

FIRST PRINCIPLES
OF
CHEMISTRY

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FROM THE PREFACE TO THE FIRST EDITION

IN selecting their material for this book, the authors have been governed wholly by what they considered of intrinsic value to the elementary student, without reference to its traditional place in a text-book. This has led to the omission of some subjects commonly found in books for beginners. To the subjects selected they have striven to give a discussion simple enough to be readily comprehended by the beginner, and complete enough to furnish him with a clear idea of the underlying principles of Chemistry and a definite knowledge of its more important facts.

The experimental determination of chemical facts is, then, emphasized from the first. When sufficient facts have been given to make explanation necessary, the generalizations of the science have been introduced. In some of the theoretical chapters, particularly those on solution and ionization, it may be advisable to omit certain portions at first and to take them up afterwards as need arises.

The authors have attempted to bring out the fundamental principles first by a simple statement, which is later developed and driven home by illustrations, exercises, and problems, all designed to stimulate the pupil to think for himself, and constantly to connect his new facts with the facts and principles already learned.

In order to give the pupil some idea of the great commercial importance of Chemistry, a number of typical manufacturing

processes have been described and illustrated. Where a substance is manufactured in several ways, the authors have tried to avoid confusion by giving a description of one process only, selecting the one which they believe is, or will become, most extensively used in this country. The commercial production of copper, aluminum, iron, and carborundum has been described somewhat in detail, for these are notable examples of modern chemical processes.

NEW YORK, August, 1907.

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FIRST PRINCIPLES OF CHEMISTRY

CHAPTER I

INTRODUCTION

1. The Effect of the Great War on Chemical Industry.—The period of the Great War was a time in which chemical industry met with astounding development. In addition to the poison gases, explosives, and many other chemical products used directly in connection with the war, the country was also obliged to produce enormous quantities of glass, dyes, photographic chemicals, and pharmaceutical preparations, which were formerly imported from Europe.

In 1914, the United States imported nearly 6,000,000 pounds of dyestuffs and exported none. In 1918, this country not only supplied its own needs with dyes of the highest quality, but exported 8,000,000 pounds. Before the war, the world was dependent on Germany for the potash indispensable to the growth of plants. By the development of previously unexploited saline deposits, and the recovery of potash compounds from the flue dust of cement kilns and blast furnaces, 60,000 tons of potash were produced in this country in 1918. Sulphuric acid production doubled; a new nitric acid and a new ammonia industry sprang up almost overnight.

Our output of explosives during the war increased from 6,000,000 to 400,000,000 pounds, and the rate of production of poison gas some time before the signing of the Armistice equaled that of any of the allied countries. The vast production of metals, cement, sulphuric acid, coal-tar products, and other essential chemicals left the country with enormous stocks of these materials available for the production of peace-time chemical products. Many of the war plants are now adapted to the manufacture of chemicals used in normal times.

The establishment of chemistry on a sound basis as one of the great permanent industries of the country, equipped for production on a large scale, has created a wide demand for skilled chemists and trained chemical engineers, as well as for a host of intelligent workers in the plants. Thus the student has added to the natural interest inherent to the study of chemistry an increased opportunity for using the subject in his life work.

2. Chemical Change. — Chemistry is the name given to the science which has grown out of the study of chemical changes and the effort to control or modify them. The most striking chemical change that goes on about us is that which occurs when a substance burns. If the burning substance is coal or wood, it seems to disappear except for a small quantity of ashes.

Early investigators did not discover the true nature of this process. They adopted a wrong explanation, and, as a result, the science of chemistry did not advance. A true explanation was stated only a little more than a hundred years ago. Since that time chemistry has progressed at an astonishing rate. The true explanation of burning was found by studying the change that many metals undergo when heated in air.

3. Heating Metals in Air. — A few metals — for example, magnesium — burn when heated in the air. Most metals undergo a similar, but much slower, change, without the production of light. If a piece of bright copper is heated, it assumes a black color; on bending or scraping it gently, a black powder separates from it. If the metal is heated again, another layer of the black substance forms. By repeating the process a sufficient number of times, the piece of copper can be entirely changed into the black powder.

The black powder in no way resembles the original piece of copper. Lead after melting gives a yellowish powder; zinc, if in the form of a powder, will take fire and yield a white powder. Gold, silver, and platinum show no change on heating in air. Most other metals, however, when thus heated produce powdered substances which bear little or no resemblance to the original metal. In all these changes the metals have lost their identity, and substances with new characteristics are formed. Such alterations are called *chemical changes*. Changes in which a material does not lose the characteristics by which we identify it are called *physical changes*.

Several things may be thought of as explanations of the change which the metals undergo. It may be that by the effect of the heat, without the aid of any substance, the metal is transformed into a new kind of matter; possibly the metal in being heated has lost some of its substance, which has passed off as gas; possibly the metal has absorbed something from the air.

As an aid in testing these possible explanations, it will be advisable to weigh the metal before and after it is heated. When this is done, it will be found that *the powder always weighs more than the metal* from which it was formed. This seems to indicate that during the heating the metal adds to itself more substance, and that this substance is taken from the air. To further test this conclusion, a piece of metal can be sealed in a glass tube from which the air has been exhausted; *heated under these conditions, the metal is not changed*.

4. Lavoisier's Experiment. — Another conclusive experiment showing the change of metals on being heated in the air is one that was performed by Lavoisier, the French chemist, to whom is given the credit of discovering the

nature of this kind of chemical change. He put some tin in a good-sized glass flask and sealed it so that the air could neither enter nor leave it. He then heated the flask carefully for several days. At the end of this time, he noticed that a certain amount of white powder had been formed. He next ascertained that the flask with its contents had not changed in weight. He then opened the neck of the flask and noticed that air rushed in. On again weighing the flask and its contents, he found that there was an increase in weight, and that this increase was equal to the increase which the tin had undergone on being converted into the white powder. He explained these facts as follows: the tin on being heated combined with some of the air in the flask, producing the white powder. The flask as a whole did not increase in weight because no air entered the flask to take the place of that which had combined with the tin. When the flask was opened, the air entered, causing the increase in weight.

Since experience has shown that matter can be neither created nor destroyed, it appears probable that the powdered substances are more complex than the metals from which they are formed; that is, they contain the metal plus something which has been taken from the air. Lavoisier undertook to find out the nature of the substance which was taken from the air.

5. Heating Mercury in the Air.—Mercury, heated in the air, underwent a much less rapid change than the metals of which we have been speaking. Kept at a temperature a little below its boiling point for several days a small quantity of red powder was gradually formed (Fig. 1). A quantity of this powder was heated in a glass tube to a temperature above the boiling point of mercury, and a colorless gas was given off.

A glowing splinter was inserted into the tube. It burst into flame and burned brilliantly. The gas could not have been ordinary air, for a splinter does not behave so in air. A quantity of the gas was collected and was shown to be very different from ordinary air by the fact that substances burned in it with extraordinary vigor.

On examining the tube it was found that a part or all

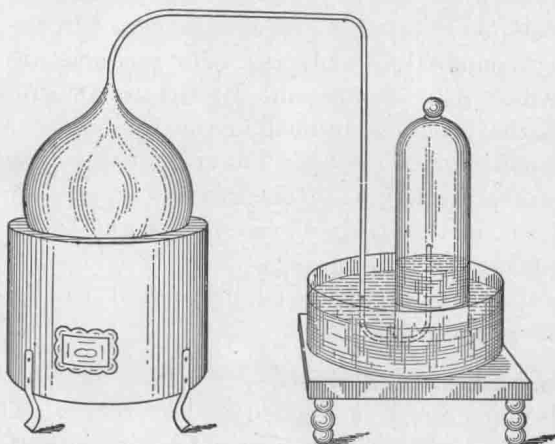


FIG. 1. — LAVOISIER'S APPARATUS FOR HEATING MERCURY.

of the red powder had disappeared and that drops of mercury had collected on the sides of the tube. It appears from this experiment that *the red powder had decomposed into mercury and a gas* which readily supports combustion. Lavoisier named this gas *oxygen*.

Since the red powder was made by heating mercury in the air, and was not formed unless air was present, *the oxygen must have come from the air*. Hence air must contain oxygen. That air is not all oxygen is shown by the fact that only about one fifth, and not all, of the air was absorbed in Lavoisier's experiments; and also by the fact that substances do not burn as readily in air as in oxygen.

The powders obtained by burning tin or copper or iron weigh more than the original piece of metal, because the metal has combined with a noticeable weight of oxygen from the air. In these cases, it is not practical to separate the metal from the oxygen by heat alone.

6. Burning. — The burning of wood or other substances is a process that closely resembles the change of a metal into a compound of the metal and oxygen. In the case of ordinary combustible materials, the products are chiefly gases which pass off unseen. By the use of suitable apparatus, the products formed in the burning of a candle can be collected, and it is found that their weight is greater than the weight of the candle burned. As in the case of the metals, this increase in weight is due to the oxygen taken up from the air. If air is excluded, the burning substance is extinguished, because it can no longer combine with oxygen.

7. Compounds and Elements. — We have shown that the red substance contains oxygen and mercury. The substance formed on heating copper in the air contains oxygen and copper. As these substances formed are composed of more than one kind of material, they are called *compounds*. A compound is a substance that can be separated into two or more substances. No one has changed copper or mercury into anything else, without *adding something*. So far as we know, gold, iron, oxygen, and about eighty other things are not composed of anything else. They are simple substances, or, as we say, *elements*. An element is a substance that has not been separated into other substances by man. A list of elements is given in Table I, Appendix.

8. Solids, Liquids, and Gases. — We have spoken of metals, powders, air, and oxygen as things that may be

weighed. They are forms of *matter*. Matter is generally defined as anything that occupies space. The different kinds of matter are called *substances*. Substances differ in the way they fill space, and it is this difference that determines their *physical state*. The three physical states of matter are the solid, the liquid, and the gaseous.

A solid has a definite shape or *form*, and a definite *volume*. A *liquid* has no definite form, but has a definite *volume*. It can fill a vessel only to the extent of its volume and takes the shape of the containing vessel so far as it fills it. *Gases* have neither a definite form nor a definite volume. They tend to distribute themselves in all directions and fill completely any vessel into which they are brought. Their only boundaries are the containing walls.

9. Identifying Substances. — The different kinds of matter are identified by their properties or peculiarities. The more important of these are given in the table below.

Physical properties used in identifying substances:

SOLID STATE	LIQUID STATE	GASEOUS STATE
Density or relative weight; melting point; luster, hardness; color, taste, or smell; solubility.	Density or relative weight; freezing point; boiling point; color, taste, or smell; solubility.	Density or relative weight; condensing point; color, taste, or smell; solubility.

Chemical properties used in identifying substances:

Reactions with air or oxygen;

Reactions with water;

Reactions with acids or bases;

Actions peculiar to the substance or its constituents.

SUMMARY

Chemical changes involve changes in the identity of the material. The composition of the substance is usually altered, and energy changes are also involved.

A **compound** is a substance that can be separated into two or more substances. An **element** is a substance which has not been separated into other substances by man.

So far as known, matter cannot be created or destroyed. (This statement is known as the **Law of the Conservation of Matter**.)

When a substance burns in air, it combines with oxygen, forming a new compound.

Lavoisier obtained oxygen from air by heating mercury in it and then decomposing the material produced.

EXERCISES

1. Air and water were formerly called elements. Why are they not now?
2. How could you prove that air contains oxygen?
3. What kind of change is involved in the withering of a leaf? Making cloth from wool? Baking bread? Burning coal? Extinguishing the fire? Rusting of iron? Decay of fruit? Fermenting fruit juices?
4. Why is a burning candle extinguished by blowing?
5. Describe experiments that you performed in the laboratory which illustrate the difference between physical and chemical change.
6. Distinguish between the terms *element* and *compound*.
7. When 2 grams of a certain substance were heated, all the oxygen which the substance contained was given off, and a residue weighing 1.07 grams was left. Calculate the percentage of oxygen in the substance.
8. Why is the crushing of glass not a chemical change?

9. Name three chemical changes which occur in the kitchen; three physical changes.

10. What kind of changes are involved: in the digestion of food? The tanning of hides? The raising of your arm? The ripening of fruits? Paring of potatoes?

11. How would you show that lead, when heated in the air, combines with something to form a yellowish powder?

12. What is the difficulty in proving that the products formed by burning a candle weigh more than the candle?

13. What always happens when a substance burns in air?

14. How did the failure of the earlier investigators to use a balance prevent them from finding the true explanation of burning?

CHAPTER II

GASES AND THEIR MEASUREMENT¹

10. Gas Pressure. — The peculiar properties of gases are due to the fact that the particles composing them are

at considerable distances from each other and are in rapid motion. As these particles pelt against the walls of the containing vessel, they exert a pressure on the walls. If a gas is compressed into a smaller space, more particles will strike a square inch in a given time, and so the pressure measured in pounds per square inch is increased. The in-

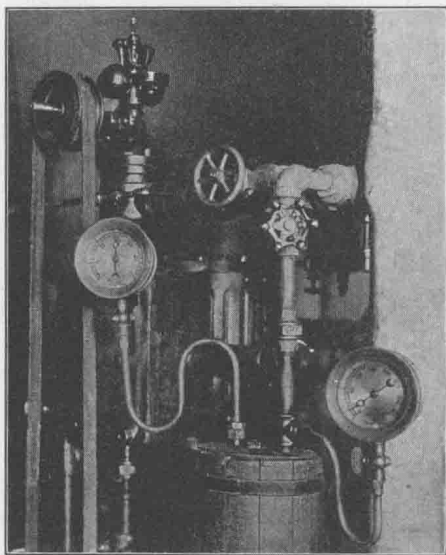


FIG. 2. — STEAM GAUGES.

creasing pressure of the air in a bicycle pump, as the piston is forced down, illustrates this. If a gas is heated without being allowed to expand, its pressure on

¹ If the instructor prefers, this chapter may be introduced later or used for reference in connection with the laboratory work, without interfering with the continuity of the course.

the walls of the vessel containing it will be increased, because the heat increases the speed of the particles.

The air which surrounds us is compressed by the weight of the atmosphere above it. The pressure due to the weight of atmosphere is about 15 pounds per square inch at sea level and is less at higher altitudes. It is not, however, a constant quantity, but varies with weather conditions. While the pressure of confined gases, like steam or compressed air, is measured by a pressure gauge (Fig. 2), atmospheric pressure is measured by the height of the column of mercury that it supports in a barometer (Fig. 3).

The barometer consists of a tube which has been entirely filled with mercury and then inverted into a reservoir of the same liquid. A pressure of 14.7 pounds per square inch is equal to the weight of a column of mercury 1 in. square, and 30 in. or 760 mm. high. As the gases whose volume we measure in the laboratory are usually subject to atmospheric pressure, gas pressures in chemical work are usually expressed in *millimeters of mercury* instead of pounds per square inch.

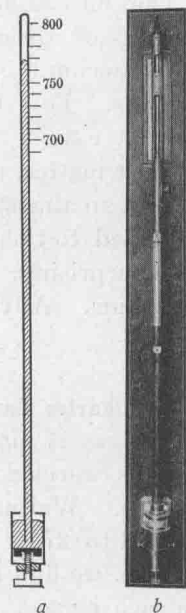


FIG. 3. — BAROMETER

a, Section; b, External view.

11. Effect of Temperature and Pressure Changes on Volumes of Gases. — The measurement of the volume of gases usually involves a *correction of the gas volume*. This is necessary because the volume of a given quantity of gas is considerably affected by even slight changes in temperature and