PRINCIPLES
OF
GENERAL CHEMISTRY

BY

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PREFACE

This text is the outgrowth of several years' study of the problems involved in presenting the subject to those students who have had a preparatory school course in chemistry. Such students enter their first year college course with an acquaintance with the field of chemistry, sufficient to dull their interest if the college course is merely a review of the school course with some added material. Nevertheless their knowledge of the fundamental principles of chemistry is not broad enough to justify their admission into advanced courses. The college course should use the previous training of the student as a foundation, and should furnish a broader survey of the subject than is possible in the limited time of the school course. Many of the specific subjects of the beginning course must be repeated in order that they may be used in the logical development of the science, but this repetition should be progressive.

The introduction of the modern concept of atomic structure at the beginning of the course furnishes material which the student finds interesting, and the use of this concept throughout the course affords a simple and logical interpretation of many of the phenomena which are encountered. The name "oxidation" has been retained in the discussion of reactions which involve valence changes. Although the name is a misnomer, it has long since lost its original significance. The application of the electron concept to oxidation-reduction phenomena furnishes a tangible basis for the study of the essential changes involved and a simple method of representing these changes.

The classification of substances according to the kinds of reactions which they exhibit, instead of according to the elements which they contain, makes it possible to emphasize the generality of the reactions instead of studying each as a specific change. The author has, therefore, adopted the classification of compounds under the general types: basic oxides; acidic oxides; acids; bases; and salts. The reactions exhibited by these compounds are of much more general application than most of those exhibited by the elementary substances. Because of these facts and because of their lesser importance, the specific elementary substances are discussed toward the end of the text, although many of their more general reactions, for obvious reasons, are included in the study of the compounds. The chapters dealing with the metals have been devoted primarily to a discussion of some of the principles involved in metallurgy. For the most part specific description of metallurgical processes has been omitted, because the details of operation differ and for the general student are not of very great importance.

By using this scheme of classification, general principles are stressed and the student who continues his study of chemistry no further than the first year college course gains an insight into the scientific method of study, and acquires something of the point of view of the chemist and a concept of the importance of the science. At the same time the student who goes on to more advanced courses in chemistry is equipped with the tools he requires without the necessity of memorizing a large number of apparently unrelated facts. Many of the specific facts, such as numerical data for the melting point, boiling point, etc., for the most part have been omitted from the body of the text, and some of these values have been included in the Appendix. Numerous compounds have been omitted arbitrarily, because they are soon forgotten and their study adds little to the general knowledge of the subject. Under each of the types of compounds, the general reactions are studied first, after which specific substances are considered. It thus becomes possible to make further omissions, if the time devoted to the course makes this desirable, without detracting from the general survey of the subject.

Several of the chapters, *e.g.*, Hydrolysis and Oxidation-Reduction, are summarizing chapters. In such chapters, subjects which have been developed gradually in preceding portions of the text are more fully developed and explained.

Many students find the normal rate of progress of a class in the study of chemistry too slow to maintain their interest. Such students should be encouraged to keep up a series of systematic readings outside of the regular text assignments. It has seemed wise, therefore, to place at the end of each chapter a list of supplementary readings. Most of the articles to which reference is made are written from the point of view of the non-technical reader, but a few will require careful study and should be assigned to only the better students in the course. Such a list is necessarily incomplete and the teacher will desire to supplement the list.

The author takes pleasure in acknowledging the assistance given by his colleagues. Professors P. T. Walden, E. B. Kelsey, D. T. Keach, Dr. E. J. Fischer, Dr. J. A. Timm, and Mr. H. G. Dietrich have given freely of their time in discussing the results obtained in the classroom use of the material upon which this text is based and have made numerous helpful criticisms. Suggestions made by Professors A. J. Hill, Blair Saxton, and H. A. Curtis have aided greatly in the preparation of some of the specific topics.

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CHAPTER I

VARIETIES OF MATTER

Introductory. Chemistry is a science which deals with substances and the changes which they undergo. The chemist studies the characteristic properties of substances so that they may be recognized and separated from each other. In some cases complex substances are decomposed in order to obtain simpler ones. In other cases the object is just the reverse, and the simple substances are used as raw materials for making complex products. Since there are an enormous number of different substances the study of chemistry is simplified by the development of general principles and theories.

Subdivisions of Chemistry. The scope of chemistry is so broad that many subdivisions of the science are made. The field is thus limited and emphasis is placed on certain aspects of the subject. *Organic Chemistry* includes a study of substances which, at the time the name was introduced, were thought to be formed only under the mystic influence of life processes. We know now that this concept is incorrect, but retain the name for convenience and call the study of the compounds of carbon by the name, organic chemistry. *Inorganic Chemistry* is a study of the mineral constituents of the earth and of the changes which they undergo. In *Analytical Chemistry* the methods which are used for the separation and detection of various substances are discussed. *Physical Chemistry* involves the development of theories and of general principles in the light of which the facts of chemistry are systematically arranged. *Chemical Engineering* is a study of the engineering problems which face the chemist in carrying out industrial operations in chemistry on a large scale. *General Chemistry* deals with facts which belong in each of these subdivisions. Since any one of these subdivisions is a field for years of specialization, a course in general chemistry can do little more than include a survey of the field as a whole and develop a scientific method of attack. The descriptive facts pertaining to substances are so numerous that remembering each fact as an isolated case is out of the question. Within the subject of general chemistry, however, it is possible to classify substances according to the kinds of reactions which they show and thus obtain general principles. A few well-grounded theories furnish a picture which enables us to interpret the changes observed and thereby secure a systematic (scientific) treatment.

Importance of Chemistry. Chemistry has played a very important part in the development of civilization and under modern conditions of life its contribution to our welfare has become increasingly important. To some, chemistry is the tool of war and is used for the perfection of engines of destruction and for the spread of misery and suffering; but in the hands of others it is being used to make war impossible and to alleviate suffering. The extension of human knowledge, the perfection of industrial operations, the development of agriculture, the improvement of sanitary conditions, the discovery and manufacture of new medicinal products, and the production of many luxuries as well as necessities are some of the contributions made by chemistry to the development of humanity.

Objects in the Study of Chemistry. The study of chemistry is undertaken with various motives in mind. Some begin the study of chemistry because they desire to have a part in its scientific developments and to use it as a profession; while to others the subject is one of general information. Changes in matter are going on about us all the time and play an important part in all that we do. We, therefore, desire to know something about the nature of these changes. The place of chemistry in general education is one of great importance because its progress is sure, its developments are rapid, its methods are systematic, and its applications bear an intimate relation to our lives. In the beginning of our work it would be futile to attempt to study the chemistry of the processes going on within our bodies, or indeed the processes of most of the great industrial operations about us. We can, however, gradually develop an insight into many of the important applications of this subject. We can also learn the chemist's view of matter and its changes and thereby broaden our intellectual horizon by a new point of view in the study of facts and methods which are peculiar to chemistry. The facts of chemistry are obtained from experimental observations. Theories and laws are developed by reasoning from these facts. Since our knowledge is incomplete and our reasoning subject to human error in interpretation, theories are amended, corrected, or entirely discarded as knowledge based on facts seems to demand. The laws of science are general statements of the observed effects of conditions upon changes in matter. These laws are not unchangeable, but are amended as additional descriptive facts demand. The theories and laws are used as a basis for the correlation of facts so that the whole structure of the science is systematically developed.

Properties of Substances. Different varieties of matter are recognized by the properties which they exhibit. *The characteristics which are used in identifying and describing substances are the physical properties of the substances.* Physical properties are characteristics which can be perceived by the senses, or which can be directly measured by physical means. At ordinary temperatures some materials are solids, some are liquids, and some are gases. Definite boiling and freezing points are characteristic of pure substances. The common properties which are used in describing and identifying substances are, in addition to those mentioned above, the color, odor, taste, density, solubility in water, and the conductivity of heat and electricity. In the case of solids the crystalline structure is a characteristic property. Many of the uses to which we put common substances depend on one or more of their physical properties. For example, copper is an exceptionally good conductor of electricity and is used most extensively in this capacity. It possesses properties which make it especially useful for this purpose: it is ductile and can readily be drawn into wire of the desired size, it is sufficiently strong to be held easily in place, and it is not extensively corroded under ordinary atmospheric conditions.

The *chemical properties* of a substance are the changes in composition which it may undergo when subjected to various conditions. Some substances, such as potassium chlorate, decompose when they are heated. In such cases, instability toward heat is a characteristic chemical property of the substance. In other cases, the change which takes place involves two or more substances. Thus, the burning of magnesium in oxygen results in the combination of the two substances to form a third substance, magnesium oxide. The ability of magnesium to combine with oxygen is a chemical property of magnesium, and that of oxygen to combine with magnesium is a chemical property of oxygen. The chemical properties of different substances are due to their composition and are responsible for the various chemical changes which they exhibit. The phenomena which accompany chemical changes are more fully discussed in succeeding paragraphs of this chapter.

Classification of Substances. Different varieties of matter are classified according to their composition and not according to the objects into which they are shaped. All pure substances are homogeneous; that is, they are of uniform composition throughout. There are a very large number of pure substances but they may be grouped according to their composition into simple substances and compounds.

Elements. Most of the common materials can be decomposed into simpler ones. *There are, however, about 90 known substances which have not been decomposed by chemical means. These are called elements.* This concept of elementary substances does not involve the assumption that they are composed of only one kind of matter. For a long time, water was regarded as a simple substance; but now we know that it can be decomposed into two simpler ones, hydrogen and oxygen. It does not follow from the above definition that it is impossible for elements to be decomposed. In recent years it has been discovered that the elementary substance radium spontaneously decomposes. No one has yet been able to affect in any way the decomposition of this substance or to build it up from its decomposition products. Rutherford and Chadwick report that the elements nitrogen, boron, fluorine, sodium, aluminum, and phosphorus can be decomposed by subjecting them to a bombardment with the particles thrown off in the disintegration of radium. Such work has led to the belief that the elementary substances are themselves of a complex structure and may be decomposed as soon as suitable conditions can be obtained.

For practical purposes, chemists retain the former view of the element. There is no violent contradiction between this concept and the experimental results of Rutherford, for, under the conditions of chemical experiments, the substances which we call elements are not decomposed.

Abundance of the Elements. Only a few of the almost ninety known elements are abundant. Oxygen constitutes half of the earth and its atmosphere, and silicon accounts for half of the remainder. An estimate of the abundance of the elements in the solid crust of the earth, the sea, and the air, has been made by F. W. Clarke. Below is given a list of the eight most abundant elements which together make up about 97% of the matter in the crust of the earth and in its atmosphere.

ABUNDANCE OF THE ELEMENTS

Oxygen	50.02%	Calcium	3.22%
Silicon	25.80	Sodium	2.36
Aluminum	7.30	Potassium	2.28
Iron	4.18	Magnesium	2.08

Compounds. Compounds represent one of the classes of complex materials, *i.e.*, materials which contain more than one element. Pure substances which contain two or more elementary substances are called compounds. Compounds are ***homogeneous*** and possess ***definite properties*** which differ from those of the constituent elements. Compounds are also characterized by a ***definite composition***. The proportions by weight of the constituent elements in a compound cannot be changed.

Mixtures. A mechanical mixture differs from a compound in that it is ***heterogeneous***, and possesses no single set of properties by which it may be described. Each of the substances present in the mixture retains its own properties. ***The composition of a mixture is not definite*** and the proportions by weight of the components may be varied at will. In mixtures, the components are merely placed together and may be separated without chemical change.

Solutions. Solutions constitute a third kind of complex materials. When sugar dissolves in water, the particles disappear and the resulting solution is ***homogeneous***. Some of the properties of sugar are altered but its characteristic taste can still be noted. Similarly, some of the properties of water, for example, the freezing and boiling points, are affected. The amount of sugar which is present in a given volume of the solution may be varied, within certain limits, at will. Solutions resemble compounds in that they are homogeneous, but are unlike compounds in that the ***composition of the solution is variable.*** The observed changes of properties in the case of solutions are due to the fact that the particles are in a very fine state of subdivision. They are, however, still particles of the dissolved substance.

Changes in Substances. The changes which substances may undergo are of two types. In one type, ***a physical change,*** some of the properties of the substance are altered, but the substance is still the same. When ice melts there is a change in the state of the substance, its crystalline form is lost, and it becomes a liquid. Yet the substance is still of the same composition and contains the same relative amounts of its constituents, 8 parts by weight of oxygen to 1.008 parts of hydrogen. When liquid water is sufficiently cooled, ice is formed again.

The other type of change, ***a chemical change,*** involves the production of substances which are of different composition from those used at the beginning of the experiment. If a piece of magnesium ribbon is heated, it takes fire and continues to burn when it is withdrawn from the flame. When all of the magnesium has burned, a white powder remains. ***The properties of the substance have been abruptly altered.*** During this change magnesium combines with oxygen and if the products from several such experiments are analyzed, it is found that the substance produced always contains the same percentage of magnesium and of oxygen. A second characteristic of chemical changes is the fact that ***the relative amounts of the reacting substances are always the same for the same reaction.*** A third characteristic of chemical changes is the fact that they ***are accompanied by energy changes.*** Magnesium burns with a very hot flame and continues to burn even when it is withdrawn from the flame. Energy is liberated during this reaction. There is an energy change in all chemical reactions. Sometimes there is an absorption of energy, but, in common reactions, a liberation is more frequently observed. Energy is the capacity of a body or system of bodies to accomplish work, and heat is one of the forms of energy. The energy which a body possesses by virtue of its composition is called *chemical energy.* Chemical energy is most frequently manifested in the form of heat. Hence, the unit of heat is also the unit of chemical energy. This unit, the *calorie,* is the amount of heat required to raise the temperature of one gram of water one degree. (All temperatures mentioned in this book are *Centigrade.*) The actual amount of the energy change during a reaction is characteristic of the reaction.

Laws of Chemical Combination. In all changes which involve the union of two simple substances there are certain general observations which can be made. These results of experimental observation which appear to be universally applicable are called the Laws of Chemical Combination.

The Law of Conservation of Mass. This generalization applies to all reactions whether they are reactions of combination or of some other type. *Mass denotes the amount of matter and is measured in terms of weight.* The units of weight are units for measuring the intensity of the earth's attraction for an object. The unit of weight is the *gram,* which is the weight of 1 cc. of water at 4°, its temperature of maximum density. ***When the amount of all of the substances taking part in a chemical reaction is measured it is found that there is no change in the total mass.***

The Law of Definite Composition. A second general characteristic of chemical changes has been mentioned previously. When magnesium burns in air, the proportions by weight in which it combines with oxygen are 24.32 to 16, although there is, of course, a large excess of oxygen present. If the conditions are changed and an excess of magnesium is started burning in a vessel in which there is a limited supply of oxygen, the reacting proportions are still the same, and the excess of magnesium is left unburned. Magnesium oxide may be formed by other methods, *e.g.*, by heating the nitrate, carbonate, or hydroxide. No matter which of these methods is used, the product always contains magnesium and oxygen in the ratio by weight of 24.32 to 16. When other pure compounds are analyzed, constancy in composition is observed. ***The Law of Definite Composition is a statement of the fact that a pure compound always contains the same proportion by weight of the constituent elements.***

Equivalent Weights. Most of the elementary substances will combine directly with oxygen under the proper experimental conditions, and the proportions by weight of the constituent elements in the compounds produced will be definite in each case. It is possible to determine by experiment what weight of each of the elementary substances will combine with some fixed weight of oxygen, or will be equivalent to a fixed weight of oxygen. The numbers which express these weights are the combining or equivalent weights. If the fixed weight of oxygen is taken as 8 parts, the proportional numbers which represent the reacting weights of the other elements are never less than one. It may be shown experimentally that 8 parts by weight of oxygen are equivalent to or combine with 1.008 parts of hydrogen, 3 of carbon, 12.16 of magnesium, and 35.46 of chlorine. These numbers show not only the ratio by weight in which these elements are present in compounds with oxygen, but also the ratio in which they combine with each other, if they combine at all. Thus, 12.16 parts by weight of magnesium combine with 35.46 of chlorine and any excess of either substance is left unchanged if weights of a different ratio are used. Similar numbers may be determined for all of the elements. ***The numbers which tell how many parts by weight of each of the elements combine with or are equivalent to 8 parts by weight of oxygen, are called the equivalent weights.***

The Law of Multiple Proportions. In some cases, the same two elements may combine in different ratios so as to produce two or more different compounds. So long as a given compound is produced the proportions by weight are the same; but if two different compounds are possible the elements may show two different combining weights. When iron and sulfur combine directly, the combining ratio is 16 parts by weight of sulfur to 27.92 parts by weight of iron. In the naturally occurring substance pyrite, there are 32 parts by weight of sulfur to 27.92 of iron. It will be noticed at once that one of these equivalent weights of sulfur is just twice the other. In other cases in which two different compounds contain the same elements, a similar relation is noticed. A generalization, known as the ***Law of Multiple Proportions***, may be stated as follows: ***if two or more elements yield a series of compounds, the different weights of the one, which combine with a fixed weight of the other, are in the ratio of small whole numbers.*** In the above example, the different weights of sulfur (16 and 32), combined with a fixed weight of iron (27.92) bear to each other (weight of sulfur in the one case to weight of sulfur in the other) a ratio expressible in small whole numbers (16 : 32 or 1 : 2).

The Atomic Theory. Speculations as to the ultimate nature of matter have been made from the time of the Greek philosophers. In an attempt to picture the composition of substances which would explain the generalizations noted above, John Dalton (1766–1844), an English schoolmaster at Manchester, first stated the theory which in an amended form is accepted today, and which has had a profound influence upon the development of chemistry. He was influenced by the speculations of the philosophers and by the work of Newton and others who shortly preceded him, but to him belongs the credit for working out the theory which he advanced in 1802.

The important assumptions of this theory, somewhat modified in statement, follow:

> *The elements are composed of minute particles* of matter. These were given the name of *atoms* in the belief that they could not be subdivided. Atoms of the same element are alike in properties and have the same weight. Atoms of different elements differ in properties and have different weights. *A definite weight is characteristic of the atom of each element.*
>
> *The atom is the reactive unit.* That is, chemical combination is the result of the union of the atoms of the combining substances in simple numerical ratios.

Dalton's postulates included no concept of molecules. This term was introduced by Avogadro in 1811. The smallest particle of a substance which exhibits the properties of the substance is called a molecule. In the case of the elements the molecule is sometimes the same as the atom; but the molecules of some of the elements consist of aggregates of two or more atoms. In the case of compounds the molecules are made up of the atoms of the constituent elements. In pure compounds the molecules are all alike. In mixtures the molecules of the different component substances are present. The modern idea of the atom, for which see later paragraphs in this chapter, retains the concept of the atom as the reactive unit, but assigns to it a definite structure.

The Laws of Combination and the Atomic Theory. The laws of chemical combination may be more clearly understood by interpreting them in terms of this very important theory. The molecules of the reacting substances are changed during the reaction and their atoms unite to form molecules of different substances. Hence, there is a complete change in properties. Atoms retain their own characteristic weights and there is no change in mass during reaction, because all of the atoms of the substances entering into the reaction are found in the products.

When an element combines with another, a definite number of atoms of the one substance unite with a definite number of atoms of the other. Therefore, the Law of Definite Composition merely means that the molecules of pure substances always contain the same number of atoms of their constituent elements. The equivalent weights are numbers which are proportional to the weights of the atoms and to the number of the atoms entering into the formation of a molecule of the product. They therefore express the ratio by weight in which the substances react.

While seeking evidence in support of his theory, Dalton found that in two different compounds of carbon and hydrogen, the weights of hydrogen combined with a fixed weight of carbon bore the ratio of 2 : 1. In terms of the theory, this means that for the same number of atoms of carbon there are twice as many hydrogen atoms in one case as in the other.

Atomic and Molecular Weights. The fact was mentioned above that the weight of the atom is characteristic for each elementary substance. The exact weight of these atoms is of little significance, but their relative weights are very important numbers. In order to express these relative weights in a systematic manner, it is necessary to choose the atom of some substance as a standard and to assign to it a number to which the weights of the other atoms may be compared. Different units have been used for this basis. For convenience the oxygen atom, with an arbitrarily assigned value of 16, has been adopted as the standard. Since oxygen forms compounds with most of the other elements, the determination of the ratio of combination is more simply made in terms of this element than any other. The number 16 is used because it gives to hydrogen, the lightest of the elements, a value slightly larger than one. ***The atomic weight of an element is a number which expresses the relative weight of an atom of that element when the number 16 is assigned to the oxygen atom.*** To say that the atomic weight of chlorine is 35.46 merely means that the ratio of the weight of the chlorine atom to that of the oxygen atom is 35.46 : 16. Atomic weights do not represent definite weights. The *gram atomic weight* is, however, a definite weight. It is equal numerically to the atomic weight multiplied by one gram. Thus, 35.46 g. constitutes the gram atomic weight, which is a definite amount of chlorine.

Since molecules are composed of atoms, the molecular weight of a substance depends on the weight of the atoms in the molecule. ***The molecular weight of a substance is a number which expresses the ratio between the weight of one molecule of the substance and the***