CHEMISTRY FOR ENVIRONMENTAL ENGINEERING

Third Edition

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PREFACE

Education in environmental engineering is usually conducted at the graduate level, and up to the present time has drawn mainly on students with a civil engineering background. In general, civil engineering training does not prepare a student well in chemistry and biology. Since a knowledge of these sciences is vital to the environmental engineer, the graduate program must be designed to correct this deficiency. In recent years students from other engineering disciplines and from the natural sciences have been attracted to this field. Some have a deficiency in chemistry and biology similar to that of the civil engineer and need an exposure to general concepts of importance.

This book is written to serve as a textbook for a first course in chemistry for environmental engineering students with one year of college-level chemistry. Environmental engineers need a wide background in chemistry, and in recognition of this need, the book summarizes the important aspects from various areas of chemistry. This treatment should help orient the students' thinking, aid them in their choice of areas for advanced study, and help them develop a better concept of what they should expect to derive from further study.

The purpose of this book is twofold: (1) It attempts to bring into focus those aspects of chemistry which are particularly valuable to environmental engineering practice, and (2) it attempts to lay a groundwork of understanding in the area of specialized quantitative analysis, commonly referred to as water and wastewater analysis, that will serve the student as a basis in all the common phases of environmental engineering practice and research.

Substantial changes continue to occur in the emphasis of courses for environmental engineers. The trend is toward a more fundamental understanding of the chemical phenomena causing changes in the quality of natural waters and of water undergoing treatment. In addition, emphasis is being directed toward more advanced methods of analysis, which are required to help solve many of the complex modern problems facing the environmental engineer.

This new edition is organized to better meet the current needs. Part One is concerned solely with fundamentals of chemistry for engineers. It includes chapters on general chemistry, organic chemistry, physical chemistry, colloid chemistry, biochemistry, and nuclear chemistry, and a new chapter on equilibrium chemistry. Each gives emphasis to environmental engineering applications. Many schools offer a lecture course on chemical principles, and it is felt that the revisions in Part One make the text more suitable for this purpose.

All chapters concerned with analytical measurements are now together in Part Two of the book. The first several chapters here contain general information on quantitative, qualitative, and instrumental methods of analysis, which can be used as background material for the subsequent chapters concerned with water and wastewater analyses of particular value to environmental engineers. These chapters are written to stress the basic chemistry of each analysis and to point out their significance in environmental engineering practice. They should be particularly useful when employed with "Standard Methods for the Examination of Water and Wastewater," published by the American Public Health Association, which gives the details for carrying out each analytical determination. Part Two is considered to be most useful as lecture material to be utilized along with a laboratory course on water and wastewater analysis.

Problems are included at the end of most chapters to stress fundamentals and to increase the usefulness of this book as a classroom text. Example problems are also given throughout the text to help increase the students' understanding of the principles outlined. In the first portion of the text, where the emphasis is on chemical fundamentals, answers are included after many of the problems to allow students to evaluate independently their understanding of the principles emphasized.

In order to meet the requirements of a textbook, brevity has been an important consideration throughout. For those who believe that we have been too brief, we can only beg their indulgence and recommend that they seek further information in standard references on the subject. References of particular value are listed at the end of each chapter in the first portion of the book.

We wish to continue to express our thanks to Dr. Wertheim for his permission to use certain material from the book by Wertheim and Jeskey entitled "Introductory Organic Chemistry." Special thanks are also due to Dr. Alonzo W. Lawrence of Koppers Company, Inc., and Dr. James J. Bisogni, Jr., of Cornell University for their many helpful suggestions for reorganizing this book, and to Dr. George A. Parks of Stanford University for his comments on Chapter 5. In addition, we greatly appreciate the several suggestions made by Dr. Irvine W. Wei, Northeastern University, a reviewer selected by the publishers.

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PART ONE

FUNDAMENTALS OF CHEMISTRY FOR ENVIRONMENTAL ENGINEERING

CHAPTER
ONE
INTRODUCTION

The important role that environmental and public health engineers have played in providing us with pure and adequate water supplies, facilities for wastewater and refuse disposal, safe recreational areas, and a healthy environment within our homes and places of employment is not generally appreciated by the public at large. Those who have experienced living in the underprivileged areas of the world usually return home with a new sense of respect for the guardians of the public health. Among these guardians are the engineers who are in the front lines of defense, employing their knowledge of science and engineering to erect barriers against the ever-present onslaught of diseases and plagues, the most terrible of the "Four Horsemen of the Apocalypse."

For many years the attention of environmental engineering was devoted largely to the development of safe water supplies and the sanitary disposal of human wastes. Because of the success in controlling the spread of enteric diseases through the application of engineering principles, a new concept of the potentialities of preventive medicine was born. Expanding populations with resultant increased industrial operations, power production and use of motor-driven vehicles, plus new industries based upon new technology have intensified old problems and created new ones in the fields of water supply, waste disposal, and air pollution. Many of these have offered a real challenge to environmental engineers, and the profession as a whole has been ready to accept the challenge.

Over the years, intensification of old problems and the introduction of new ones have led to basic changes in the philosophy of environmental engineering practice. Originally the major objectives were to produce hygienically safe water supplies and to dispose of wastes in a manner that would prevent the development of nuisance conditions. Many other factors concerned with aesthetics, economics, recreation, and other elements of better living are important considerations and have become part of the responsibilities of the modern environmental engineer.

1-1 WATER

Water is one of the materials required to sustain life and has long been suspected of being the source of many of the illnesses of man. It was not until a little over 100 years ago that definite proof of disease transmission through water was established. For many years following, the major consideration was to produce adequate supplies that were hygienically safe. The public has been more exacting in its demands as time has passed, and today water engineers are expected to produce finished waters that are free of color, turbidity, taste, odor, and harmful metal ions. In addition, the public desires water which is low in hardness and total solids, noncorrosive, and non-scale-forming. To provide such water, chemists, biologists, and engineers must combine their efforts and talents. The chemist, through his knowledge of colloidal and physical chemistry, is especially helpful in solving problems related to the removal of color, turbidity, hardness, and harmful metal ions and to the control of corrosion and scaling. The biologist is often of great help in taste and odor problems that derive from aquatic growths. In a true sense, therefore, all who cooperate in the effort regardless of discipline are environmental engineers.

As populations increase, the demand for water grows accordingly and at a much more rapid rate if the population growth is accompanied by improved living standards. The combination of these two factors is placing greater and greater stress upon water engineers to find adequate supplies. In many cases inferior-quality, and often polluted, water supplies must be utilized to meet the demand. It is to be expected that this condition will continue and grow more complicated as long as population growth occurs. In many situations in water-short areas, purposeful recycling of treated wastewaters will be required in some degree to avoid serious curtailing of per-capita usage. The ingenuity of scientists and engineers will be taxed to the limit to meet this need.

1-2 WASTEWATER AND STREAM POLLUTION CONTROL

The disposal of human wastes has always constituted a serious problem. With the development of urban areas, it became necessary, from public health and aesthetic considerations, to provide drainage or sewer systems to carry such wastes away from the area. The normal repository was usually the nearest watercourse. It soon became apparent that rivers and other receiving bodies of water have a limited ability to handle waste materials without creating nuisance conditions. This led to the development of purification or treatment facilities in which chemists, biologists, and engineers have played important roles. The chemist in particular has been responsible for the development of test methods for evaluating the effectiveness of treatment processes and providing a knowledge of the biochemical and physicochemical changes involved. Great strides have been made in the art and science of waste treatment in the past few decades. These have been made possible by the fundamental knowledge of wastewater treatment established by scientists with a wide variety of training. It has been the responsibility of the engineers to synthesize this basic knowledge into practical systems of wastewater treatment that are effective and economical.

It has long been known that all natural bodies of water have the ability to oxidize organic matter without the development of nuisance conditions, provided that the organic loading is kept within the limits of the oxygen resources of the water. It is also known that certain levels of dissolved oxygen must be maintained at all times if certain forms of aquatic life are to be preserved. A great deal of research has been conducted to establish these limits, and undoubtedly a great deal more is needed. Such surveys require the combined efforts of biologists, chemists, and engineers if their full value is to be realized. In the past, streams have been classified into the following four broad categories: (1) those to be used for the transportation of wastes without regard to aquatic growths but maintained to avoid the development of nuisance conditions, (2) those in which the pollutional load will be restricted to allow fish to flourish, (3) those to be used for recreational purposes, and (4) those that are used for water supplies.

The consensus at the present time in the United States is to require the highest practical degree of treatment of all wastewaters, regardless of stream purification capability. Thus, effluent quality or effluent standards have superseded stream standards.

1-3 INDUSTRIAL WASTES

Perhaps the most challenging field in environmental engineering practice at the present time is the treatment and disposal of industrial wastes. Because of the great variety of wastes produced from established industries and the introduction of wastes from new processes, a knowledge of chemistry is essential to a solution of most of the problems. Some may be solved with a knowledge of inorganic chemistry; others may require a knowledge of organic, physical, or colloidal chemistry, biochemistry, or even radiochemistry. It is to be expected that, as further technological advances are made and industrial wastes of even greater variety appear, chemistry will serve as the basis for the development and selection of treatment methods.

1-4 ENVIRONMENTAL SANITATION

Although the problems of water supply and liquid-waste disposal are of major importance to urban populations, their solution alone does not ensure a completely satisfactory environment. Pollution of the atmosphere increases in almost direct ratio to the population density and is largely related to the products of combustion from heating plants, incinerators, and automobiles, plus gases, fumes, and smokes arising from industrial processes. The intensity of most air pollution problems is usually related to the amount of particulate matter emitted into the atmosphere and to the atmospheric conditions that exist. In general, visible particulate matter can be controlled by adequate regulations. The most serious situations develop where local conditions favor atmospheric inversions and the products of combustion and of industrial processing are contained within a confined air mass. A notable example is the situation at Los Angeles, where inversions occur frequently; they also occur, though less often, at several other metropolitan areas.

In cases where atmospheric inversions occur over metropolitan areas under cloudless skies, a haze commonly called "smog" is produced in the atmosphere. Under such conditions the atmosphere is often highly irritating to the eyes and to the respiratory tract and is far too intense to be accounted for by the materials emitted to the atmosphere from the separate sources. Research on this problem has been extensive in the Los Angeles area. Many theories have been advanced as to the cause, but the consensus at present is that photochemical action between nitrogen dioxide and unsaturated hydrocarbons from automobile exhaust gases combine to form the irritating substance. This substance condenses on particulate matter in the atmosphere to form a fog. A knowledge of chemistry has played an important role in finding the cause of this enigma.

Air pollution of quite another type was of major concern a few years ago. This resulted from radioactive materials that gained entrance to the atmosphere through nuclear explosions. The nuclides that were dispersed and settled as "fallout" varied greatly in their effect upon living plants and animals. Although limitations on atmospheric nuclear testing have greatly lessened this problem, other uses of nuclear energy have raised new fears over release of radioactive materials to the atmosphere. These fears have resulted from the development and installation of nuclear power plants. Experience has indicated these particular fears have little basis, however. The major threat to the environment results from the transportation of "nuclear ash," separation, and safe disposal of the waste radioactive materials. This constitutes a major challenge to the environmental engineering profession, for with ever-diminishing supplies of fossil fuels, nuclear power (perhaps together with renewable sources such as solar energy) must replace them or living standards will have to be lowered.

1-5 OTHER TECHNOLOGICAL DEVELOPMENTS

During the past few years, many new chemicals have been produced for agricultural purposes. Some of them are used for weed control, others for pest control. Residues of these materials are often carried to water courses during periods of heavy rainfall and have had serious effects upon the biota of streams. A great deal of research by chemists and biologists has demonstrated which of the materials have been most damaging to the environment and many products have been outlawed. Continuing studies will be needed, but hopefully new products will be kept from general use until proven equal or even less harmful than those in current use.

1-6 SUMMARY

From the discussions presented it should be apparent that the solution of many problems in environmental engineering has required the concerted efforts of scientists and engineers and that chemists, in many instances, have played an indispensable role. It is to be expected that problems arising in the future will be fully as complex as those of the past and that chemistry will continue to be an important factor. Engineers with sound chemical training should find that their knowledge is a great aid and advantage in conquering unsolved problems and that liaison with scientists working on the same or allied problems will be facilitated. The chapters following are dedicated to that purpose.

CHAPTER

TWO

BASIC CONCEPTS FROM GENERAL CHEMISTRY

The factual information and basic concepts taught in freshman chemistry vary considerably, depending upon the institution and the interests of the students. In many schools, engineers are given a considerably different course from that given to science majors. Because of these differences and because certain fundamental information is essential for environmental engineering, a review of certain phases of general chemistry is indicated.

2-1 ELEMENTS, SYMBOLS, ATOMIC WEIGHTS, GRAM ATOMIC WEIGHTS

Remembering the names of the common elements poses no particular problem to the average student. However, the proper symbol does not always come to mind. This is mainly because many of the symbols are derived from Latin, Greek, or German names of the elements, and sometimes because of a similarity of names which makes a multiple choice of symbols possible. This similarity is well illustrated by the symbols for magnesium, Mg, and manganese, Mn, which are commonly confused.

To remember the symbols for magnesium, manganese, and those derived from Latin or other foreign names, one must rely entirely upon memory or association with the uncommon name. A list of the elements whose symbols are derived from Latin, Greek, or German names is given in Table 2-1.

Table 2-1 List of elements whose symbols are derived from Latin, Greek, or German names

Element	Name from which symbol is derived	Symbol
Antimony	Stibium, L.	Sb
Copper	Cuprum, L.	Cu
Gold	Aurium, L.	Au
Iron	Ferrum, L.	Fe
Lead	Plumbum, L.	Pb
Mercury	Hydrargyrum, Gr.	Hg
Potassium	Kalium, L.	K
Silver	Argentum, L.	Ag
Sodium	Natrium, L.	Na
Tin	Stannum, L.	Sn
Tungsten	Wolfram, G.	W

Atomic weights of the elements refer to the relative weights of the atoms as compared with some standard. In 1961 the C^{12} isotope of carbon was adopted as the atomic weight standard with a value of exactly 12. According to this standard, the atomic weight of oxygen is 15.9994, or 16 for all practical purposes.

It is not necessary to remember the atomic weights of the elements, because tables giving these values are readily available. It will save time, however, to remember the weight of the more commonly used elements such as hydrogen, oxygen, carbon, calcium, magnesium, sodium, sulfur, aluminum, chlorine, and a few others. It is usually sufficient for all practical purposes to round off the atomic weights at three significant figures; thus aluminum is called 27.0, chlorine 35.5, gold 197, iodine 127, and so on.

In general, elements do not have atomic weights that are whole numbers because they consist of a mixture of isotopes. Chlorine is a good example. Its atomic weight of 35.45 is due to the fact that it consists of two isotopes with atomic weights of 35 and 37. Cadmium contains eight isotopes whose atomic weights range from 110 to 116.

The *gram atomic weight* of an element refers to a quantity of the element in grams corresponding to the atomic weight. It has principal significance in the solution of problems involving weight relationships.

2-2 COMPOUNDS, FORMULAS, MOLECULAR WEIGHTS, GRAM MOLECULAR WEIGHTS, MOLE

Although the concept of chemical compounds is readily established, association of the proper and correct formula for each compound does not always follow. This difficulty is sometimes due to faulty use of symbols but much more often to a lack of knowledge regarding valence. The subject of valence will be discussed presently. If strict attention is paid to correct symbols and valences, errors in writing formulas will be eliminated.

Calculation of molecular weights poses no real problem except when rather complex formulas are involved. Most difficulties in this regard can be overcome by writing structural formulas and applying some effort in the form of practice. The importance of correct molecular weights as the basis for engineering calculations should be emphasized.

The term *gram molecular weight* (GMW) refers to the molecular weight in grams of any particular compound. It is also referred to as a *mole*. Its chief significance is in the preparation of *molar* or *molal* solutions. A molar solution consists of 1 gram molecular weight dissolved in enough water to make 1 liter of solution, whereas a molal solution consists of 1 gram molecular weight dissolved in 1 liter of water, the resulting solution having a volume slightly in excess of 1 liter.

2-3 AVOGADRO'S NUMBER

A significant fact is that the gram molecular weight contains the same number of molecules, whatever the compound. The number of molecules present is called Avogadro's number, and is approximately equal to 6.02×10^{23}. By definition, a mole of a substance contains an Avogadro's number of elementary entities. It is expressed as atoms per mole, molecules per mole, ions per mole, electrons per mole, or particles per mole, depending on the context.

$$6.02 \times 10^{23} \text{ O atoms} = 16.0 \text{ g O}$$
$$6.02 \times 10^{23} \text{ H atoms} = 1.01 \text{ g H}$$
$$6.02 \times 10^{23} \text{ H}_2\text{O molecules} = 18.0 \text{ g H}_2\text{O}$$
$$6.02 \times 10^{23} \text{ OH}^- \text{ ions} = 17.0 \text{ g OH}^-$$

The enormous size of this number is incomprehensible. Some concept of its magnitude may be gained from a consideration that the life span of the average United States citizen is of the order of 2.2×10^9 seconds (s) and that a person would have to live about 3×10^{14} lives to count to Avogadro's number.

2-4 VALENCY, OXIDATION STATE, AND BONDING

A knowledge of valency and bonding theory serves as the key to correct formulas. In general, the writing of formulas with elements and radicals that have a fixed valence (or *oxidation state*) is easy, if a knowledge of electrostatics is applied. The real difficulty stems from elements that can assume several oxidation states, the variety of radicals that results, and a lack of knowledge of nomenclature, which is not always consistent.