CHEMISTRY: PRINCIPLES AND APPLICATIONS

Sienko / Plane

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CHEMISTRY: Principles and Applications

A major revision and reorganization of *Chemical Principles and Properties*.

PREFACE

In preparing this edition, we came to the conclusion that a new title was necessary to emphasize that this is a major reorganization and revision of *Chemical Principles and Properties*. So, we have chosen the title *Chemistry: Principles and Applications*.

Unlike preceding editions, which assumed that high school chemistry courses would become more mathematical and more abstract with time, this edition recognizes that present-day college students need more help than ever to cope with both the theoretical and experimental sides of freshman chemistry. As a result, there has been a major recasting of our approach. Although the basic sequence of topics—atoms to molecules to more complex systems—is retained, the development is more gradual and starts with a broader base. We begin in Chapter 1 with a description of what chemistry is and what vocabulary and notation are associated with it. Then, in Chapter 2, we move on to stoichiometry, partly to increase students' abilities to handle chemical notation and partly to allow instructors to begin meaningful related laboratory work early in the course. Chapter 3 provides an overview of some descriptive chemistry based on the periodic table. This sets the stage for Chapters 4 and 5, where we start to examine the details of atomic structure, the nature of molecules, and chemical bonding. From these chapters, the student should develop sufficient ease in handling the ideas of molecular shapes and molecular reactivity to go rather extensively into states of matter, solutions, solution reactions, kinetics, and equilibrium (Chapters 6 to 15). Chemical thermodynamics is introduced in Chapter 10, considerably later than before, and used subsequently to tie in with electrochemistry (Chapter 11) and equilibrium (Chapter 13). Chemical equilibrium is handled in two chapters. First, Chapter 13 develops the basic ideas of equilibria using gaseous systems. Chapter 14, devoted to the chemistry of hydrogen, oxygen, and water, provides a bridge to Chapter 15, where we undertake a consideration of the more complex equilibria in aqueous solutions. In Chapter 16 we return to take a harder look at the problem of describing electrons in atoms and molecules, first explored in Chapter 5.

There has been considerable revision of the descriptive chemistry that constituted Part II of the second edition. Some has been brought forward and integrated with the discussion of chemical principles; some, particularly

that of the less common elements, has been omitted entirely; the rest has been rearranged to make a more practical, coherent package. The typical metals are discussed in Chapter 17; the transition metals, in Chapters 18 and 19; and the nonmetals, in Chapter 21. The material on carbon, Chapter 20, has been expanded to give a better idea of the scope of organic chemistry: We have more on organic functional groups, more on mechanisms of reaction, and new material on carbohydrates, proteins, and nucleic acids.

Freshman chemistry texts tend to add or expand topics without dropping any. In this edition, pruning has been necessary to keep the depth and breadth of coverage manageable. Although new subjects have been added, such as valence-shell–electron-pair repulsion (Chapter 5), osmotic pressure (Chapter 8), photoelectrolysis (Chapter 11), polymers (Chapter 20), and applications of radioactivity (Chapter 22), a page has been deleted for each one added.

The number of worked-out problems has been increased, and they have been tied more closely to the development in the text. The exercises at the ends of chapters—more than 900 of them at varying levels of difficulty—are all new. As in the second edition, asterisks are used to designate the level of difficulty: easy*, moderate**, hard***. The relative number of one-asterisk problems has been increased, and the relative number of three-asterisk problems has been reduced. Answers to some of the exercises have been included. The remaining answers as well as worked-out solutions are included in a *Student/Instructor Solution Supplement* available from the publisher.

This book is designed for careful study, and a student who makes such effort will be repaid with a comprehensive grasp of chemistry. The book is intended for college students who have had one year of high school chemistry. A knowledge of calculus is not assumed, and none is used. The text is designed mainly for those interested in science or science-related subjects. It is directed toward premedical students, engineers, students of agriculture and biological science, and all those who may have a need for knowledge of chemistry in their careers. It can also be used by students majoring in chemistry.

For students whose high school chemistry preparation is not strong or who simply wish to refresh their memories or review material covered in this text, a *Study Guide* is available from the publisher. It includes a complete glossary of the key terms and concepts, skills to master, step-by-step worked problems covering the skills, and chapter self-tests.

For the preparation of this edition, we wish to express our deep appreciation to reviewers David L. Adams, Robert C. Atkins, Jon M. Bellama, Ellen A. Keiter, and Fred H. Redmore for their perceptive criticism; to the McGraw-Hill staff for their help and guidance; to Ann Lemley for checking the problems; and especially to Christina Fuiman for expertly and cheerfully working her way through typescripts of the several versions that ended up as the chapters that follow.

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Chapter 1

CHEMISTRY AND CHEMICAL NOMENCLATURE

In the irrigation ditches of North Africa and the jungle swamps of Brazil lives a fresh-water snail that is the intermediate host for a debilitating human parasite, the schistosome, or blood-fluke. The disease that results, *schistosomiasis,* is widespread throughout Africa and Brazil. It takes a fearful economic toll because it drains all a person's energy so that just living becomes an ultimate chore. How can this disease be cured? Early diagnosis is important. Chemotherapy, the treatment of disease by chemical agents, has been somewhat effective, but the compounds used, such as those of the element antimony, are exceedingly toxic, and there are frequently unwanted side effects. One of the desperate calls currently sounded by the World Health Organization is for a systematic search for a cure to this disease. Specifically, what is needed is a replacement of older, dangerous drugs by a safe, effective remedy.

On the other side of the world, in the sunlit deserts of Arizona, experts gather for a symposium to discuss the utilization of solar energy. We all know that the time of fossil fuels, petroleum and natural gas, is running out. New sources of energy have to be developed. Can we perhaps design an electrochemical cell that will directly use solar energy to split water into its component elements, hydrogen and oxygen, and thus provide the cleanest fuel of all, hydrogen? What materials might be used? What new compounds should be invented to exploit this mode of energy conversion and make it most efficient?

These are but two of the problems that chemistry is currently involved in. They may appear to be very far from questions such as why the bond angle in the water molecule is only 104.5° or why potassium chloride spontaneously dissolves in water even though the process is energetically unfavorable, but the experience of the past tells us that knowledge of fundamentals is generally the key to successful solution of an applied problem.

In this chapter we concern ourselves with an introduction to the language of chemistry. We will need it before undertaking the systematic study of chemistry in later chapters. Precision in language is a distinctive feature of science. Although much of the material in these sections will be familiar to most readers, importance of its mastery cannot be overemphasized.

1.1
CHEMISTRY

Chemistry concerns itself with the composition of matter, the changes that matter undergoes, and the relation between changes in composition and changes in energy. The scope of the subject is vast, as vast as the universe.

Astrochemistry relies for its information about the composition of the stars on analysis of the radiation that comes to us through space and time. Even for the closest star, the sun, it takes 8 min for the information to reach us. What

changes have occurred in those 8 min? How much greater are the changes for the next closest star where it takes 4 years for the light to reach us? How much do we really know at the present time about other stars, so far distant that light, traveling at its constant speed of 3×10^{10} cm/sec through the centuries, has barely had time to reach us? Let us confine our study of chemistry to the earth.

Geochemistry concerns itself with the composition of the earth. Much can be learned by gathering pebbles on the surface of the earth and analyzing them for chemical content, but what about the earth's interior? Most people believe that the core, almost as inaccessible as the farthest star, is composed of iron and nickel. How do we know? We get information indirectly. We observe echo waves of earthquakes that pass through the earth's interior; we observe the behavior of liquid iron and nickel in the laboratory; we calculate how properties are affected by the enormous pressures under the earth's surface. We proceed indirectly, and eventually we are led to a belief that we all accept because our hypothesis, our suggested assumption, turns out to predict so many things that are consistent with observation.

This is generally the way science proceeds—collection of facts, interpretation of facts in terms of a proposed model, and then acceptance of the model as "fact." Few of us realize how great a portion of our thinking is not really fact but only a model that was suggested to explain some facts. Consider the atom. For most chemists, it is a real entity that is the building block of all materials. Yet no one has ever seen an atom. Even the most sophisticated, modern, high-resolution electron microscope gives only indirect evidence of an atom's existence. Why then do we have so much faith in it? The answer is that the body of knowledge we can account for is so vast and so elegantly simplified by thinking in terms of atoms that we accept the atom as a physical actuality.

Chemistry is traditionally divided into four broad areas: analytical, physical, organic, and inorganic. *Analytical chemistry* emphasizes the techniques that are used to find out about the composition of matter: What are the atoms that make up a given substance? How are they arranged in clusters? What is their relative arrangement in space? *Physical chemistry* is concerned rather with the general laws that govern the behavior of all matter: What governs the particular arrangements of atoms in space? How do these generally change with time? What are the great driving forces that generate the particular material or combination of materials that we have at hand? *Organic chemistry* is special only in that it concentrates on the compounds of the element carbon. *Inorganic chemistry* has for its province the compounds of all the other 100 or so elements.

When chemistry started some 500 years ago in the dim mysterious reaches of alchemy, it was primarily an experimental science. Main interest then was in discovering new recipes: How to extract metals from the earth; how to make medicines from plants; how to convert lead into gold. As the recipes patiently accumulated, chemistry became more abstract. Venturesome thinkers wondered why certain general patterns of observation existed and began to create models of the underlying structure. At present,

chemistry stands on the scale of abstraction about midway between biology and physics. It shares with biology the need to systematize an extraordinarily large body of observations on complex systems. It shares with physics the effort to explain observed laws of behavior in terms of a few principles applied to simple particles.

Recently, as with most sciences, chemistry has spread out to overlap neighboring disciplines and thereby produce challenging new areas of interdisciplinary study. *Biochemistry,* concerned with the chemical reactions that occur in living tissues, came from a fusion of biology and chemistry; it has long been recognized as an important adjunct for the study of medicine. *Molecular biology,* which is closely related to biochemistry, concentrates on biological events such as growth and reproduction in terms of molecules in the cell; it came from a fusion of biochemistry and genetics. It is particularly concerned with the replication of giant molecules (macromolecules) in living systems. Toward the other end of the scale of abstraction lies *theoretical chemistry,* where generalized statements of chemical phenomena are subjected to the most powerful methods of mathematics for rigorous solution. Because mathematics is highly abstract and divorces itself from specific materials or reactions, it is capable of giving great insight for predicting the general behavior of chemical substances. On a more practical side, chemistry has merged with engineering to give, for example, *chemical engineering;* it concentrates on the problem of translating a basic discovery in a research laboratory into plant production of a real product in a real economic world. Another example is *materials engineering,* where synthetic and analytical aspects of chemistry have been applied to understand why there are limits to desirable properties in specific materials and thereby lay the basis for rational improvement of these properties. Noteworthy also is a relatively new but rapidly growing field, *solid-state chemistry;* it straddles chemistry and physics and addresses itself to the problem of how physical properties, i.e., those that can be described without reference to interaction with other substances (e.g., electric conductivity), are related to composition and arrangement of atoms in the solid state.

All these interdisciplinary fields have one thing in common. They demand equally comprehensive knowledge of the two disciplines that are being merged. For basis, they all go back to chemistry. The fact that schools of agriculture, medicine, life sciences, engineering, etc., all require knowledge of chemistry underlines its widespread importance.

1.2
ELEMENTS, COMPOUNDS, SOLUTIONS, AND PHASES

One of the most promising areas of current technological research is the development of *composite materials.* These are usually made as mixtures of materials in which a binder, e.g., epoxy resin, has some type of reinforcement, e.g., boron fibers, dispersed through it. The goal is to optimize combinations of high strength, high stiffness, and light weight that are required for applications such as rocket-motor casings and structural components of aircraft. Clearly the properties of a composite are a complex blend of the properties of

binder, fibers, and interfacial surface between the two. One can well imagine how difficult it would be to work back from the observed properties of the mixture to deduce the properties of pure boron alone. Yet this is the problem constantly faced in chemistry. We make a new compound; we wish to catalog its properties. How do we know we have a pure compound? How do we know the properties we are measuring are not due to an impurity or, worse yet, to some cooperative effect in which impurity and compound work together to produce an observed effect? The constant fussing of the chemist to establish clearly the distinction between *mixture, compound,* and *phase* stems from a desire to avoid such traps.

First, let us get together on some fundamental terms. *Matter* is anything that has mass and occupies space. It can occur in any of three states: solid, liquid, or gas. The *solid state* is characterized by retention of shape, of form, and of volume, no matter what the shape of the container. The *liquid state* retains volume when a sample is transferred from container to container, but the shape of the sample adjusts itself to take on the shape of the bottom of the container in which the sample is confined. The *gas state* is characterized by retention of neither shape nor volume since the sample expands to fill any container accessible to it. As an example of the foregoing, water is a sample of matter. In the solid state, it exists as *ice;* in the liquid state, as *liquid water;* in the gaseous state, as *water vapor.* Note that, in describing the gaseous state of water, we have not said steam. The reason for this is that the term "steam" is ambiguous. Sometimes it is used to refer to the invisible vapor into which water is converted when heated to the boiling point; more often it is used to describe the visible mist formed by condensation on cooling of water vapor (as at the spout of a teakettle). When terms are ambiguous, it is better to avoid them unless the meaning is not critical.

By *element* we mean one of the 100 or so fundamental chemical substances, composed of atoms of only one kind, into which all matter can be resolved. By *compound* we mean a complex substance, composed of two or more elements, which has the property that no change in composition (i.e., no change in the percent of the different elements) occurs when a sample is partly put through a change of state. Why do we include the restriction as to change of state? Why make such an involved definition? It is necessary if we want to make a clear distinction between a *compound* and a *solution.* Some people differentiate the two by saying *a compound has a fixed composition,* whereas *the composition of a solution is variable.* It is important to note that "fixed" and "variable" are being used here in two contexts: going from sample to sample and going from one state of matter to another. The latter is the more significant. Given a single sample of a compound and a single sample of a solution, both will have fixed compositions. The compound, however, will not change in percent composition when the sample is partly put through a change of state; the solution will. As a specific illustration, when a sample of pure liquid water is partly boiled, the vapor (gas) that is formed consists of 11% by weight hydrogen and 89% by weight oxygen just as does the starting liquid water; this is typical of a compound's behavior. On the contrary, if a 10% salt-90% water solution is partially boiled, the gaseous substance that first forms is practically

pure water; i.e., it is much richer in the water component than is the starting water-salt solution. *This is typical of a solution's behavior. When a solution starts to go through a change of state, one of the components of the solution generally tends to separate out more than the other.*

Another useful but sometimes confused term is *phase*. It applies to the region (or regions) of a sample characterized by the same set of properties. As a simple example we can consider several ice cubes floating in liquid water. All the ice cubes taken together represent the ice phase; all the liquid water represents another phase. This is a two-phase system, no matter what the relative amounts of ice and liquid water are. The distinctive feature about a phase is that properties change when one crosses a *phase boundary*, i.e., when one goes out from one phase into another. Thus, for example, in going from the ice phase into the liquid-water phase there is a change in density from 0.9 g/cm^3 (gram per cubic centimeter) to 1.0 g/cm^3. Confusion in the use of the word *phase* comes from the fact that occasionally the word *phase* can be substituted for the word *compound* without saying anything wrong. For instance, when a solution of sodium chloride dissolved in water is mixed with a solution of silver nitrate in water, the *compound* that separates out as a white precipitate is silver chloride. One could equally well say the *phase* that separates out is silver chloride. In the former case, the emphasis is on formation of a complex material composed of the elements silver and chlorine; in the latter, emphasis is on a new region that has appeared in which properties are different from those in the starting system.

1.3
SYMBOLS AND FORMULAS

The chemical elements are generally represented by *symbols*, such as H for hydrogen and O for oxygen. A symbol represents not only an element in general but also a specific amount of that element, either one atom or, as described in the next chapter, a standard large number (6 × 10^{23}) of such atoms. The latter is called a *mole* of atoms. Thus, N stands for nitrogen, one atom of nitrogen, and also for 1 mol of nitrogen atoms.

In many cases the symbol for an element is just the capitalized first letter of the name, for example, P for phosphorus. If several elements have the same initial letter, a second small letter may be included in the symbol, for example, Pt for platinum, Pu for plutonium. In some cases, particularly for elements known since antiquity, the symbols are derived from Latin names, for example, Ag for silver from *argentum*, Au for gold from *aurum*, Cu for copper from *cuprum*, Fe for iron from *ferrum*. A complete list of element names and symbols is given on the inside back cover of this book.

Chemical compounds are represented by *formulas*, such as H$_2$O, which are combinations of the symbols of the constituent elements. The subscript numbers, 2 for H and 1 (understood) for O, designate the relative numbers of atoms of the different kinds. Again the formula does triple duty: It represents the compound in general, it represents 1 formula-unit of the compound

(a formula-unit is the set of atoms shown by the subscripts in the formula), and it represents a standard large number (6×10^{23}) of such formula-units. The term *mole* is used for 6×10^{23} formula-units. Thus, H_2O stands for water, 1 formula-unit of water, and also for 1 mol of water. In some cases, as with water, the formula-unit exists as a separate discrete entity, in which case it may be called a *molecule*. In other cases, as with SiO_2, there is no simple molecule and only the ratio of atoms is indicated.

Chemical formulas are usually determined from experimental analysis of a compound to determine what atoms make up the compound and how the atoms are connected. One technique, which is discussed in more detail in Sec. 2.3, uses weight relations in chemical reactions to fix the ratio of the number of atoms of each kind. This gives us what is called the *empirical formula,* or the *simplest formula;* it tells nothing about how the atoms are joined together. Another technique, which is particularly applicable to organic compounds, is to break the compound apart and analyze for the masses of the various fragments. Computer analysis of the fragments can often tell us which atoms are connected to which and how many atoms of each kind there are in the molecule. The term *molecule* is used to designate the discrete unit which includes all the atoms that are strongly joined together. Thus, we can get not only the *molecular formula* but also some idea of the specific atomic groupings that occur in the molecule. Common groupings that we will frequently encounter are hydroxyl (OH), methyl (CH_3), and ethyl (C_2H_5). The compound methyl alcohol shows the groupings CH_3 and OH and is usually written CH_3OH. There are various other techniques for finding out which atoms are connected to which and how they are arranged in space, but we shall postpone consideration of them until after we have developed more background information.

Names of chemical compounds are usually described as being trivial or systematic. *Trivial names,* such as wood alcohol for CH_3OH, are like nicknames; they generally reflect some characteristic of the compound, and having grown to be accepted through repeated usage, they are likely to be commonly used in informal conversation. Thus, the name "wood alcohol" for CH_3OH reflects the fact that the compound was originally obtained by destructive distillation of wood, i.e., by heating wood in a closed container and collecting the volatile products of the decomposition. *Systematic names,* as the term implies, are more formal; they generally reflect the classification of the compound and often tell something about the atomic arrangement. For example, CH_3OH is called *methanol.* The ending *-ol* indicates that the compound is classified as an alcohol (characterized by OH groups attached to C). The root *methan-* is derived from the parent compound methane, CH_4. Another systematic name for CH_3OH would be hydroxymethane, emphasizing that CH_3OH is derived from CH_4 by replacing an OH group for one of the H's.

The rules for giving systematic names of organic compounds are rather involved, because there are over a million such compounds and it requires some care to spell out the rules so as to cover all possibilities. A brief summary of the rules is given in Appendix A2.2.

Systematic naming of inorganic compounds is a bit simpler. A summary

of the rules is given in Appendix A2.1. Here we simply mention a few of the rules that will be most useful for the early part of this book. Compounds composed of but two elements have names derived directly from the elements, with the second element generally given an *-ide* ending. Thus, CaO, for which the trivial name is *lime*, is called calcium oxide. If we want to emphasize the number of atoms of a given element, prefixes such as *mono* (for 1), *di* (for 2), *tri* (for 3), *tetra* (for 4), *penta* (for 5), and *hexa* (for 6) can be used to precede the name of the element. Thus, carbon monoxide (CO) is distinguished from carbon dioxide (CO_2).

Compounds containing more than two elements are usually named to reflect classification of the compound as an acid, a base, or a salt, or to emphasize certain characteristic groupings that commonly occur. We shall discuss acids, bases, and salts in considerable detail later in this text, but here we give a few preliminary definitions. *Acids* are a class of substances that have the following characteristic properties: (1) sour taste, (2) ability to turn litmus red, (3) ability to react with most metals to liberate hydrogen, and (4) ability to neutralize, or destroy, bases. *Bases* are substances that have the following properties: (1) bitter taste, (2) ability to turn litmus blue, and (3) ability to neutralize acids. *Salts* are the products of neutralization reactions between acids and bases. Two hundred years ago, the French chemist Lavoisier suggested that to have acid properties, a compound needs to contain oxygen. A hundred years later, the Swedish chemist Arrhenius argued that to have acid properties, a compound needs to contain hydrogen. The Arrhenius view is more in keeping with modern ideas. However, as we shall see later, it will need to be broadened considerably. In the Arrhenius view, acid properties are attributable to the presence of an easily detachable hydrogen ion, H^+. The superscript + indicates the electric charge of the particle, and the word *ion* describes in general any grouping of one or more atoms that carries a charge. The formulas of acids are generally written to show the detachable hydrogen first. Thus, as common examples we have the following:

HCl	hydrochloric acid, or hydrogen chloride
HNO_3	nitric acid, or hydrogen nitrate
H_2SO_4	sulfuric acid, or dihydrogen sulfate
H_3PO_4	phosphoric acid, or trihydrogen phosphate
$HC_2H_3O_2$	acetic acid, or hydrogen acetate

The first of the names are trivial names; the second, systematic. The systematic names illustrate the special names that go with certain characteristic groupings: nitrate for NO_3^-, sulfate for SO_4^{2-}, phosphate for PO_4^{3-}, and acetate for $C_2H_3O_2^-$.

Bases can be interpreted as owing their characteristic properties to action of the hydroxide ion OH^-. Typical bases are:

NaOH	sodium hydroxide
$Ca(OH)_2$	calcium hydroxide

When an acid such as HCl neutralizes a base such as NaOH, it is believed that the H^+ of the acid combines with the OH^- of the base to form the compound HOH, that is, water. If the water is now boiled off, the Na^+ of the base and the Cl^- of the acid are left to combine with each other as the salt sodium chloride, NaCl. The formulas of salts are generally written with the residue from the parent base first and the residue from the parent acid second. The systematic name is then simply the combination of the names of the two groupings. As a further example, neutralization of H_2SO_4 by NaOH produces the salt Na_2SO_4, for which the name is sodium sulfate.

1.4
CHEMICAL REACTIONS AND CHEMICAL EQUATIONS

The simplest kind of chemical reaction is one in which one chemical element combines with another chemical element to form a compound. In shorthand form, this is usually written as a *chemical equation,* which is simply a symbolic statement of observed chemical facts. As an example, let us consider the reaction of the element zinc with the element sulfur to produce the compound zinc sulfide. We write this as

$$Zn + S \longrightarrow ZnS$$

where the arrow is read as "reacts to give." The symbols $Zn + S$ to the left of the arrow represent *reactants,* i.e., starting materials; the formula ZnS to the right of the arrow represents the *product.* If the direction of the arrow were reversed, the role of starting reactants and final products would be interchanged. Specifically,

$$Zn + S \longleftarrow ZnS$$

stands for a chemical reaction in which the starting material ZnS is decomposed (broken down) into constituent elements Zn and S.

To be valid, a chemical equation needs to satisfy two conditions: It must be consistent with the observed facts, and it must be balanced. The word "balanced" means that atoms must be conserved in a chemical reaction; i.e., each atom on the left side of a chemical equation must also show up on the right side of the equation.

There are systematic ways to go about balancing a chemical equation which we shall consider in later chapters, but the essence of the procedure is to adjust the coefficients of the equation (the numbers that go in front of each symbol and each formula) to ensure that all the atoms are accounted for. It should be emphasized that the *subscripts* in a formula cannot be changed to achieve balance, because that would imply a different chemical species.

Suppose, for example, we are asked to write a balanced equation for the reaction of calcium (Ca) with oxygen (O_2) to form calcium oxide (CaO). We first write

Step (1) $\qquad ?Ca + ?O_2 \longrightarrow ?CaO$