides*, such as asparagine and urea; the *extractives* of meat, such as creatine and creatinine.

These substances are chemically simpler than the proteins; in other words, they are made up of smaller molecules. But their relative abundance is so small that when a chemist wishes to estimate the quantity of protein in a food, he commonly ignores the presence of these simpler nitrogenous compounds and calculates the quantity of protein by multiplying the total quantity of nitrogen found by 6.25.

The reason for using this factor is that, on the average, proteins contain 16 per cent of nitrogen, and $16 \times 6.25 = 100$.

It will be realized that this is only a rough way of determining the quantity of protein in a food, but it is the method almost universally used.

The proteins resemble the polysaccharides in having very complex molecules, in forming colloidal solutions, and in being hydrolyzable into crystalloid substances. The crystalloid substances into which the proteins are ultimately converted by hydrolysis are the so-called *amino acids*.



EMIL FISCHER.—1852—.

A distinguished German chemist, whose researches upon the chemistry of the carbohydrates and proteins have contributed much to our knowledge of both these classes of compounds.

In all, about twenty amino acids have been obtained from the various proteins by hydrolysis, and a single protein may yield all of them, and usually does yield the greater number of them. Some of these twenty-odd amino acids contain more than one amino group, some more than one carboxyl group, some contain sulphur, and there are various other complications.

The proportions of the various amino acids yielded by the various proteins differ widely. For instance, comparing the following proteins — *casein* from milk, *gelatin* prepared from the tendons of beef, *gliadin* from wheat, and *zein* from corn — we find that no glycine is yielded by casein, gliadin, or zein, while the amount yielded by gelatin amounts to one sixth of the weight of the gelatin. Again, while gelatin yields only 0.6 per cent of alanine, casein yields 1.5, gliadin 2, and zein nearly 10 per cent of this amino acid. Once more, *tryptophane*, one of the very complex amino acids, is not found among the hydrolysis products of gelatin or of zein, but gliadin yields 1 per cent and casein $1\frac{1}{2}$ per cent of this substance.

In addition to amino acids, *ammonia* is formed in the hydrolysis of proteins, and from certain classes of proteins — the so-called “conjugated” proteins — still other products are obtained. Thus, *hemoglobin*, the red coloring matter of the blood, yields a pigment containing iron; *casein* (the curd of milk) and *vitellin* of egg yolk yield phosphorus compounds; the *mucins* yield carbohydrates; and *nucleins* yield nucleic acid, a complex organic acid containing phosphorus. The amino acids and the other groups which enter into the molecules of the more complex proteins are often referred to figuratively as the “building stones” of the protein molecules. “Native” proteins (*i.e.* such as exist in plant and animal tissues and fluids) may be divided into two classes:

1. **Simple proteins**, which yield no hydrolysis products other than amino acids and ammonia.
2. **Conjugated proteins**, which yield other hydrolysis products in addition to amino acids and ammonia.

Just as in the hydrolysis of starch, intermediate products—soluble starch, dextrins, maltose—between the starch and its ultimate product, glucose, were obtained, so also in the hydrolytic cleavage of proteins, intermediate products are obtained. Some of these products have still the essential characteristics of proteins. When egg-white is heated above 73° C. (160° F.), for example, it hardens or “coagulates.” It is thus converted from a substance soluble in water into one which is insoluble but is still essentially a protein. It is believed that this change is due to slight hydrolysis or hydration of the protein molecule. Similarly, the soluble *caseinogen* of milk is readily converted into the insoluble protein, casein, by the action of the ferment rennin; and the soluble *fibrinogen* of the blood clots into *fibrin* when the blood is exposed to air. Such slightly altered proteins are called “derived proteins” or *protein derivatives*. Another class of derived proteins are obtained by further hydrolysis of such primary derivatives as coagulated egg albumin, fibrin, and casein. Such hydrolysis can be accomplished by the action of digestive ferments (such as the pepsin found in the stomach and the trypsin found in the small intestines) and the products are substances soluble in water and not coagulated by heat. The substances so produced are called *proteoses* and *peptones*. Proteoses are more complex and less soluble in salt solutions than peptones, but no very sharp line of distinction can be drawn between the two classes of compounds. The term peptone was formerly applied to both, and commercial “peptone” consists largely of proteoses.

Protein Tests

The following are some of the most general tests for proteins:

1. **Decomposition Test.**—Proteins when subjected to dry heat (*e.g.* in a test tube) give off vapors having an alkaline

reaction and a characteristic, disagreeable, "empyreumatic" odor — that of burning meat, feathers, leather, hair, wool, etc.

When the protein is mixed with lime and heated, the odor of ammonia is distinctly noticeable.

Experiment 104.

Materials :

- Egg albumin, dry.
- Blood albumin, dry.
- Gelatin.
- Casein.
- Quicklime.
- Turmeric paper.
- Red litmus paper.

Heat a little of each of the proteins in a dry test tube. Note the odor. Add quicklime and heat again. Note odor and hold turmeric paper and red litmus paper at the mouth of the test tube. Also expose turmeric paper and red litmus paper to ammonia gas by holding them to the open mouth of the ammonium hydroxide reagent bottle.

2. **Xanthoproteic Test** (Greek, *xanthos* = yellow). — Proteins heated with concentrated nitric acid impart a yellow color to the acid, owing to the formation of xanthoproteic acid. If the acid be then neutralized with ammonia, the color deepens.

Experiment 105.

Materials :

- The same proteins as for Experiment 104.
- Sugar.

Gently heat a little of each of the proteins with concentrated nitric acid. Note the coloration. Cool the tube, and then neutralize the acid with ammonium hydroxide. Heat a very little sugar with nitric acid in the same manner as the proteins. Is the acid colored by the sugar? Cool and neutralize with ammonia. In making the xanthoproteic tests on the proteins notice the difference in behavior between gelatin and the other proteins. Chemically pure gelatin gives no xanthoproteic test. This test is due to the action of nitric acid upon the amino acids of a certain

class, none of which is yielded by the hydrolysis of pure gelatin. Commercial gelatin, however, contains small quantities of other proteins.

3. **Millon's Test.** Proteins boiled with Millon's reagent (prepared by dissolving mercury in its own weight of concentrated nitric acid, diluting with twice the volume of water, and allowing to settle) yield a red precipitate which collects at the surface of the liquid.

Experiment 106.

Materials :

The same proteins as for Experiment 104.

Boil small portions of the proteins in test tubes with Millon's reagent. Note the difference in behavior between gelatin and the others. Pure gelatin gives no Millon's test, this reaction being due to an amino acid of the same class as those to which the xanthoproteic test is due.

4. **Biuret Test.** — Proteins dissolved in strong alkali and treated with minute quantities of copper sulphate give a violet to blue coloration. The test takes its name from the substance with which it was first obtained. Biuret, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, although neither a protein, a peptide, nor an amino acid, gives a coloration like that given by the proteins.

Experiment 107.

Materials :

The proteins used in Experiment 104.

Peptone.

Dissolve a little of each in a 50 per cent solution of potassium hydroxide. To a test-tubeful of water add a drop or two of copper sulphate solution. Add a few drops of this diluted copper sulphate solution to the alkaline solutions of the proteins. Note any differences observed.

CHAPTER XXXV

THE PROTEINS. II

WE have seen that the "building stones" which go to make up the molecules of proteins are numerous and varied. We have also seen that a single pair of these amino acids can be joined together into two different products, *e.g.* glycine and alanine into either glycyl alanine or alanyl glycine. Remembering, now, that the protein molecules are built up, not of two, but of a large number of building stones, we can realize that a great many different kinds of protein molecules might be constructed, not only by varying the selection of the building stones, but also by varying their arrangement.

Whether this be the explanation or not, it is certainly true that the proteins exhibit a remarkable diversity of physical properties, particularly as regards their solubilities. It is customary to attempt to classify the proteins according to their solubilities in a number of solvents.

The **albumins** dissolve in water and are coagulated by heat. *Egg albumin* (ovalbumin), *milk albumin* (lactalbumin), and *blood albumin* (seralbumin) are typical examples.

The term *albumins* has been much used as the general class name for proteins. The definition here given is that now recognized by the leading American and British societies of physiology and biological chemistry. Other terms formerly used as synonyms for the modern term *proteins* are *proteids* and *albuminoids*. The societies referred to have agreed to drop the word *proteid* altogether. The English societies also drop *albuminoid*, while the American societies use it to designate a special class of proteins. (See below.)

Experiment 108. — Coagulation of Egg Albumin.*Materials :*

Fresh white of egg.

Thermometer.

Fill a test tube to the depth of $1\frac{1}{2}$ to 2 inches with fresh white of egg. Put a thermometer into the liquid and place the tube in a beaker of cold water over a low flame. Note the temperature at which the albumin coagulates (whitens). Express this temperature in Fahrenheit and in Centigrade degrees.

It is because of the coagulating effect of heat on albumins and on some other classes of proteins that in washing dishes which have held uncooked foods, such as milk or eggs, it is better to rinse with cold water before applying hot water.

The **globulins** are insoluble in water but soluble in dilute solutions of the neutral salts of strong acids with strong bases. They are, however, insoluble in concentrated solutions of these same salts. (The albumins are soluble both in dilute and in saturated sodium chloride and magnesium sulphate.)

Among the globulins are the *myosin* of meat, the *fibrinogen* of blood (the change of which into *fibrin* is the cause of blood clotting), *serum globulin*, which remains in solution in the serum of blood, and *ovoglobulin*, a constituent of egg-white. *Edestin* is a globulin found in many plant seeds, including the cereals, flaxseed, and hempseed. *Legumin* is a globulin found in peas and beans.

Experiment 109.*Materials :*

Hempseed, crushed.

5 per cent solution of common salt.

Cover a handful of crushed hempseed with 5 per cent sodium chloride and heat to 60° C. for about half an hour. Moisten a filter with hot 5 per cent sodium chloride solution and filter the hot liquid through it. Allow the filtrate to cool. Part of the edestin crystallizes out on cooling. Filter off a little of this crystallized edestin and wash it in test tubes with water. Boil a

little of it with Millon's reagent. Does it behave like a protein? Treat three equal portions of the edestin with, respectively, (a) distilled water, (b) a 5 per cent sodium chloride solution, (c) a saturated sodium chloride solution, warming each to about 60° C. Which of these three liquids is the best solvent for edestin?

The most important proteins of the interior of the wheat grain (and therefore of white flour) are those which are contained in the **gluten**. Gluten, which — as is evident from the method of its preparation from flour — is insoluble in water, contains as its chief constituents two proteins called *glutenin* and *gliadin*. Both of these constituents are insoluble in water. **Glutenin**, however, is soluble in very dilute acids and alkalis and is representative of a class of proteins known as **glutelins**, which behave similarly. **Gliadin** is soluble in a mixture of alcohol and water containing 60 to 70 per cent of the former. It is, however, insoluble in absolute alcohol.

Experiment 110. — Preparation of Wheat Gluten from Flour.

Materials :

Wheat flour, strong and not over nine months old.

Cheesecloth.

Mix 30 grams flour with 5 cc. water to form a stiff dough. Knead in the hand in a stream of running water until the water runs through clear. (What constituent of the flour is carried out by the water, rendering it turbid?) Examine the residue of gluten left in the hand. Note its color and elasticity. The quality of flour depends not only on the quantity, but also on the quality of the gluten contained in it. The gluten of good flour is yellow, tough, and elastic. That of aged flour is grayish and "short" or friable.

Experiment 111. — Gliadin.

Materials :

Gluten from Experiment 110.

Mortar and pestle.

Put the gluten from Experiment 110 in a mortar, cover it with a mixture of 5 cc. water and 15 cc. alcohol and rub well with the pestle. Filter. To one portion of the filtrate add water, to another alcohol. What effect does each have? Explain.

The **albuminoids** or **scleroproteins** (from the Greek, *skleros*, hard) are a class of simple proteins characterized by great insolubility. They include *collagen*, the protein of cartilage, skin, and bone; and *keratin*, the protein of hair, horns, hoofs, nails, etc. Collagen is converted by hydrolysis into **gelatin** which is soluble in hot water, forming a solution which sets to a jelly on cooling. Commercial gelatin is usually made from bones by treatment with hydrochloric acid, followed by treatment with boiling water or steam. *Glue* is a crude form of gelatin made from hoofs and hide clippings. *Isinglass* is a natural gelatin found in the swimming bladders of certain fishes.

The *keratins* contain a high proportion of sulphur. Hair and wool are therefore characterized by decided tests for sulphur — a fact which is used to distinguish these fibers from silk, which is also essentially protein but contains no sulphur. (See Chapter XL.)

Experiment 112.

Materials :

Sulphur.

Wool, undyed.

Egg albumin, raw, coagulated (hard boiled), or dried.

Egg yolk, raw or coagulated.

Silk.

(a) Prepare sodium plumbite solution by adding sufficient sodium hydroxide solution (5 to 10 cc.) to 1 cc. lead acetate solution to redissolve (on warming) the precipitate which forms at first.

(b) Boil a little sulphur with sodium hydroxide solution. Add a little of the sodium plumbite. The black precipitate which forms is lead sulphide, PbS .

(c) Boil a small quantity of the wool with sodium hydroxide. Add to sodium plumbite solution and boil. Add sufficient water to enable you to see through the liquid. Has a black precipitate (lead sulphide) formed?

(d) Repeat (c) using egg albumin instead of wool.

(e) Repeat (c) using yolk of egg.

(f) Repeat (c) using silk.

CHAPTER XXXVI

THE FUNCTIONS OF FOOD

THE functions of food are:

1. *To supply building material* for the growth and repair of body tissue.
2. *To furnish energy* for the internal and external work of the body *and heat* to keep the body warm.
3. *To regulate the physiological processes, i.e.* the chemical and physical changes occurring in the body.

I. Food as Building Material

The human body is composed of the same classes of substances as foods. It is made up approximately as follows:

APPROXIMATE COMPOSITION OF HUMAN BODY

	PER CENT
Water, about	65
Proteins, about	18
Fat, about	12 (varying greatly)
Carbohydrates, less than	1
Ash, about	4 to 5.

The amount of carbohydrates in the body is not only very small, but also exceedingly variable. The amount of fat is also widely variable and may fall very low without interfering with the normal physiological processes.

Proteins are essential constituents of all living cells, both vegetable and animal. There can be no life without them. Plants manufacture their own proteins from inorganic materials, making use of the carbon dioxide which they obtain from the air and of the water and nitrogen compounds which



WILBUR OLIN ATWATER. — 1844-1907.

Distinguished for his researches on the chemistry of nutrition. Professor of Chemistry in Wesleyan University, Middletown, Connecticut, from 1873, the first director of an American agricultural experiment station, and the first Director of the Office of Experiment Stations of the United States Department of Agriculture, Atwater devoted special attention to agricultural chemistry and to problems of human nutrition. Under his direction numerous analyses and determinations of digestibility of American food materials were made. The respiration calorimeter described in the text was devised for the purposes of these nutrition investigations.

they obtain from the soil to build up the large and complex protein molecules.

Animals have not this power of building up proteins from inorganic materials. It appears doubtful whether they can synthesize them even from simpler organic substances not derived from other proteins. For the most part, at any rate, they merely take proteins ready-made and convert them into other proteins.

Since animals must have proteins to form and repair their body tissues, and since they cannot make proteins except from other proteins, it follows that proteins are absolutely essential constituents of the food of all animals. However generous the supply of carbohydrates and fats, the animal cannot thrive nor even continue to live without a constantly renewed supply of protein. The term "protein" (from a Greek verb signifying *to take the first place*) is applied to this class of compounds on account of its unique and preëminent importance in relation to life.

Some of the ash constituents of food are also of special importance as building material. Bones contain a large proportion of calcium phosphate. This salt constitutes more than half the weight of the dry, or more than one-fourth the weight of the fresh, bone. Calcium salts and phosphorus compounds are therefore of great importance in foods in relation to the growth and maintenance of the skeletal framework of the body. Iron is an essential constituent of hemoglobin, the protein of the red corpuscles of the blood. Hence, an abundant supply of iron in the food is important for the maintenance of health, and still more so when the blood requires enrichment; *e.g.* in cases of anæmia.

II. Food as Fuel

The chief ultimate products of the chemical changes which occur in the body are the carbon dioxide given off from the

lungs; the water excreted by the lungs, skin, and kidneys; and the urea and salts excreted by the kidneys. Urea is a nitrogenous organic compound of the formula, CON_2H_4 , and is plainly derived from the proteins. As far as the organic foodstuffs are concerned, then, we may summarize the chemical reactions of the body as follows:

Fats and carbohydrates oxidize to carbon dioxide and water.

Proteins oxidize to carbon dioxide, water, and urea.

The foregoing paragraph must be understood, not as an adequate account of the chemistry of nutrition, but only as the roughest outline of the sum of the numerous changes involved. The reactions by which the different classes of foods are digested, absorbed, stored, and utilized as fuel are very complicated. Some reference to these processes — especially to digestion and absorption — will be made later.

Again, the products enumerated above are by no means all the compounds excreted from the body. In addition to water, salts, and urea, the urine contains notable quantities of three other nitrogenous compounds of importance, namely, *uric acid*, *creatinine*, and *hippuric acid*, and also notable quantities of a number of sulphur compounds. The bowel excrement (feces), although consisting in part of undigested food — more or less fermented and putrefied by bacteria — also contains a certain proportion of substances derived from the digested and absorbed food. Among these are compounds of iron, phosphorus, magnesium, and calcium.

These ultimate products of the chemical changes occurring in the body are produced by the combining of the oxygen of the air with the elements of the digested and assimilated food. And it is to be noted that the products of oxidation of the fats and carbohydrates in the body are exactly the same as those which are produced by the rapid oxidation, *i.e.* combustion, of these substances.

When food is oxidized in the body, then, the chief chemical products are the same as those which would be obtained if the food were burned in a stove or in a calorimeter. (See p. 52.) For fats and carbohydrates this statement is literally

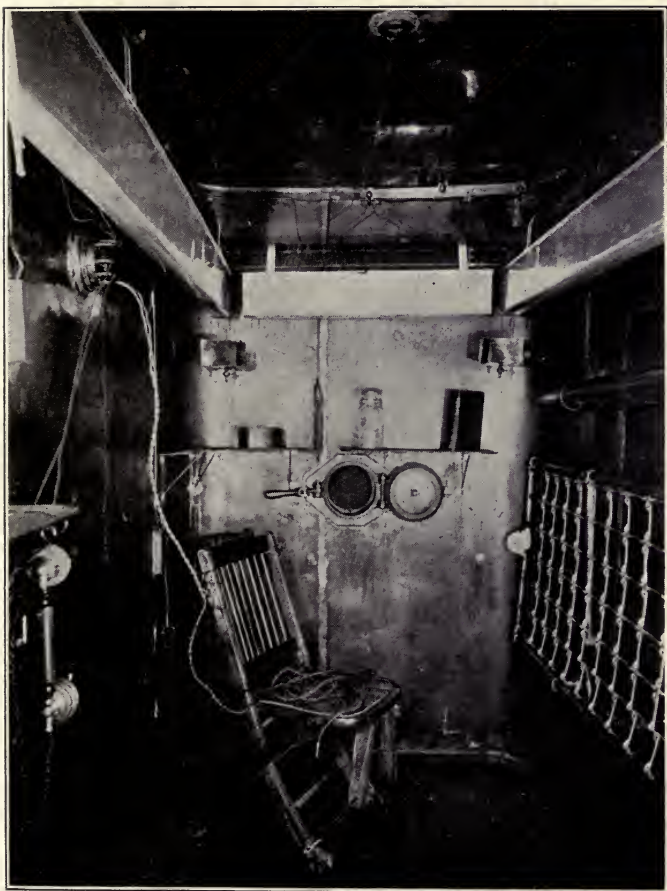


FIG. 39. — *The Atwater-Rosa Respiration Calorimeter. Interior View.*
From Bulletin 175, Office of Experiment Stations, U. S. Department of Agriculture,
by permission.



true. In the case of proteins it requires the modification that the nitrogen, which in combustion is given off as the free element, is excreted from the body combined with a certain amount of carbon, hydrogen, and oxygen, chiefly as urea, CON_2H_4 , a compound which can itself be further oxidized (*e.g.* by combustion) to carbon dioxide, water, and free nitrogen.

When burned in a furnace, fats and other organic food constituents produce heat, a part of which may be converted into work by such a device as a steam engine. A fat oxidized in the body also produces work and heat, the work-producing mechanism being the muscles.

We can easily measure the quantity of heat which any pure foodstuff or any mixed food is capable of producing when rapidly oxidized. This measurement can be made in exactly the same way as in the case of fuels, *i.e.* by burning a small weighed sample of the food or foodstuff in compressed oxygen in the bomb calorimeter (see Fig. 32, p. 55), and noting the quantity of heat set free. It is also possible to measure the quantity of heat set free by a man or an animal maintained on a certain diet. This is done by confining the man or animal to the chamber of an *animal calorimeter* — an apparatus which measures the quantity of heat given off from his body.

Figure 39 is an interior view of a "respiration" calorimeter designed by the late Professor W. O. Atwater of Wesleyan University, Middletown, Conn., and Professor E. B. Rosa of the same institution, for experiments upon man. This apparatus was so constructed that no heat could escape through the walls of the chamber. The heat given off by the occupant was absorbed by a current of water flowing through the pipes at the top of the chamber.¹ The quantity of water flowing through these pipes was measured and also its temperature as it entered, and again

¹ In the illustration these pipes are partly, but not entirely, concealed by metal "shields," which could be raised or lowered to regulate the rate at which the heat was taken up by the water.

as it left, the chamber. The product of the quantity of water flowing in a given time and its rise of temperature represented the number of Calories given off by the occupant of the chamber. The chamber had a tightly sealed window and a porthole or large pipe through which food and other materials could be passed in and out, the porthole being kept closed at one end whenever it was opened at the other. Provision was also made for continually renewing the supply of oxygen, and the apparatus owes its name of "respiration" calorimeter to the fact that it was so designed that not only the heat, but also the amounts of carbon dioxide and water produced, and (as later developed) the quantity of oxygen used by the subject of the experiment could be measured. Experiments with this apparatus were sometimes continued for periods of ten or twelve days.

This apparatus was greatly improved and eventually rebuilt by Dr. F. G. Benedict. Figure 40 gives a view of one form of apparatus now in use, showing the *exterior* of the respiration chamber and the apparatus used in measuring the heat given off and the carbon dioxide and water excreted by the occupant of the chamber. An observer is shown seated at the observer's table, a post which is manned night and day during the course of an experiment. This observer is making the temperature observations and so controlling the instrument that no heat can pass through the walls of the respiration chamber. In front of the observer is a hanging support for the galvanometer, an electrical instrument used in the temperature measurements. On the floor in front of the observer (at the right of the picture) is a rack or table holding the apparatus through which the circulating air is passed for purification and analysis before being returned to the respiration chamber. Behind the observer's platform (*i.e.* to the reader's left) near the floor is a large cylindrical vessel in which the water, which passes through the pipes in the chamber to absorb the heat, is collected and weighed. And on the extreme left of the picture a second experimenter is seen talking through a telephone to the man inside the chamber who is serving as the subject of the experiment.

When such measurements are made, it is found that the quantity of heat produced by the oxidation of a fat is exactly the same when this oxidation takes place slowly in the human body as when it takes place instantaneously in the bomb

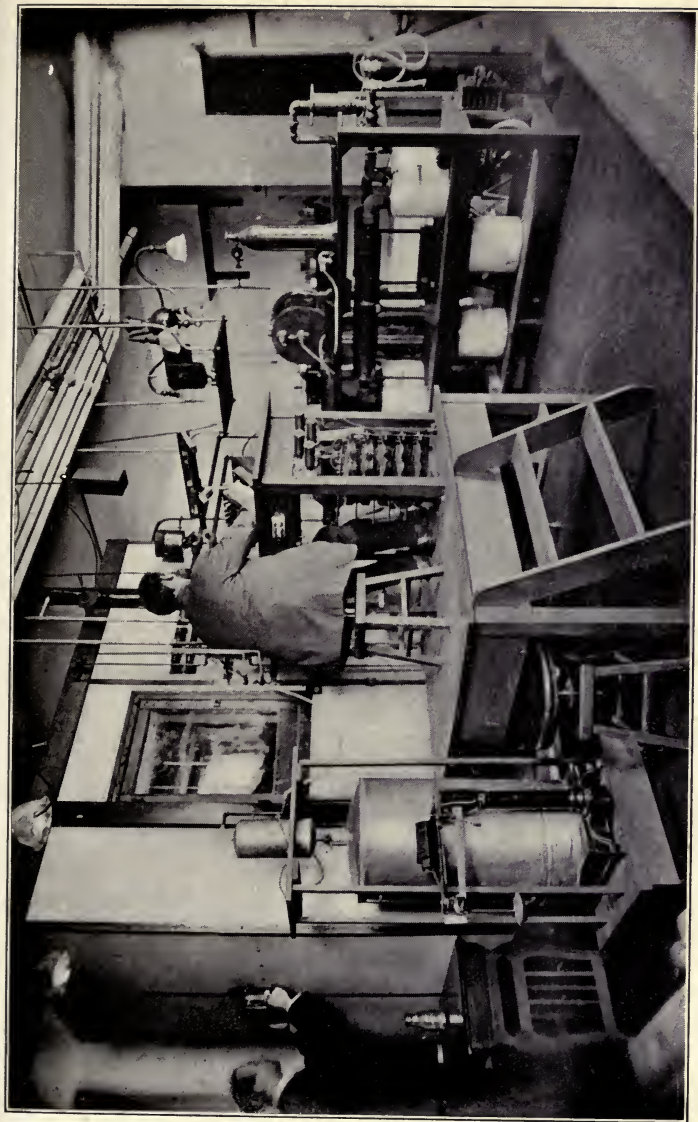


FIG. 40. — *The Atwater-Rosa-Benedict Respiration Calorimeter as modified by Langworthy and Milner. Exterior View.*
From the Yearbook of the U. S. Department of Agriculture, 1910, by permission.

calorimeter. The same is true of a carbohydrate such as starch or sugar. The quantity of heat produced by the oxidation of a protein in the body is less than that produced by the combustion of the protein in the bomb; but the difference is just the quantity of heat yielded by the combustion of that quantity of *urea* and other nitrogenous end products which would be formed in the body from the given quantity of protein. In other words, if we were to allow the oxidation of the protein to go on in the body of the man in the respiration calorimeter and then burn in the bomb calorimeter the excreta of the man, the total heat obtained would be the same as if we had burned the protein directly in the bomb calorimeter.

Making allowance for the average quantities of each class of foodstuffs lost in digestion (*i.e.* excreted in the feces), it is found that a pound of carbohydrate in the food yields about 1815 Calories, and a pound of protein the same; but a pound of fat yields 4080 Calories.

One pound of fat is therefore equal in fuel value to 2 $\frac{1}{2}$ pounds of either protein or carbohydrate.

Stated according to the metric system of weights these fuel values are:

Carbohydrates and proteins	4 Calories per gram
Fats	9 Calories per gram

When muscular work is done, the heart beats more rapidly and the breathing becomes both faster and deeper. The result is a quickening of the oxidation processes in the body. A larger quantity of assimilated food material is oxidized in a given time, and of course a larger quantity of heat is produced. But the quantity of heat given off from the body does not now amount to 1815 Calories for each pound of protein and each pound of carbohydrate and 4080 Calories for each pound of fat oxidized, for a part of the "fuel value" of the food is converted into mechanical work.

This partial conversion of the fuel value or *energy* of the food into work is accomplished by the muscles of the body in a way that is not fully understood. In the steam engine *all* the energy of the fuel is first converted into heat and then a part of the heat is converted into work. In the muscles only a part of the original energy is converted into heat. The remainder is apparently converted directly into work. As much as one-fifth of the fuel value of the foodstuffs oxidized may be converted into work by the engine of the human body, *i.e.* the muscular system. The work done may be reconverted into heat, and when this is done, the total quantity of heat produced — that evolved directly as heat *plus* that produced as work and then converted into heat — is equal to 1815 Calories per pound of carbohydrate and protein and 4080 Calories per pound of fat oxidized.

In some of the experiments with the respiration calorimeter the man in the chamber turned the wheel of a stationary bicycle which was attached to an electric dynamo, the current produced by which was passed through an incandescent electric light bulb. This device enabled the experimenters to estimate the quantity of work done and at the same time provided for the reversion of the work into heat within the calorimeter.

III. Food as a Regulator of Physiological Processes

Much less is definitely known about this function of food than about the other two. It is certain, however, that some foods have a greater tendency to stimulate the activity of the intestines than have others. In other words some foods are laxative, others constipating. Among the laxative foods are fruits, green vegetables, and the coarser cereal products. Fruits and green vegetables contain much water and ash constituents or "mineral matter" (salts of organic as well as of inorganic acids). The outer portion of the wheat

kernel (the bran) contains not only a larger proportion of mineral matter, but also a larger proportion of cellulose — a carbohydrate which largely escapes digestion. Cellulose is also a prominent constituent of green vegetables, such as celery, lettuce, radishes, asparagus, etc. The laxative effect of coarse foods is commonly regarded as due to their mechanical stimulation of the intestinal lining. But it has been shown in experiments upon cows that wheat bran, which in its natural state contains the potassium, magnesium, and calcium salts of an organic acid, called phytic acid, loses its laxative effect when these salts are removed from it. It has been found that persons living exclusively or very largely on a diet of rice suffer from the disease *beriberi* if the bran of the rice has been polished off. While, therefore, the mechanical effect of coarse foods in stimulating the bowels may be important, it seems probable that the chemical effects of certain foods may be equally or in some cases even more important.

Certain of the body fluids, such as the gastric juice, the digestive fluid of the stomach, have an acid reaction; certain others, such as the saliva, the bile, and the blood, have an alkaline reaction. It is necessary to health that the acidity of the former and the alkalinity of the latter should remain within certain limits. The gastric juice, for example, must not become either neutral or too strongly acid. Now in the oxidation processes which go on in the body certain constituents of food are converted into acid products, certain others into alkaline products. Thus in the oxidation of proteins, sulphuric acid is produced from the sulphur of the protein molecule, while the phosphorus of phospho- and nucleo-proteins and of phosphorized fats, such as lecithin, yields phosphoric acid. On the other hand, the salts of all organic acids oxidize to bicarbonates, which may act as alkalis.

An excess of acid-producing constituents in the food is

apt to lead to physiological disturbances. The foods in which acid-producing elements predominate are meats, eggs, and cereals. In vegetables, fruits, and milk the base-forming elements predominate.

For a fuller discussion of the chemistry of nutrition the reader is referred to Sherman's "Chemistry of Food and Nutrition." New York, 1911.

CHAPTER XXXVII

THE DIGESTION OF FOOD

IN order to reach the tissues it is to repair or the muscles for whose activities it is to serve as fuel material, the food taken into the alimentary canal must be *absorbed* into the circulating fluids of the body, the blood and lymph. To get into these fluids it must pass through the membranous envelopes of the vessels containing them, the *capillaries* (small blood vessels) and *lacteals* (lymph vessels). These vessels are especially abundant in the folds and villi of the small intestine, which is the chief seat of absorption. Absorption, however, occurs also to a slight extent in the stomach and to a considerable extent in the large (lower) intestine.

Now, chemical compounds of different classes show striking differences in their ability to pass through membranes of a colloidal nature, such as make up the linings of the digestive organs and the envelopes of the capillaries and lacteals. Such differences are illustrated in the following experiments, although it is only fair to premise that some substances which do pass through the membranes used in the experiments do *not* pass through the *living* membranes of the digestive organs.

Experiment 113.

Materials:

Parchment filters or parchment tubing.

Glass jars or large beakers.

Glucose (dextrose).

Fructose (levulose).

Cane sugar.

Maltose.

Dextrin.

Starch paste, prepared as in Experiment 101 (p. 170).

Put solutions of the carbohydrates named above (about one part carbohydrate to ten parts water) into the parchment filters or into pieces of the tubing, being careful to get none of the solution on the outer surface of the parchment. Add a drop of chloroform to each to prevent the growth of microorganisms.

Suspend the papers in jars or beakers of distilled water. If tubing is used, both ends should be suspended above the surface

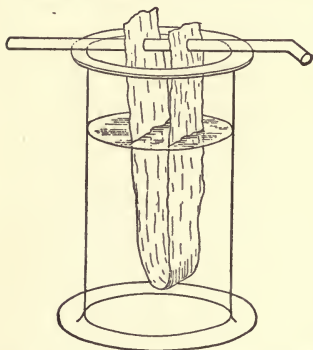


FIG. 41.— *Apparatus for the study of the diffusibility of carbohydrates through parchment paper.*

of the water, making a U-shaped tube dipping beneath the surface of the water. (See Fig. 41.) Allow to stand overnight. Then carefully withdraw portions of the outer liquids from the bottom of the jars with pipettes and test for the carbohydrates used, making parallel tests with some of the liquids from the interior of the parchment vessels. For tests see your record of Experiments 99 to 101. Dextrin is tested for by adding the liquid to a solution of iodine diluted so as to appear yellow. Dextrin changes the color to red.

Parchment paper is made by dipping paper into strong sulphuric acid and then thoroughly washing. This treatment greatly reduces the porosity of the paper by converting some of the cellulose into a more bulky substance. (See Experiment 139, p. 232.)

Experiment 114.

Materials :

Goldbeater's skin.

The same carbohydrates as in preceding experiment.

Select test tubes with evenly flanged tops; heat the closed ends in the flame and blow them out while soft, thus forming a tube open at both ends. Cut the goldbeater's skin into squares of about $1\frac{1}{2}$ inches and bind these tightly over the flanged ends of the tubes with thread. To make sure that the tubes are tightly closed with the skin, fill them with water. The water will gradually pass *through* the skins, but will not flow in a stream nor drop rapidly if the skin is perfect and is properly bound to the tube.

Fill these tubes about three-fourths with the carbohydrate

solutions used in Experiment 113, being careful to avoid wetting the outside surface. Place them in beakers of distilled water, and allow to stand overnight. Pipette off portions of the outer liquids from the bottom of the beakers and test for the carbohydrates as in the preceding experiment.

Goldbeater's skin is made from the inner lining of the intestines of cattle.

The above experiments show that colloiddally dissolved carbohydrates will not pass through the membranes used, while the substances in true solution (the crystalloids) do pass through. From the observations which have been made upon living animals, however, it appears that even some of the crystalloid substances cannot pass through the envelopes of the blood and lymph vessels. The substances which will not pass through are those made up of large molecules. Thus in some cases monosaccharides pass through but disaccharides do not.

It would appear from experiments upon animals that, as a preliminary to absorption and utilization, all carbohydrates must be changed into monosaccharides. Similarly, fats are not absorbed until converted into fatty acids (or salts of fatty acids, *i.e.* soaps) and glycerol; and proteins not until converted into amino acids and, perhaps, relatively simple polypeptides.

It will be noticed that the chemical changes which all these nutrients undergo preliminary to absorption are hydrolytic. In other words, all nutrients incapable of direct absorption are converted into absorbable nutrients by reaction with water. But this hydrolysis of the complex molecules of polysaccharides, proteins, and fats takes place only in contact with certain organic catalytic reagents, known as *enzymes* or "digestive ferments."

These enzymes are contained in the digestive juices secreted by cells in the linings of the digestive organs or by glands which communicate with those organs. The digestive juices are:

(1) The *saliva*, secreted by glands in or delivering their secretions into the mouth.

(2) The *gastric* juice, secreted by certain cells of the stomach wall, chiefly in the middle division of the stomach.

(3) The *pancreatic* juice, secreted by the pancreas and delivered into the small intestine (duodenum).

(4) The *bile*, secreted by the liver and delivered into the small intestine.

(5) The *intestinal* juice, secreted by certain cells of the intestinal lining.

All of these but the bile are known to contain enzymes that promote the hydrolysis of organic nutrients. Of such enzymes the following are well known :

HYDROLYTIC ENZYMES OF THE DIGESTIVE FLUIDS.

DIGESTIVE SECRETION	ENZYME	SEAT OF ACTION	COMPOUNDS AFFECTED	PRODUCTS (OR CHIEF PRODUCTS)
Saliva	Ptyalin	Mouth and cardiac (anterior) end of stomach	Starch	Dextrin and maltose
Gastric juice	Pepsin	Pyloric (posterior) end of stomach	Proteins	Proteoses and peptones
	Gastric lipase	Stomach	Emulsified fats, such as cream	Fatty acids and glycerol
Pancreatic juice	Amylopsin	Intestines	Starch and dextrin	Maltose
	Trypsin	Intestines	Proteins	Proteoses, peptones, polypeptides, and amino acids
	Steapsin	Intestines	Fats (emulsified by bile)	Fatty acids and glycerol
Intestinal juice	Sucrase (invertase)	Intestines	Sucrose	Glucose and fructose
	Maltase	Intestines	Maltose	Glucose
	Lactase	Intestines	Lactose	Glucose and galactose
	Erepsin	Intestines	Proteoses and peptones	Amino acids and ammonia

EXERCISES

1. Classify these enzymes as (1) Amylases, (2) Disaccharases, (3) Lipases, (4) Proteases.
2. Write equations for the hydrolysis of: (a) Sucrose, (b) Tristearin, (c) Glycyl glycine.

The following experiments will serve to illustrate the effects of enzymes:

Experiment 115. — Action of Ptyalin on Starch.*Materials:*

Starch solution.

Prepare a starch solution as in Experiment 101 (p. 171), dilute it with two or three times its volume of water, cool to the temperature of the hand, add a little of your own saliva, mix well and place in a beaker of water at the temperature of the hand (about 38° C.). After five or ten minutes pour off a little of the liquid into a test tube containing iodine solution. If this test shows starch to be still present, add more saliva, allow the test tube to stand longer in the beaker, and repeat the iodine test at intervals. When this test shows all the starch to have been transformed, pour off a little of the liquid remaining in the test tube into Fehling-Benedict solution and boil. What kind of substance has been formed from the starch? For comparison a little of the starch solution *without saliva* may be similarly treated and tested.

Experiment 116. — Action of Proteolytic Ferments (Proteases) on Fibrin.*Materials:*

Fibrin.¹

Pepsin solution.

Trypsin solution.

0.4 per cent solution hydrochloric acid.

1.0 per cent solution sodium carbonate.

¹ The fibrin, pepsin, and trypsin may be most conveniently bought in the dried condition. The fibrin should be soaked in water for an hour or more before beginning the experiment. For the pepsin and trypsin solutions 0.1 gram of the commercial ferments are to be dissolved in one liter of water. If preferred, fresh fibrin may be made by whipping freshly drawn ox blood with twigs to promote clotting and then washing the clot with cold water until the

Into each of six test tubes put a piece of fibrin. Add respectively (1) 5 cc. water, (2) 5 cc. pepsin solution, (3) 5 cc. 0.4 per cent hydrochloric acid, (4) 2.5 cc. pepsin solution and 2.5 cc. 0.4 per cent hydrochloric acid, (5) 5 cc. trypsin solution, (6) 2.5 cc. trypsin solution and 2.5 cc. sodium carbonate solution.

Set the test tubes (labeled) in an empty beaker or in a suitable rack and place in a water oven at 40° C. Examine after 24 hours. In which of the tubes has the fibrin been dissolved? Filter and make the biuret test on a portion of the filtrate. Boil another portion. What do you infer from the results? Does the hydrochloric acid alone affect the fibrin in any way? Is the action of the pepsin affected by the addition of hydrochloric acid? Is that of the trypsin affected by the sodium carbonate?

It is extremely difficult to separate an enzyme from the substances accompanying it, and it is also difficult to determine whether any given preparation is to be regarded as pure. The best preparations that have been made, however, resemble the proteins in composition and behavior, and it is probable that enzymes are themselves proteins. A pepsin preparation has been made which was capable of digesting 500,000 times its weight of fibrin; also a pancreatic amylase (amylpsin) capable of digesting 1,000,000 times its weight of starch.

red color is gone. Pepsin solution may be prepared fresh by extracting the finely cut mucous membrane of a pig's stomach for 24 hours either with 0.4 per cent hydrochloric acid at 38-40° C. or with glycerin at room temperature. Fresh trypsin solution can be made by extracting the finely divided pancreas of the pig or sheep for three days with water containing 5-10 cc. of chloroform or with glycerin. The 0.4 per cent hydrochloric acid may be made from the reagent (2 N) dilute hydrochloric acid by diluting with 18 times its volume of water. The sodium carbonate solution may be made directly by dissolving 1 gram anhydrous sodium carbonate in 100 cc. water.

CHAPTER XXXVIII

FOODS OF VEGETABLE ORIGIN

TABLES giving the average composition and fuel value of American food materials are given in Appendix A. Table I (pp. 271-277) comprises a classified selection of foods of vegetable origin. The last four columns of the table give the essential information about the edible portion of each food. The first column gives the percentage of refuse in the food as purchased. In comparing costs this must, of course, be taken into consideration. Thus, the 100-Calorie portion of the edible part of a banana (the first item in the table) is 3.6 ounces. But the average amount of refuse in a banana as purchased is 35 per cent. Thus with every 65 ounces of edible banana we purchase 35 ounces of banana peel. The 100-Calorie portion of banana as purchased is therefore 100 sixty-fifths of 3.6 ounces, which is equal to 5.5 ounces.

EXERCISES

1. Calculate similarly the 100-Calorie portion of the following foods as purchased: (a) Grapes, (b) Lemons, (c) Squash, (d) Green peas, (e) Butternuts.
2. From the percentage composition of ten selected foods, as given in the second to fifth columns of the table, calculate the number of Calories per pound, the number of ounces yielding 100 Calories and the number of Calories out of every 100 yielded by proteins, fats, and carbohydrates, respectively. For methods see Appendix A, pp. 268-270.
3. From the percentage composition of the following foods calculate as in Exercise 2 the number of Calories per pound, the weight of the 100-Calorie portion in ounces, and the distribution of the 100 Calories among the three classes of organic nutrients; also in ounces the 100-Calorie portion of the food as purchased:

FOOD	REFUSE	EDIBLE PORTION							100-CALORIE PORTION AS PURCHASED		
		PER CENT OF				CALORIES PER POUND	100-CALORIE PORTION OUNCES	CALORIES FROM			
		Water	Protein	Fat	Carbo- hydrate			Protein		Fat	Carbo- hydrate
						85.0	1.1				
Apricots . . .	6	85.0	1.1	—	13.4						
Muskmelons . .	50	89.5	0.6	—	9.3						
Artichokes . . .		79.5	2.6	0.2	16.7						
Succotash . . .		75.9	3.6	1.0	18.6						
Brussels sprouts		93.7	1.5	0.1	3.4						
Lentils, dried . .		8.4	25.7	1.0	59.2						
Buckwheat flour		13.6	6.4	1.2	77.9						
Oatmeal, boiled .		84.5	2.8	0.5	11.5						
Oatmeal gruel . .		91.6	1.2	0.4	6.3						
Jumbles . . .		14.3	7.4	13.5	63.7						

The most marked general characteristic of vegetable foods is the large proportion of carbohydrates contained in them. If we except olives and chocolate, which contain a large proportion of fat (olive oil and cocoa butter); nuts and oatmeal, which are rich in both fat and protein; and mushrooms, lettuce, and the legumes, which are rich in protein, we may say that all the vegetable foods have over three-quarters of their total fuel value in the form of carbohydrates. In many, such as potatoes and all products of the cereal grains, the predominating carbohydrate is starch. In others, such as fruits, sugars and pectins are predominant. In a few, such as green vegetables and coarse roots, *e.g.* turnips and radishes, cellulose abounds. But carbohydrates in some form characterize them all.

Experiment 117.

Materials:

Potatoes.

(a) Pare and grate one quarter of a potato. Add a little water and filter. Boil a portion of the filtrate. Make the biuret test on another portion. What kind of substance have you thus detected in potato juice?

(b) Add a portion of the filtrate to Fehling-Benedict solution and boil. What kind of substance does this test show the potato juice to contain?

(c) Place the potato pulp in a cheesecloth bag. Allow a stream of water to run through the bag into a beaker and knead the bag. Continue until the water runs through clear. Allow the contents of the beaker to settle. Examine the residue left in the bag. It consists mainly of "fiber" or "cellulose."

(d) When the contents of the beaker have settled, remove a portion of the sediment, boil it with water, cool, and test with iodine. What do you infer that the sediment was?

What three kinds of carbohydrates have you detected in the potato?

The water in the potato may be determined as in Expt. 96 (p. 163), and the ash by burning the dried material in the dish, avoiding heating above dull redness. For average results consult Table I, p. 272. The ash averages 1.0 per cent.

Experiment 118.*Materials:*

Carrots.

Beets.

Grate a carrot. Test a portion of the pulp for proteins, using two appropriate tests. Digest a portion of the pulp with cold water; filter and test the filtrate for (a) reducing sugars, (b) sucrose. (How?) Boil a portion of the pulp with water, cool, and test for starch.

Make the same tests on beets.

Experiment 119.*Materials:*

Orange.

Apple.

Test some of the orange juice and some of the apple juice for reducing sugars. Also test the juices with litmus. Test the pulp for starch by boiling with water, cooling, and adding iodine.

Experiment 120.*Materials:*

Oatmeal.

Beans, ground.

Walnuts, ground.

Test each for starch and for proteins. Shake a portion of each with benzine, filter through a dry filter on to a clean watch glass, set in a warm place to evaporate the benzine. If a residue remains, add Sudan III solution and warm water. What do you infer from the result?

Very few of the foods of vegetable origin contain as large a proportion of **proteins** as is demanded by the older "dietary standards," which, in general, require 15 to 16 Calories out of every 100 to come from protein. Reference to the tables will show that mushrooms, peas, beans, peanuts, butternuts, cocoa, and oatmeal have more than this proportion of protein. So also have several of the foods known as "vegetables" in cookery — including most of those derived from the *stalks* and *leaves* of plants, and also *pumpkins*, *tomatoes*, and *radishes*. In the case of these latter, however, it is to

be remembered that a considerable proportion of the nitrogen calculated as protein is really not in true protein compounds, and that, being bulky foods containing much water, these "vegetables" do not, as a rule, contribute a very large proportion of the total fuel value of the diet.

On the basis of the more recently proposed "dietary standards" — not only the radically low protein one of Chittenden but also the more moderate standards such as that of Langworthy¹ — a much larger number of foods of vegetable origin contain an adequate proportion of proteins. These would include *wheat flour* and *bread*, *potatoes* and most varieties of *roots*, and the greater number of *varieties of nuts*.

As a rule the quantity of fat in vegetable foods is small. Conspicuous exceptions are the *nuts* (including *peanuts*), *chocolate* and its derivative *cocoa*, and *olives*. The *germs* of cereal grains are also rich in fat. But in the manufacture of some commercial foods from cereals — particularly in that of white flour and cornmeal — the germ is removed because of the tendency of the fat to become rancid and thus cause deterioration of the product. *Oatmeal* and *rolled oats*, on the other hand, contain fat sufficient to yield a fuel value equal to that of their proteins, and are thus the best balanced of all the cereal products. In cooking cereals and vegetables it is common to add fat to compensate for the natural deficiency of such foods in this nutrient. Hence the division of the table entitled "Baked Foods" (pp. 274-5) shows in many instances a liberal proportion of fats to carbohydrates.

As to the quantities of the important **mineral** elements — calcium, phosphorus and iron — that they contain, foods of vegetable origin differ greatly. Table II in Appendix A (pp. 278-9) gives the quantities of these three elements (the calcium and phosphorus stated in terms of milligrams of their oxides, the iron as milligrams of the element) contained in the 100-Calorie portion of a number of vegetable foods,

¹ Sherman's "Chemistry of Food and Nutrition," Chapter VIII.

classified as in Table I. To compare the foods on the basis of equal weights, one must divide these quantities by the weight of the 100-Calorie portion. Thus, while per 100-Calorie portion spinach is much richer than ripe beans in all three of these constituents, it is much poorer in all per 100 grams or per pound.

	SPINACH	BEANS
100-Calorie portion in grams	412	29
CaO per 100-Calorie portion	370 mg.	63 mg.
CaO per 100 grams	89 mg.	217 mg.
P ₂ O ₅ per 100-Calorie portion	540 mg.	336 mg.
P ₂ O ₅ per 100 grams	129 mg.	1140 mg.
Fe per 100-Calorie portion	13.3 mg.	2.0 mg.
Fe per 100 grams	3.2 mg.	6.9 mg.

Among foods of its own class, however, *spinach* stands conspicuously high as regards its content of *iron* and *phosphorus* and fairly high also as regards calcium. *Cauliflower* and *celery*, however, are much richer in *calcium*. The *legumes* are also rich in all three of the important mineral elements. Among the cereals, those containing *the outer layers of the grain* (oatmeal and Graham flour) are richest in all three of these elements.

An adequate supply of the bone-forming materials, lime and phosphoric acid, is of special importance in children's dietaries. Table II shows that *green vegetables* and *roots* (especially turnips, carrots, and parsnips) are conspicuously rich in these ingredients. *Some fruits* also (for example, oranges) contain much calcium in the form of organic salts.

As noted in Chapter XXXVI (p. 200) the cereals contain a small excess of acid-forming constituents, while in the vegetables, fruits, and legumes base-forming elements predominate.

CHAPTER XXXIX

FOODS OF ANIMAL ORIGIN

IF the foods of vegetable origin are to be regarded as mainly carbohydrate foods, those of animal origin are, on the whole, to be regarded as protein and fat foods. To be sure, honey contains practically no nutrient but the carbohydrates, glucose, fructose, and a little sucrose; but it is exceptional. Other than honey, the only animal foods containing any proportion of carbohydrates worthy of consideration are milk and some of its products (particularly skim milk, buttermilk, and whey), and shellfish, such as oysters and clams. Liver, cream, cheese, and shad roe contain minor quantities of carbohydrates. All the other animal foods are made up (as regards their organic nutrients) almost exclusively of protein and fat.

The proportions of these two classes of nutrients, protein and fats, vary widely in the different animal foods. Egg-white is fat free, consisting of pure protein matter with some ash and much water. Gelatin is all protein also, but, curiously enough, it is not by itself capable of building muscular tissue — a fact that is probably related to the absence of certain amino acids (particularly tyrosine and tryptophane) from among its hydrolysis products. The protein of frogs' legs and of codfish yields over 95 per cent of the total fuel value of these foods. On the other hand, the energy of fat pork, of cream, and of butter comes nearly all from the fat; and lard and tallow are, of course, practically pure fats.

Meats vary greatly in composition with the variety, the cut, and the condition of the animal when killed. The tongue, breast, and shoulder, for instance, are much more muscular than the ribs, loin, and rump. Hence we find a

larger proportion of protein in cuts of the former class, and a larger proportion of fat in those of the latter.

Table III of Appendix A (p. 280) gives the average composition and nutritive value of several varieties and cuts of meats. Table IV (p. 282) illustrates how widely the same cuts may vary according as they are from fat or lean animals. The figures given in the latter table are not the extreme values found in individual cuts of meat, but are in each instance the average of the results of analysis of several pieces classed as fat, medium fat, lean, etc. It will be observed that as the percentage of fat in the meat increases the percentages of water and protein decrease. But even the leanest meat is not entirely devoid of fat.

Experiment 121.

Materials :

Lean beef.

Remove all visible fat from the beef; then cut it up into fine pieces or put it through a mincer. Place some of the minced meat in a dish, cover with alcohol, and knead to extract the water from the tissues. Pour off this alcohol, add more, and knead again. Pour off the alcohol, add benzine, and knead or shake. Filter off the benzine, allow it to evaporate, and test the residue for fat with Sudan III solution.

Experiment 122.

Materials :

Lean beef.

Mince the beef, put it in a cheesecloth bag, and knead in running water until the tissues are white. Apply Millon's test and the xanthoproteic test to these tissues.

Reference to Table III (Appendix A) will show that pork, mutton, and lamb are, as a rule, fatter than beef, and beef is usually fatter than veal. The average fore quarter or hind quarter of beef yields out of every 100 Calories about 30 Calories from protein and 70 Calories from fat. The fore quarter or hind quarter of mutton yields about 20 Calories

from protein and 80 from fat. The average pork ham yields about 17 Calories from protein to 83 from fat, and the average side of pork only 7 Calories from protein out of every 100. Average veal, on the other hand, has about half of its fuel value in the form of protein.

When the fat is largely trimmed off by the butcher or cook or rejected at table, there is, of course, not only a great loss of fuel value, but the proportions of protein and fat in the food actually eaten are greatly altered. Rejected fat is not included in the *refuse* as estimated in the tables. These tables, therefore, give higher energy values to the meats than are usually realized from them.

Table V (Appendix A, p. 283) gives the average composition and nutritive value of fish of several varieties.

Most fish have over half their fuel value in the form of protein. A few of the fatter varieties, such as sardines, salmon, trout, shad, and eels, have a little less than half (43 to 50 per cent) of their fuel value in the protein form, while the leanest varieties, such as cod, haddock, and pickerel, may have as much as 90 Calories out of every 100 from protein.

Table VI (Appendix A, p. 284) gives the average composition and fuel value of dairy products. Here a column must be provided for the carbohydrates, viz. the lactose. In whole milk, evaporated milk, and milk powder this provides about 29 per cent of the total fuel value. In the dairy products richer in fat (butter, cream, and cheese) the lactose plays a minor part. In skim milk, buttermilk, and whey, on the other hand, it becomes the most prominent nutrient. In sweetened condensed milk the cane sugar added constitutes about four fifths of the total carbohydrates and the milk sugar only one fifth.

Table VII (Appendix A, p. 285) gives the composition and nutritive value of miscellaneous foods of animal origin. Eggs, it will be noted, are protein and fat foods. The whites, how-

ever, contribute protein only, while the yolks have twice as much fat as protein by weight and between four and five times as much by calories. Shad roe and the shellfish, in spite of the presence of carbohydrates (glycogen), are highly nitrogenous foods. The shellfish, white of eggs, and frogs' legs have high 100-Calorie portions on account of their high water content and low fat content. In other words, although their dry matter is highly nitrogenous, they contain only a small amount of dry matter per pound.

Meats are poor in calcium, and eggs contain only a moderate amount. See Table VIII (Appendix A, p. 286). Milk, however, is extraordinarily rich in this element, and the same is true of some of its products, especially cheese and buttermilk. As pointed out by Sherman, a quart of milk contains rather more calcium than a quart of clear, saturated limewater, and one would need to take 25 hundred-Calorie portions of round steak and white bread to get as much calcium as one could obtain in 1 hundred-Calorie portion of whole milk or of cheese.

The majority of animal foods contain a liberal supply of phosphorus. In egg yolk this exists in the form of phosphorized fats and phospho-proteins — forms in which it is more readily assimilated than in the inorganic phosphates. In meat and fish it is mainly in the inorganic forms. In milk it is present in both inorganic and organic forms; in cheese, chiefly in organic combination, viz. as casein.

Iron in readily assimilable form is abundant in egg yolk. It is from the organic iron compounds contained in the yolk that the hemoglobin of the chick's blood is formed, and there is good reason to believe that it serves a similar purpose in the human diet. The iron in lean meats is chiefly present as hemoglobin in the blood retained in the tissues. It is, however, not certain that this iron is as useful in the human diet as that of eggs, milk, and vegetables, because hemoglobin is not readily digested.

Milk and eggs are especially valuable foods for children, not only on account of their protein content and the emulsified condition of their fats, but also on account of the kinds of mineral matter they contain. Per 100-Calories of fuel value milk contains far more calcium than any other food. It is also rich in phosphorus, being surpassed, however, in this respect by a few foods, such as lean beef and beans. Eggs are also among the richest foods in phosphorus content, and contain a fair proportion of calcium as well.

CHAPTER XL

TEXTILE FIBERS OF ANIMAL ORIGIN. WOOL AND SILK

TEXTILES for clothing and for household furnishings can be made from any kind of fiber, natural or artificial, which has sufficient length, strength, and elasticity. The mineral kingdom furnishes some such fibers — asbestos, spun gold and silver, and spun glass. On account of their costliness and other defects, however, the mineral fibers find only limited application. Both the vegetable and the animal kingdoms, on the other hand, yield us fibers of very wide utility.

The **animal fibers** are of two classes, viz. (1) *Hair fibers*, of which *wool* is by far the most important; (2) *Silk fibers*. Both classes are composed of protein substances, but the silks are sulphur-free, while the hair-fibers, being keratins, are rich in sulphur. (See Expt. 112, p. 191.)

Experiment 123.

Materials:

Wool.

Silk.

Burn a little of each kind of fiber in a flame, noting the odor and the shape which the end of the fiber assumes. Heat portions in small, dry test tubes and test the evolved gases for ammonia with red litmus paper, and for hydrogen sulphide gas, H_2S , with paper moistened with lead acetate solution. Hydrogen sulphide reacts with lead acetate to give lead sulphide, PbS , which is black.

Make the xanthoproteic test (Expt. 105, p. 186) and Millon's test (Expt. 106, p. 187) on other portions of the wool and silk.

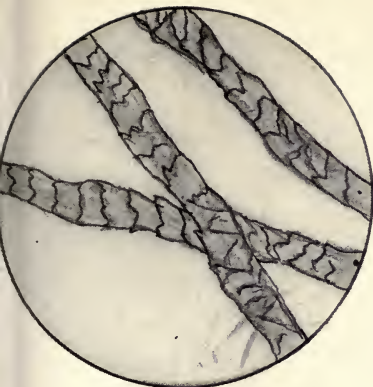


FIG. 42. — *Wool fibers magnified.*

From Kinne and Cooley's "Shelter and Clothing,"
by kind permission.

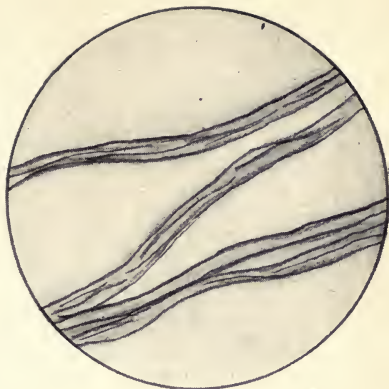


FIG. 43. — *Silk fibers magnified.*

From Kinne and Cooley's "Shelter and Clothing,"
by kind permission.

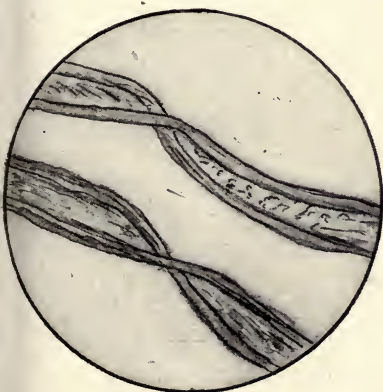


FIG. 44. — *Cotton fibers magnified.*

From Kinne and Cooley's "Shelter and Clothing,"
by kind permission.

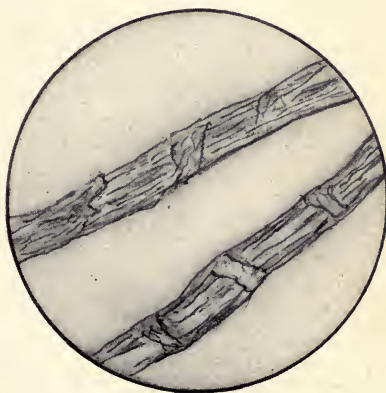
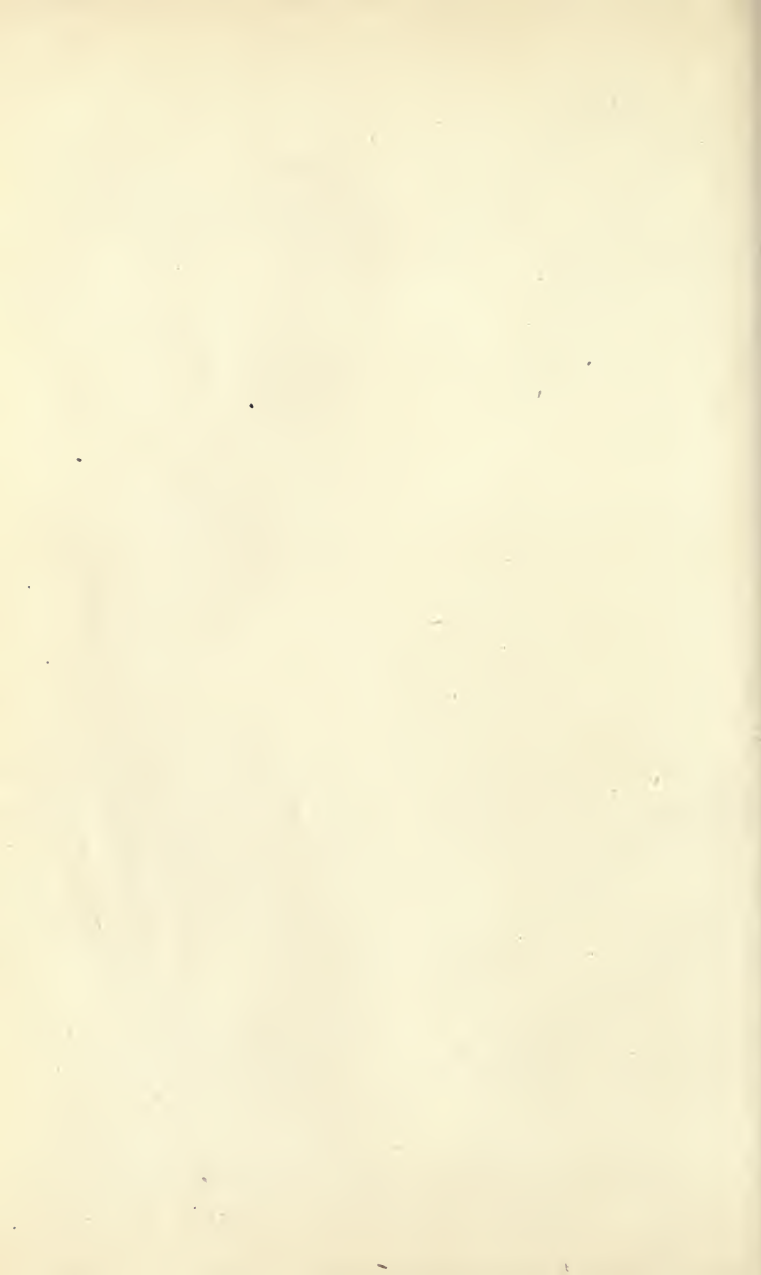


FIG. 45. — *Flax fibers magnified.*

From Kinne and Cooley's "Shelter and Clothing,"
by kind permission.



Experiment 124.*Materials :*

Silk fibers.

Wool.

Human hair.

Cat's hair.

Apparatus :

Microscope and slides.

Examine the fibers, noting points of similarity among the various hair fibers and differences of these from the silk. Observe particularly the scaly surface of the hair fibers. Is there any noticeable difference between wool and the coarser hair fibers in regard to (a) diameter, (b) appearance of the scales?

Wool

A hair fiber comprises' three distinct portions: (1) the *medulla*, a cellular marrow, which frequently contains the pigment to which the wool owes its color; (2) the fibrous *cortical* tissue, to which the fiber owes most of its strength and elasticity; (3) the *epidermis* of horny scales, consisting of flattened cells, overlapping one another like shingles.

The characteristics which distinguish wool from other hair fiber are its fineness, its softness, and the abundance of its scales or serrations. To these scales is due the characteristic "felting" property of wool; that is to say, the tendency of the fibers to mat together, and also the tendency of woollen goods to shrink, the scales catching upon one another and so preventing the fibers returning to their original position.

The length and fineness of wool depend chiefly upon the breed of sheep producing it, but these qualities, as well as the strength and luster, are influenced also by the climate in which the sheep are grown, by the nature of the soil providing the pasture, and by the condition of the animals' health. Ordinarily, the length of the fibers is between 1 and 8 inches and the diameter between $\frac{1}{3000}$ and $\frac{1}{500}$ inch. The quality of the wool varies not only in different fleeces, but also in the different parts of the same fleece, the wool of the shoulders and sides excelling in length, strength, and uniformity,

while that from the upper parts of the legs is coarse and that from the head, chest, and lower parts of the legs is likely to be coarse, stiff, and dirty. The uses of the wool depend upon its quality, which in turn depends upon such physical properties as the length, diameter, strength, elasticity, and glossiness of the fibers.

Only the longer and brighter fibers, for instance, are suitable for the manufacture of worsteds. The wool manufacturer grades and sorts his wool and uses the different kinds for the manufacture of different classes of goods.

Raw wool contains a large proportion of impurities. In some merino wools these impurities constitute as much as 70 per cent of the total dry weight of the fleece. The impurities consist of:

(a) *Wool grease*, a fatty substance, which serves as a protective covering to the fibers.

(b) *Suint*, that is, dried perspiration, consisting chiefly of potassium soaps.

(c) *Vegetable matter*, such as burrs, straw, and vegetable fibers from sacks and twine.

(d) *Mineral matter*, such as clay.

Unwashed wool contains from 4 to 24 per cent of moisture; from 12 to 47 per cent of yolk (grease and suint); from 3 to 24 per cent of dirt; and from 15 to 72 per cent of true wool fiber.

Wool grease, the chief constituent of which is an alcohol, called *cholesterol*, is the source of a product known as *lanolin*. Lanolin has remarkable capacity for forming emulsions with water and aqueous solutions, and is readily absorbed by the skin. On this account it is used in many pharmaceutical ointments and cosmetics.

The impurities are removed from the wool by "scouring," that is, washing with soap and an alkali. Only the milder alkalies, such as the carbonates of potassium and sodium, ammonia or borax, may be used, not the caustic alkalies. By this treatment the soaps in the wool are dissolved, the fats are emulsified and removed from the wool fibers, and the earthy matters are thereby loosened and washed out. Much of the vegetable matter, however, remains in the wool and is removed by subsequent treatment. In the *worsted* pro-

cess this subsequent treatment is simply a combing, which removes not only the vegetable matter, but also those wool fibers which are too short to be used in worsted yarns. In the manufacture of *woolens*, where these shorter wool fibers are used, the vegetable matter is removed by a chemical process known as *carbonizing*.

Carbonizing.—The washed wool is treated with dilute sulphuric acid (sp. gr. 1.03) and then subjected to a temperature of 140° to 180° F. (60–80° C.), at which temperature the vegetable matter is rendered brittle by the conversion of the cellulose into hydrocellulose. The brittle residue is then shaken out of the wool, and the sulphuric acid is neutralized with soda and washed out.

With the exception of the bleaching and dyeing, which will receive consideration later (Chapters XLII and XLIII), the remaining operations of the woolen industry—the carding, spinning, weaving, and finishing—involve no chemistry, but are purely mechanical.¹

Experiment 125.

Material:

Scoured wool or woolen yarn.

Weigh the wool (about 5 grams) on a balance accurate in the second decimal place. Dry for one hour in a water oven. Remove from the oven, place in a corked test tube, the weight of which has previously been determined, and as soon as the wool is cool, weigh again. Reheat for half an hour, weigh again, and repeat until the wool ceases to lose weight. Calculate the percentage of moisture. The wool should be allowed to cool in dry air. If a desiccator—*i.e.* an apparatus in which air is kept dry by exposure to sulphuric acid or calcium chloride—is at hand, the wool may be placed in it.

Dry wool absorbs moisture from the air. Substances which do this are said to be *hygroscopic*. Dry wool is capable of taking up an average of 16 per cent of its own weight of

¹ For a description of these processes the reader is referred to Woolman and McGowan's "Textiles." (See p. 228.)

water from ordinary air, while cotton absorbs only 8 or $8\frac{1}{2}$ per cent of its weight. The amount of hygroscopic moisture in wool at any given time depends upon the humidity of the atmosphere to which it has been exposed.

In addition to the hygroscopic water, which is condensed on the surface of the fibers, wool contains some water chemically combined with the protein compounds. Such water is known as "water of hydration." When in the manufacture or subsequent treatment of woolen goods the water of hydration is driven off by overheating, the luster and strength of the fibers are irrecoverably lost. In pressing wool goods, therefore, care must be taken to avoid subjecting them to dry heat.

Experiment 126. — Action of Acids.

Material :

White woolen yarn.

Treat wool with (a) dilute sulphuric acid, (b) concentrated sulphuric acid, (c) dilute hydrochloric acid, (d) concentrated hydrochloric acid, (e) concentrated nitric acid. If no action occurs in the cold, heat the acid. Which of the acids affects wool? Can you account for the effect of the nitric acid? Neutralize the nitric acid solution with ammonia and note effect on color.

Experiment 127. — Action of Alkalies.

Treat white wool yarn with (a) sodium hydroxide solution, cold (allow to stand several hours); (b) sodium hydroxide, boiling; (c) sodium carbonate, boiling; (d) borax, boiling; (e) ammonia.

Where the yarn is not destroyed, pour off the reagent, rinse with water, and compare the strength of the treated yarn with that of a piece of the same yarn, untreated.

Wool is not affected by dilute acids, but is very sensitive to alkalies, which, it will be remembered, readily attack most proteins. Soap containing free alkali should therefore be avoided in washing woolen goods. The free alkali dissolves off the scales and renders the fibers hard and weak.

Soda (sodium carbonate), if free from caustic soda, is less harmful than soap containing caustic soda (free alkali). But soda is not without a certain amount of effect. Ammonia, borax, and neutral soap are permissible alkalies for the washing of woolen goods.

Silk

Experiment 128.

Material :

Silk.

Apparatus :

Microscope.

Examine silk fibers under the microscope, comparing them with wool and hair fibers, as regards fineness and structure.

Silk is obtained from the cocoons of a species of caterpillar, which feeds upon the leaves of the mulberry tree. In making silk the silkworm secretes a viscous liquid, *fibroin*, in two glands in its body, and forces this liquid through two minute channels in its head into a single exit tube. Two other glands deliver into the same tube a cementing fluid, known as *sericin*. As it emerges from the head of the worm the fibroin coagulates, thus forming a double thread cemented with sericin.

Besides the silkworm proper there are other kinds of caterpillars which produce silk. Since these latter worms are not cultivated by man, as are the mulberry silkworms, their products are known as *wild silks*. The best-known wild silk is tussah (or tussur) silk used in the manufacture of pongee. The wild silk fibers are coarser and hence stronger, but more broken than those of the mulberry silkworm. They are also commonly dark in color and hard to bleach. Wild silks find use in the manufacture of pile fabrics, such as velvet, plush, and imitation sealskin.

The true silk fiber is notable for its great length and extreme fineness. The cocoon threads are only .0005 to .0007

inch in diameter (1430 to 2000 threads in the inch), but the length may be as much as 1300 to 1400 yards. Silk is also distinguished by its high luster and by its great strength and elasticity.

About 75 per cent of the weight of the raw silk is *fibroin*, the fiber proper, and 25 per cent the cementing substance, *sericin*, also known as *silk gum* or *silk glue*. Both fibroin and sericin, although sulphur-free, behave like, and are classed as, proteins. Sericin, however, is soluble in hot water and forms a jelly on cooling. In this respect it closely resembles gelatin, hence the name "silk gelatin" sometimes applied to it. In the manufacture of silk more or less of the sericin is removed by treatment with hot soap solution, the process being known as *boiling off*, *stripping*, or *degumming*.

Ecrú silk is silk which has lost 2 to 5 per cent of its total weight, *i.e.* $\frac{1}{12}$ to $\frac{1}{5}$ of its sericin, in boiling off.

Souple silk is that which has lost 12 to 14 per cent of its weight, *i.e.* about half its sericin.

Boiled-off silk is that which has lost 22 to 25 per cent of its weight, *i.e.* practically all its sericin.

Silk is, like wool, a hygroscopic substance. Under favorable atmospheric conditions raw silk will absorb as much as 30 per cent of its weight of moisture without appearing wet. Boiled-off silk is, however, much less hygroscopic. Ordinarily, air-dry silk contains about 10 to 12 per cent of moisture, and it is the custom in the trade to buy and sell silk on the basis of its perfectly dry weight plus 11 per cent; in other words the quantity of silk which when perfectly dried weighs 100 pounds is sold as 111 pounds of silk.

Experiment 129.

Weigh about 5 grams silk. Dry in oven at 100° C. to constant weight, as in Experiment 125. What would be the legal weight of this piece of silk?

Experiment 130. — Action of Acids.*Material :*

White silk thread.

Treat silk thread with acids, as in Experiment 126, and either compare with the results obtained on wool in that experiment or make the experiments on wool and silk in parallel. Compare the rates of solution in concentrated nitric acid. Note particularly the difference in the effect of cold concentrated hydrochloric acid on the two materials. The violet coloration produced by the action of concentrated hydrochloric acid on boiling or long standing is one of the characteristic reactions of proteins.

Experiment 131. — Action of Alkalies.

Make experiments on silk parallel to those of Experiment 127. Which of the two materials is the more susceptible to the action of alkalies? Which to the action of acids?

Experiment 132. — Action of Basic Zinc Chloride (Elsner's Reagent¹).

Heat Elsner's reagent to boiling. Tie a silk thread on to a glass rod and dip into the hot liquid. Make the same experiment with a piece of woollen yarn.

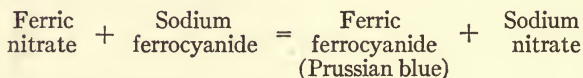
The above experiments suggest methods of quantitatively determining the proportion of silk in a mixed fabric of wool and silk. The silk may be dissolved out with either concentrated hydrochloric acid or boiling basic zinc chloride, and the undissolved residue of wool washed, dried, and weighed.

The Weighting of Silk

Silk absorbs and combines with the *tannins* or *tannic acids*, — organic substances contained in various plants and used in tanning leather, — and the tannins, in turn, react with iron salts, giving dark-colored dye products. By successively treating silk with an iron salt and a tannin the weight of the

¹ Dissolve 500 grams zinc chloride and 20 grams zinc oxide in 425 cc. water, warming till clear. The liquid becomes turbid on standing in the cold, but clears again on heating.

fibers can be greatly increased. Sometimes potassium or sodium ferrocyanide is used in place of, or in addition to, the tannin. Ferrocyanides and ferric salts react together to form Prussian blue, an insoluble substance which precipitates in the fibers. Thus:



Experiment 133.

Materials:

Tannin of gallnuts.

Cutch (catechu).

Infuse 10 grams of each of the tannin materials separately with 100 cc. water. Filter.

In test tubes mix solutions of: (a) Ferric chloride and gallnut tannin (gallotannic acid), (b) Ferric chloride and cutch infusion (containing catechutannic acid), (c) Ferric chloride and potassium ferrocyanide.

Dilute the dark products until you can see through the liquid. In which instance is a precipitate formed?

Experiment 134.

Materials:

Cutch.

Ferric nitrate or ferric acetate.

Piece of woven ecru silk.

Infuse 10 grams cutch with 100 cc. water. Dissolve 10 grams ferric nitrate in 100 cc. water. Weigh the piece of silk (1 to 2 grams). Heat the ferric nitrate solution to 70–80° C. and immerse the silk in it for 10 minutes. Squeeze out, transfer to the cutch bath, and heat to boiling. Repeat the treatment with ferric nitrate and that with cutch several times. Rinse with hot water, dry, and weigh. If heat is applied in drying, allow the silk to stand in the room for a few hours before weighing. Calculate the percentage gain in weight.

A few crystals of stannous chloride added to the cutch bath may produce a greater gain of weight.

Weighting with iron compounds is only practicable where the silk is to be dyed black or a dark color. For white and

light-colored silks soluble substances such as sugar, glucose, and magnesium chloride were formerly and are still sometimes used, but the most successful weighting materials are insoluble compounds of tin. Tin silico-phosphate is one of the most common of these weighting materials for light-colored silk. It is obtained by treating the goods first with stannic chloride, then with sodium phosphate, and finally with sodium silicate.

Experiment 135.

Materials :

Ecreu silk.

Stannic chloride crystals (or anhydrous stannic chloride).

Disodium phosphate crystals.

Sodium silicate (or water-glass solution).

Dissolve 40 grams stannic chloride crystals ($\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$) or 30 grams (13 cc.) anhydrous stannic chloride in 70 cc. of water. Dissolve 13 grams sodium phosphate crystals ($\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$) in 87 cc. water. Dilute water-glass solution to a specific gravity of 1.04.

Weigh a piece of ecreu silk (1 or 2 grams). Place it in the stannic chloride solution and let stand one hour. Heat the sodium phosphate solution and the sodium silicate solution to 60°C . (140°F). Remove the silk from the stannic chloride, rinse it with water, and immerse in the sodium phosphate solution for 10 minutes, then in the sodium silicate for the same length of time. Rinse, dry, and weigh.

The process may be repeated five or six times, the weight increasing with each treatment.

Compare the weighted silk with an untreated piece of the same goods, noting particularly the relative strength of the fibers.

Burn a thread of heavily weighted and a thread of unweighted silk. What differences of behavior are observed?

Silk experts maintain that moderate weighting — up to about 25 per cent of the weight of the boiled-off silk — is not injurious, but rather improves the wearing quality of the silk. Indeed, the term “ pure silk ” is used in the trade to designate a silk which has been weighted just sufficiently to compensate

for the loss of weight sustained in boiling off. It is generally agreed, however, that excessive weighting is very injurious. Goods weighted with tin compounds are especially liable to deterioration on exposure to air and light. It is thought that this may be due to the hydrolytic effect of moisture on the stannic chloride retained in the fibers. Such hydrolysis would liberate hydrochloric acid, which, as we have seen, has a solvent action on silk. Proceeding on this assumption, some manufacturers treat tin-weighted goods with mildly basic organic compounds, and this is said to mitigate the evil to some extent at least.

The most satisfactory methods of estimating the amount of weighting in silk are:

(1) Treatment with dilute hydrofluoric acid, which dissolves the weighting without affecting the silk.

(2) Determination of the amount of nitrogen in the material after first freeing it from nitrogenous weighting materials, such as Prussian blue, ammonium phosphate, glue, and gelatin. Since pure boiled-off silk containing 11 per cent of moisture contains 17.6 per cent of nitrogen, every gram of nitrogen found in the weighted goods represents $100 \div 17.6 = 5.68$ grams of air-dry silk. The difference between the original air-dry weight and the estimated air-dry weight of real silk represents the weight of the filling material.

(3) Burning the goods and weighing the ash. This is a simple method which gives good results with light-colored goods. Unweighted silk leaves less than 1 per cent of its weight of ash. Silk legitimately weighted leaves not over 25 per cent. Silks yielding more than 25 per cent of ash are overweighted. In the case of black goods the amount of weighting may considerably exceed the amount of ash, since some of the weighting substances, *e.g.* tannin, are combustible.

For an account of the silk industry and of the properties of silk fibers and fabrics which should influence their selection and use, reference may be made to Woolman and McGowan's "Textiles: A Handbook for the Student and the Consumer" (New York, 1913).

CHAPTER XLI

TEXTILE FIBERS OF VEGETABLE ORIGIN. COTTON, LINEN, AND ARTIFICIAL SILK

VEGETABLE fibers are of great variety if we include such materials as are used in the manufacture of furniture and floor coverings — twigs, canes, rushes, grasses, leaf fibers (*e.g.* manila, sisal), etc. Leaving these coarse materials out of consideration, the **natural** vegetable fibers resolve themselves into two classes:

(1) **Seed hairs**, of which *cotton* is the only important example.

(2) **Bast fibers**, including *linen*, *ramie*, *jute*, and *hemp*. *Artificial silks* (lustracelluloses) are **artificial** fibers made from vegetable materials.

All these materials are carbohydrate in composition and all belong to that class of carbohydrates known as *celluloses*. Between the cellulose of cotton and that of linen there is little, if any, difference.

Wood-pulp paper and jute consist of lignocellulose, a distinctly different substance from true cellulose. Hemp probably contains both these kinds of cellulose.

Cotton

Cotton fibers are the seed hairs of several varieties of the cotton plant (genus, *Gossypium*), most species of which grow as shrubs in warm climates.

The seed hairs are inclosed with the seed in a sort of pod, known as a boll. The bolls are harvested when they burst open, exposing the ripe cotton.

Experiment 136.

Examine cotton fibers under the microscope at a magnification of about 150 to 300. Note the ribbon-like form and the characteristic twist. Under a higher magnification (about 700) note the inner canal of the fiber.

Cotton fibers (or *staple*, as they are technically termed) of American growth vary in length from $\frac{3}{4}$ inch in Texas to $1\frac{1}{2}$ inches in Uplands, and in diameter from $\frac{1}{2000}$ to $\frac{1}{1000}$ inch, the longer fibers having the smaller diameters.

They are, accordingly, comparable in diameter with silk and fine wool, but much shorter than either silk, wool, or linen fibers. (See pp. 223, 219 and 236). Sea Island cotton, originally grown in the West Indies, and Egyptian cotton, which has been developed from Sea Island stock, have a longer staple and are finer than that from the American mainland. It is this finer variety of cotton which is employed in the manufacture of mercerized lawns.

Cotton fibers consist of a single cell, the structure of which is represented in Figure 44. During growth the interior tube (*lumen*) is filled with a liquid, and the fiber is cylindrical. On ripening, the liquid withdraws and the fiber flattens irregularly into a twisted ribbon. The twist is not only a valuable mark of identification of cotton fibers, but is also of great practical importance in facilitating spinning. As a means of interknitting the fibers it plays a part similar to that played by the epidermal scales in wool. Raw cotton fibers have 300 to 500 twists per inch.

The raw fiber is mixed with, and attached to, the cotton seed. The seed is removed by mechanical processes (*ginning*) — not, however, without some injury to the fibers. A waxy coating also covers the fiber. The quantity of wax is small — usually between 0.3 and 0.5 per cent. After the cotton is spun, this wax is removed by boiling the cotton 6 or 8 hours in a dilute (1 per cent) solution of caustic soda under slight pressure. The bleaching of cotton is not undertaken until the wax has been removed.

Chemical Behavior

Boiled-off cotton is practically pure cellulose. To most reagents cellulose is much more resistant than the protein substances which constitute the animal fibers.

Experiment 137. — Action of Acids.

Treat wisps of absorbent cotton in test tubes with (a) concentrated sulphuric acid, (b) concentrated hydrochloric acid, (c) concentrated nitric acid, allowing it to stand in the cold for 5 or 10 minutes. Afterwards heat tubes (b) and (c). Cool tube (c) and neutralize the nitric acid with ammonia. Record the effect of each of the three acids, and compare with the effects on wool and silk. How could the results be utilized to distinguish (1) cotton from wool and silk, (2) cotton and wool from silk?

Experiment 138. — Action of Acids.

Immerse two pieces of woven cotton goods for a few minutes in dilute sulphuric acid and two similar pieces in a saturated solution of oxalic acid. Without rinsing, immerse one piece from each acid in ammonia. Dry the four pieces on watch glasses in a water oven at 60–80° C. (140 to 180° F.). Note how the acids have affected the strength of the fabric. Is this effect produced by the cold solutions of the acids? (Compare the pieces in which the acid was neutralized by the ammonia before drying.)

It is sometimes stated that the injury produced by organic acids, such as oxalic and tartaric, is purely mechanical, due to the crystallizing of the acids in the fibers. Do your results support this view? Can you suggest other methods of testing this theory?

When acids are accidentally spilled upon cotton goods, what means should be taken to prevent injury to the fabrics?

When strong alkalis are spilled upon cotton goods, how are they best neutralized? What acids may be used and what precautions should be observed in their use?

Explain the use of dilute sulphuric acid in the purification of wool from burrs and other vegetable matter. (See p. 221.)

Cellulose proper — e.g. that of boiled-off cotton and bleached linen — dissolves readily in the cold in concen-

trated sulphuric acid and in strong solutions of certain salts in concentrated hydrochloric acid. Among such salts are mercuric chloride and zinc chloride. A hot concentrated solution of the latter salt (being much hydrolyzed) will dissolve cellulose without the addition of any hydrochloric acid.

Before going into solution in any of these reagents the fibers swell and soften, probably on account of the combining of water with the cellulose. This swelling is utilized in the manufacture of parchment paper and in one of the processes of waterproofing cotton goods.

Experiment 139.

Pour 20 cc. concentrated sulphuric acid into 10 cc. water in a beaker or dish. Allow to cool to room temperature. Provide another beaker or dish of water. Dip a strip of filter paper into the acid for about five seconds, then transfer it quickly to the water. Wash thoroughly. Compare the appearance and strength of the treated paper with that of wet untreated filter paper. Treat each with iodine solution.

Cellulose, being carbohydrate, has the characteristics of an alcohol (with many —OH groups). It is, therefore, capable of reacting with acids to form esters and, having many —OH groups, it can form several esters with one acid. The nitrates of cellulose are made commercially, not only for use as explosives, but also for the manufacture of collodion and artificial silk. Cellulose is nitrated by treatment with a mixture of nitric acid and concentrated sulphuric acid. Cellulose nitrates are commonly called nitrocelluloses.

Experiment 140.

Mix 20 cc. concentrated sulphuric acid and 10 cc. concentrated nitric acid. Allow to cool to room temperature. Immerse absorbent cotton in this mixture for about one minute. Wash thoroughly with cold water, wring out, and allow to dry on filter paper. Set a piece of the dry product and a piece of the untreated cotton on fire and compare the rapidity with which they burn.

This product is a "nitrocellulose" (guncotton or pyroxylin). Shake a portion of the dry guncotton with a mixture of alcohol and ether. (A residue of unchanged cellulose will remain.) The clear liquid (a solution of nitrocellulose in ether and alcohol) is collodion. Pour a little of it on a glass plate and allow to evaporate. (Keep flames away.) Surgeons sometimes use collodion to form a coating over wounds. Such a coating is adherent, flexible, and impermeable to air and water.

Experiment 141.

Material:

Collodion prepared in the preceding experiment.

Pour a little of the collodion solution on water in a test tube. Note that it forms a clear layer above the water. Shake the tube. The precipitate is nitrocellulose.

Experiment 142. — Action of Alkalies.

Boil a piece of cotton yarn or woven cotton goods for a few minutes with dilute sodium hydroxide solution. Wash, neutralize the alkali by dipping into water containing a little acetic acid, and wash again. Compare the strength of the goods with that of untreated cotton of the same kind. Contrast the effect of alkalies on cotton with that on wool and silk. How could this difference be utilized in the analysis of mixed goods?

Experiment 143. — Action of Alkalies.

Cover a piece of cotton with a strong solution of caustic soda (30 per cent) or caustic potash (50 per cent) and allow to stand 10 or 15 minutes. Remove the cotton, wash in a stream of cold water, dip into dilute acetic acid, and wash again. Note the appearance of the cotton, comparing it with that of untreated cotton.

Mercerization

Mercerization is a process to which cotton is sometimes subjected to increase its luster, its strength and wearing qualities, and its capacity for taking dyes. The cotton is stretched on a frame and subjected to the action of a strong cold solution of sodium hydroxide (about 30 per cent NaOH), after which it is washed with water. The effect of the strong

solution of alkali on unstretched cotton is to swell and shorten the fiber, causing shrinkage of the goods. When the goods are stretched, the shrinkage is overcome or prevented, but the fibers are untwisted and acquire a high luster. It is supposed that the alkali hydroxide combines chemically with the cellulose, and that, on washing, the metal of the alkali is replaced by hydrogen, leaving hydrated cellulose, *i.e.* a compound of cellulose with water.

The process takes its name from John Mercer, who in 1844 first observed the action of concentrated solutions of the caustic alkalies on cotton, and in 1850 took out a patent on the process. The stretching of the fabric to prevent shrinkage and produce a high luster was a later development introduced by Lowe in 1889. It is only since this later discovery that the process has become commercially successful. Long-stapled cottons (Egyptian and Sea Island), which are naturally more glossy than the commoner short-stapled varieties, are preferred in the manufacture of mercerized goods.

Sizing, or Dressing of Cotton Goods

Cotton goods are commonly sized or otherwise finished to give an attractive (sometimes a deceptively attractive) appearance. In the trade, the term *sizing* is commonly used to designate the process of applying dressing materials to the warps, while the application of the same materials to the *woven fabric* is termed *finishing*. Among the materials used for various purposes are :

- (a) Stiffening agents: *starch, flour, dextrin, glue, gelatin, gums.*
- (b) Softening agents: *fats, waxes, soaps.*
- (c) Filling and weighting agents: *aluminium silicate (China clay), calcium sulphate (gypsum), magnesium silicate (talc), calcium carbonate (whiting), barium sulphate (blanc fixe).*
- (d) Hygroscopic agents — which both add weight and soften: *magnesium chloride, calcium chloride, glycerin.*
- (e) Preservative agents — to prevent the growth of mildew and other organisms: *zinc chloride, carbolic acid, cresols, salicylic acid, boric acid.*

The basis of the size is practically always starch. This can be removed by boiling with dilute acid, which hydrolyzes it and thus loosens the filling materials. Subsequent treatment with dilute alkali removes the fats and waxes.

Experiment 144. — Determination of Dressing Materials.

Material:

White cotton goods, unwashed.

Wet a small portion of the goods and test with iodine solution for starch. Prepare a 3 per cent solution of hydrochloric acid (by diluting 400 cc. of the reagent dilute hydrochloric acid to 1 liter) and a 1 per cent solution of sodium carbonate (by diluting 100 cc. of the reagent solution to 1 liter).

Weigh a piece of the dry goods (2 to 5 grams). Boil 10 or 15 minutes in the 3 per cent hydrochloric acid. Cool, rinse, and test for starch. If present, boil again with the acid. Rinse and boil 5 minutes in 1 per cent sodium carbonate solution. Rinse thoroughly, dry, allow to stand in the air of the room for 2 or 3 hours, and weigh. The difference between the initial and the final weight is the weight of the dressing materials.

Linen

Linen is a bast (*i.e.* inner bark) fiber obtained from flax stalks. These are cut or pulled, while still somewhat green, stripped of seeds and leaves by a machine, and then subjected to a fermentation known as "retting" — *i.e.* rotting. Retting is conducted either in water (tanks or running streams) or by exposure to the weather (dew retting) or both. Its effect is to convert the substances holding the fibers together into soluble compounds which are washed out. Thus an enzyme (pectinase) secreted by certain bacteria acts upon the calcium pectate between the cells, converting it into pectin, sugars and soluble calcium salts. The remaining impurities — bark, woody tissue, etc. — are removed by mechanical processes, and the fiber then undergoes much the same treatment as cotton.

Experiment 145.

Examine unbleached and bleached linen fibers under the microscope, comparing them with cotton fibers. Moisten with a dilute solution of iodine and examine again.

Note particularly the absence of twist and the presence of cross-markings at the junctions of the cells — similar to the “knots” in straw.

Linen fibers are from 8 inches to 5 feet long, averaging 20 inches, and from $\frac{1}{2000}$ to $\frac{1}{600}$ inch in diameter, averaging about $\frac{1}{1000}$ inch. They are thus much longer, and on the average a little coarser than cotton fibers. Under the microscope the flax fiber appears as a long, straight, cylindrical tube with a narrow lumen, often appearing as a mere black streak. There are cross markings on the cylinder, and nodes resembling the knots on straw. These markings, which are emphasized by treatment with iodine, constitute one of the best means of identifying linen fibers. The natural ends of the flax fibers are narrow and pointed.

The flax fiber is not, like the cotton fiber, a single cell, but consists of a bundle of cells, averaging about 1 inch in length and $\frac{1}{1700}$ inch in diameter at the middle. The fiber of flax is more porous than that of cotton, and the following very good test, particularly for bleached goods, is based upon this property.

Experiment 146. — Oil Test for Linen.

Free the sample from dressing by boiling in 3 per cent hydrochloric (or 5 per cent oxalic) acid. Treat with 1 per cent sodium carbonate solution, rinse with distilled water, and dry. Fringe out the goods on two adjacent edges, so as to expose ends of warp and weft threads. Moisten the piece thoroughly with olive oil or glycerin. Press between filter papers and place against a dark background. The linen fibers or threads appear translucent, the cotton fibers remain opaque white.

The linen fiber is stronger, but harder and less resilient (elastic) than cotton. It is also a better conductor of heat

and therefore feels cooler to the touch. Experts can sometimes distinguish cotton goods from linen by feeling them. Dressings, however, may interfere here.

Bleached linen, like bleached cotton, is almost pure cellulose. Unbleached flax fiber, however, contains from 0.5 to 2 per cent of a wax-like substance and 2.5 to 10 per cent of intercellular substance and pectins. Unbleached or incompletely bleached linen often shows a noticeable difference from cotton on treatment with staining materials. Many distinguishing tests have been based upon this fact.

Experiment 147.

Materials:

Rosolic acid solution (0.5 gram in 50 cc. water and 50 cc. alcohol).

Samples of pure cotton and pure linen goods.

Sample with linen warp and cotton weft.

Warm the mixture. Fringe out the samples on two adjacent edges and immerse in the solution for five minutes. Remove, wash with water, with dilute ammonia, and again with water. Dip into concentrated sodium hydroxide solution; again wash thoroughly, and allow to dry. Note which of the materials is permanently reddened.

Experiment 148.

Materials:

Cyanin solution (0.1 gram in 50 cc. alcohol and 50 cc. water).

The same fabrics as in Experiment 147.

Fringe out the samples, warm them in the cyanin solution for 3 minutes. Wash. Lay in water acidulated with sulphuric acid, then treat with dilute ammonia.

One of the most useful tests for distinguishing cotton from, and detecting cotton in, linen goods is treatment with cold concentrated sulphuric acid. This test is most successful with coarse-woven goods, such as towelings, but by varying the time of immersion may be made to succeed even with a handkerchief weave.

Experiment 149.

Free the material completely from dressing by boiling with 3 per cent hydrochloric or 5 per cent oxalic acid, treating with 1 per cent sodium carbonate solution and rinsing with distilled water. Dry the goods. Immerse in concentrated sulphuric acid from $1\frac{1}{2}$ to 2 minutes, according to the texture of the material. Remove, wash thoroughly with water, then with dilute ammonia. Cotton fibers are destroyed, linen fibers remain.

Linen warp threads in goods with cotton weft can be retained in position in this test by tying the goods to microscope slides with strong linen thread.

Although linen is more resistant to sulphuric acid than cotton, it is less resistant to boiling alkaline solutions and to bleaching powder and other oxidizing agents.

The dressing materials applied to linen goods are similar to those used for cottons. The amount of hygroscopic moisture in linen is about the same as that in cotton, viz. 6 to 8 per cent.

Lustracellulose (“ Artificial Silk ”)

“ Artificial silk ” fibers are made from cellulose (cotton or wood pulp) by dissolving it in a suitable solvent, forcing the solution through minute openings, and reconverting it into a solid form as it issues in fine streams. The threads thus produced resemble silk in structure, being formed by a process similar to that used by the silk worm. In size (both length and diameter) and in luster they approximate much more closely to silk fibers than do mercerized cotton fibers. Chemically they are not protein, like the fibroin of silk, but carbohydrate, viz. cellulose. From the chemical standpoint, therefore, the name *lustracellulose* is preferable to *artificial silk*.

Attempts have been made to manufacture artificial protein fibers from gelatin and from casein. These processes, however, have not been commercially successful.

The three leading processes of manufacturing artificial silk are:

1. That known from its inventor as the **Chardonnet Process** and from its intermediate products as the **Pyroxylin** or **Collodion Process**. The cellulose is converted into *nitrocellulose* by treatment with nitric and sulphuric acids. (See Expt. 140, p. 232.) The nitrocellulose is dissolved in ether and alcohol and the resulting *collodion* forced through the narrow openings into a warm chamber. The alcohol and ether evaporating from the threads are recovered and used over and over again. The nitrocellulose fibers are reconverted into cellulose ("denitrated") by immersion in a solution of ammonium sulphide.

The Chardonnet Process, although expensive, is still in use in France.

2. The **Cuprate** or **Cuprammonium Process**. The cellulose is dissolved in an ammoniacal solution of copper hydroxide and the threads delivered into an acid, which reprecipitates the cellulose. This process is used principally in Germany.

3. The **Viscose Process**. The cellulose (usually wood pulp) is treated with a strong caustic soda solution such as is used in mercerizing. The alkali cellulose thus obtained is treated with carbon disulphide. Combination occurs with the production of a compound soluble in water, but insoluble in alcohol and in brine. This compound is called "viscose" on account of the extraordinary viscosity of its solution in water. The viscous solution is forced through fine openings into a concentrated solution of sodium chloride or ammonium chloride which precipitates the viscose in threads. The latter is then decomposed by heat into cellulose and water-soluble products, which latter are washed out.

The chemical reactions involved in the Pyroxylin Process are illustrated by Experiments 140 and 141 above.

Experiment 150. — The Cuprate Process.

Dilute 10 cc. copper sulphate solution to about 150 cc. in a beaker. Add a few drops ammonium chloride solution, and, without heating, add sodium hydroxide solution until the precipitate formed just begins to darken in color. Allow to settle, filter, and wash the precipitate with cold water. (What is this precipitate?) Remove the precipitate from the filter paper, place it in a dish, cover with ammonium hydroxide, and stir. Pour off the clear solution into a test tube, add some absorbent cotton, and shake. Pour a little of the solution thus obtained into dilute acid in a test tube. The precipitate is the regenerated cellulose.

Experiment 151. — The Viscose Process.

Cover a little absorbent cotton in a beaker with 30 per cent sodium hydroxide (or 50 per cent potassium hydroxide) solution and allow to stand for an hour or longer. Remove the alkali-cellulose from the liquid by use of a glass rod. (Better results will be obtained if the moist mass is now placed in a stoppered bottle or test tube and allowed to stand two or three days. This, however, is not essential to the success of the experiment.)

Cover the moist mass with carbon disulphide, shake vigorously, and allow to stand until quite yellow (about 3 hours). Pour off the excess of carbon disulphide, cover the product with water, and again allow to stand for an hour or more. Shake, and add enough additional water to give a thick brown liquid. This is the *viscose* solution. Pour portions of it into (a) alcohol, (b) a saturated solution of ammonium chloride. A portion may also be forced through a piece of glass tubing drawn to a capillary. Dip the capillary end of the tube under the surface of alcohol or saturated ammonium chloride solution and blow steadily into the tube. The viscose will precipitate in threads.

Pour the main portion of viscose solution into a small, flat-bottomed dish (a crystallizing dish), cover it with alcohol, and allow to stand half an hour. Pour off the alcohol, being careful not to disturb the sediment of viscose. Rinse two or three times with alcohol, then heat on a water bath. The viscose is decomposed by the heat. Rinse the dry residue several times with water. This removes the other decomposition products, leaving the cellulose in the form of a film.

Experiment 152.*Materials :*

Artificial silk.

True silk.

Mercerized cotton.

Ravel out threads of each. Could the mercerized cotton be recognized by the length of the fibers?

Break equal-sized threads of each, comparing the strength of the threads.

Wet each thoroughly and again compare the strength of the threads.

Burn a little of each and note odor.

How can you distinguish :

(a) Artificial silk from mercerized cotton.

(b) Lustracellulose from silk.

The following methods may be used for the quantitative analysis of mixtures of cotton and wool and of cotton and silk.

Experiment 153. — Analysis of a Wool-cotton Fabric.*Materials :*

Fabric containing wool and cotton.

5 per cent solution of potassium hydroxide.

1 per cent solution of hydrochloric acid.

0.05 per cent solution of sodium carbonate.

Weigh the sample. Remove the finishing materials by boiling 30 minutes in 1 per cent hydrochloric acid, rinsing, and boiling thirty minutes in 0.05 per cent sodium carbonate. Wash thoroughly, air-dry, and weigh. The loss represents finishing materials. Dry to constant weight in a water oven. The loss represents moisture, and the residue is dry fiber.

Boil for 20 minutes in 5 per cent caustic potash. Wash well, dry in the water oven to constant weight. Add 5 per cent to the weight of the residue, because the cotton is attacked to about that extent. The residue is the weight of dry cotton, the loss that of dry wool.

Experiment 154. — Analysis of a Silk-cotton Fabric.*Materials :*

Fabric of silk and cotton.

Elsner's reagent (basic zinc chloride).

Determine the quantities of finishing material and moisture as in Experiment 153.

Immerse in the boiling basic zinc chloride solution for one minute. Wash thoroughly with 1 per cent hydrochloric acid, then with water; dry and weigh. Add $1\frac{1}{2}$ per cent to the weight of the residue. The result represents the amount of cotton.

The silk may also be dissolved by immersion for 5 minutes at room temperature in Richardson's reagent (an ammoniacal solution of nickel hydroxide) or for 15 minutes at 50° C. in Löwe's reagent (an alkaline solution of copper hydroxide and glycerol).

Richardson's reagent is prepared by dissolving 25 grams nickel sulphate in 500 cc. water, precipitating completely with sodium hydroxide, washing thoroughly by settling and decantation, dissolving in 125 cc. concentrated ammonia and making up to 250 cc.

Löwe's reagent is prepared by dissolving 25 grams copper sulphate in 250 cc. water, adding 12 cc. glycerol and just sufficient sodium hydroxide solution to redissolve the precipitate which forms at first.

The methods of manufacturing cotton and linen fabrics and their properties in relation to selection and use are fully discussed by Woolman and McGowan in the work already referred to (p. 228).

CHAPTER XLII

BLEACHING AND BLUEING

WHILE a great many chemical compounds are white — *e.g.* sugar, salt, starch — there are many others that are characterized by certain colors. When such compounds undergo chemical change, their characteristic colors disappear and the colors of the products of the chemical change make their appearance. Indeed, a change of color is commonly accepted as an indication of chemical change.

A change of color is only an indication, not a *proof*, that chemical change has taken place. The color of a solid substance may be materially altered by a change of physical condition. Thus large copper sulphate crystals appear dark blue, while small crystals are lighter blue; cold zinc oxide is white, but hot zinc oxide yellow.

To bleach a textile, whether for the purpose of removing the natural color of the fiber or to take out a stain or to remove a dye, what must be done is to convert the color-bearing compound or compounds into colorless products. The natural coloring matters of textile fibers, and practically all the dyes which are used upon textiles, are *organic substances*, *i.e.* *carbon compounds*. There are two general methods of converting organic coloring matters into colorless products:

1. **By Oxidation.** — This may be accomplished by the action of free oxygen, especially under the influence of direct sunlight. The “grass bleaching” of linen is a familiar example. More rapid action can, as a rule, be attained by the use of an *oxidizing agent*, *i.e.* a compound which readily gives up oxygen to other substances. Among the oxidizing agents used in bleaching are *calcium hypochlorite*, *sodium hypochlorite*, *hydrogen peroxide*, and *potassium permanganate*.

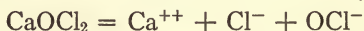
2. By **Action of Sulphurous Acid, H_2SO_3** . — Sulphurous acid is a *reducing agent* (see Expt. 98, p. 169), being readily oxidized to sulphuric acid, H_2SO_4 . No doubt in many instances it bleaches by removing oxygen from the color-bearing compound. But it also has the power of *combining with* some kinds of organic substances, and its bleaching action may often be due to combination rather than to reduction. Its action is in many instances not fully understood.

In the removal of the natural colors from textile fabrics the choice of a bleaching agent must be governed by its effect upon the fiber substance itself, as well as by its cost and its effectiveness in destroying the coloring matter. In household bleaching, likewise, the effect of the bleaching agent upon the material to be bleached must be known and borne in mind.

Hypochlorites

The most active bleaching agent, and the cheapest except atmospheric oxygen, is **bleaching powder**.

This is made by the combining of chlorine with lime, whence the alternative name, *chloride of lime*. It has the composition represented by the formula $CaOCl_2$, and when dissolved in water ionizes thus:



The hypochlorite ions, OCl^- , readily give up oxygen, especially in presence of acid, where they first unite with hydrogen ions, H^+ , to give the unstable hypochlorous acid, $HClO$. Bleaching-powder solutions, therefore, especially when acidified, act as strong oxidizing agents.

Experiment 155. — Bleaching Powder.

Materials:

Bleaching powder.

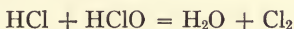
Mortar and pestle.

Cobalt nitrate solution (10 per cent).

Grind about 10 grams bleaching powder in a mortar, and gradually add about 5 grams of water so as to form a paste. Add an additional 25 cc. water, mix thoroughly, and filter. Note the odor of the filtrate. Heat a portion of it and note whether the odor becomes stronger. Also note whether a precipitate forms. The odor is that of hypochlorous acid and the precipitate is calcium hydroxide. What effect do you infer that heat has on the hydrolysis of calcium hypochlorite?

To a portion of the filtrate add a few drops of cobalt nitrate solution, cover the test tube with the thumb for a minute or so, then test the evolving gas with a glowing splint. What is the gas? Is it pure? (Note odor.) The black precipitate, which is an oxide of cobalt, acts as a catalytic agent, causing rapid decomposition of the hypochlorous acid.

To a portion of the original filtrate add dilute hydrochloric acid. Note color and odor. These are due to *chlorine*, hydrochloric and hypochlorous acids reacting thus:



Experiment 156. — Bleaching Effect.

Materials:

Bleaching-powder solution prepared as in Experiment 155.

Small pieces of cotton fabric dyed or printed in various colors.

Immerse the pieces of cotton in the bleaching-powder solution for a few minutes. Then dip in dilute hydrochloric acid. Repeat the treatment with bleaching powder and dilute hydrochloric acid several times, noting the effect on the colors.

Experiment 157. — Effect on Textile Materials.

Materials:

Bleaching-powder solution prepared as in Experiment 155.

Sodium bisulphite solution or sodium thiosulphate solution.

White or unbleached cotton, linen, silk, and wool, in yarns or light fabrics.

Immerse the textiles in the bleaching-powder solution for a few minutes, then dip in dilute hydrochloric acid, and finally in sodium bisulphite solution. Rinse and dry. Note how the color and strength of the materials have been affected.

Experiment 158. — Formation of Oxycellulose.*Materials :*

White cotton or linen goods.

Bleaching-powder solution.

Sodium bisulphite solution.

Immerse three equal-sized pieces of the goods in the bleaching-powder solution for about five minutes. Dry one without rinsing. Treat the second with dilute hydrochloric acid and the third with sodium bisulphite (or with sodium thiosulphate) solution; rinse and dry.

When the three pieces are dry, compare their strengths and colors.

Experiment 159. — Detection of Oxycellulose.

Thoroughly wash the piece of cotton dried with the bleaching powder in it (Expt. 158). Cover it with Fehling-Benedict solution and boil. For comparison boil a piece of untreated cotton with Fehling-Benedict solution. Oxycellulose reduces the solution, the precipitate of cuprous hydroxide being deposited upon the fiber.

Industrially, *silk* is never treated with bleaching powder or other hypochlorites. In the *woolen* industry bleaching powder is not used for bleaching purposes, though it is sometimes used to render woolen goods unshrinkable — not, however, without injury to the wearing qualities. In the commercial bleaching of *cotton* and *linen*, however, it is universally used. Great care has to be exercised to prevent the formation of oxycellulose, which both tenders the goods and makes them dye unevenly. Special care is necessary in the case of linen, which has more natural color to remove and at the same time has a more easily injured fiber than cotton. Weaker solutions are used for linen, the treatments being more numerous and the bleaching-powder treatment (“chemicking”) being alternated with treatments with alkalis and supplemented by grass bleaching.

Cotton bleaching is accomplished by alternate treatments with bleaching-powder solution (“chemicking”) and with

dilute hydrochloric acid ("souring"). The acid acts on the bleaching powder left in the material, converting it into chlorine and calcium chloride, which are readily washed out.

If solid particles of bleaching powder are allowed to come into contact with the goods, or if the goods are exposed to air and light before the hypochlorite has been completely removed, oxycellulose is apt to be formed. Much damage is no doubt done in domestic and commercial laundries through the ignorant use of bleaching powder. Washing with water ought not to be depended upon to remove the reagent from the goods. Effective materials for this purpose, less disagreeable in their effects than the hydrochloric acid (which is preferred in factory practice for economical reasons), are *sodium bisulphite*, NaHSO_3 , and *sodium thiosulphate*, $\text{Na}_2\text{S}_2\text{O}_3$, commonly known as *hyposulphite of soda*.

Experiment 160.

Materials :

Bleaching-powder solution.

Pieces of dyed or printed cotton.

To a filtered solution of bleaching powder add sodium carbonate solution as long as a precipitate is formed. The precipitate is calcium carbonate. Write equation for the reaction. What compounds are left in solution? Filter.

Immerse pieces of colored cotton in the liquid, afterwards treating with dilute hydrochloric acid.

The solution obtained by the interaction of sodium carbonate and chloride of lime contains sodium chloride and **sodium hypochlorite**. The latter has a bleaching action similar to that of the calcium compound and has the advantage of avoiding the impregnation of the goods with calcium salts which may afterwards react with soaps, producing deposits of the insoluble lime soaps. It finds use in the household for the removal of stains from fabrics by bleaching.

Sodium hypochlorite can also be prepared by passing chlorine gas into a dilute, cold solution of sodium hydroxide or sodium

carbonate and by passing an electric current through a solution of common salt. In either case the solution obtained contains sodium chloride as well as sodium hypochlorite.

This solution is popularly known as *Javel water* (commonly misspelled *Javelle* or *Javelles*) although that name belonged originally to the corresponding potassium product, which was first made in the Javel bleach works near Paris in 1792. In pharmacy the sodium solution is known as *Labarraque's solution*.

Hydrogen Peroxide

Hydrogen peroxide is a compound of hydrogen and oxygen containing a higher percentage of oxygen than does water. Its formula, H_2O_2 , expresses the fact that the proportion of oxygen to hydrogen is twice as great as in water, H_2O ; in other words, that its molecule contains two atoms of oxygen combined with two atoms of hydrogen. In acting as an oxidizing agent hydrogen peroxide gives up half its oxygen (*i.e.* one atom from each molecule), and water remains.

Pure hydrogen peroxide is a liquid resembling water, but heavier and more viscous. It is an unstable substance, decomposing spontaneously into water and oxygen. For this reason it is not easy to make or to keep, and the common commercial hydrogen peroxide is only a 3 per cent aqueous solution.

As a bleaching agent hydrogen peroxide has the advantages over all others, except oxygen and ozone, that it does not injure the most sensitive of the textile fibers and that it leaves no solid residue in the goods. It is used in a mildly alkaline medium, being less stable in alkaline than in acid solutions and therefore more rapid in its action. It is employed in the bleaching of feathers and ivory.

Experiment 161.

Materials :

- Hydrogen peroxide solution.
- Manganese dioxide, powdered.
- Feather.

Colored hair.

Ecru silk.

To 5 cc. hydrogen peroxide in a test tube add a little powdered manganese dioxide. Test the evolved gas with a glowing splint. What is the gas?

To 10 cc. hydrogen peroxide in a beaker add ammonium hydroxide little by little until small bubbles begin to form. Immerse the feather, hair, and ecru silk, and examine from time to time.

The great disadvantage of hydrogen peroxide as a bleaching agent is its high price. This can to some extent be obviated by preparing the hydrogen peroxide in the bleaching bath itself from cheaper materials. *Sodium peroxide*, Na_2O_2 , is one of the materials from which it is obtained. Sodium peroxide reacts with acids, liberating hydrogen peroxide, thus:



In use the sodium peroxide is gradually added to cold water. The solution thus obtained is neutralized with dilute sulphuric acid and then rendered mildly alkaline by the addition of sodium silicate.

Sodium perborate, $\text{NaBO}_3 \cdot 4 \text{H}_2\text{O}$, is also used as a bleaching agent, its solution behaving like one of borax and hydrogen peroxide.

Potassium permanganate, KMnO_4 , is occasionally used as a bleaching agent. In acting as an oxidizing agent it yields a brown solid residue. This residue is removed by treatment with sodium bisulphite.

The nature of sunlight bleaching is obscure. It is possible that the action of the sunlight on the evaporating water produces hydrogen peroxide or ozone (an active form of oxygen), and that this product acts upon the coloring matters.

Sulphurous Acid

Experiment 162.

Materials :

Sulphur.

Red flower or fresh grass.

Pieces of colored cotton.

Apparatus :

- Deflagrating spoon.
- Glass cylinder or beaker.
- Glass plate.

Ignite a small quantity ($\frac{1}{4}$ gram) sulphur in a deflagrating spoon, lower the spoon into the beaker and cover with the glass plate. Note odor of gas evolved. This gas is sulphur dioxide, SO_2 . Suspend in the beaker a red flower (*e.g.* rose or carnation) or some grass and some pieces of colored cotton.

Experiment 163.*Materials :*

- Sodium bisulphite.
- Potassium permanganate solution.

Apparatus :

Test tube with one-holed rubber stopper or cork, through which passes a delivery tube bent twice at right angles so as to reach the bottom of a second test tube.

Place in the generator test tube 1-2 grams sodium bisulphite, cover with water, and add a few cubic centimeters of dilute sulphuric acid. Fill the other test tube with water and pass the gas from the generator into the water. Note the odor of the gas and compare it with that obtained by burning sulphur (Expt. 162). What is the gas? Write equation for its formation. Does it appear to be absorbed by the water? (Compare size of bubbles as they leave the tube with those which escape from the water.) Test the water with blue litmus paper. What do you infer as to the character of the substance formed by the combining of the gas with water? Write equation for this reaction. The solution contains sulphurous acid. Try the action of this solution on the same materials as were exposed to the action of the gas in Experiment 162. Add a little of the solution to a dilute solution of potassium permanganate.

Experiment 164.*Materials :*

- Sodium bisulphite.
- Indigo carmine solution, prepared by dissolving indigo carmine in water or by warming 1 gram indigo with 8 cc. fuming sulphuric acid for one to two hours, rinsing into a flask and making up to 1 liter.

To indigo carmine solution add sodium bisulphite solution sufficient to discharge the blue color. To one portion of the product add dilute sulphuric acid, to a second ammonium hydroxide.

Sulphurous acid, H_2SO_3 , is known only in solution. Its *anhydride* is the gas *sulphur dioxide*, SO_2 . Being dibasic, sulphurous acid forms acid salts, *e.g.* sodium bisulphite, $NaHSO_3$, as well as the normal salts, such as sodium sulphite, Na_2SO_3 . The *anhydride*, the *acid*, and the *acid sodium salt* are all used as bleaching agents in the textile industries. The gaseous anhydride, sulphur dioxide, finds the widest use. The usual method of bleaching wool and silk is to burn sulphur in iron or brick pans in a chamber in which the goods are suspended. The process is known technically as "stoving." As a little sulphuric acid is formed in the burning of sulphur, thorough washing should follow stoving.

For bleaching on a small scale sodium bisulphite is convenient. The goods may either be steeped for some hours in a fairly strong (about 15 per cent) solution of the bisulphite, then passed through very dilute hydrochloric acid, and finally washed with water; or a weak solution of the bisulphite may be acidified with hydrochloric acid and the goods soaked several hours in the mixture, which, of course, contains free sulphurous acid.

Wool bleached with sulphurous acid or bisulphite is readily affected by alkalis, the natural yellow color returning on washing with soap or soda.

A more permanent bleach is obtained by the use of hydrogen peroxide. Black or brown wools and hair cannot be bleached white, but assume a golden color when treated with peroxide.

Blueing

In addition to bleaching, *i.e.* chemical alteration of the coloring matters, there is another device used, both industrially and in the household, to give yellowish goods a pure

white appearance. Blue and yellow, being complementary colors, neutralize each other in their optical effect. Yellowish goods can therefore be made white by treatment with a suitable quantity of blue coloring matter. The materials used for this purpose are :

1. **Ultramarine**, a complex compound of the elements sodium, aluminium, silicon, sulphur, and oxygen. Originally found as a rather rare mineral, *lapis lazuli*, ultramarine is now made synthetically from sodium sulphate, clay, and sulphur by heating with a carbonaceous reducing agent, such as charcoal or tar. Ultramarine is insoluble in water, but in a finely divided condition remains suspended long enough to be evenly distributed over the goods. It is not affected by air, light, or alkalies, but is decomposed by dilute acids.

2. **Indigo**, a dye formerly, and to some extent still, obtained by the fermentation of the juices of certain species of plants known as *Indigoferæ*, but now manufactured in a purer form from coal-tar products. Indigo is insoluble in water, but can be suspended in it in the same way as ultramarine. By treatment with fuming sulphuric acid it can be converted into *indigo carmine* (*sulphindigotic acid*), a soluble product retaining the blue color. It is not decolorized by acids, soap, or soda, and is fast to light. Suspended indigo can be decolorized by treatment with sodium bisulphite and zinc dust, indigo carmine by sodium bisulphite alone.

3. **Soluble Coal-tar Products**. — Blues of this class can often be recognized by making one portion of the solution acid and another alkaline and comparing colors. The two will usually differ in shade. The best coal-tar blues are not actual dyes, which would permanently color the textile, but rather substances which will readily wash out, *e.g.* the *alkali blues* and *indigo carmine*.

All the above are good stable blues. The soluble blues —

including indigo carmine — have the advantage over the insoluble that they give a more even coloring to the fabric. Some of them, however, are treated with oxalic acid in the laundry to set them in the goods, and the acid, drying in the fabric, corrodes the textile fibers.

A cheap but very objectionable laundry blue is *Prussian*, or Berlin, *blue*. This is a compound of iron, carbon, and nitrogen, the chemical name for which is *ferric ferrocyanide*. It is decomposed by alkalies with production of *ferric hydroxide*, $\text{Fe}(\text{OH})_3$. Goods treated with it are apt to show rust stains, particularly if they contain any soap or soda when blued.

Experiment 165.

Materials:

Ultramarine.

Prussian blue.

Indigo.

Soluble blues.

Soap solution.

Place a minute quantity of each blue in a separate test tube. Fill with water and shake until the blue is evenly distributed through the water.

Test portions of each liquid with the following solutions:

(a) Dilute hydrochloric acid. Note the odor from the ultramarine. Moisten a piece of filter paper with lead acetate solution and hold at the mouth of the test tube.

(b) Sodium hydroxide. Compare the colors with those of the acidified solutions from (a).

(c) Sodium carbonate.

(d) Soap, boiling.

Allow the main portions to stand for a few days and note which form sediments.

CHAPTER XLIII

DYEING

DYEING consists in attaching a colored substance to the fibers of the textile in such a manner that it is not readily removed by rubbing or washing. Whether dyeing involves a chemical union between the fiber and the coloring matter is a disputed question. There are some facts which appear to indicate that such combinations of fiber and dye do occur in some instances. The animal fibers (and leather), being protein and having, therefore, basic and acid radicles, will combine directly with certain dyes which are acid and basic, whereas the same dyes will not become attached to the vegetable fibers. On the other hand, the product of the deposition of the dye in the fiber does not appear to have properties distinct from those of the dye and of the fiber, which ought to be the case if actual combination has occurred; nor does the combination seem to occur in the definite proportions in which substances react in chemical processes, but this may be because the enormous size of the protein molecules makes possible an almost unlimited number of compounds. The fact that cotton fibers from which the lumen is absent refuse to take dyes furnishes another argument in favor of a physical theory of dyeing.

The protein fibers are so different in character from the cellulose fibers, and the diversity of chemical nature among dyestuffs is so great, that it is not likely that all cases of dyeing can be explained in the same way. Physical phenomena may play the more important part in some instances, chemical phenomena in others.

Many dyes that will not attach themselves directly to a

given kind of fiber will dye the fiber after it has been first treated with a substance called a *mordant* (from the Latin, *mordeo*, I bite). The mordant is used to attach to the fiber a compound capable of combining with the dye to form an insoluble product. The insoluble product is known as a *lake*.

A dye that will dye fibers without the intervention of a mordant is called a **substantive dye**.

A dye that will only attach itself to the fiber through the intervention of a mordant is called an **adjective** or **mordant dye**.

Practically all the modern dyes are organic compounds. A buff color of iron oxide is sometimes produced by treating the fabric first with an iron solution (such as ferrous sulphate), then with an alkali (*e.g.* sodium hydroxide or sodium carbonate), and then exposing it to the air to oxidize the ferrous hydroxide, $\text{Fe}(\text{OH})_2$, formed at first, to ferric hydroxide, $\text{Fe}(\text{OH})_3$. "Khaki" is obtained by adding a chromium salt (chrome alum) to the iron solution and treating in this way, thus producing a mixture of ferric and chromic oxides. Manganese brown, composed of an oxide (or hydroxide) of manganese, can be similarly produced from solutions of manganese salts. Chrome yellow is produced as a precipitate in the fibers when the goods are treated first with lead acetate and then with potassium dichromate. These **inorganic** dyes are sometimes called "mineral pigments."

Of the **organic** dyes a few are still obtained from *plant* or *animal* sources. *Logwood*, a dye extracted from the heart wood of a large South and Central American tree, the *Haematoxylon campechianum* (literally, *blood-red wood of Campeachy*), is used extensively in the silk industry and in calico printing for the production of a full black. Quercitrin bark and Persian berry are still used in dyeing yellow, although better effects are, as a rule, obtained with synthetic dyes.

Natural *indigo*, obtained by exposing to the air the juice

of the leaves of various species of plants of the genus *Indigofera*, formerly cultivated on a large scale in India, has within the last decade been almost entirely replaced by synthetic indigo, the same compound in purer form manufactured from coal-tar products.

Madder, obtained from the dried roots of the madder plant and used for the production of *Turkey red*, has long been replaced by synthetic *alizarin*, a compound identical with one of those contained in the natural product. Alizarin is manufactured from coal-tar products, and derivatives of the compound are in use which enable the dyer to obtain blues, purples, yellows, etc., chemically similar to Turkey red and equally fast to light and washing. Such vegetable dyes as *sandalwood*, *archil*, *alkanet*, *fustic*, *turmeric*, and *cudbear*, and such insect dyes as *cochineal*, *kermes*, and *lac dye*, have been replaced almost completely by coal-tar derivatives, not identical with the natural coloring matter of these substances, but superior to them in fastness, in convenience, in economy, or in beauty. Cochineal, however, is still used to some extent.

The **synthetic** (*i.e.* built-up) **dyes** are all derived from products of *coal tar*. The first to be manufactured were made from aniline, $C_6H_5NH_2$, and the term "aniline dyes" is sometimes applied in popular language to the whole group of substances. Only a few of them, however, are actually made from aniline. *Coal-tar dyes* and *synthetic dyes* are more appropriate names for the class. Coal tar is obtained as a by-product when coal is heated out of contact with air, which is done in the manufacture of coke for fuel and coal gas for illuminating purposes. (See Chapter XII.) The tar is a mixture of an enormous number of organic compounds. Prominent among them are the hydrocarbons *benzene*, C_6H_6 , *naphthalene*, $C_{10}H_8$, and *anthracene*, $C_{14}H_{10}$; the phenols, *carbolic acid* (phenol proper), C_6H_5OH , and the three *cresols*, C_7H_7OH ; and the amine, *aniline*, $C_6H_5NH_2$.

From these coal-tar products are derived, directly or indirectly, thousands of chemical compounds, among which are many coloring matters. Of these a considerable number make good dyes.

The coal-tar dyes may be classified as follows :

1. Direct or Substantive Cotton Dyes.
2. Developed Dyes.
3. Mordant or Adjective Dyes.
4. Acid Dyes.
5. Basic Dyes.

1. Direct or Substantive Cotton Dyes

These dye cotton without the intervention of a mordant. Their application is so simple and inexpensive that they are very commonly used, although as a class they are excelled in fastness by the mordant dyes and in brilliance by the basic colors. The transfer of dyes of this class from solution to the fibers is accelerated by the addition of salts, especially sodium chloride and sodium sulphate, to the solution. Hence the name "salt colors" sometimes applied to this class of dyes. Alkalies, on the other hand, tend to retard the precipitation of the coloring matter into the fiber. Sodium carbonate, sodium phosphate, and soap are sometimes added to the bath to render the dyeing slower and more penetrative.

In washing goods dyed with dyes of this class the soda and soap used tend to cause "bleeding" of the dye, while salt added to the water will sometimes prevent this trouble. In many instances the fastness of a substantive dye to washing is improved by after treatment with metallic salts or with formaldehyde.

In other instances the material originally deposited is converted into another and faster dye by a developing process. Many of the dyestuffs contain *amino* ($-\text{NH}_2$) groups, and it is these which are used for this purpose. After the sub-

stantive dye containing an amino group is applied, the goods are treated with *nitrous acid* (HNO_2). This reagent converts the amines in the fiber into unstable compounds known as *diazonium salts*. The conversion of an amine into a diazonium salt is called *diazotizing*. When a diazonium salt is brought into a solution containing another amine or a phenol, a reaction takes place by which the molecule of the amine or phenol is combined with that of the substantive dye through two nitrogen atoms, the product being a dye faster than that originally applied and sometimes also of a different color. The yellow dye, primuline, for instance, can be developed into a red dye by diazotizing and coupling with β -naphthol.

Experiment 166. — Dyeing Cotton with a Substantive Dye.

Materials :

Skein of cotton yarn.

Primuline.

Salt.

Dissolve 0.3 gram of primuline and 1 gram of salt in just sufficient water to cover 5 grams of the cotton. Add about $\frac{1}{2}$ cc. sodium carbonate solution. Heat to 60°C . (140°F .), introduce the 5 grams of cotton, and gradually heat to boiling. Boil 15 to 30 minutes. Note the color. Rinse in cold water.

Experiment 167. — Development of a Substantive Dye by Diazotizing.

Materials :

Dyed skein of cotton from preceding experiment.

Sodium nitrite.

β -naphthol.

Dissolve 0.25 gram sodium nitrite in sufficient water to cover the goods. Add 3 cc. dilute sulphuric acid. What acid is produced? Immerse the dyed skein of cotton for 10 minutes, keeping the bath cool. Does the color change?

Rinse in acidulated water and immediately transfer to a bath containing 0.1 gram β -naphthol dissolved in an equal weight of a 30 per cent solution of NaOH. Note the production of the new color.

Although called direct *cotton* dyes, many of this class give even better results on wool. This is especially true of the reds and yellows.

Closely related to the substantive dyes, at least in the manner of their application, are the so-called "sulphur dyes." These are applied in a salt bath to which sodium sulphide has been added. They are used exclusively on cotton and linen. They are exceedingly fast to washing.

2. Developed Dyes

The developed dyes are those whose colors are produced within the fiber. They may be produced (*a*) by oxidation of a soluble compound to an insoluble dye or (*b*) by combining two colorless or slightly colored compounds into a dye by diazotizing.

The "vat" dyes and aniline black are examples of the first class. The vat dyes, of which *indigo* is the oldest example, are *reduced* to so-called "leuco compounds" by strong reducing agents. The leuco compounds, being soluble, penetrate the fiber. The goods are then exposed to air for 15 to 20 minutes, after which they are boiled in a soap solution. This treatment reoxidizes the leuco compound to the insoluble dye. The vat colors are characterized by extreme fastness, not only to light and washing, but also to the action of acids, alkalis, and oxidizing agents.

The reduction of indigo was formerly accomplished by a fermentation, whence the term "vat." The reducing agent now almost universally used for all vat colors is sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4$, which is prepared by reducing sodium bisulphite with zinc dust. Sodium hydrosulphite is very readily oxidized by the oxygen of the air. A compound of sodium hydrosulphite with formaldehyde, which is less affected by the air, is sometimes used instead of the sodium hydrosulphite itself.

Experiment 168. — Vat Dyeing with Indigo.*Materials :*

Sodium bisulphite solution (30 per cent) and zinc dust.

Indigo powder or paste.

Sodium hydroxide (30 per cent).

Cotton skein or piece of cheesecloth.

To 1 gram zinc dust in a test tube add 10 cc. of the sodium bisulphite solution. Allow to stand for a few minutes, stirring gently from time to time with a glass rod. The sediment should become pale gray. What compound is produced by this action?

In another test tube place 1 gram powdered indigo or 2.5 grams indigo paste, 20 per cent. Add 8 cc. of the concentrated sodium hydroxide solution and mix. Add the contents of the other tube, heat to 50° C. (120° F.), and set in a beaker of water at 50° C. Allow to stand until the material has turned yellow (about $\frac{1}{2}$ hour). Sufficient material is obtained for 3 or 4 students to perform the actual dyeing, which is done as follows :

Into 50 cc. water put a very little zinc dust (0.1 gram) and sodium bisulphite solution (0.5 cc.). This removes the dissolved oxygen from the water. Add about one fourth of the yellow liquid. Wet the cotton, immerse it for a minute or so, squeeze it out well, and hang it exposed to the air for 5 or 10 minutes. Note the development of the color. Rinse with water, soap to remove unabsorbed dye, and rinse again.

Sodium hydrosulphite, or its formaldehyde compound, may be used instead of the zinc and sodium bisulphite. Use 2 grams sodium hydrosulphite and 20 cc. water for 2 grams indigo, and allow to stand 10 minutes before adding the sodium hydroxide, of which only half as much will be required as when the bisulphite is used. Heat to 60° C. (140° F.) and allow to stand until a glass rod dipped into the mixture gives a clear yellow drop and the liquid wetting the rod becomes blue after about half a minute's exposure to the air. A little hydrosulphite should be used to remove the dissolved oxygen from the diluting water.

Aniline black is a color so fast to washing that it forms the basis of many marking inks. It is an oxidation product of aniline, $C_6H_5NH_2$, produced not by the action of atmospheric oxygen, but by that of oxidizing agents. Pure aniline is a colorless, oily liquid, insoluble (or rather only slightly soluble) in water, and possessed of a penetrating, somewhat

nauseating odor. The ordinary "aniline oil" of commerce is, however, colored yellowish brown by impurities. Being an amine, aniline forms salts with acids, similar to the ammonium salts, *e.g.* aniline hydrochloride, $C_6H_5NH_3Cl$. These salts are soluble in water. In dyeing with aniline black the goods are impregnated with an oxidizing agent such as potassium (or sodium) chlorate, with an aniline salt, and with a catalytic agent, such as copper sulphate or sodium ferrocyanide. They are then exposed to the action of steam for half a minute and afterwards treated with soap. The heat and moisture promote the oxidation. Aniline black can also be obtained directly from aniline by oxidizing it with a mixture of potassium dichromate and sulphuric acid, as in the following experiment.

Experiment 169. — Dyeing with Aniline Black.

Materials :

Aniline oil.

Potassium dichromate solution (5 per cent).

Cotton skein or cheesecloth.

Note odor and appearance of commercial aniline. Shake about 1 cc. with water (5 cc.). Add concentrated hydrochloric acid and shake again.

To 100 cc. potassium dichromate solution add 250 cc. water and 10 cc. dilute (2 N.) sulphuric acid. Dissolve $1\frac{3}{4}$ cc. aniline in $2\frac{1}{2}$ cc. concentrated hydrochloric acid and add to the dichromate mixture. Immerse the cotton and slowly heat the bath to $80^\circ C.$ ($175^\circ F.$). Rinse well, soap, wring out, and dry without rinsing out the soap.

On account of the use of the strong "mineral" acids, aniline black dyeing is apt to injure the fiber. The use of sodium (or potassium) ferrocyanide, $Na_4Fe(CN)_6$, as a catalytic agent appears to mitigate this evil. It reacts with the mineral acid, *e.g.* hydrochloric, giving sodium chloride and ferrocyanic acid, $H_4Fe(CN)_6$, a weaker acid than hydrochloric.

The second class of developed synthetic dyes embraces

those which are produced by saturating the goods with the solution of a colorless compound (technically a "prepare"), then introducing them into a diazotized solution of an amine — in other words, into the solution of a diazonium salt. The principle is exactly the same as that of the after-development of substantive colors, described above (p. 257), and the product is an insoluble dye, precipitated within the fiber. The diazonium salts are only stable at low temperatures. Ice is therefore kept in the developing solution. On account of this circumstance colors produced by this process are called "ice colors."

The "prepare" universally used for ice colors is a solution of sodium β -naphtholate, prepared by dissolving β -naphthol in caustic soda. Several beautiful reds are produced by this process, and blue and black can also be obtained.

Experiment 170. — Dyeing with Paranitraniline Red.

Materials :

Skein of white cotton yarn or piece of cheesecloth.

Paranitraniline.

β -naphthol.

Sodium nitrite.

Sodium acetate crystals.

Sodium hydroxide solution (30 per cent).

Dissolve 3 grams β -naphthol in 100 cc. water to which have been added 3 cc. of the strong sodium hydroxide solution.

In a 250 cc. beaker, heat 7 grams paranitraniline with 4 cc. conc. hydrochloric acid and 75 cc. water. Paranitraniline hydrochloride is formed. When all has dissolved, cool quickly, stirring rapidly so as to make the hydrochloride crystallize out in small crystals. Continue the cooling below the room temperature by putting ice into the beaker. When the temperature reaches 4° C. (39 to 40° F.), gradually add 4 cc. concentrated hydrochloric acid, then throw in 3.5 grams sodium nitrite. Keep down to 4° C. by adding more ice as needed. After 10 or 15 minutes add 8 grams sodium acetate crystals.

Immerse the cotton in the β -naphthol "prepare," wring out gently, dry carefully, and immerse in the cold diazonium salt solution. Work the cotton in the solution for a minute or so.

Remove, rinse well, dip into water to which a little sodium carbonate has been added, then rinse again thoroughly.

Instead of the paranitraniline the following may be used in the experiment, the red colors obtained varying in shade from paranitraniline red: α -naphthylamine (7 grams), β -naphthylamine (7 grams), benzidine (4.5 grams), metanitraniline (7 grams).

3. Mordant or Adjective Dyes

The **mordant** or **adjective** dyes may be either of acid or of basic character. In the case of the acid dyestuffs the mordants used are of such a character that they leave upon the fiber, and firmly combined with it, metallic bases which are capable of combining with the acid dyestuff. Soluble salts or soluble basic salts of the weak bases are suitable. Those used practically are salts of aluminium, iron, chromium, tin, copper, cobalt, and nickel. The goods are immersed in solutions of the salts and then either subjected to the action of a weak alkali, or, in case the acid of the salt is a volatile one, are steamed to liberate the weak acid and drive it off as vapor.

As a rule, goods prior to drying are subjected to the process of "dunging," which in the practice of half a century ago consisted in passing the goods through cow dung. Later, arsenate of soda was substituted, but phosphate of soda has now superseded this poisonous compound. The effect of the dunging process is to fix the mordant more firmly in the fiber and thus enhance the fastness of the dye subsequently to be applied. The dunging process has also the effect of removing the surplus mordant so as to insure an even surface of the goods ("level dyeing"). Afterwards the goods are dyed, the dyestuff combining with the metallic base to form a *lake*, often different in color from the dyestuff itself.

Experiment 151. — Alizarin Lakes.

Materials:

Alizarin.

Solutions of aluminium, chromium, and ferrous salts.

Dissolve a little alizarin in ammonia. To separate portions

of the solution, add calcium sulphate and small quantities of the aluminium, chromium, and ferrous solutions. Heat to boiling and filter. Note the colors of the precipitates. Wash them on the filter. Do they retain the dye?

For comparison precipitate the hydroxides of the metals by adding ammonium hydroxide to the solutions.

As an auxiliary to the mordant base, an acid mordant or fixing agent is sometimes employed. The leading examples of this class of bodies are: (1) the *tannins*, (2) *fatty acid derivatives*. The tannins or tannic acids are much used with the basic dyes (see below) and as weighting agents for silk. (See Chapter XL.) Cotton which is to be mordanted with iron, tin, or aluminium salts is sometimes first treated with a tannin, usually *sumac extract*.

The most important fatty acid derivative used as a fixing agent is **Turkey-red oil**. This is prepared by treating castor oil or olive oil with concentrated sulphuric acid, keeping the mixture cold. The product is soluble in water, but it is customary to partially neutralize with caustic soda or ammonia to render it more soluble. It takes its name from its use in Turkey-red dyeing. The dye used in this process is alizarin, and before the discovery of Turkey-red oil the mordanting of the cotton, preliminary to dyeing with extract of madder root, was a very lengthy process, requiring several weeks for its completion. Nowadays the goods are treated with Turkey-red oil, dried overnight, mordanted in an aluminium solution, dried again overnight, treated with a mild alkali (usually chalk), dyed with synthetic alizarin, steamed, soaped, rinsed, and dried. The whole process is completed in three days, and the result compares favorably with that obtained by the old process. Slightly rancid olive oil and soaps containing a little free fatty acid are other materials used with alizarin and dyes chemically related to it. Sometimes tannins and fatty acid fixing agents are both used with these dyes.

4. Acid Dyes

The acid dyes dye wool and silk directly. They are very seldom used on cotton. They are usually sold in the form of their sodium salts, and are liberated in the dyeing bath by treatment with an acid, usually sulphuric. Sodium sulphate is used as a restraining agent, preventing too rapid absorption of the dye. This is just the opposite effect from that played by sodium sulphate in dyeing cotton with direct dyes.

There is great variety among the acid dyes, and they play a very important part in the dyeing of wool and silk. The best of them are very fast to light, although not equal to the vat dyes in this respect. They are not fast to washing with soap.

5. Basic Dyes

The basic dyes, which are the real *aniline* derivatives, are applied to wool and leather directly (rarely to silk) and to cotton mordanted with tannin. Chardonnet artificial silk (p. 239) takes these dyes better than those of any other class. They are characterized by great brilliance, but very few of them are fast to light. In cotton dyeing they are often used to "top" other dyes. The brightness of sulphur dyes can be increased by such topping, and so also can the fastness of the substantive dyes to washing.

The chief tannins used as mordants or fixing agents for the basic dyes are those derived from: (1) *gallnuts*, which are excrescences produced on oak trees and other plants as the result of insect injuries; (2) *sumac* leaves and twigs; (3) *catechu*; (4) *horse-chestnut* wood. Cotton immersed in tannin solutions absorbs more or less of the tannins. The tannin behaves as an acid, weak but polybasic, *i.e.* having several replaceable hydrogen atoms. The cotton is next treated with an antimony salt, usually potassium antimonyl tartrate, tartar emetic. An insoluble antimony tannate, or acid antimony tannate, is produced in the fiber, and this has

sufficient replaceable hydrogen left to act as an acid towards the basic dye. In dyeing, a double tannate of antimony and the dyestuff is formed in the fiber.

Calico Printing

Designs on cotton are produced by means of printing machines, which consist essentially of rollers upon which the design, or so much of it as is to be printed in one color, is engraved. The rollers may be employed either (1) to apply the dyestuff, thickened with starch or gum, directly to the goods, (2) to print upon the goods a *mordant* which will fix a dye to be subsequently applied, (3) to print upon the goods a reagent which will *resist* the action of a dye to be subsequently applied, (4) to print upon dyed goods a reagent which will *discharge* the dye by converting it into a colorless compound, or by removing the mordant which holds the dye, or (5) to print *both a discharging agent and a new dye or mordant*.

Practically all the dyes which are applicable to cotton can be used in printing processes.

APPENDIX A

LIST OF TABLES IN APPENDIX A

<i>Table</i>	<i>Subject</i>
I.	Foods of Vegetable Origin — Average Composition and Nutritive Value.
II.	Foods of Vegetable Origin — Important Ash Constituents in the One-Hundred-Calorie Portion of Edible Material.
III.	Foods of Animal Origin — Meats — Average Composition and Nutritive Values.
IV.	Foods of Animal Origin — Composition of Meats, Fat and Lean.
V.	Foods of Animal Origin — Fish — Average Composition and Nutritive Value.
VI.	Foods of Animal Origin — Dairy Products — Average Composition and Nutritive Value.
VII.	Miscellaneous Foods of Animal Origin — Average Compositions and Nutritive Value.
VIII.	Foods of Animal Origin — Important Ash Constituents in the One-Hundred-Calorie Portion of Edible Material.
IX.	Approximate Weights of One Cupful of Some Food Materials.

TABLES

The following tables of food composition are derived, for the most part, from the compilations of Atwater and Bryant,¹ of Sherman,² and of Rose.³

¹ Atwater and Bryant, "Chemical Composition of American Food Materials," Office of Experiment Stations, United States Department of Agriculture, Bulletin 28, Revised edition, 1899. These tables are also to be found in the appendix to Jordan's "Principles of Human Nutrition," New York, 1912.

² Sherman, "Chemistry of Food and Nutrition," New York, 1911.

³ Rose, "A Laboratory Hand-Book for Dietetics," New York, 1913.

NOTE. In the tables of Atwater and Bryant (Bulletin 28) and in the data drawn from them by Jordan, the fuel values are calculated by factors which are now known to have allowed too little for losses in digestion and which gave results from 2.5 to 3.3 per cent too high. The fuel values given here (as well as those in the tables of Sherman and of Rose) are recalculated by the later and more accurate factors as given in the foregoing text; viz. protein and carbohydrate, 4 Calories per gram; fat, 9 Calories per gram. These factors are equivalent to 1814 Calories per pound for protein and carbohydrates and 4082 Calories per pound for fat. The fuel values in the tables are calculated to the nearest 5 Calories and, consequently, do not coincide exactly with those given by Sherman and by Rose.

Table I gives the composition and nutritive value of selected foods of vegetable origin, arranged in groups, and Tables III-VII those of selected foods of animal origin. In these tables there is first given the per cent of refuse — peel and stems of fruit, bone and tendons of meat, etc., in short all the material that is not usable as food. The remaining columns all refer to the edible portion of the food. The percentage composition of the edible portion (omitting the ash) is next given, then fuel value in calories per pound.

From these data the remaining figures of the tables are calculated as follows:

1. *The one hundred Calorie portion in ounces by dividing 1600 by the fuel value per pound.*

EXAMPLES

*Bananas*¹

Fuel value per pound	450 Calories
450 Calories are yielded by	16 ounces
∴ 100 Calories are yielded by	$1600 \div 450 = 3.6$ ounces

*Watermelons*¹

Fuel value per pound	135 Calories
100-Calorie portion in ounces	$1600 \div 135 = 11.9$

*Dates*¹

Fuel value per pound	1575 Calories
100-Calorie portion in ounces	$1600 \div 1575 = 1.02$

2. *The distribution of the 100 Calories by multiplying the per cent of fat by 2.25, adding the per cent of protein and the per cent of carbohydrate, dividing the sum by each addend, and multiplying the result by 100.*

¹ In all cases the data given relate to the *edible portion* of the food.

EXAMPLES

Bananas

Per cent of fat in the edible portion 0.6
 0.6 lb. fat is equivalent to $0.6 \times 2.25 = 1.35$ lb. protein or carbohydrate

Per cent of protein	1.3
Per cent of carbohydrates	<u>22.0</u>
Sum	24.65

Out of every 24.65 Calories the protein contributes 1.3

Out of every 100 Calories the protein contributes $\frac{1.3 \times 100}{24.65} = 5$, approximately

Out of every 24.65 Calories the fat contributes 1.35

Out of every 100 Calories the fat contributes $\frac{1.35 \times 100}{24.65} = 6$, approximately

Out of every 24.65 Calories the carbohydrate contributes 22.0

Out of every 100 Calories the carbohydrate contributes $\frac{22.0 \times 100}{24.65} = 89$, approximately

Olives

Fat 27.6 per cent, equivalent in fuel value to $27.6 \times 2.25 = 60.1$ per cent protein or carbohydrate

Per cent of protein	1.1
Per cent of carbohydrate	<u>11.6</u>
Sum	72.8

Out of 72.8 Calories the proteins yield 1.1

Out of 100 Calories the proteins yield $\frac{1.1 \times 100}{72.8} = 1.5$ Calories

Out of 72.8 Calories the fats yield 60.1

Out of 100 Calories the fats yield $\frac{60.1 \times 100}{72.8} = 82.5$

Out of 72.8 Calories the carbohydrates yield 11.6

Out of 100 Calories the carbohydrates yield $\frac{11.6 \times 100}{72.8} = 16$

Pork, salt, clear fat

Fat 86.2 per cent, equivalent to $86.2 \times 2.25 = 194.0$ proteins or carbohydrates

Protein		<u>1.9</u>
	Sum	195.9
Out of 195.9 Calories proteins yield	19	
Out of 100 Calories proteins yield	$\frac{1.9 \times 100}{195.9} = 1$	1 Calorie
Out of 195.9 Calories fats yield	194.0	
Out of 100 Calories fats yield	$\frac{194.0 \times 100}{195.9} = 99$	99 Calories

Tables II and VIII give for foods of vegetable and of animal origin, respectively, the content of the most important ash constituents, the foods being compared on the basis of equal fuel value. Table IV gives the average composition of lean and of fat meats of the same varieties.

TABLE I.—FOODS OF VEGETABLE ORIGIN. AVERAGE COMPOSITION AND NUTRITIVE VALUE

	REFUSE	EDIBLE PORTION									
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- orie Por- tion	Calories Furnished by		Carbo- hydrate	
		per cent	per cent	per cent	per cent	Calories	ounces	Protein	Fat		per cent
FRUITS, FRESH											
Bananas	35	75.3	1.3	0.6	22.0	450	3.6	5	6	89	
Grapes	25	77.4	1.3	1.6	19.2	435	3.7	5	15	80	
Plums	5	78.4	1.0	—	20.1	380	4.2	5	—	95	
Cherries	5	80.9	1.0	0.8	16.7	355	4.5	5	9	86	
Raspberries, black	0	84.1	1.7	1.0	12.6	300	5.3	10	14	76	
Pears	10	84.4	0.6	0.5	14.1	285	5.6	4	7	89	
Apples	25	84.6	0.4	0.5	14.2	285	5.6	3	7	90	
Oranges	27	86.9	0.8	0.2	11.6	235	6.8	6	4	90	
Lemons	30	89.3	1.0	0.7	8.5	200	8.0	9	14	77	
Peaches	18	89.4	0.7	0.1	9.4	185	8.6	7	2	91	
Strawberries	5	90.4	1.0	0.6	7.4	175	9.1	10	14	76	
Watermelons	60	92.4	0.4	0.2	6.7	135	11.9	5	6	89	
FRUITS, DRIED											
Dates	10	15.4	2.1	2.8	78.4	1575	1.02	3	7	90	
Raisins	10	14.6	2.6	3.3	76.1	1560	1.03	3	9	88	
Citrons	—	19.0	0.5	1.5	78.1	1485	1.08	1	4	95	
Currants, Zante	—	17.2	2.4	1.7	74.2	1460	1.10	3	5	92	
Figs	—	18.8	4.3	0.3	74.2	1435	1.12	5	1	94	
Prunes	15	22.3	2.1	—	73.3	1370	1.17	3	—	97	
Apples	—	28.1	1.6	2.2	66.1	1320	1.21	2	7	91	

TABLE I.—FOODS OF VEGETABLE ORIGIN.—Continued

	REFUSE	EDIBLE PORTION																		
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- orie Por- tion	Calories Furnished by												
		per cent	per cent	per cent	per cent	Calories	ounces	Protein]	Fat	Carbo- hydrate										
FRUITS, SPECIALLY USED																				
<i>For Pickles</i>																				
Olives, green	27	58.0	1.1	27.6	11.6	1355	1.18	1	83	16										
Cucumbers, green	15	95.4	0.8	0.2	3.1	80	20.0	18	12	70										
<i>As "Vegetables"</i>																				
Squashes	50	88.3	1.4	0.5	9.0	210	7.6	12	10	78										
Pumpkins	50	93.1	1.0	0.1	5.2	115	13.7	16	3	81										
Tomatoes, as purchased	—	94.3	0.9	0.4	3.9	105	15.2	16	16	68										
VEGETABLES																				
<i>Roots, Tubers, and Bulbs</i>																				
Sweet potatoes	20	69.0	1.8	0.7	27.4	560	2.9	6	5	89										
Potatoes	20	78.3	2.2	0.1	18.4	380	4.2	11	1	88										
Parsnips	20	83.0	1.6	0.5	13.5	295	5.4	10	7	83										
Onions	10	87.6	1.6	0.3	9.9	220	7.3	13	6	81										
Beets	20	87.5	1.6	0.1	9.7	210	7.6	14	2	84										
Carrots	20	88.2	1.1	0.4	9.3	205	7.8	10	8	82										
Turnips	30	89.6	1.3	0.2	8.1	180	8.9	13	5	82										
Radishes	30	91.8	1.3	0.1	5.8	135	11.9	18	3	79										
<i>Stalks and Leaves</i>																				
Dandelion greens	—	81.4	2.4	1.0	10.6	275	5.8	16	14	70										
Cabbage	15	91.5	1.6	0.3	5.6	145	11.0	20	9	71										

TABLE I.—FOODS OF VEGETABLE ORIGIN.—Continued

EDIBLE PORTION

	REFUSE	EDIBLE PORTION						Calories Furnished by		
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- oric Por- tion	Protein	Fat	Carbo- hydrate
	per cent	per cent	per cent	per cent	Calories	ounces	per cent	per cent	per cent	
Cauliflower	—	92.3	1.8	0.5	4.7	140	11.4	24	14	62
Spinach	—	92.3	2.1	0.3	3.2	110	14.5	35	12	53
Rhubarb	40	94.4	0.6	0.7	3.6	105	15.2	10	28	62
Asparagus	—	94.0	1.8	0.2	3.3	100	16.0	33	7	60
Lettuce	15	94.7	1.2	0.3	2.9	85	18.7	25	15	60
Celery	20	94.5	1.1	0.1	3.3	85	18.7	24	4	72
<i>Green Legumes</i>										
Peas, green	45	74.6	7.0	0.5	16.9	455	3.5	28	4	68
Beans, string	7	89.2	2.3	0.3	7.4	190	8.4	22	7	71
<i>Ripe Legumes</i>										
Beans	—	12.6	22.5	1.8	59.6	1565	1.02	26	5	69
Peas	—	9.5	24.6	1.0	62.0	1610	1.00	28	2	70
<i>Fungi</i>										
Mushrooms	—	88.1	3.5	0.4	6.8	205	7.8	31	8	61
CEREAL PRODUCTS, UNCOOKED										
Oatmeal	—	7.3	16.1	7.2	67.5	1810	0.88	16	16	68
Rolled oats	—	7.7	16.7	7.3	66.2	1800	0.89	17	17	66
Starch, arrowroot	—	2.3	—	—	97.5	1770	0.90	0	0	100
Starch, corn	—	10.0	—	—	90.0	1630	0.98	0	0	100

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TABLE I.—FOODS OF VEGETABLE ORIGIN.—Continued

	REFUSE	EDIBLE PORTION									
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- oric Por- tion	Calories Furnished by		Carbo- hydrate	
		per cent	per cent	per cent	per cent	Calories	ounces	Protein	Fat		per cent
Shredded wheat	—	8.1	10.5	1.4	77.9	1660	0.96	12	3	85	
"Wheat germs"	—	10.4	10.5	2.0	76.0	1650	0.97	12	5	83	
Cracked wheat	—	10.1	11.1	1.7	75.5	1640	0.98	12	4	84	
Cornmeal, granular	—	12.5	9.2	1.9	75.4	1615	0.99	10	5	85	
Rice	—	12.3	8.0	0.3	79.0	1590	1.01	9	1	90	
Barley, pearled	—	11.5	8.5	1.1	77.8	1610	0.99	10	3	87	
Hominy	—	11.8	8.3	0.6	79.0	1610	0.99	9	2	89	
Macaroni	—	10.3	13.4	0.9	74.1	1625	0.98	15	2	83	
Vermicelli	—	11.0	10.9	2.0	72.0	1585	1.01	13	5	82	
Wheat flour, Graham	—	11.3	13.3	2.2	71.4	1630	0.98	15	5	80	
Wheat flour, whole wheat	—	11.4	13.8	1.9	71.9	1630	0.98	15	5	80	
Wheat flour, roller process, baker's grade	—	11.9	13.3	1.5	72.7	1625	0.98	15	4	81	
Wheat flour, roller process, family and straight grade	—	12.8	10.8	1.1	74.8	1610	0.99	12	3	85	
Rye flour	—	12.9	6.8	0.9	78.7	1590	1.01	8	2	90	
BAKED FOODS											
Doughnuts	—	18.3	6.7	21.0	53.1	1940	0.82	6	44	50	
Macaroons	—	12.3	6.5	13.2	65.2	1920	0.83	6	32	62	

EDIBLE PORTION

REFUSE	EDIBLE PORTION										Calories Furnished by	
	Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- orie Por- tion	Protein	Fat	Carbo- hydrate	per cent	per cent	per cent
	per cent	per cent	per cent	per cent	Calories	ounces	per cent	per cent	per cent	per cent	per cent	per cent
Zwieback	5.8	9.8	9.9	73.5	1915	0.84	9	21	70			
Oyster crackers	4.8	11.3	10.5	70.5	1910	0.84	11	22	67			
Butter crackers	7.2	9.6	10.1	71.6	1885	0.85	9	22	69			
Soda crackers	5.9	9.8	9.1	73.1	1875	0.85	9	20	71			
Sugar cookies	8.3	7.0	10.2	73.2	1870	0.86	7	22	71			
Ginger snaps	6.3	6.5	8.6	76.0	1850	0.86	6	19	75			
Sponge cake	15.3	6.3	10.7	65.9	1745	0.92	7	25	68			
Fruit cake	17.3	5.9	10.9	64.1	1715	0.93	6	26	68			
Frosted cake	18.2	5.9	9.0	64.8	1650	0.97	7	22	71			
Rolls, plain	25.2	9.7	4.2	59.9	1430	1.12	12	12	76			
Toast	24.0	11.5	1.6	61.2	1385	1.15	15	5	80			
Bread, white, Vienna	34.2	9.4	1.2	54.1	1200	1.33	14	4	82			
Bread, white, home-made	35.0	9.1	1.6	53.3	1200	1.33	14	5	81			
Bread, Graham	35.7	8.9	1.8	52.1	1180	1.36	14	6	80			
Bread, gluten	38.2	9.3	1.4	49.8	1130	1.42	15	5	80			
Bread, whole-wheat	38.4	9.7	0.9	49.7	1115	1.44	16	3	81			
Bread, brown	43.6	5.4	1.8	47.1	1025	1.56	10	7	83			
Mince pie	41.3	5.8	12.3	38.1	1300	1.23	8	39	53			
Apple pie	42.5	3.1	9.8	42.8	1230	1.30	5	33	62			
Tapioca pudding	64.5	3.3	3.2	28.2	700	2.29	8	19	73			

TABLE I.—FOODS OF VEGETABLE ORIGIN.—Continued

	REFUSE	EDIBLE PORTION									
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100 Cal- oric Por- tion	Calories Furnished by			
		per cent	per cent	per cent	per cent	Calories	ounces	Protein	Fat	Carbo- hydrate	
NUTS ¹											
Pecans	50	3.4	12.1	70.7	12.2	3325	0.48	6	87	7	
Hickory nuts	62	3.7	15.4	67.4	11.4	3240	0.49	9	85	6	
Brazil nuts	49	4.7	17.4	65.0	9.6	3145	0.51	10	84	6	
Filberts (hazel nuts)	52	5.4	16.5	64.0	11.7	3125	0.51	9	84	7	
Walnuts	59	3.4	18.2	60.7	16.0	3100	0.52	11	80	9	
Butternuts	87	4.5	27.9	61.2	3.4	3070	0.52	17	81	2	
Almonds	47	4.9	21.0	54.4	16.8	2905	0.55	13	76	11	
Coconuts	35	13.0	6.6	56.2	22.6	2825	0.57	4	81	15	
Peanuts	27	7.4	29.8	43.5	17.1	2625	0.61	20	68	12	
Chestnuts, dry	23	6.1	10.7	7.8	73.0	1835	0.87	10	18	72	
Chestnuts, fresh	16	43.4	6.4	6.0	42.8	1115	1.43	10	22	68	
NUT PRODUCTS ¹											
Coconuts, desiccated	—	3.5	6.3	57.4	31.5	3030	0.53	4	77	19	
Peanut butter	—	2.1	29.3	46.5	17.1	2740	0.58	19	70	11	
Almond paste	—	24.2	13.1	23.9	37.2	1890	0.85	12	51	36	
Coconut milk	—	92.7	0.4	1.5	4.6	150	10.7	5	40	55	
CHOCOLATE AND COCOA											
Chocolate	—	5.9	12.9	48.7	30.3	2770	0.58	8	72	20	
Cocoa	—	4.6	21.6	28.9	37.7	2255	0.71	17	53	30	

TABLE I.—FOODS OF VEGETABLE ORIGIN.—*Concluded*

	REFUSE	EDIBLE PORTION									
		Water	Protein	Fat	Carbo- hydrate	Fuel Value per Pound	100-Cal- orie Por- tion	Protein	Fat	Carbo- hydrate	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>Calories</i>	<i>ounces</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
SUGAR AND SIRUPS											
Sugar, white	—	—	—	100.0	1815	0.88	—	—	—	100	
Candy	—	4.0	—	96.0	1740	0.92	—	—	—	100	
Sugar, coffee or brown	—	5.0	—	93.0	1685	0.95	—	—	—	100	
Sugar, maple ²	—	5.0	—	93.0	1685	0.95	—	—	—	100	
[Honey	—	18.2	0.4	81.2	1480	1.08	—	—	—	100]	
Molasses, cane	—	25.1	2.4	69.3	1300	1.23	3	—	—	97	
Sirup, maple ²	—	34.2	—	64.0	1160	1.38	—	—	—	100	
STARCHES											
Cornstarch	—	10.0	—	—	1630	0.98	—	—	—	100	
Tapioca	—	11.4	0.4	88.0	1610	0.99	—	—	—	100	
Sago	—	12.2	9.0	78.1	1580	1.01	10	1	—	89	

¹ The figures for the composition of nuts and nut products are from Jaffa, "Nuts and their Uses as Food," U. S. Department of Agriculture, Farmers' Bulletin, 332.

² The figures for the composition of maple sirup and sugar are based upon the investigations of Bryan, U. S. Department of Agriculture, Bureau of Chemistry, Bulletin 134; McGill, Laboratory Inland Revenue Department, Ottawa, Canada, Bulletin 228; and the author, *Journal of Industrial and Engineering Chemistry*, 1913-1914.

TABLE II.—FOODS OF VEGETABLE ORIGIN

Important Ash Constituents in the One-hundred-Calorie Portion of Edible Material¹

	100-CALORIE PORTION (EDIBLE)	IMPORTANT ASH CONSTITUENTS PER 100-CALORIE PORTION		
		CaO	P ₂ O ₅	Fe
FRUITS, FRESH				
	<i>Grams</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
Bananas	101	10	55	0.6
Grapes	104	24	120	1.3
Plums	118	29	64	0.6
Cherries	128	40	90	*
Raspberries	151	110	180	*
Pears	158	32	90	0.5
Apples	159	22	50	0.5
Oranges	195	110	90	0.6
Lemons	226	120	40	1.3
Peaches	242	20	113	0.7
Strawberries	269	130	162	2.3
Watermelons	332	60	60	*
FRUITS, DRIED				
Dates	29	30	30	1.0
Raisins	29	20	80	1.0
Currants, Zante	31	40	90	*
Figs	32	89	99	1.0
Prunes	33	20	80	0.9
FRUITS, SPECIALLY USED				
<i>For Pickles</i>				
Olives, green	33	60	10	0.9
Cucumbers	575	120	450	*
<i>As "Vegetables"</i>				
Squashes	217	40	170	1.7
Pumpkins	389	110	420	*
Tomatoes	438	87	257	1.7
ROOTS, TUBERS, AND BULBS				
Sweet potatoes	81	20	80	0.4
Potatoes	120	19	166	1.5
Parsnips	154	140	290	*
Onions	206	120	240	1.1
Beets	217	60	190	1.3

* Not determined.

¹ Selected from the more comprehensive tables of Sherman, "Chemistry of Food and Nutrition," pp. 338-341.

TABLE II.—FOODS OF VEGETABLE ORIGIN.—*Continued*

	100-CALORIE PORTION (EDIBLE)	IMPORTANT ASH CONSTITUENTS PER 100-CALORIE PORTION		
		CaO	P ₂ O ₅	Fe
	<i>Grams</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
Carrots	221	168	220	1.6
Turnips	254	222	292	1.3
Radishes	341	170	300	2.0
STALKS AND LEAVES				
Cabbage	317	214	280	3.5
Cauliflower	328	550	450	*
Spinach	417	370	540	13.3
Asparagus	450	170	390	4.3
Rhubarb	433	260	300	*
Lettuce	525	260	470	5.0
Celery	542	540	540	2.7
LEGUMES, GREEN				
Peas	100	32	240	1.6
Beans, string	241	177	284	3.8
LEGUMES, RIPE				
Peas	28	40	250	1.5
Beans	29	63	326	2.0
FUNGI				
Mushrooms	223	53	530	*
CEREAL PRODUCTS				
Oatmeal	25	30	216	0.9
Cornmeal	28	4	80	0.3
Barley, pearled	28	7	127	0.4
Rice	29	3	57	0.3
Rye flour	29	5	220	*
Wheat flour, Graham	28	17	253	1.5
Wheat flour, white	28	7	50	0.4
Bread, Graham	38	19	190	1.3
Bread, white	38	11	75	0.3
Bread, "whole wheat"	41	16	160	0.6
NUTS				
Walnuts	14	15	108	0.3
Almonds	15	46	132	0.3
Peanuts	18	18	160	0.4
Chestnuts	41	17	80	0.4

* Not determined.

TABLE III. — FOODS OF ANIMAL ORIGIN — MEATS
Average Composition and Nutritive Value

VARIETY	CUT	REFUSE	EDIBLE PORTION						Calories from	
			Water	Protein	Fat	Fuel Value per Pound	100-Calorie Portion	Protein	Fat	
			per cent	per cent	per cent	Calories	ounces	per cent	per cent	
Pork, salt	Clear fat	0	7.9	1.9	86.2	3555	0.45	1	99	
do	Lean ends	11	19.9	8.4	67.1	2890	0.55	5	95	
do	Bacon, smoked	9	20.2	10.5	64.8	2835	0.56	7	93	
do	Ham, smoked	12	39.8	16.5	38.8	1885	0.85	16	84	
Pork, fresh	Side (without lard or kidney)	12	34.4	9.1	55.3	2425	0.66	7	93	
do	Ham	10	50.1	15.7	33.4	1590	0.97	17	83	
do	Shoulder	12	51.2	13.3	34.2	1635	0.98	15	85	
do	Loin (chops)	19	50.7	16.4	32.0	1605	1.00	19	81	
do	Tenderloin	—	66.5	18.9	13.0	875	1.83	39	61	
Mutton	Fore quarter	21	52.9	15.6	30.9	1545	1.04	18	82	
do	Hind quarter	17	54.8	16.7	28.1	1450	1.10	21	79	
do	Loin (without kidney or tallow)	15	47.8	15.5	36.2	1760	0.91	16	84	
do	Leg, hind	18	63.2	18.7	17.5	1055	1.52	32	68	
Lamb	Loin (without kidney or tallow)	15	53.1	18.7	28.3	1495	1.07	23	77	
do	Leg, hind	14	58.6	18.6	22.6	1260	1.27	27	73	

TABLE III. — FOODS OF ANIMAL ORIGIN. — Continued

VARIETY	CUT	REFUSE	EDIBLE PORTION							Calories from	
			Water	Protein	Fat	Fuel Value per Pound	100-Calorie Portion	Protein	Fat	per cent	per cent
			per cent	per cent	per cent	Calories	ounces	per cent	per cent		
Beef	Fore quarter	21	62.5	18.3	18.9	1105	1.45	30	70		
do	Hind quarter	16	62.2	19.3	18.3	1095	1.46	32	68		
do	Ribs	20	57.0	17.8	24.6	1325	1.21	24	76		
do	Tenderloin	—	59.2	16.2	24.4	1290	1.24	23	77		
do	Rump	19	57.9	18.7	23.1	1280	1.25	27	73		
do	Loin	13	61.3	19.0	19.1	1125	1.42	30	70		
do	Chuck, including shoulder.	17	65.0	19.2	15.4	975	1.64	36	64		
do	Round	8.5	67.8	20.9	10.6	810	1.98	47	53		
do	Tongue	—	70.8	18.9	9.2	720	2.23	48	52		
Beef, Corned		8.5	53.6	15.6	26.2	1355	1.18	21	79		
Veal	Fore quarter	24.5	71.7	20.0	8.0	690	2.32	53	47		
do	Hind quarter	21	70.9	20.7	8.3	715	2.24	53	47		
do	Breast	24.5	68.2	20.3	11.0	815	1.96	45	55		
do	Loin	19	69.5	19.9	10.0	770	2.08	47	53		
do	Leg	12	71.7	20.7	6.7	650	2.46	58	42		
do	Liver	—	73.0	19.0	5.3	560	2.85	62	38		
Poultry	Goose	18	46.7	16.3	36.2	1775	0.90	17	83		
do	Turkey	23	55.5	21.1	22.9	1320	1.21	29	71		
do	Fowl	26	63.7	19.3	16.3	1015	1.58	35	65		
do	Chickens (broilers)	42	74.8	21.5	2.5	490	3.27	21	79		

TABLE IV. — FOODS OF ANIMAL ORIGIN
Composition of Meats, Fat and Lean

VARIETY AND CUT	CONDITION	REFUSE	EDIBLE PORTION						
			Water	Protein, ¹	Fat	Fuel Value per Pound	100-Calorie Portion	Protein	Calories from Fat
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>Calories</i>	<i>ounces</i>	<i>per cent</i>	<i>per cent</i>
Pork, ham, smoked	Fat	3.5	27.9	14.8	52.3	2405	0.67	11	89
do.	Medium fat	14	40.3	16.3	38.8	1880	0.85	16	89
do.	Lean.	11.5	53.5	19.8	20.8	1205	1.32	30	70
Pork, ham, fresh	Fat	13	38.7	12.4	50.0	2265	0.71	10	90
do.	Medium fat	11	53.9	15.3	28.9	1455	1.10	19	81
do.	Lean	9	60.0	25.0	14.4	1040	1.54	44	56
Beef ribs	Fat	17	48.5	15.0	35.6	1725	0.93	16	84
do.	Medium fat	21	55.5	17.5	26.6	1405	1.14	23	77
do.	Lean	23	67.9	19.6	12.0	845	1.89	42	58
do.	Very lean	23	70.9	25.0	3.5	595	2.69	76	24
Beef loin	Very fat	10	49.7	17.8	32.3	1645	0.97	20	80
do.	Fat	10	54.7	17.5	27.6	1445	1.11	22	78
do.	Medium fat	13	60.6	18.5	20.2	1160	1.38	29	71
do.	Lean	13	67.0	19.7	12.7	875	1.83	41	59
do.	Very lean	23	70.8	24.6	3.7	600	2.67	75	25
Veal loin	Fat	18	61.6	18.7	18.9	1110	1.44	30	70
do.	Medium fat	16.5	69.0	19.9	10.8	800	2.00	45	55
do.	Lean	22	73.3	20.4	5.6	600	2.67	62	33

NOTE. — The data of this table represent in all instances the average of several analyses. The figures for very fat beef loin, for instance, give not the composition of the fattest beef loin that has been analyzed, but the average composition of three samples, classed as very fat.

TABLE V.—FOODS OF ANIMAL ORIGIN.—FISH
Average Composition and Nutritive Value

VARIETY	EDIBLE PORTION							
	Refuse	Water	Protein	Fat	Fuel Value per Pound	100-Calorie Portion	Calories from	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>Calories</i>	<i>ounces</i>	<i>per cent</i>	<i>per cent</i>
Sardines, canned	5	52.3	23.0	19.7	1220	1.31	44	56
Salmon, whole	35	64.6	22.0	12.8	920	1.75	43	57
Salmon, canned	14	63.5	21.8	12.1	890	1.80	44	56
Trout, salmon or lake	49	70.8	17.8	10.3	745	2.15	43	57
Shad, whole	50	70.6	18.8	9.5	730	2.19	47	53
Eels, salt-water—head, skin, and en- trails removed	20	71.6	18.6	9.1	710	2.26	48	52
Whitefish, whole	54	69.8	22.9	6.5	680	2.35	61	39
Herring, whole	43	72.5	19.5	7.1	645	2.49	55	45
Mackerel, whole	45	73.4	18.7	7.1	630	2.54	54	46
Halibut, steak or sections	18	75.4	18.6	5.2	550	2.93	61	39
Perch, white, whole	63	75.7	19.3	4.0	515	3.11	68	32
Cod, salt	25	53.5	25.4	0.3	475	3.38	97	3
Bass, striped, whole	55	77.7	18.6	2.8	450	3.54	74	26
Bass, black, whole	55	76.7	20.6	1.7	440	3.64	84	16
Trout, brook, whole	48	77.8	19.2	2.1	435	3.68	80	20
Smelt, whole	42	79.2	17.6	1.8	395	4.07	81	19
Blackfish, whole	60	79.1	18.7	1.3	390	4.11	87	13
Pickarel, pike, whole	47	79.8	18.7	0.5	360	4.45	94	6
Haddock, entrails removed	51	81.7	17.2	0.3	325	4.92	96	4
Cod, fresh, whole	53	82.6	16.5	0.4	315	5.08	95	5
Flounder, whole	62	84.2	14.2	0.6	280	5.72	91	9

TABLE VI. — FOODS OF ANIMAL ORIGIN. — DAIRY PRODUCTS
Average Composition and Nutritive Value

FOOD	REF-USE	EDIBLE PORTION										100-Calorie Portion by Measure
		Water	Protein	Fat	Carbo-hydr.	Fuel Value per Pound	100-Cal-orie Portion	Calories from		Carbo-hydr.		
		per cent	per cent	per cent	per cent	Calories	ounces	Protein	Fat		per cent	
Milk, whole	—	87.0	3.3	4.0	5.0	315	5.1	19	52	29	Small glass	
Milk, skim	—	90.5	3.4	0.3	5.1	165	9.6	37	7	56	1½ glasses	
Buttermilk	—	91.0	3.0	0.5	4.8	160	9.9	33	13	54	1½ glasses	
Whey	—	93.0	1.0	0.3	5.0	120	13.2	15	10	75	2 glasses	
Condensed milk (sweetened)	—	26.9	8.8	8.3	54.1	1480	1.08	10	23	67		
Evaporated milk	—	68.2	9.6	9.3	11.2	755	2.11	23	50	27		
Cream (18.5 per cent fat)	—	74.0	2.5	18.5	4.5	880	1.81	5	86	9	¼ glass	
Cream, thick (40 per cent fat)	—	54.5	2.2	40.0	3.0	1725	0.93	1	97	2	⅓ glass	
Butter	—	11.0	1.0	85.0	—	3490	0.46	0.5	99.5	0	1 ordinary ball	
Cheese, Cheddar	—	27.4	27.7	36.8	4.1	2080	0.77	24	72	4		
Cheese, full-cream	—	34.2	25.9	33.7	2.4	1890	0.85	25	73	2		
Cheese, skim-milk	—	45.7	31.5	16.4	2.2	1280	1.25	45	52	3	1½ cubic inches	
Cheese, cottage	—	72.0	20.9	1.0	4.3	500	3.2	76	8	16		

Average Composition and Nutritive Value

FOOD	REF-USE	EDIBLE PORTION										100-Calorie Portion by Measure
		Water	Protein	Fat	Carbo-hydr.	Fuel Value per Pound	100-Cal-oric Portion	Calories from			Carbo-hydr.	
		per cent	per cent	per cent	per cent	Calories	ounces	Protein	Fat	per cent		
SHELLFISH												
Lobsters, fresh	62	79.2	16.4	1.8	0.4	380	4.2	78	20	2		
Lobsters, canned	—	77.8	18.1	1.1	0.5	380	4.2	86	12	2		
Oysters, canned	—	83.4	8.8	2.4	3.9	330	4.9	49	30	21		
Oysters, fresh, solids	—	88.3	6.0	1.3	3.3	220	7.2	49	24	27		1 dozen
Clams, long, in shell	42	85.8	8.6	1.0	2.0	195	8.1	67	17	16		
EGGS, HENS'												
Yolks	—	49.5	15.7	33.3	—	1645	0.97	18	82	0		1½ yolks
Whole	11	73.7	13.4	10.5	—	670	2.38	38	62	0		1½ eggs
Whites	—	86.2	12.3	0.2	—	230	6.9	100	0	0		5½ whites
FATS												
Lard or tallow, refined	—	—	—	100	—	4082	0.39	0	100	0		
Lard, unrefined	—	4.8	1.1	94.0	—	3855	0.41	1	99	0		
Suet	—	13.7	4.7	81.8	—	3425	0.47	2.5	97.5	0		
Oleomargarine	—	9.5	1.2	83.0	—	3410	0.47	0.5	99.5	0		
MISCELLANEOUS												
Gelatin	—	13.6	84.2	0.1	—	1530	1.05	100	0	0		1 tablespoon
Honey	—	18.2	0.4	—	81.2	1480	1.08	1	0	99		
Shad roe	—	71.2	20.9	3.8	2.6	580	2.75	65	27	8		
Frogs' legs	32	83.7	15.5	0.2	—	290	5.5	98	2	0		

TABLE VIII.—FOODS OF ANIMAL ORIGIN

Important Ash Constituents in the One-hundred Calorie Portion
of Edible Material ¹

	*100- CALORIE PORTION (EDIBLE)	ASH CONSTITUENTS PER 100-CALORIES		
		CaO	P ₂ O ₅	Fe
MEATS				
	<i>Grams</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
Bacon	16	1	40	0.2
Ham	44	5	180	1.1
Beef, lean	50	9	420	3.2
Veal, lean	65	12	370	*
Chicken	92	7	250	*
Frogs' flesh	153	42	670	*
FISH				
Salmon	49	5	200	0.7
Herring	70	50	380	*
Halibut	83	10	300	0.2
Pike	123	60	600	*
Haddock	140	40	500	*
Cod	150	21	600	0.6
DAIRY PRODUCTS				
Butter	13	3	4	*
Cheese	22	250	329	*
Cream	50	70	100	0.1
Milk	145	239	303	0.3
Buttermilk	280	415	610	*
EGGS				
Whole	68	60	240	1.9
Yolk	28	50	270	2.3
White	182	28	50	0.2

* Not determined.

¹ From Sherman, *Chemistry of Food and Nutrition*, pp. 338-341.

TABLE IX.—APPROXIMATE WEIGHTS OF ONE CUPFUL OF
COMMON FOOD MATERIALS

	Ounces
Almonds, shelled	5
Baking powder	7
Butter	8
Beans, dried	12
Chocolate, grated	3½
Coconut, shredded.	3
Cocoa	4
Coffee, ground	3
Cornmeal	5
Currants, Zante	4¾
Farina	5½
Figs, dried	4
Flour, pastry, sifted	3¾
Flour, pastry, unsifted	4
Flour, bread, sifted	4
Flour, bread, unsifted	4¼
Gelatin	4
Grape nuts	5
Hominy	5½
Lard	6¼
Lentils	6½
Macaroni	4
Milk	8½
Molasses	11½
Oatmeal	6¾
Oats, rolled	2½
Olive oil	7½
Peas, split	6½
Prunes	6
Raisins	4¾
Raisins, seeded	5¾
Rice	8
Sugar, brown	4¾
Sugar, granulated	7
Sugar, powdered	5½
Sugar, icing	4¾
Sugar, loaf	4¾
Tea	2
Tapioca (pearl)	6
Walnuts, shelled	3

APPENDIX B

REAGENTS

A *mole*, or *gram-molecule*, of a substance is the molecular weight in grams.

An *equivalent weight*, or *gram-equivalent*, of a substance is the quantity which is chemically equivalent to one gram-atom (1.008 grams) of hydrogen.

A *molar* solution of any substance contains one mole of the substance per liter. A twice-molar solution (2 M) contains twice this quantity per liter, a half-molar solution (M/2) half the quantity per liter, and so on.

A *normal* solution of any substance contains one equivalent weight of the substance per liter. A twice-normal solution (2 N) contains twice this quantity per liter, a half-normal solution one half this quantity per liter, and so on.

EXAMPLES

HCl	Molecular weight	36.5
	Mole	36.5 grams
	Equivalent weight	36.5 grams
	Molar solution (M)	contains 36.5 grams hydrogen chloride per liter. This is also the normal solution (N) of hydrogen chloride.
	A twice-molar solution (2 M, also 2 N)	contains 73 grams hydrogen chloride per liter.
H ₂ SO ₄	Molecular weight	98
	Mole	98 grams
	Equivalent weight	49 grams
	A molar solution of sulphuric acid	contains 98 grams pure sulphuric acid per liter. This solution is twice-normal, 2 N.
	A half-molar (M/2) solution of sulphuric acid	contains 49 grams per liter. This is a normal solution.

$\text{Al}_2(\text{SO}_4)_3$ Molecular weight 342.

Since there are two atoms of aluminium, each equivalent to three atoms of hydrogen, the mole of aluminium sulphate is equal to six equivalent weights. The equivalent weight is, therefore, 57.

A molar solution (M) of aluminium sulphate is a six times normal (6 N) solution.

A normal solution (N) is one-sixth molar (M/6).

Reagents for General Use

Acetic Acid, 2 N. Dilute 115 cc. glacial acetic acid to one liter.

Alcohol. 95 per cent alcohol, or methylated spirits.

Ammonium Chloride, 2 N. 107 grams to one liter.

Ammonium Hydroxide, 5 N. Specific gravity 0.96. Dilute 340 cc. concentrated ammonium hydroxide (sp. gr. 0.90) to one liter.

Ammonium Oxalate, N/2 (M/4). 35 grams crystals, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, to one liter.

Barium Chloride, N (M/2). 122 grams crystals, $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$, to one liter.

Benzine. Commercial.

Calcium Chloride, N (M/2). 56 grams anhydrous calcium chloride or 110 grams crystals, $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, to one liter.

Calcium Hydroxide, Saturated. Slake a lump of quicklime, weighing about half a pound, by pouring upon it as much warm water as it will absorb and allowing it to stand for about ten minutes. Put the slaked lime in a two-liter bottle, fill the bottle with distilled water, and shake well, allow to settle, and decant the clear liquid. By refilling the bottle with water many batches of lime-water may be prepared from the same portion of lime.

Calcium Sulphate, Saturated. About 2.5 grams crystals, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, to one liter.

Copper Sulphate, N/2 (M/4). 62 grams crystals, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, to one liter.

Ether.

Fehling-Benedict Solution.

17.3 grams copper sulphate crystals, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	} to one liter
173 grams sodium citrate	
100 grams sodium carbonate, anhydrous, or 270 grams sodium carbonate crystals, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$	

Ferric Chloride, N (M/3). 90 grams crystals, $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, to one liter.

Hydrochloric Acid, Concentrated. About 13 N. Specific gravity 1.20.

Hydrochloric Acid, Dilute, 2 N. Specific gravity 1.035. Dilute 170 cc. concentrated hydrochloric acid to one liter.

Iodine. 20 grams potassium iodide } to one
1 gram iodine } liter

Lead Acetate, N (M/2). 190 grams crystals, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$, to one liter.

Litmus. Heat 10 grams commercial cubes with about 200 cc. water. Filter. Wash the residue several times with hot water. Make up to one liter.

Magnesium Chloride, N (M/2). 102 grams crystals, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, to one liter.

Mercuric Chloride, N/5 (M/10). 27 grams to one liter.

Millon's Reagent. Treat mercury with twice its weight of concentrated nitric acid (in a porcelain dish under the hood). Warm gently towards the last. When all is dissolved, add the liquid to twice its volume of water. Allow to settle a few hours and decant the clear liquid.

Nitric Acid, Concentrated. About 16 N. Specific gravity 1.42.

Nitric Acid, Dilute, 2 N. Specific gravity 1.065. Dilute 130 cc. concentrated nitric acid to one liter.

Phenolphthalein. 5 grams in one liter of alcohol (or of 60 per cent alcohol).

Potassium Ferrocyanide, N (M/4). 106 grams crystals, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$, to one liter.

Potassium Hydroxide, 50 per cent. 770 grams to one liter.

Potassium Iodide, N/5. 33 grams to one liter.

Potassium Permanganate, M/10. 16 grams to one liter.

Silver Nitrate, N/10. 17 grams to one liter.

Soap. Shave 50 grams white castile soap. Dissolve in one liter hot water and filter.

Sodium Carbonate, N (M/2). 53 grams anhydrous, or 143 grams crystals, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, per liter.

Sodium Hydroxide, 30 per cent. 400 grams to one liter.

Sodium Hydroxide, 2 N. About 85 grams sodium hydroxide sticks to one liter.

Sodium Phosphate, N (M/3). 119 grams crystals $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ to one liter.

Sulphuric Acid, Concentrated. About 36 N (18 M). Specific gravity 1.84.

Sulphuric Acid, Dilute, 2 N. Specific gravity 1.065. Dilute 59 cc. concentrated sulphuric acid to one liter.

Reagents for Special Use

Acetic Acid, N. *Experiments 62 and 63.* Dilute the reagent acetic acid to twice its volume; or dilute 57.1 cc. glacial acetic acid to one liter.

Aluminium Chloride, N/2 (M/6). *Experiment 57.* 22 grams crystals, $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$, to one liter.

Barium Acetate, N/2 (M/4). *Experiment 57.* 62 grams crystals, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, to one liter.

Barium Nitrate, N/2 (M/4). *Experiment 57.* 65 grams to one liter.

Bleaching Powder. *Experiments 155-160.* Grind 100 grams bleaching powder in a mortar and gradually add about 50 cc. water, so as to form a paste. Add 250 cc. water, mix thoroughly, and filter.

Calcium Bicarbonate (Artificial Hard Water). *Experiments 69-71.* Dilute limewater with an equal volume of distilled water. Pass in carbon dioxide until the precipitate formed at first is redissolved. If a little precipitate persists, filter the liquid.

Chromic Sulphate, N/2 (M/12). *Experiment 151.* 60 grams crystals, $\text{Cr}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$, to one liter.

Copper Sulphate for Fehling's Solution. *Experiment 98.* 17.3 grams crystals, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, to one liter.

Cyanin. *Experiment 148.* 0.1 gram in a mixture of 50 cc. alcohol and 50 cc. water.

Elsner's Reagent (Basic Zinc Chloride). *Experiment 132.*

500 grams zinc chloride

20 grams zinc oxide

425 cc. water

Warm until clear.

Ferrous Sulphate, N/2 (M/4). *Experiment 151.* 70 grams crystals, $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, to one liter.

Formic Acid, Concentrated. About 36.5 N. *Experiment 33.* Specific gravity 1.22.

Formic Acid, N. *Experiments 62 and 63.* Dilute 37.7 cc. pure formic acid (sp. gr. 1.22) to one liter; or dilute 173.6 cc. formic acid of sp. gr. 1.06 to one liter.

Hydrochloric Acid, N. *Experiments 62 and 63.* Dilute the reagent dilute (2 N) hydrochloric acid to twice its original volume.

Hydrochloric Acid, 3 per cent. *Experiments 144, 146, 149.* Dilute 400 cc. of the reagent dilute (2 N) hydrochloric acid to one liter.

Hydrochloric Acid, 0.4 per cent. *Experiment 116.* 55 cc. dilute (2 N) hydrochloric acid to one liter.

Indigo Carmine. *Experiment 164.* 1 gram indigo carmine to one liter.

Löwe's Reagent. *Experiment 154.* Dissolve 25 grams copper sulphate and 12 cc. glycerol in 250 cc. water. Add just sufficient sodium hydroxide solution to redissolve the precipitate formed.

Oxalic Acid, Saturated. 120 grams crystals, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, to one liter.

Oxalic Acid, 5 per cent. *Experiments 146 and 149.* 50 grams crystals $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ to one liter.

Pepsin. *Experiment 116.* 0.1 gram commercial dry pepsin to one liter.

Potassium Chloride, N/2. *Experiment 57.* 37 grams to one liter.

Potassium Dichromate, N (M/6). *Experiment 169.* 49 grams to one liter.

Potassium Hydroxide, 30 per cent. *Experiment 32.* 385 grams to one liter.

Potassium Hydroxide, 5 per cent. *Experiment 153.* 50 grams to one liter; or dilute the 50 per cent solution to 15 times its volume.

Potassium Hydroxide in Alcohol. *Experiment 82.* 100 grams to one liter alcohol.

Potassium Sulphate, N/2 (M/4). *Experiment 57.* 44 grams to one liter.

Richardson's Reagent. *Experiment 154.* Dissolve 25 grams nickel sulphate crystals, $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$, in 500 cc. hot water. Precipitate with sodium hydroxide solution. Wash thoroughly by settling and decantation. Dissolve in 125 cc. concentrated ammonia (sp. gr. 0.90) and make up to 250 cc. with water.

Rosolic Acid. *Experiment 147.* 0.5 gram in a mixture of 50 cc. alcohol and 50 cc. water.

Silver Sulphate, Saturated. 7 grams to one liter.

Sodium Bisulphite, 30 per cent. *Experiment 168.* 385 grams to one liter.

Sodium Bisulphite, M. *Experiments 157, 158, and 164.* 104

grams to one liter; or dilute the 30 per cent solution to three times its volume.

Sodium Carbonate, 1 per cent. *Experiment 116 and 144.* 10 grams anhydrous sodium carbonate to one liter; or dilute the reagent N. sodium carbonate solution to five times its volume.

Sodium Carbonate, 0.05 per cent. *Experiment 153.* Dilute the reagent sodium carbonate to 100 times its volume.

Sodium Chloride, 5 per cent. *Experiments 57 and 109.* 50 grams to one liter.

Sodium Citrate. *Experiment 98.* 173 grams to one liter.

Sodium Sulphate, N/2 (M/4). *Experiment 57.* 80 grams crystals, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, to one liter.

Sodium Potassium Tartrate for Fehling's Solution. *Experiment 98.* 346 grams crystals, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$, to one liter.

Sodium Thiosulphate, M./2. *Experiment 157.* 124 grams crystals, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, to one liter.

Trypsin. *Experiment 116.* 0.1 gram commercial dry trypsin to one liter.

APPENDIX C

THE METRIC SYSTEM

Meanings of the Prefixes

Milli- = one-thousandth, .001. Compare *mill* = one one-thousandth of a dollar.

Centi- = one-hundredth, .01. Compare *cent* = one one-hundredth of a dollar.

Deci- = tenth, .1. Compare *dime* = one tenth of a dollar.

Deca- = ten, 10. Compare *decalogue* = ten commandments.

Hecto- = one hundred, 100. Compare *hectograph* = a gelatin pad for multiplying copies of a writing or drawing.

Kilo- = one thousand, 1000.

Length

10 millimeters (mm.)	= 1 centimeter (cm.)
10 centimeters	= 1 decimeter (dm.)
10 decimeters	= 1 meter (m.)
1000 meters	= 1 kilometer (km)

Area

100 square millimeters (mm. ²)	= 1 square centimeter (cm. ²)
100 square centimeters	= 1 square decimeter (dm. ²)
100 square decimeters	= 1 square meter (or centare)(m. ²)
100 square meters	= 1 are (a.)
100 ares	= 1 hectare (ha.)

Volume (Capacity)

1000 cubic millimeters (mm. ³)	= 1 cubic centimeter (cm. ³ or cc.)
1000 cubic centimeters	(milliliters) = 1 liter
1000 liters	= 1 cubic meter (or stere) (m. ³)

Weight

10 milligrams (mg.) = 1 centigram (cg.)

10 centigrams = 1 decigram (dg.)

10 decigrams = 1 gram (g.)

1000 grams = 1 kilogram (kg.)

1 gram is the weight of 1 cubic centimeter of water at 4° C.

1 kilogram is the weight of 1 liter of water at 4° C.

TABLES OF EQUIVALENTS

Length

1 millimeter = .0394 inch = about $\frac{1}{25}$ inch

1 centimeter = .394 inch = about $\frac{2}{5}$ inch

1 decimeter = 3.94 inches = nearly 4 inches

1 meter = 39.37 inches = about $1\frac{1}{10}$ yards

1 kilometer = .62 mile = about $\frac{5}{8}$ mile

1 inch = 2.54 centimeters = about $2\frac{1}{2}$ centimeters

1 foot = 3.05 decimeters = about 30 centimeters

1 yard = 9.15 decimeters = about $1\frac{1}{10}$ meter

1 mile = 1.61 kilometers = about $1\frac{3}{5}$ kilometers

Area

1 centare (square meter) = 1550 square inches = about $1\frac{1}{2}$ square yards.

1 hectare = 2.47 acres = nearly $2\frac{1}{2}$ acres.

Volume

1 cubic centimeter (milliliter) = .06 cubic inch

10 cubic centimeters (1 centiliter) = .61 cubic inch

100 cubic centimeters (1 deciliter) = 6.10 cubic inches

1 liter = 61.03 cubic inches

1 cubic inch = 16.39 cubic centimeters

Capacity

1. Dry Measure

1 liter	= .908 quart
1 hectoliter	= 2.84 bushels
1 quart	= 1.10 liters,
1 gallon	= 4.40 liters
1 bushel	= .35 hectoliter

2. United States Liquid Measure (Wine Measure)

1 liter	= 1.057 quarts
1 fluid ounce	= $\frac{1}{16}$ pint = 29.6 cubic centimeters
1 quart	= .946 liter
1 gallon	= 3.79 liters

1 United States gallon = 231 cubic inches = almost exactly the capacity of a cylinder 7 inches in internal diameter and 6 inches in height.

3. British Imperial Liquid Measure

1 liter	= .881 quart = about $1\frac{3}{4}$ pints
1 fluid ounce	= $\frac{1}{20}$ pint = 28.4 cubic centimeters
1 quart	= 1.135 liters
1 gallon	= 4.54 liters

1 Imperial gallon = 277.274 cubic inches = the volume of 10 pounds of water at 62° F. (about 16° C.).

Weight

1 gram	= 15.43 grains
1 kilogram	= 2.20 pounds
1 ounce Avoirdupois	= 437.5 grains = 28.4 grams
1 pound Avoirdupois	= 7000 grains = 453.6 grams

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