GENERAL UNIVERSITY CHEMISTRY

VOLUME I

A Developmental Approach

SIDNEY GOLDEN

G E N E R A L   U N I V E R S I T Y   C H E M I S T R Y

A DEVELOPMENTAL APPROACH

Volume I

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Preface

This book, to the extent that it deals with the subject matter usually considered in a first-year chemistry course, is a textbook in General Chemistry. It provides an exposition that places primary emphasis on chemical facts, but one which makes full use of the physical ideas that have become increasingly incorporated into the subject and the mathematical language by which they are expressed. It is something more than a technical exposition, however, since it integrates the latter with a comprehensive and connected account of the historical background of modern chemistry—one designed to help its readers learn what chemistry is all about.

For this purpose, the topics that are considered, the treatments which are accorded them and the order in which they are presented all have been chosen so that they best reflect the fundamental developments which chemistry has undergone during the past two centuries. Involving some departure from convention, as a result, the topics are somewhat more numerous than those ordinarily dealt with in a first-year course and the treatments given them are more detailed than usual. The order in which the topics are presented, however, is a decidedly unconventional one.

With history serving as a guide, but not as a taskmaster, most topics occur in the book in an order that simulates the one in which they arose in the developing chemistry. Accordingly, how they are treated is largely determined by where they do occur in the book and by what chemical and physical principles have been established by then—or which may be inferred from the topic itself. For some topics, this means that little more can be done when they are first introduced other than to organize the relevant facts so as to raise questions which can be answered only in terms of material yet to be considered. The answers to such questions appear, in due course, later in the book. To the extent that readers of this book will become involved in these questions, and the answers which have been found for them, they will surely benefit from the experience. For then, their technical mastery of the subject will be augmented by an appreciable insight into the basis for our present knowledge of chemistry.

The book's unconventional topical order, from my own experience, is well suited to be used in an Advanced General Chemistry course. With a judicious balance of student-effort and teacher-demand, both the topics and their treatments can be covered properly in such a course—as I have, in my own.

In the first volume, the initial fourteen chapters of the book provide traditionally basic information about the macroscopic physical and chemical properties of materials and substances, as well as some of the simpler ideas which have been developed to account for them in atomic, ionic and molecular terms. These chapters supply the "raw material" with which a more fundamental microscopic treatment of chemical phenomena must be concerned. This treatment is given in the second volume, which consists of the final twelve chapters of the book. In addition to providing a fuller elaboration of some of the material considered earlier, it is in these chapters that the comprehensive correlating role of the Periodic System is developed and, where possible, exploited. With the Periodic System serving as the primary motivation, detailed attention is given here to atoms, ions and molecules and how their properties are determined and accounted for in terms of those of their constituent electrons and nuclei.

Each chapter of the book concludes with a section giving a number of queries, problems and exercises that have been devised to illustrate and illuminate its contents. Readers may find it to their benefit if, before beginning a given chapter, they examine the concluding section and the summary that precedes it. This can often give a good preview of the chapter's contents and objectives. Detailed responses to the queries, problems and exercises are all to be found in a separate companion volume to this book.

Throughout the writing of this book, I have been fortunate in having the help, support and encouragement of many people—colleagues, students and friends. I will not attempt here to list all of them by name; they each know the extent of their help and my thanks for having received it.

A few individuals warrant special mention, however. The confidence first expressed by Mr. G. F. McCauley in my being able to write the present book ensured my undertaking to do so. The suggestions of Professor R. Stevenson, of Brandeis University, and of Professor H. H. Patterson, of the University of Maine, coming early in the course of the writing, were of immense value to me in settling on the form of presentation used in the book. The beautifully executed typescript of Mrs. E. P. Goodwin, carried out with accuracy and dispatch, ultimately determined the present format of the book, to a far greater extent than was anticipated while it was being done. The constant encouragement given me by my wife, Muriel, not only made it possible for me to do the extensive writing and rewriting that this book entailed: it could not have been done without that.

To all these individuals I give my special thanks.

S.G.
Waltham, Mass.
February 1975

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GENERAL UNIVERSITY CHEMISTRY

Chapter I. Introduction

1. Chemistry: the name of the game.

In answer to the question: "What is Chemistry?", a variety of responses may be expected. Each will reflect the knowledge, experience and interest of the person giving it; many may be incomplete but not entirely incorrect. All the answers of those who are involved with the subject combine to give a good idea of what chemistry is: Chemistry is what Chemists do.

The last statement is useless as a "definition" of chemistry unless a person already happens to know what it is; if he does, the "definition" is unnecessary. The requisite knowledge, however, includes a variety of things that is truly enormous. Thus, there now exist reasonably distinct specialized fields of Analytical chemistry, Biological chemistry, Colloid chemistry,--- Metallurgical chemistry, Nuclear chemistry, Organic chemistry, Physical chemistry,---, to indicate only a few. Nevertheless, despite their differences, the various specialities have a basic approach that is common to all of them, which we shall emphasize in this book. Admittedly we shall not then know all of chemistry, but we will be able to have a reasonable knowledge of what chemistry is all about.

Chemists are concerned primarily with material substances from four basically different but related aspects. They are:

(1) Analytic: What a substance is and what are its characteristics and properties;

(2) Synthetic: How each particular substance may be prepared and under what conditions;

(3) Quantitative: How much can be prepared of various substances;

(4) Kinetic: How much time is required to prepare them.

Although no explicit mention of atoms or molecules is necessary to deal with these aspects, the most natural language at present makes extensive use of such terms and we shall do so in due course. Initially, however, the approach we shall take will be similar to learning a language—the language of chemistry.

There are many ways of learning a language. Perhaps the simplest is the way we learn our mother tongue: we grow up in its presence and learn it by continued exposure, by imitation, by making errors and correcting them, by association of various words with the objects of our experience. Learning a second language usually is more difficult: we usually cannot overcome the temptation to compare it with the first, even though differences between the two languages often may be irreconcilable. Nevertheless, the structure existing in one language can be useful in learning another, if only to emphasize the similarities and differences existing between them.

The parallel between learning a new language and the study of chemistry should not be overemphasized since there are obvious differences. First, chemical terminology—the analogue of vocabulary in a language—is extremely limited in its range of application. Second, the rules for relating chemical terms to one another—the analogue of grammar in a language—are not entirely a matter of prevailing taste and fashion; there are further restrictions. Third, existing languages develop and enlarge mainly by a process of invention of new words, phrases and constructions while, by contrast, the growth of a subject like chemistry depends primarily upon a process of discovery. These discoveries, in the past, have frequently required a complete revision of the language of chemistry used previously and a knowledge of them is essential for a proper understanding of present chemistry. Attention will be given to them throughout this book.

The prospect of discovery in chemistry warrants our maintaining an attitude of restraint regarding the range of validity of the subject, as we now know it. Such an attitude need not be so extreme that it totally undermines our confidence in what we learn. It can be valuable to the extent that a critical and questioning approach to the subject is stimulated by it. For then, the basis for the present form and structure of chemistry will be understood, as well as the changes it may undergo in the future.

2. Scientific Methodology

Chemistry is one of several subjects which comprise the Natural Sciences. Others include Astronomy, Biology, Geology and Physics. All the fields mentioned have mutual connections, but obvious differences make their distinction reasonable and convenient. They all exploit, and are restricted by, what is called the Scientific Method. Most persons already have some idea of what scientific methodology consists. A set of related statements that summarize it can easily be written down, but such a summary cannot convey properly how it is used by most practicing scientists in their investigations and studies. A somewhat better idea of what is involved can be gotten from the following.

Suppose that you—the reader—encounter some person. Ask the person to make an impersonal and declarative statement. Then, no matter what the statement may be (assuming, of course, that there is one), ask him: "How do you know that what you say is true?" Notice that the question being asked does not inquire into the truth of the statement; only the basis of judging its truth on the part of the person making it is involved. A variety of answers may be expected.

If the person happens to be a scientist, the answer might be something like: "I noticed that such-and-so occurred whenever this-and-that happened. It seemed to me that the observed behavior could be accounted for by the statement I have just made. To test this notion, I did the following things." At this point, the person would give a reasonably detailed description of the procedures employed. "After this, I saw that certain other things happened"—here again a detailed list would follow—"which could not have occurred if the statement I made to you were incorrect. Hence I believe the statement to be true."

Now, if the procedures described are repeated and the individual is a good scientist, you will undoubtedly see what he saw and come essentially to the same conclusion as he did. This result, basically, is the objective of the scientific methodology in current use.

However, suppose the person happens to be a poet. He might very well reply to your question: "How do I know that what I say is true? I feel it!" If he is a good poet, in all likelihood you will feel it also. Current scientific methodology sometimes acquires an esthetic character usually associated with poetry and art. The words are different, but the feelings they arouse are often the same.

Any impression that scientific methodology is not at all a rigid and exactingly difficult procedure is to be encouraged. What is involved is merely an interplay of three activities: (1) Observational, (2) Rational, and (3) Experimental.

Observation involves a use of the senses: sight, touch, hearing, etc. Assistance by various machines of one kind or another introduces no qualitative change.

Rationality involves thinking and reasoning. Here, also, assistance provided by mathematics, logic and analogy introduces no qualitative change.

Experiment is basically inventive in nature, and usually involves the manipulation of objects and materials in a predetermined manner.

The interplay of these activities can be represented by Fig. 1.1, in which the varying extents of overlap between the regions of the figure suggest that different amounts of interplay can occur between them.

Not each activity need be of equal importance at every stage in the development of a typical science. For example, astronomy has developed largely as the result of observation and reasoning; geology has been able to employ experiment to a limited extent; biology, chemistry and physics have developed as the result of having involved all three activities. At