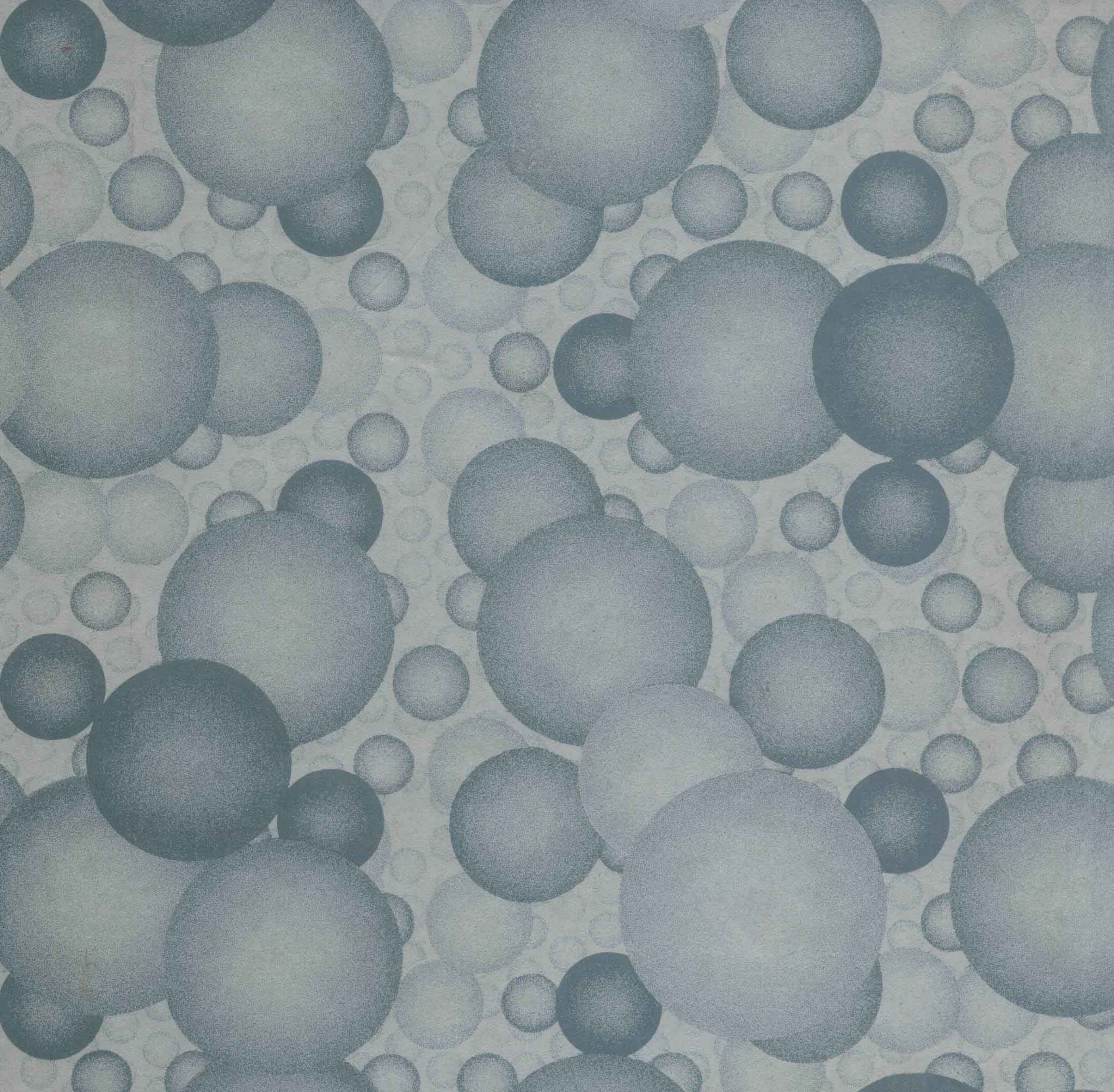
J.A. Campbell

CHEMISTRY: THE UNENDING FRONTIER



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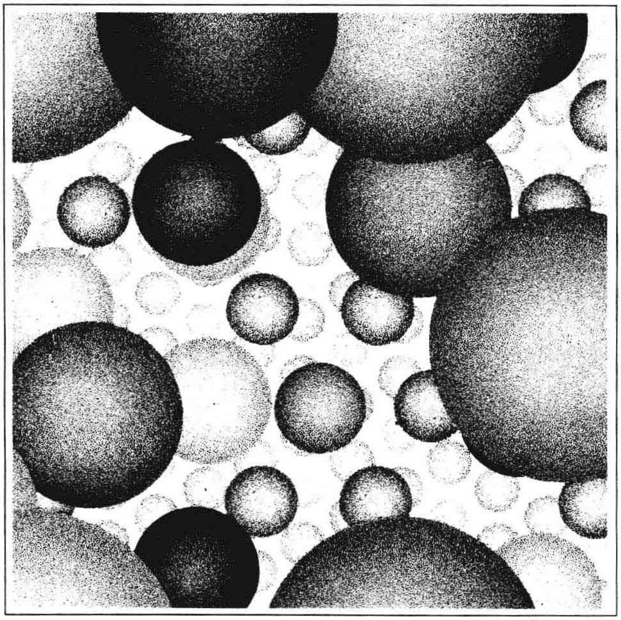

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The only persons free to choose
are those who know the choices.

The persons best prepared to choose
will know the likely outcomes.

PREFACE

Most chemistry students are not going to be chemists. This book is designed for them. My assumptions include the idea that such students wish to understand themselves and the world around them in terms of molecular behavior, a principal point of view in chemistry. My emphasis is on familiar, practical systems with interpretations in terms of clear, direct, and correct scientific ideas and experiments. Environmental and health questions are dealt with throughout the book. Those students who find chemistry attractive enough to wish further study should be able to continue in other courses. But they will need a higher level of mathematical background than is required here. This book requires no calculus and little algebra.

Most of this book follows a much-used sequence. It begins with atomic theory in the early chapters, followed by a discussion of the nucleus (Chapters 3 and 4), the periodic table (Chapter 5), and then proceeds through an introduction to chemical bonding, behavior of gases, rates and mechanisms of reaction, and chemical equilibrium, with separate chapters on general equilibrium and Le Châtelier's principle (Chapter 15), acids and bases (Chapter 16), redox (Chapter 17), solubility (Chapter 18), and thermodynamics—here optional as Chapter 19. The sequence continues with chapters on polymers (Chapter 21) and biochemistry (Chapters 22 and 23).

But, unlike most texts, I have no separate chapter on carbon (organic) chemistry, nor on the chemistry of any other element or group of elements. This material is introduced in contexts that involve knowledge already available to the student—contexts that encourage the development, correlation, and application of chemical ideas. For example, hydrocarbons are used to illustrate the unlimited number of possible chemical compounds (Chapter 8). The structure of graphite is used to introduce the alkenes and unsaturated ring compounds (Chapter 9), including delocalized electrons as contrasted to the localized electrons in diamond and alkenes. Functional groups (ether, ester, amine, amide, and so on) are introduced in terms of interesting compounds, not as a catalog in one place. Nomenclature of both inorganic and organic compounds is discussed as needed throughout the book, but the main ideas are tied together in Appendix B. References to particular ideas, types of compounds, or even individual compounds are readily available through use of the index.

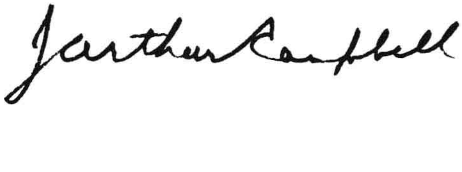
The periodic table is presented early (in both Chapters 1 and 5) as a valuable guide and aid in learning, understanding, and even predicting properties. The chemistry of the individual elements and their families is taken up as needed to provide emphasis and to supply useful, interesting, and long-lasting correlations with what the student already knows and what he or she is apt to meet in the future. For example, iron is discussed in terms of its preparation (as in the blast furnace, Chapter 6) and in terms of rusting (Chapters 14 and 17).

The book is a tapestry of many threads, but some are more continuous than others. Omission of some of the chapters causes little interruption in alternate study patterns. Furthermore, their deletion does not eliminate ideas fundamental or necessary to what follows. At worst, a few minor deletions might be required to bridge the thin places in the total web. The chapters designed for optional deletion are: 4, 11, 14, 21, and 23. If further pruning (for a one-term course, for example) is required, Chapters 6, 9, 12, 16, 17, 18, and 19 could be added to the list.

These chapters are neither dangling threads nor patches whose removal leads to a torn fabric. They are, rather, complements to the other chapters. They make the pattern richer in detail and fill in examples that enhance the overall design. Making these deletions would leave a one-term course providing excellent coverage of and insights into chemistry. And there would be ample additional material for those ever-present students who wish "more."

It is impossible to give individual credit to all who have been instrumental in exploring, selecting, winnowing, and polishing the ideas presented here. I would have to list all my teachers, students, and fellow authors whose questions, suggestions, and ideas have not only penetrated my senses but circulated in my brain. But three institutions merit special mention: Harvey Mudd College for providing an exceptionally stimulating atmosphere plus a sabbatical to tie things together, the Chinese University of Hong Kong for a perfect sabbatical site plus two fine typists (Grace Poon Suet Lin and Steven Chan Ping Chung, who deciphered my English hieroglyphics as well as they did Chinese ones), and the Rockefeller Foundation for three grandly effective weeks at the Villa Serbelloni. Finally, whereas copy editors can often be a nuisance to authors, I must cite Larry McCombs and Gloria Joyce as an exceptional pair. If you notice any expressions of which Mr. Fowler's *English Usage* would disapprove, please let me know. Please do! But rest assured that the editors have gone through the manuscript with great care, as have my much appreciated reviewers: James P. Birk, Daniel R. Decious, James E. Byrd, Charles H. Carlin, T. Cassen, John H. Harrison, Lawrence P. Elbin, Lavier J. Lokke, and Perry Reeves. Thanks once more to all of them.

May I wish you as much fun in the reading as I had in the writing.



J. Arthur Campbell
Harvey Mudd College, 1978

CONTENTS

To Mrs. Jimmy, who taught me most of what this book is about

Any chemicals here?

1 DIVE IN!

"Begin at the beginning." One difficulty in following this advice when writing a book is that every reader is different. Each one begins with a different background. You may know that there is a limited number of chemical elements and that these elements combine to form compounds. But some individuals do not know these things. You may know that ozone is made from oxygen, that gasoline is made up mostly of hydrocarbons, that combustion usually produces carbon dioxide, and that incomplete combustion yields carbon monoxide, a deadly poison to humans. You may have noticed the chemical names on bottles of vitamins—vitamin C is ascorbic acid, vitamin B_1 is thiamine, vitamin B_2 is riboflavin—and that an increasing number of foods bear labels identifying the chemicals in them. Then again you may not have noticed. Not every reader has the same background, nor does each one understand equally what the chemical words indicate.

When you look at Figure 1.1, you might see only a carefree diver. But, with a shift in viewpoint, you might describe the diver as wearing nylon shorts and leaping from a wooden board into water. You might even add that the liquid water is continuously evaporating into an atmosphere of nitrogen and oxygen, through which the gaseous water rises and later condenses into white clouds of water droplets. You might have learned that nylon is a synthetic polymer, and that wood is mainly cellulose—a polymeric carbohydrate, $C_n(H_2O)_m$. You might also know that water contains molecules of H_2O and that air is mainly molecules of N_2 and O_2 (nitrogen and oxygen respectively, each containing two atoms per molecule). But somewhere in this sequence your background—and your understanding—may have run out. Nor is this surprising; as you shall find, words and symbols used in chemistry are a very concise means of expressing a large number of experimental observations. They require care and precision in use.

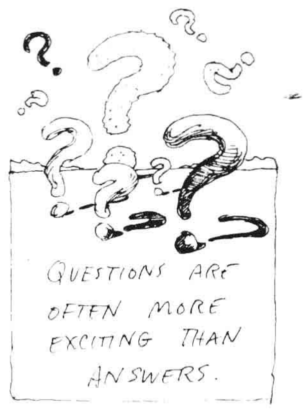
Because of these differences in background, I begin many chapters with questions and/or observations on widely known phenomena. I hope these beginnings will encourage you to search your background for some things you already know, things that will give you a frame of reference for reading and studying the chapter. You need not be able to answer the questions nor to recall all the observations mentioned. Each chapter will further develop the ideas involved.

Certain key ideas in each chapter are set out by colored type, forming a "microchapter" that gives a quick overview of the main ideas.

"Begin at the beginning," the King said, very gravely, "and go on till you come to the end: then stop."—*Lewis Carroll,* Through the Looking Glass.

POINT TO PONDER
Expressions like $C_n(H_2O)_m$ are called *chemical formulas.* C, H, and O are *symbols* used to represent carbon, hydrogen, and oxygen atoms, respectively. This symbolism is discussed in Chapter 2. See if you can understand some of the symbolism even before it is explained. But just ponder, don't fret!

Remember that the Points to Ponder are intended to provide opportunities for you to exercise your mind as creative scientists do. Treat them as puzzles or ideas to stretch your "mental muscles," ideas whose development will continue as you learn more and more about them. After all, solving puzzles and developing ideas can be exciting lifelong activities.



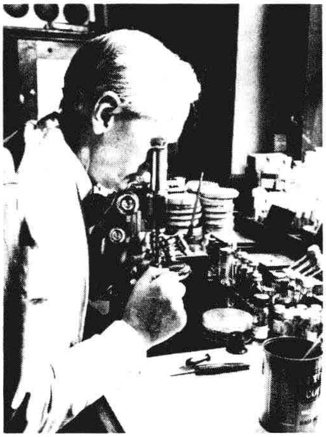


Figure 1.2
What do scientists do?
(The Bettmann Archive, Inc.)

I strongly encourage you to scan the section headings, the illustrations and tables, and the "microchapter" before starting to read the material intensively. You should next read the problems at the end of the chapter—again, before you read the chapter. The first problem provides a preview of the chapter in the form of a checklist of the new terms and equations presented. Later this checklist and the microchapter can be used for quick review and self-testing. You will probably be able to handle a few of the problems at once; the rest will give a framework for your reading.

So scan the headings, the illustrations and tables, and the microchapter; read the problems and try to think of some possible answers. Then read the text. As you do so, try the exercises in the margin. These exercises cover many of the more obvious objectives of the chapter. You should be able to work out many of them in your head.

The words, symbols, and ideas will sometimes come thick and fast, but I'll try not to drown you. In fact, the idea is to float, flow, and have fun. Dive in!

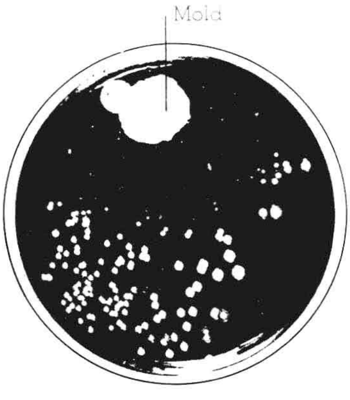
The White Coat Syndrome

What does Figure 1.2 suggest to you? Most likely the white coat is translated as "scientist," the background as "laboratory." You may envision a person remote from everyday life, engaged in difficult research—research that is unknown by and uninteresting to the general public. Or you may see a "mad scientist," a threat to the safety of humanity.

The man in Figure 1.2 is actually Alexander Fleming, one of the discoverers of penicillin. Born of a poor family, he became the winner of a Nobel Prize. It is true that Fleming, like most scientists, worked in a laboratory remote from public observation, and it is true that his projects interested few outside the laboratory. But occasionally something unexpected happens. Then a keen observer with a lively curiosity may see marvelous surprises unfold.

In Fleming's case, he noticed that one of his bacterial cultures failed to grow where it had become contaminated with a mold. By chance, Fleming's culture was next to a window (open by chance) through which blew a mold from the manure of the horse stables that were (by chance) across the street. Suppose the laboratory had been air-conditioned, hence had no open windows! Or suppose the city zoning laws had forbidden a stable there—the effect might never have been observed.

But chance favors the prepared mind. All the chances just mentioned could have remained just that—chance occurrences. But in this case, the result was noticed, recorded, pondered, further explored, and discussed with others by a person with a well-prepared mind. Even so, penicillin was not used for humans until 13 years after Fleming's initial



Why no bacteria near the mold?

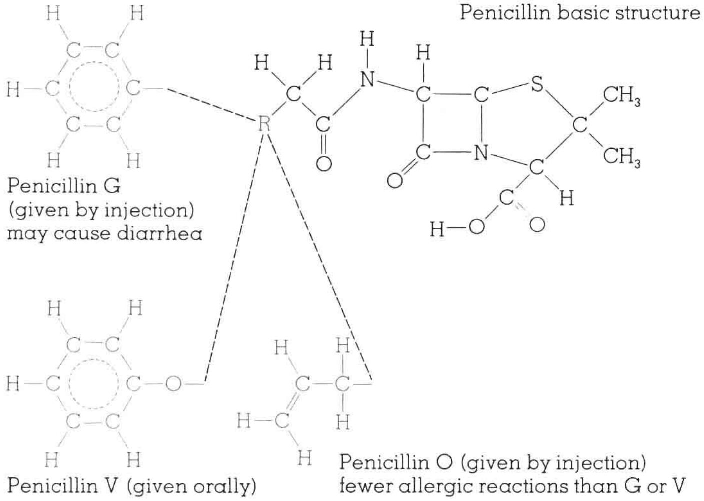


Figure 1.3
Some penicillins. All types of penicillin have the same basic formula, but each type has a unique R group.

discovery in 1928. Many scientists were involved in its development. It then proved so effective as an antibacterial drug that it was quickly added to the list of approved medical treatments. But there were still plenty of problems. My younger daughter, for instance, was placed in serious danger when the penicillin administered to her in 1946 proved to be from a faulty batch. At that time, the chemistry of penicillin was not understood; it could be synthesized only by molds. Its structure was unknown until 1949, when Dorothy Hodgkins determined it.

Once the structure was known, modifications were synthesized, so that there are now many varieties of penicillin. The physician can now match drug to patient to maximize effectiveness and minimize bad side reactions. Much of the drug's detailed chemistry is also understood. We now know that its principal effect is to interfere with the chemical synthesis of bacterial cell walls. Figure 1.3 lists structural formulas for some of the penicillins.

Yet penicillin is still dangerous. Every year several hundred persons who have unusual body chemistries are killed by careless dosage with penicillin. All discoveries by those in "white coats" are both potentially good and potentially bad.

Every chemical—whether called food, medicine, drug, or whatever—is fatal if taken internally by humans in large enough doses. Yet many chemicals are most helpful in moderate amounts, and some are essential if life is to survive. Paracelsus, in the sixteenth century, put it well: "Poisoning is not a matter of chemicals, it is a matter of dose size." This statement has not been contradicted by discoveries made since Paracelsus' time.

POINT TO PONDER
Alexander Fleming once saved another youth from drowning. The youth's family responded by paying for Fleming's education. Some 50 years later, Fleming's penicillin saved the same individual from dying of pneumonia. That man was Winston Churchill, only one of untold millions whose lives Fleming extended. Quite a return on providing for one education!

POINT TO PONDER
There are no good chemicals and there are no bad chemicals. There *are* good and bad uses. And their "goodness" and "badness" may vary from individual to individual.