COLLEGE GENERAL CHEMISTRY

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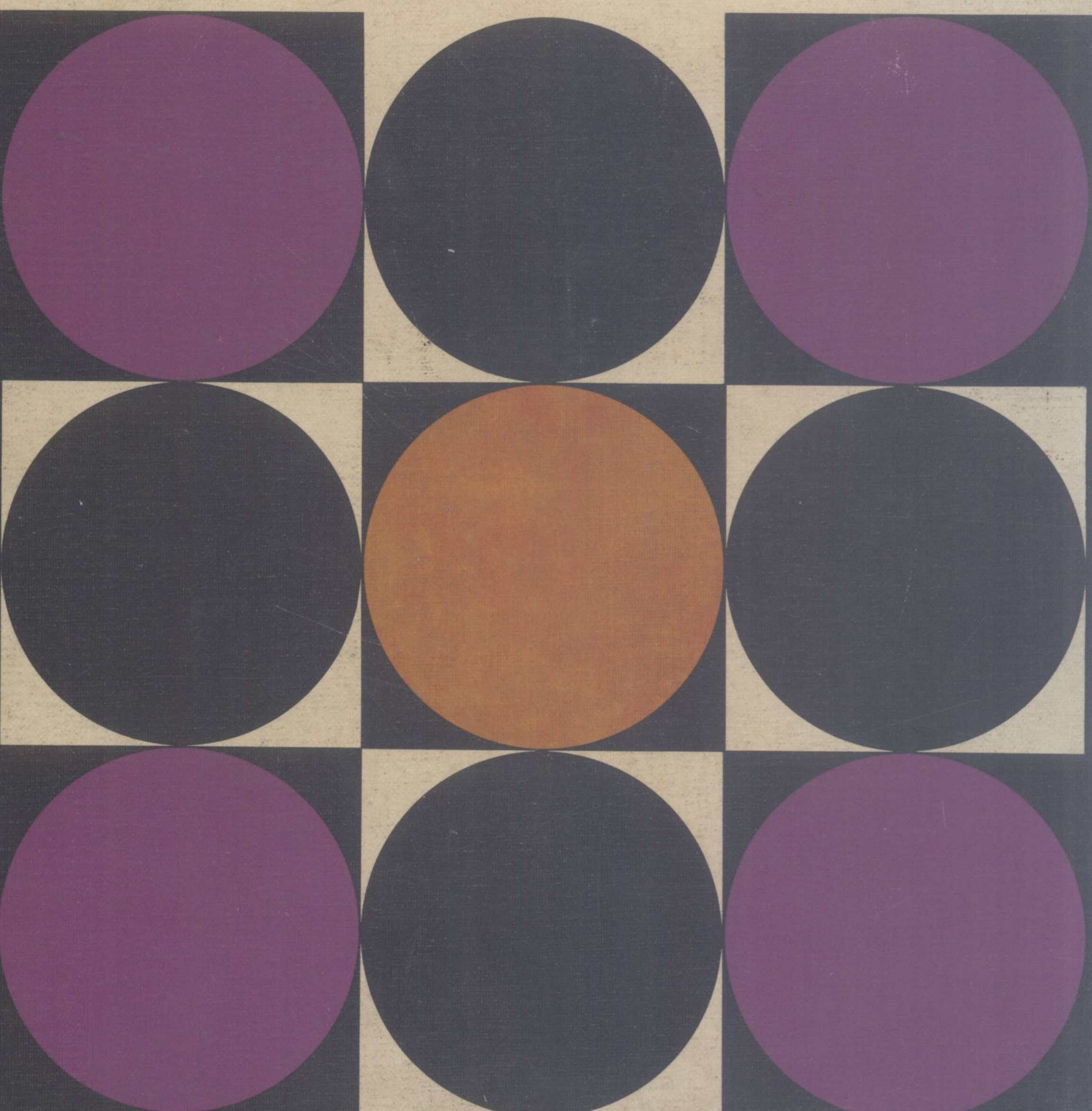

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COLLEGE GENERAL CHEMISTRY

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Preface

A liberal education that has as its goal the development of a broad understanding of various fields of study must, of necessity, include some instruction in a given science. Quite often, students who are not chemistry majors are given a first-year course that consists primarily of inorganic chemistry, leaving practically untouched other large areas such as organic chemistry and biochemistry. Our basic philosophy is that chemistry is as much a liberal arts subject as is English or French, and because chemistry is the only science that many liberal arts students will encounter in college, we intend to give a balanced picture of this field without, hopefully, making it superficial.

One objective of this book is to demonstrate the wide scope of chemistry practiced in the twentieth century as well as discuss the slow, gradual development of the various scientific concepts and the laborious searching for relationships and generalizations. We hope to show how various types of instrumental analyses have been influential in the development and modification of chemical theories. The basic principles of modern techniques such as nuclear magnetic resonance, infrared spectroscopy, and gas chromatography as well as nuclear instrumentation are covered. General trends in atomic and ionic size, ionization potentials, and electronegativities are explained, and the percent ionic character of bonds are related to differences in electronegativity. General principles are stressed because of their value in organizing data. In short, this is not an *inorganic* text but a broad *general* chemistry text which incorporates some elements from all of the major branches of chemistry.

A majority of the freshman college students today have studied some science in high school. This book is written, however, so that those without any chemistry background will be able to understand the material. We are aware that a non-science major may be unfamiliar with much of the terminology of chemistry and so attempt to explain difficult concepts thoroughly. It is our hope that this book will, therefore, be useful not only to students in liberal arts colleges who are not planning careers in science, but also to students who are going on in some field of science, especially those in the biological or medical fields.

"No man is an island to himself," and as Kekulé said, "We all stand on the shoulders of our predecessors." It is impossible to specifically acknowledge all of the help and assistance we received in the preparation of this book, but we want to mention some who have been of special help. Two of our colleagues, Dr. Johann Schulz and Dr. J. Keith Addy have kindly read portions of the manuscript and made suggestions. We also want to express our appreciation to Dr. Arthur Davidson, President of Wagner College, for a Summer Creativity

Grant to one of the authors, and for encouragement in this effort. Dr. Adolph Stern, as Dean of the College and as a friend and fellow chemist, has through the years been an inspiration and a help. We want especially to thank Mrs. Eleanor Sweatman for her patient and efficient typing of the various forms of the manuscript, and to Mr. Christopher Zazakos for his help with the drawings. We also want to acknowledge the support of the staff of the Charles E. Merrill Publishing Company; we are particularly indebted to Mr. Patrick Hearne, Science Editor, Professor Theodore Brown, Series Editor, and Miss Patricia Jayson and Miss Cynthia Meeks, Production Editors. Finally we want to express our thanks to our wives for their patience and encouragement during the preparation of the book. The analogue to the "golf widow" must be the "textbook-writer widow."

Suggestions and criticisms from teachers and students using the book will be appreciated.

W. P. Ferren
J. T. Jensen

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Table of Contents

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Chemistry and Matter

What Is Chemistry?

Your life started as the result of a series of chemical reactions. Your body is composed of chemical structures, small and large. Your existence from hour to hour depends upon the proper integration of a fantastically large number of complicated chemical reactions. Your death will return the chemical elements in your body to a cycle which will ultimately place some part of you in some other living form. The stuff from which you are made is the same (in part, possibly, the *very* same) chemical elements which were Julius Caesar or Cleopatra. You, in truth, *are* chemistry. You are the most important collection of chemical elements and reactions in the world. Every motion in your body, no matter how small, involves a series of complex chemical reactions. Every thought in your mind involves chemical and energy changes. In short, every part of your physical and mental being involves chemical reactions which are staggering in their complexities and inspiring in their beauty. The purpose of this book is to introduce you to the science of chemistry, to demonstrate the relevance of chemistry to your existence.

Chemistry may also be viewed as a collection of organized knowledge devised and conceived by human minds to interpret the world around us, or as something which existed prior to the appearance of mankind on this planet. In fact, the birth of chemistry may be thought of as having occurred when the energy of creation was converted to the simple entities of matter which we now call atoms. If we consider it to be organized knowledge, a simple workable definition of chemistry is as follows: chemistry is the study of the *properties* and *composition* of *matter*, and of the changes or transformations that matter undergoes. Let us attempt to obtain a clear concept of the precise meaning of the italicized terms in this definition.

Matter, in a common sense view, is something which occupies space. Certainly it seems self-evident that matter, whether it be an MG sports car or an eager young chemistry student, takes up space. The older view of matter was that it not only occupied space, but was also continuous. The modern view—one that makes *uncommon* sense—is that matter is something which is occupied chiefly *by* space. However, this change in viewpoint was slowly made after two thousand years and at the cost of the sacrifices and dedicated labors of numerous chemists. The modern or the atomistic view of matter we will reserve for future consideration.

Another definition that we can use is that matter is something which occupies space and has a certain mass. This is a more complete working definition.

In addition to having mass and occupying space, matter may be defined in terms of its internal mobility. We may think of a book or a chair as being a static entity, but just as a peaceful, quiet meadow is part of a planet undergoing numerous forms of rotational and translational or linear motion, so any matter has numerous complex internal motions.

The three states of matter—gaseous, liquid, and solid—differ in the amount of order and energy. This will be discussed in later chapters.

Composition is the arrangement of the ingredients of which matter is composed. Actually, the chemist uses the word composition in three ways. First of all, he may ask, "What are the ingredients?" Second, "What are the percentages of each component?" Third, he may ask how these components are arranged; that is, "Is it in a cubic, octahedral, or some other spatial arrangement?"

Properties are characteristics by which one kind of matter may be distinguished from or compared with other kinds of matter. Just as "five foot two, eyes of blue" describes a pretty girl in the song, so a chemical entity must be described in terms of some characteristics.

Properties may be either *physical* or *chemical* properties. Examples of physical properties are color, density, shape, taste, boiling point, freezing point, hardness, ductility, and physical state. Chemical properties are shown by the change in composition of a substance. For example, the tendency of a piece of wood to burn is a chemical property. That is, it has a tendency to undergo a certain chemical change. A chemical property is, therefore, a characteristic way in which the substance reacts with another substance.

Just as the American Revolution had Thomas Paine, so the chemical revolution had its champion and spokesman, Robert Boyle, whose credo was: "First to doubt, then to inquire, and then to discover." Other chemists in less enlightened lands found such a credo quite difficult to live with—for the year was 1661, and free inquiry was not in vogue throughout continental Europe.

Many of those who did pursue the scientific craft at this time were motivated by a desire to find eternal youth or to convert lead into gold. These people, called alchemists, were often so imbued with the mysticism of their time that any contribution they might have made to mankind was often limited. Compare, for example, the following two styles of writing. The first is an alchemist's recipe for preparing the philosopher's stone. The second is Robert Boyle's definition of the term *element.*

> You will separate the earth from the fire, the subtle from the compact, gently, with great skill. It ascends from earth to heaven, then descends again to earth, and receives the force of those above and those below . . . this is the strong strength of all strength, because it will overcome every subtle thing and penetrate every solid.

> The elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted.

The alchemist's recipe reflects his total commitment to the Aristotelian doctrine that matter was continuous and consisted of four elements—fire, earth, air, and water—and the quintescence, or spirit, of the matter. The preoccupation of those people who should have been chemists was to perform whatever mental gymnastics were necessary to make the facts suit the words. Happily for mankind, Robert Boyle placed the horse before the cart and gave us words to suit the facts.

The publication of Boyle's epic book, *The Skeptical Chymist*, in 1661, was probably the first example of the method of scientific inquiry. Boyle's work was a search for truth based on experimentation rather than the escape from truth into mysticism. Further, Boyle's definition of the word element, written in the seventeenth century, has a simplicity and clarity which permits the modern reader to understand and accept it as a meaningful definition. All we need add at this point is that *the atom is the smallest unit into which an element can be divided and still maintain its identity as an element.*

We may, therefore, return to our definition of the word *matter*, and in view of Boyle's statement classify matter as follows: matter is either a *mixture* or a *substance*. A *mixture* is matter which varies in homogeneity and composition. The word "homogeneous" means it is of the same composition, is uniform, throughout. The opposite of this is "heterogeneous." A *substance* is matter which is homogeneous and has an exact composition. A substance may either be an element or a compound. Boyle has defined the word element for us. A compound is merely two or more combined elements. These terms should extend our understanding of the word matter.

However, the fact that matter is mostly empty space is indeed a concept which involves a drastic reorientation of our everyday thinking. Ancient philosophers of the atomistic school led by Democritus (470–360 B.C.) thought of matter as consisting of simple, indivisible particles (atoms) floating about in a vast empty void. They visualized these atoms as having various sizes and shapes depending upon the kind of matter they constituted. Unfortunately, the opposing view of the Peripatetic school of thought led by Aristotle (384–322 B.C.) taught that all matter was continuous and therefore infinitely divisible. The Aristotelian view dominated and directed almost all further thinking until the clear voice of Boyle was heard in 1661.

The basic problem one faces here is to consider the old saying, "No matter how thin you slice it, it is still baloney." Now is this a valid statement? According to the Aristotelian dogma that matter can be divided an infinite number of times, one can go on slicing baloney forever. On the other hand, if you can accept the viewpoint that nothing can be subdivided indefinitely without at some point destroying the basic integrity of the substance, then the view of Aristotle becomes untenable. For example, let us consider a city having a population of two million people. Can we divide the human population of the city into two units? Of course. Each unit will then contain one million people. It is further possible to divide the city's population into units of thousands, hundreds, or tens, etc. However, we cannot divide the population into units of a billion without performing major surgery on the inhabitants of our hypothetical city. So it is with matter. A cube of copper may be divided and subdivided, but at some point it will become necessary to destroy that smallest subdivision, the individual copper atom.

An English schoolteacher, John Dalton (1766–1844), stated the atomistic view of matter in 1803. The major points of his theory are:

1. Each element is composed of very small, indestructible and indivisible particles called *atoms*.
2. The atoms of the same element have the same weight while those of different elements have different weights.
3. The union of a definite whole number of atoms is a compound.

The clarity of this statement and the endurance of its general propositions is similar to the statement of Boyle regarding the nature of the element. It must be remembered that it was not until the twentieth century that methods of instrumental analysis became available to verify this and other hypotheses.

The Scientific Process

We have already indicated that the method of scientific inquiry is based upon experimentation and that it attempts to suit theories to facts rather than facts to theories. Aristotle, as mentioned earlier, exerted great influence on philosophy for nearly 2000 years. Unfortunately, he did not believe that observations of nature could give the truth; he believed that it was only through the mind, through reasoning, that truth could be found. This view delayed the progress of science until the English philosopher, Francis Bacon (1561–1626), developed a plan of careful observation and experimentation in order to find the general relationships that might be present in a certain situation. He felt that if all possible experiments were made, the generalization would become apparent.

Bacon is usually credited with being the father of the so-called *scientific method*. This procedure was formally developed three hundred years later by the philosopher and educator, John Dewey (1859–1952). Dewey thought that, first of all, we must have a problem. Then, we must look for facts, for bits of information that seem to have some bearing on the problem. After a while, we seem to detect some pattern or trend in the information, and we can make up a *tentative hypothesis*, which we test by devising experiments that will either prove or disprove it. If we find after many tests that the results always agree with our hypothesis, we tend to accept that hypothesis, and to call it a theory, or, finally, a law. However, one negative case is enough to cause us to discard the hypothesis. Here we are at the heart of the scientific method: it is a deep respect for the facts. In science, we do not disregard or "brush under the rug" an unpleasant fact merely because it does not agree with our hypothesis. That would truly be placing the cart before the horse. Yet, this is what we often tend to do in everyday life. Science brings in the facts.

Another aspect of the scientific method is the use of *controlled* experiments. A controlled experiment is one in which all elements are kept constant except the one we are testing, which we call the independent variable. We then change the value of the independent variable to see what effect it has on the dependent variable. The control of variables is relatively easy in the physical sciences, but it is very difficult in areas such as psychology, education, and economics, where people are involved.

Scientific theories are often derived by the *inductive* method of reasoning. This means that a theory is built, proceeding from the specific facts to the general principle. Employing scientific principles, we often use the reverse, or *deductive*, method. The value of this is that in a new situation we do not have to experiment, try out what will happen, but can predict on the basis of the theory what should happen.

The scientific process has been a valuable tool in the development of knowledge about the physical universe. However, there has been a tendency to overemphasize the importance of the step-by-step procedure. Much of our knowledge has not come in an organized manner, but rather in flashes of insight, in "brainstorms," and in hunches. The free spirit of inquiry is a characteristic of science. It is a search for relationships among seemingly unrelated facts. It is a valuable method in the search for truth, but it is not the only one, and it is not infallible. A scientific "law" is not the final, ultimate answer, but the best explanation of the present facts, and it is open to revision as new information is found.

Science is built on sense perceptions, and only those phenomena that are observable can be used as facts in science. This does not mean that areas outside of science are not important. Quite the contrary. Our affections and sympathies, loves and hates, joys and sorrows are all very real and important to human life, but science, because of its selectivity, may not speak to these. The famous British astronomer, Arthur Eddington (1882–1944), has a good illustration of the selectivity of science:

> Let us suppose that an ichthyologist is exploring the life of the ocean. He casts a net into the water and brings up a fishy assortment. Surveying his catch he proceeds in the usual manner of a scientist to systematise what it reveals. He arrives at two generalisations.
>
> 1. No sea-creature is less than two inches long.
> 2. All sea-creatures have gills.
>
> These are both true of his catch, and he assumes tentatively that they will remain true however often he repeats it.
>
> . . . .
>
> In applying this analog, the catch stands for the body of knowledge which constitutes physical science, and the net for the sensory and intellectual equipment which we use in obtaining it. The casting of the net corresponds to observation: for knowledge which has not been or could not be obtained by observation is not admitted into physical science.
>
> An onlooker may object that the first generalisation is wrong. "There are plenty of sea-creatures under two inches long, only your net is not adapted to catch them." The ichthyologist dismisses the objection contemptuously. "Anything uncatchable by my net is *ipso facto* outside the scope of ichthyological knowledge, and is not part of the kingdom of fishes which has been defined as the theme of ichthyological knowledge. In short, what my net can't catch isn't fish."*

It is important to realize the limitations of science at the same time that we appreciate its value.

How Do We "See" Atoms?

No one has ever seen an atom. Then how do we have the temerity to give such detailed descriptions of atoms? Much of our knowledge is based upon indirect proof. We will see more of this in Chapter 4, but at this point, we shall take a look at what we call the "bear tracks."

Radiation from radioactive material cannot be seen, but we know that it exists because of the damage it sometimes does to living tissue, and because it blackens photographic film. We can also detect radiation by the use of the Wilson cloud chamber or the liquid helium bubble chamber. As the radiation goes through the chamber it causes ionization (removing electrons from neutral atoms and causing them to become charged), and wherever ionization occurs, in the case of the cloud chamber, condensation of the vapor takes place and we see droplets of liquid. Thus, the track is a series of droplets. These droplets

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**The Philosophy of Science* (New York: The Macmillan Company, 1939).

formed where condensation occurred, and this, in turn, was the result of ionization caused by the radiation.

Suppose that I came home from a hunting trip and told you about a large bear with brown fur and a fierce face, and then you discovered that I had never seen the bear, but only the bear tracks. Wouldn't you think that I had a great deal of imagination? Actually, scientists must be men of much imagination. The model of the atom is based upon such "bear tracks." The number of the particles, and their weight, speed, and life is deduced from these tracks. Some of them exist for less than a billionth of a second.

Scientists are popularly thought of as being coldly logical, devoid of whimsy, and lacking in esthetic sensibility; this is far from the truth. It takes a great deal of imagination to propose some new model of a structure or a mechanism. In fact, someone said that "common sense is the enemy of progress in science." Why? Because common sense is only what we are accustomed to. Much of what has been discovered on the microcosmic scale of the sub-atomic seems to contradict common sense and common science.

The word *serendipity* is often used to indicate the ability to make fortunate accidental discoveries. The word is based on Horace Walpole's story, *The Three Princes of Serendip* (Ceylon). The princes had an apparent aptitude for making valuable or agreeable discoveries accidentally. We should point out, however, that "success comes to the prepared mind," and that the scientists who make such "accidental" discoveries actually have to have a great deal of preparation in the field, in order to be able to recognize the importance of the event.

A classic example of this is the discovery of penicillin by Alexander Fleming in 1928, in London. He found that a mold growing in a germ culture seemed to stop the germs from growing. So he then grew this mold in some nutrient broth and found that it was effective in preventing the growth of disease-causing micro-organisms. Fleming's work is an outstanding example of how one scientist can *see* and grasp the significance of a phenomenon that numerous other scientists have only observed failed to appreciate.

SUMMARY

The science of chemistry has relevancy for all human beings in a very personal sense. This is true because every life begins, continues, and will ultimately cease as a result of numerous, complex chemical reactions. In considering matter, we must learn to look beyond the obvious continuous view as set forth in error by Aristotle, and to adopt the "atomistic" view. Chemistry is the study of the properties and composition of matter and its transformations. Matter has mass and occupies space. The universal law of gravitation states that all matter is attracted to itself in direct proportion to the masses involved and inversely with the square of the distance. A scientific theory is generally derived inductively and is used deductively.