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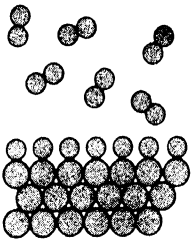
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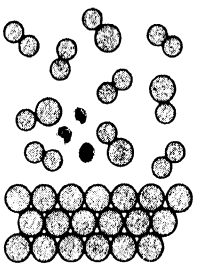
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Principles of Chemistry

SANDERSON (R.T.)
Principles of Chemistry

SANDERSON (R. T.) AND BENNETT (W. E.)
Laboratory Manual for Introduction to Chemistry





Principles of Chemistry

R. T. Sanderson Professor of Chemistry

Arizona State University, Tempe, Arizona

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Preface

THIS BOOK might well be subtitled, or even titled, "Atoms and Their Consequences." Chemistry is the science of atoms. Whoever knows the fundamental nature of atoms knows how they must behave when they come together. From this, he knows what the combination must be like and how the atoms must behave after they have come together. Only by knowing these things can he attain a true understanding of chemistry. So, seeking to help students toward such an understanding, this book begins with atoms, and emphasizes throughout the cause-and-effect relationship between the nature of atoms and the physical and chemical properties of matter.

The book has been written because I firmly believe that much more can be accomplished toward imparting a real understanding of chemistry in its introductory presentation. Fundamental chemistry is not simple chemistry. Yet I think we have been too reluctant to break away from the timeworn traditional descriptive approach, and I say this fully aware of the ever increasing emphasis on physical principles in most recent textbooks. Despite this emphasis, the courage of conviction seems to have been lacking, or else we have been too timid, or perhaps too unimaginative, to realize the vast potential of teaching values derivable from modern theoretical chemistry. We have become too easily persuaded of the awesome complexities of matter to recognize its concurrent simplicities.

For nature, it seems to me, has a dual character. Its truths are at once too complex to be attainable yet beautifully simple. These aspects are not incompatible, they are not mutually contradictory; they are but

variations of the viewpoint, while the scene remains unchanging. I think we do students a disservice when, out of reverence for "rigor," we withhold the simplicities for fear of instilling misconceptions. The temptation to present chemistry *only* as an *exact* science, subject to rigid laws and therefore exclusive of more approximate interpretations, is a temptation that permits only a narrow and restricted view of a subject very broad and rich. Actually, little chemistry can be explained with ultimate exactness. When we pretend otherwise we only deceive ourselves and our students, and indeed conceal the true nature of science. On the other hand, all degrees of reasonable approximations are available, from which a good, practical, simple understanding can be achieved even by beginning students.

Yet in the deliberate oversimplification of knowledge, two kinds of error are possible. A teacher may aim in the wrong direction, or he may aim in the right direction but fall short. The first kind of error is unjustifiable; students should never be led down an easier path if it is wrong. Errors of the second kind are, in my opinion, far less serious, and much to be preferred over pretending no target exists. I would rather try to explain, freely admitting whatever inadequacies there may be, than fail to recognize and point out to the students that a question exists. For the recognition of questions is of the essence of scientific research. The student who does not ask why is not thinking, and the instructor who does not stress the existence of questions is derelict in his duty.

In this book, therefore, I have tried to explain chemistry as thoroughly and as simply as I can, pointing out questions and attempting to answer if possible. I have done my best to help students learn with a minimum of formal guidance, and to help their memories retain this learning by the glue of understanding, without which most knowledge leaks away. This goal has prompted a new type of self-testing section at the end of each chapter. Our precollege educational system seems to have provided most students with far too little exercise in independent reasoning, and the tendency for many college courses to continue this lack is deplorable. Under the heading, "Test Your Understanding," are questions to which direct answers are not available in the book. Students can think out their own answers, and then refer to detailed answers at the back of the book. The importance of these sections is suggested by the fact that the answers comprise about 10 per cent of the book.

To the extent that an author succeeds in writing clearly and simply, especially on a technical subject, he risks creating the superficial impression that the book is not "rigorous," that it is not suitable for "upper-level" courses, that it would not "challenge the student" sufficiently,

Should a reader gain such an impression from this book at first glance, I would beg him to look again. The student who has mastered this book should be well prepared for his advanced chemistry courses, besides being, I would hope, more adaptable to, and appreciative of, a world of swift technological change.

No textbook can reach its highest level of usefulness without the intermediate assistance of a competent instructor. For the instructor, not the author, knows his students, their needs, their abilities, their limitations. I hope this book will make easier the difficult task of teaching, and that students will find herein a source of stimulation and understanding.

R. T. SANDERSON

Iowa City, Iowa
April, 1962

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1

Introduction

FROM THE BIG STONES behind the glowing embers, the welcome warmth still reflected into the open cave where the family slept. But the flames no longer flickered, and only the closest stones were faintly pink with ember glow. All else was black. Not even the stars shone through the murky overcast. Suddenly the silence of the night was shattered by piercing screams, and the thrashing sounds of struggle, abruptly terminated. John Earlyman sat up and grasped his stout stone axe firmly, peering apprehensively into the blackness. Behind him, his woman stirred uneasily and the child whimpered softly under the covering of furry hide. To their ears, keenly attuned to the dangers of the darkness, came unmistakable sounds of a rending and chomping of flesh and bone. In a few moments these sounds gave way to silence, broken only by the distant calls of tree toads and the faint fluttering of bats swooping close overhead. Then dull, heavy thuds and the snapping of shrubs, slowly coming closer. The woman's leathery fingers closed over a large stone, suitable as a weapon. John Earlyman's muscles tensed and his jaw dropped open, the better to listen. His breath came short and sharp. Fearfully they waited.

The sounds came closer, and stopped. There was deep sniffing and a loud snort. The brush parted and some shadowy beast of enormous bulk stepped heavily toward the cave. John Earlyman grabbed up an armful of dead grass and threw it on the embers. There was an agonizing moment of dull, dark smouldering, and then at last the bright, crackling flame shot forth high in the air. The colossus hesitated, its beady eyes gleaming balefully in the firelight. The woman hurled her stone and it struck with a sound like a coconut landing on soft sand. With heavy, gutteral grunts, the great brute clumsily stepped back, swung away, and pressed ponderously into the jungle. John Earlyman hastened to bring dead branches and heavier logs, and built up the fire until it blazed forth defiantly toward the sky. Then, squatting back on his haunches, his axe by his side, and a boulder at his back, he stoically awaited the blessed light of dawn. The woman and the child settled back to sleep.



Figure 1. Before chemistry.

So it was only fifty thousand years ago, with our ancestor, John Earlyman. The same physical world that is ours today was his, except that its resources were untouched. Beneath the virgin forests and under the grassy plains were soils that could be enormously productive, and under them or in the rocks lay rich deposits of all the minerals necessary for building a flourishing civilization. Far more raw materials were at man's disposal then than now. Yet, instead of being master of his physical environment, he was its slave. His existence on earth was barely tolerated, the awesome forces of nature threatening to wipe him out at any moment.

What has brought about this miraculous change in the relative positions of man and his environment?

The development of material civilization came slowly—for thousands of years, almost imperceptibly. But with each new fragment of knowledge, the frontier broadened. Wider horizons came into view with each successful exploration into the vast unknown. Expansion and development have therefore been constantly accelerated. But most of this acceleration has come only within the past three centuries—a fleeting moment in the eons of time since the emergence of man. Why?

Of course, it would be ridiculous to claim that any single influence has brought about this rapid change. Yet one important development has certainly played a major role. John Earlyman, and all his descendents for thousands of years, and all his ancestors for millions of years, used only the matter, the substance, of their environment without significantly changing its nature. Thus they were limited to products found in nature or relatively easily shaped or built from natural materials. The best material civilization that could be developed was therefore of necessity quite crude. Slowly over the last four thousand years, much faster over the last three hundred years, and extremely rapidly within the last century, man has removed this limitation. He has learned how to extricate valuable substances which, as found in nature, are too tangled to be used, and even more important, how to transform matter available in nature into entirely new substances with useful properties unequalled by anything nature can provide.

The importance of this new information can readily be appreciated by comparing the situation of John Earlyman and his contemporaries with our situation today. John's raw materials were more abundant and better than we have. His basic needs were identical. Surely he would have enjoyed the comforts of our civilization, even under threat of nuclear annihilation, far more than the precariousness of his incessant struggle against the prehistoric hazards surrounding him. The greatest difference is that John knew only how to use sticks and stones and

animal skins and vines. Modern man knows much better how to use his physical environment. Modern man knows chemistry.

WHAT IS CHEMISTRY?

Look at this book. Look at it carefully and thoughtfully. You can observe that it has weight, that it occupies space. You can observe that all its pages are, like this one, white, and of a material called paper. The print is of a different material, black, called ink. Both paper and ink are very familiar substances, and doubtless you feel that you are very well acquainted with them. But think, now—what do you *really* know about paper and ink? Do you know what they are composed of? Do you know why the paper is white, why the ink is black, why the paper can bend without breaking, why the ink cannot easily be erased, why the whole book would disappear, leaving only a grey ash and invisible gases, if you threw it on a fire?

These are questions of the kind with which chemists are concerned. Anything that, like this book, occupies space and has weight is classed as matter. Everyone makes use of matter, but it is the special province of the chemist to learn about the *fundamentals* of matter. What is it made of? Why does it have the qualities that are observed? Under what conditions can it be changed to other kinds of matter, and to what other kinds of matter can it be changed? How can such changes be prevented, and how can such changes be brought about? For chemistry is at once two things: it is a vast body of *accumulated* knowledge about the fundamental nature and properties of matter, and it is an intensive search, ceaselessly continuing, for *new* knowledge about matter. No one begins the study of chemistry too late to have a hand in the discovery of new knowledge about it. Herein lies a fascination that can never be equalled by any body of knowledge, however profound, that is complete, discovered, and sufficient unto itself. You yourself can, if you choose, stand one day at the frontiers of chemistry, and write your name into the record of those who, living constantly in the fun and excitement of quest and discovery, become at the same time benefactors of their fellow men.

WHY STUDY CHEMISTRY?

But even if you choose some other career than chemistry, the knowledge that you can gain from these studies will enrich your life forever.

Such knowledge is not only an essential for many other specializations, such as physics, botany, physiology, pharmacy, medicine, zoology, and engineering. Should you wind up as poet, artist, musician, politician, or mother of ten, a more penetrating knowledge, a more fundamental familiarity with the matter that is both you and your environment cannot help but broaden your view and deepen your appreciation of life. It is sad but true that many chemists are not broadly educated. At the same time it must be emphasized that no person can be considered broadly educated who knows nothing of chemistry.

Dealing, as it does, with all kinds of matter in the universe, chemistry is a science that includes millions of facts. Fortunately, however, for those of us who seek to know this science, these facts are secondary to a much smaller number of primary facts and fundamental principles. One might waste a lifetime trying in vain to memorize all the secondary facts about matter. But by staying closer to the fundamentals, one can, within a two-semester course, attain at least a fair appreciation of what chemistry is and why it exerts so vital an influence on everyday living. At the same time, one cannot help but acquire some degree of feeling for the inherent orderliness, the paradox of beautiful simplicity yet infinite complexity, that characterize this physical world of which we are so significant yet so insignificant a part. Finally, one cannot study a subject like chemistry without marveling at the powers of the human intellect, which, operating in the minds of thousands of men, has through the years made such admirable progress in beginning to understand the seeming chaos that surrounds us. For most of this progress, thanks are due to the development of that most happy combination of thought and experiment known as the "Scientific Method."

THE SCIENTIFIC METHOD AND SCIENTISTS

Man has always been a thinking animal, and his thinking has had a dominant influence in the development of civilization. But one of man's most serious faults from the beginning has been his tendency not to consider, in evaluating his own thoughts, the limitations that his human experience and human qualities inevitably place upon those thoughts. Too often, in other words, he has failed to recognize or admit the possibility that he might be mistaken. This tendency has had its advantages, for it has given man the confidence for necessary, positive action. But it has also had severe disadvantages, for it has led not only to disastrous and futile conflicts, but also to prejudices that

repeatedly have blinded man to the truth, and indeed still do. It has led, and still does, to unthinking subservience to "authority," when in fact said authority is only mortal and highly fallible man.

So for many centuries human progress remained retarded under a tyranny of human "authority," an authority of ignorance, an authority of despotism in government, of intolerance and bigotry in religion, of intellectual arrogance in philosophy, despite an almost total lack of understanding of the nature of the physical world. Natural phenomena were explainable only in terms of pseudo-human activities of purely imaginary gnome-like or god-like creatures, in terms of mystery and superstition. Then gradually man began to recognize that, at least so far as his material world is concerned, it is possible to make *reproducible observations* of natural phenomena. When a number of independent observers could make identical observations of a given phenomenon, and when the same phenomenon, repeated many times, always resulted in the same way, here was an almost absolute basis for establishing these observations as facts. No longer was it necessary to speculate or philosophize about what *might* happen, if instead one could watch it actually happen. And although a dozen men, all learned and intelligent, might easily speculate to a dozen different conclusions, a dozen men making careful observations of the same phenomenon could reasonably be expected to make identical observations. The fallibility of thinking was no longer so significant a factor in determining a fact.

The possibilities for observation of physical phenomena became greatly expanded when man began to realize that he need not necessarily sit around waiting for such phenomena to occur under the conditions set for them by nature. Neither need he always speculate about the results without observing their occurrence. For often these phenomena could be staged under controlled conditions, at convenient times, when one could observe closely the action and the results. In other words, one could discover new facts by *deliberately* designing and carrying out *experiments*. Thenceforth man began to use his mind, not so much to guess at what the facts "ought" to be, but to improvise apparatus by use of which he could carry out carefully controlled, and therefore exactly reproducible, experiments to find out those facts. He began to recognize his own mental limitations, for he discovered that frequently —indeed more often than not—the experimental facts were not at all as he would have predicted. He began to appreciate the necessity of trusting his senses farther than his impulses or emotions, and of recording honestly his best observations without regard to whether or not they fulfilled expectations based on speculations and theories. And then, as his experience in scientific experimentation increased and

reliable data accumulated, he began to develop confidence in an inherent reasonableness of physical phenomena, to perceive that mystery is only a manifestation of ignorance, and to notice that when the ignorance is removed the mystery disappears. He had developed the "Scientific Method."

The Scientific Method is the most effective approach to the discovery of new knowledge and the interpretation of old knowledge that has yet been devised. It involves three processes. One is the intelligent planning of experimental procedures to test the behavior of matter under controlled conditions. A second is the testing of this behavior of matter by careful and honest observation, accurate measurement, and faithful recording of observations and results, impartially and as freed of prejudice as is humanly possible. The third is the thoughtful study of the observations and results, attempting to recognize unifying principles and reason out logical explanations. The validity of such principles and explanations can then be tested by further experimentation.

You can see that the successful application of the Scientific Method places a strain on ordinary human qualities, for it requires ideally a complete absence of prejudice, as well as a high degree of ingenuity and the capacity to think thoroughly on subjects that are frequently very complex. Therefore you must not expect too much of scientists, who, after all, are inescapably human and subject to the very human limitations that plague us all. Scientists do know a lot, because their business is to know as much as they can, and they attend seriously to this business, studying all their lives. But they do not know everything. In fact, the exacting concentration required in their specialization makes impossible as broad a comprehension of all knowledge as they ideally should have. Scientists are intelligent people because their work requires a high degree of intelligence, but they certainly cannot be infallible. Scientists try to keep open minds, because they must be constantly alert to recognize the unexpected, which is most frequently the way in which great discoveries are made. But although there is abundant evidence that prejudice arises from ignorance, there is a less well-recognized perversity of learning that causes prejudice to accompany knowledge. For every fact that you learn builds up your resistance to other facts if they seem somewhat contrary to those learned first. This is true, unfortunately, even if the first "facts" happen to be false!

Perhaps you can understand better how knowledge might build prejudice from the following crude example. If you knew nothing about common animals, you would have little difficulty in believing that there could be a breed of dogs with only three legs. If you were

acquainted with a few other animals, however, such as horses and cows and hippopotami, your knowledge that all these are normally four-legged would tend to make you surprised, at least, to learn of the three-legged dogs. But since in fact you have been familiar with all kinds of four-legged animals, including dogs, all your life, if someone reported that the dogs on a certain island were all of a three-legged breed, you would doubtless be highly skeptical. Those dogs you would have to see for yourself.

So it is with scientists. Although ideally the scientific method requires them to maintain open-mindedness, as they learn more facts in a particular field of specialization it is less easy for them to accept new facts that do not appear to fit in with what they already know. Thus, although constantly increasing knowledge is essential to the continuing development of a scientist, its acquisition also makes it increasingly difficult for him to maintain an open mind. It is a human weakness that one cannot become an expert without simultaneously becoming prejudiced. Fortunately, as the result of the training and mental discipline of a good scientist, despite the strength of his prejudices he is able to accept new ideas and new facts if the experimental evidence is adequate. The point of this whole discussion, then, is that it would be both unrealistic and unfair to expect any human being to practice to perfection the ideals of the Scientific Method. You must understand that the methods actually employed in past and present scientific research only represent *a practical approach to what are really unattainable standards.* In practice, nevertheless, the Scientific Method has become established as an extremely effective method of developing new knowledge.

Where, you may ask, does chemistry fit into this picture? The field of chemistry, like the other sciences, is populated with normal human beings dedicated to the ideal of the Scientific Method, but subject like everyone else to the limitations inherent in being human. Despite these limitations, the application of the Scientific Method by these people to the problems of chemistry has been enormously successful. In the two centuries since the advent of this method in chemistry, man's material way of life has changed more than it had in all the centuries since his earliest beginnings. There is today hardly a single aspect of life that is not influenced by chemistry. We live in an Age of Chemistry, certainly destined to become no less so with the development of nuclear power. Let us make haste, then, to learn what we can about chemistry.

PART ONE

The Chemical Elements

2

Occurrence and Description of the Elements

YOU WILL HARDLY need to think deeply to be mindful of the wide variety of materials with which we are all familiar. The summer zephyrs that waft away the mosquitoes, and the scent of blossoms that the zephyrs bring, are as truly material as the lamppost that slows the wandering motor car, or the oaken footstool lurking in the dark. Think of water and of oil, of vegetable and mineral, of concrete and cotton, of arsenic and applesauce, of chocolate bars and nails, and you will agree that the matter on earth has myriad forms and qualities. Chemistry is the knowledge, and the search for new knowledge, of what all this stuff is made of, and why it has the qualities we perceive.

Now, think again, and this time not of familiar things but of familiar changes. Think of the grass and air and water that enter the cow, becoming food for people and food for plants. Think of the seasoned hickory that burns to gases, smoke, and ash, of the golden motor oil becoming black in service, of the shiny metal that disintegrates into rust, and you will agree that there are also myriad ways in which matter can change from one form to others. Chemistry is likewise the knowledge, and the search for new knowledge, of the changes in matter.

Think, please, yet again on the changes in matter, of the changes in energy which accompany them. The hickory gives out much heat when it changes to gases and ash. The robin in the blizzard does not freeze as long as he has food, for by changing it into other substances he derives heat. Conversely, many changes absorb heat. Heated rubber, for example, begins to decompose and stink long before it is hot enough to catch fire. When changes in matter are carefully studied, they are found always to involve changes in energy. Chemistry must therefore be concerned also with the energy changes that accompany the transformation of matter.

Chemistry, in summary, is the science of matter. What is it made of? How is it put together, and how could one put it together or take it apart? What are its properties, and why does it have them? How can it be changed into different kinds of stuff, and how can one prevent or control these changes? How can one use these changes to provide useful energy? How can substances with prespecified properties be created?

An exposition of chemistry might logically begin by considering first the question: What is matter made of?

This question has intrigued man for thousands of years. Could all matter have certain components in common? Might certain basic substances exist from which all the myriad forms of matter could be constructed? To the ancient and medieval philosophers, these possibilities seemed quite reasonable, and they speculated that all matter was made from earth, water, fire, and air. But these men were abstract thinkers, not experimentalists. When men began to experiment with matter, to study its properties and particularly the transformations from one kind to another, such speculations became less and less satisfying. Yet for many centuries there was no clear distinction among kinds of matter except, and this was not always true, to recognize their individuality.

Gradually, however, two classes of matter began to be recognized, one capable of breaking down to other substances under the influence of heat or other agency, and the other seemingly incapable of breaking down under any conditions. Not until near the end of the seventeenth century was a clear distinction made between these two kinds of matter. Robert Boyle, one of the earliest and most famous of the *scientific* chemists, described the latter kind as *elements,* or elementary; simple forms of matter that are not made of any other bodies or of one another. During the next half century the concept of these simple elementary substances, as contrasted to the more complex kinds of matter which are composed of the elements and decomposed into them, became much

more fully developed and recognized. Possibly the most important single fact about chemistry is: *All matter, whether solid, liquid, or gas, pink, green, or colorless, hard or soft, living or inanimate, is made up entirely of these basic substances called the chemical elements, and of nothing else whatever.*

You have already given thought to the vast variety of matter that exists on earth. Nearly a million distinct kinds of matter have been identified to date, new ones are being discovered even as you read this, and there is no practical limit for the future. Each kind has its own individual properties, not exactly like the properties of any other kind of matter, and thus each kind is entirely unique. Surely it must take an enormous number of basic substances, or elements, to form so amazing a number and variety of kinds of matter. Or, so one might well think. But the fascinating fact is that there are actually only about 90 different chemical elements found in nature, to which man has so far added a dozen more. And by far the great majority of different kinds of matter are composed only of a very few (about 30) of these elements! How can this be?

A major purpose of this book is to explain, as simply as possible, how this can be. In a nutshell, the different chemical elements are able to enter into combination with one another. In the process of combination, they abandon completely the properties which were theirs when uncombined, concealing their identity as long as the combination endures. The combination, called a "chemical compound," has an entirely new and different set of properties all its own. The nature of the compound will depend on the kinds of elements combining, on their relative quantities, and on the way in which they are held together in the combination. By variation of any or all of these three factors, millions of different compounds, each unique in its properties, are possible. Later, you will be able to achieve a satisfying understanding of all this, even though at present it may seem complex. But before you attempt to understand the principles of chemistry, you will find it useful to learn something about these individual chemical elements.

The earth's crust—the lithosphere (surface rocks and soil), the hydrosphere (oceans), and the atmosphere—is all we really know about. Yet no reason has ever been discovered for suspecting that the interior of the earth, or even other bodies in the universe, are not composed of the same chemical elements as the crust. Meteorites which come to us from outer space are made entirely of familiar elements, and even the light from the stars discloses, through ingenious instruments, only elements already recognized in the crust of the earth. Thus, by learning of the world about you, you will also learn something of those vaster

horizons in which our earth is only an infinitesimal speck. In this chapter we will consider some of the more familiar facts about these elements and their compounds, as a preliminary to a study of their fundamental nature. First, however, it will be useful to introduce a means of classifying the various compositions of matter that exist.

PURE SUBSTANCES AND MIXTURES

If a given portion of matter consists of only one element, or of only one compound, it is called a "pure substance." If (*a*) it contains more than one element but they are not chemically combined, (*b*) it consists of one or more elements and also one or more compounds, or (*c*) it contains two or more compounds, it is called a "mixture." The significance of this distinction is that the properties of matter depend on its composition. Any one element has a uniform, constant composition, and all portions of it have the same properties. Any one compound, for reasons to be explained in detail in later chapters, is likewise of uniform, constant, definite composition. This is a fundamental characteristic of a chemical compound. All portions of it will therefore likewise have the same properties. But whenever two or more substances—each of different composition—are contained in the same portion of matter, all portions cannot possibly have the same properties. A pure substance is homogeneous with respect to composition and properties. A mixture is homogeneous neither in composition nor in properties.

Pure substances seldom occur in nature. Almost all naturally occuring matter is mixed. Often one can observe distinct inhomogeneities in matter that clearly identify it as a mixture. A close look at a handful of soil, for example, will reveal its mixed nature. On the other hand, many mixtures have a homogeneous appearance. This is truer, the more intimately mixed its components are. When the matter is mixed so thoroughly that its individual atoms or molecules are separated from one another by atoms or molecules of another kind, it is called a "solution." Sugar, for example, is a definite chemical compound: a pure substance. Its basic components are identical particles called "sugar molecules." Water is likewise a definite chemical compound, whose basic units are called "water molecules." When sugar and water come in contact, sugar molecules become intimately mixed with water molecules. The sugar disappears into the water, and we say it "dissolves" to form a solution. Air is a somewhat similar mixture, in which molecules of oxygen and nitrogen are thoroughly interdis-

persed. Many metal alloys consist of similar mixtures of atoms of different metallic elements, called "solid solutions." To ordinary inspection, all such solutions are completely homogeneous and might therefore pass superficially as pure substances.

Composition

Three features of all mixtures, including solutions, prevent their classification as pure substance. One is their composition, which ordinarily can be varied within rather wide limits. For instance, a sugar solution may contain a trace of sugar, quite a lot of sugar, or any concentration in between. The composition of elements is invariable. The composition of all liquid and gaseous compounds is also invariable, as is that of most solid compounds. For instance, limestone, a chemical compound, is exactly 40 per cent calcium, no more, no less. The composition of a relatively few chemical compounds is variable, but only within relatively very narrow limits. In other words a solution, or any mixture, may have a range of properties depending on its composition. The properties of a pure substance are fixed.

Physical Properties and Physical Separations

The second distinguishing feature of all mixtures, including solutions, is their separability into dissimilar portions by means which do not effect any change in the component particles. Such means are usually called "physical." The kind of properties of matter on which such methods depend are called "physical properties." Physical properties in general are those that can be measured without causing a change in the identity of the substance. They include density, color, odor, appearance, temperature of melting (if the heat does not cause it to change identity), strength, hardness, electrical conductivity, volatility, and ability to dissolve in liquids (provided that evaporation of the liquid leaves the original substance). However homogeneous a mixture may appear, some physical method of separating its components can always be found.

For example, one component of the mixture may be solid and another liquid. Advantage can be taken of the difference in physical state to separate them, for a liquid will flow through a porous barrier but a solid, unless it is extremely finely divided, will not. In the laboratory a

circular piece of porous paper is folded in quarters to form a cone to fit a funnel, and the mixture is poured into it. This apparatus is called a "filter." The liquid runs through the paper, and the solid is retained. The process is called "**filtration,**" and the filtered liquid, the "filtrate."

Liquids are usually more volatile than solids, and commonly can be evaporated and condensed again without changing their identity. The liquid portion of the above mixture could have been removed from the solid by vaporizing the liquid and collecting the vapor elsewhere, cooling it to condense it to liquid again. If the solid had been dissolved in the liquid, separation could have been accomplished in the same way. Or a mixture of liquid substances can be separated by taking advantage of their difference in volatility. When the mixture is heated to boiling, the lowest boiling substance evaporates most rapidly. This method of separation is called "distillation." When separate portions of condensed vapors are collected in "fractions" differing in boiling temperatures, the process is called "**fractional distillation,**" and the vaporized portions the "distillate." For example, alcohol can be distilled away from its solution in water, and gasoline from petroleum.

Different substances differ in their solubility in any given liquid. If only one component of a mixture is soluble in a certain liquid, this component can be separated by extracting it with that liquid. A liquid that dissolves something is called a "solvent," and this process of separation is known as "**solvent extraction.**" The most common methods of separating the components of mixtures are the three just described: filtration, fractional distillation, and solvent extraction.

A reliable criterion for deciding whether a given portion of matter is a pure substance or a mixture is this: If by any physical means the matter can be separated into two or more parts with different composition and properties, the original matter must have been a mixture. Otherwise it is a pure substance.

We must avoid misunderstanding here by emphasizing that a pure substance may exist in different forms, most notably solid, liquid, and vapor. Water, for example, may be in the form of ice, liquid, or steam. A mixture of such forms is not a "mixture" by the above classification, but a pure substance. These forms differ, as will be explained later, in their energy content but not in their composition. For example, before arguing that ice is solid and therefore different from liquid water (which in some respects it is), remember that melting of the ice is a physical change and does not alter the fundamental composition. Properties, to be meaningful for comparison, must be measured under the same conditions. Under the same conditions water, ice, and steam become identical.

Chemical Differentiation

The third distinguishing feature of mixtures is their chemical inhomogeneity. Each component has its own unique ability to react chemically —to change composition by rearranging its own atoms or by exchanging atoms with another substance. All portions of a pure substance will undergo such a change in composition in exactly the same way under the same conditions. This is not true of mixtures. For example, sugar will burn but sand will not. A mixture of sand and sugar, no matter how thoroughly mixed, would be changed under burning conditions to sand and gases. Often such differences in susceptibility to change in chemical composition can be used to isolate pure substances from mixtures, or at least to remove unwanted components.

SUMMARY

In summary, most of the matter with which we are familiar on earth consists of mixtures of compounds. Compounds in turn consist of two or more chemical elements, joined together in a definite manner. The individual elements are the fundamental substances of which all matter is composed.

GASEOUS ELEMENTS AND SOME OF THEIR COMPOUNDS

Eleven of the elements are gases under ordinary conditions. These are: hydrogen (H), oxygen (O), nitrogen (N), fluorine (F), chlorine (Cl), helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). The letters following each name are the **chemical symbols** that represent the elements. Such symbols are commonly used in chemistry instead of the full names.

Hydrogen occurs in the free state in traces only, in the atmosphere and in the rocks, but when substantial quantities are needed it can be isolated from its compounds, which are very abundant and familiar. In the free state, being the lightest of substances, it can be used to fill balloons which then can rise high into the atmosphere. It burns with an extremely hot, almost invisible flame, making it useful in certain welding operations and in melting quartz. At one time, lighter-than-air craft, such as dirigibles, were filled with hydrogen, but its inflammability made this too frequently disastrous. In combined form hydrogen is very common. Combined with oxygen, it is contained in water and in hydrogen peroxide. Com-

bined with carbon, it comprises the bulk of petroleum and petroleum products such as gasoline, and is also a major constituent of natural gas. With nitrogen, it is combined as ammonia. With both carbon and oxygen, hydrogen forms thousands of different substances, including cellulose, starch, sugars, and fats. There is enough hydrogen in you to fill, in the form of a gas under ordinary conditions, a large room, or, mixed with air, to blow up a building.

Oxygen, both free and combined, makes up more than half the weight of the surface of the earth. In the free state, it occurs as about one-fifth of the atmosphere, a lucky circumstance for those of us who enjoy living, for without oxygen to breathe and distribute via the blood stream the end would come quickly. In the combined state, oxygen is all about us. Combinations with hydrogen and carbon have already been mentioned. In addition, almost nothing but oxygen, combined with silicon, is in quartz and sand. Most of the mineral matter of the rocks and soil of the earth's crust is oxygen combined with silicon and various metals. Oxygen makes up two-thirds of your own weight, and this would equal the oxygen content of all the air within a six-room house.

Nitrogen, in the free state, makes up most of the four-fifths of the atmosphere that is not composed of oxygen. In compounds, nitrogen is a very important element; a component of all proteins, an essential to all life. Gunpowder contains, along with other elements such as sulfur (S), and carbon (C), nitrogen combined with oxygen. Many explosives, such as TNT (trinitrotoluene), are compounds of nitrogen with carbon, hydrogen, and oxygen. In your body is enough nitrogen to make about 18 pounds of TNT. Nitrogen, combined with hydrogen or oxygen, is an essential ingredient in fertilizers. The nitrogen within you could make 20 pounds of sodium nitrate for plant food. Intimately combined with carbon, nitrogen forms cyanides, notoriously toxic.

Fluorine never occurs in the free state until it is deliberately liberated from its compounds with other elements, which are widely distributed. But although you have probably never seen any fluorine gas, you undoubtedly know of the use of its compound with sodium (Na) sodium fluoride, which, in extremely small concentrations in drinking water, helps prevent decay of teeth, and in very much higher concentrations substantially diminishes the life expectancy of rats or roaches.

Chlorine likewise never occurs in the free state unless someone deliberately prepares it from its compounds, but its great utility justifies its commercial preparation in large quantities. Small concentrations of chlorine are very useful for purifying drinking water, whether the water is to be drunk intentionally, as from fountains, or unintentionally, as from swimming pools. In you is enough chlorine to purify 100,000

gallons of drinking water, or in much higher concentrations to kill several people. Combined with the element sodium (Na), chlorine forms the very familiar table salt, sodium chloride. Combined with carbon, it forms the useful solvent carbon tetrachloride. Combined with both carbon and hydrogen, it forms many different substances, including a kind of synthetic rubber (chloroprene) which has valuable properties.

Helium, neon, argon, krypton, xenon, and radon (He, Ne, Ar, Kr, Xe, and Rn) are all alike and distinct from other elements in that they occur only in the free state, refusing to combine with any other elements under most conditions. Because of this aloofness, these elements are sometimes called the "noble gases." Except helium, which occurs in extensive accumulations of underground gas in the American Southwest, and radon, which is extremely unstable and found only in the vicinity of certain radioactive substances, these elements are not found in nature except in the atmosphere, only argon being present in more than minute traces. For this reason, they are often called the "rare gases." The preferred term, however, is "inert elements."

Helium is the second lightest element, next to hydrogen, and can therefore also be used in lighter-than-air craft and balloons that can rise rapidly through the atmosphere. It has the great advantage over hydrogen of being completely noncombustible. Neon gives its name to neon lights, with which surely you are familiar. These are glass tubes containing neon gas, which gives out that cheery red glow when electricity passes through it. Argon you may not have heard much of, but it is by far the most abundant of these gases in the atmosphere, of which it makes up nearly 1 per cent. Some light bulbs are filled with argon, which cannot corrode the metal filament and which impedes the evaporation of the filament at high temperatures, thus extending the life of the bulb. Krypton, xenon, and radon are very rare. You may not have heard of them before, but you take in minute traces of the first two every time you breathe. Xenon has been found effective in anaesthesia, but, being rare, it is far too expensive for general application.

So much, for the present, about the gaseous elements. Probably seven of the entire eleven are familiar to you either in the free state or in the form of some of their common compounds.

LIQUID ELEMENTS AND SOME OF THEIR COMPOUNDS

Only two of all the elements, mercury (Hg), and bromine (Br), are liquids at ordinary temperatures. (Two other metallic elements, both

relatively rare, are melted very easily by the heat of the hand or in a warm room. These are cesium, and gallium, and both are probably unfamiliar to you either in the free state or as compounds with other elements.) Mercury you know as the silvery, heavy liquid often used in thermometers and barometers. Perhaps you have played with some of it; it is an unusual liquid, for you can dip your finger into it without getting it wet. Also, it is quite dense—an ordinary drinking glass full would weigh seven or eight pounds. Mercury is very poisonous, as are most of the other heavy metals, and even mercury vapor, which forms only very slowly under ordinary conditions, is highly toxic and causes disagreeable symptoms. Despite its liquid nature mercury is a metallic element, having a characteristic metallic luster and ability to conduct the electric current in common with most metals. Certain mercury compounds are occasionally found in the home, examples being the red antiseptics, "mercurochrome" and "merthiolate."

Bromine is a deep red, corrosive liquid that gives off an irritating reddish vapor. It is never found in the free state in nature, but certain of its compounds occur and have important uses. Perhaps you do not realize that very small amounts of a compound of bromine with carbon and hydrogen are present in the anti-knock fluid used in gasoline.

SOLID ELEMENTS AND SOME OF THEIR COMPOUNDS: NONMETALS

All the remaining elements are solids. Most of them are metals, with their characteristic luster and sheen, mirror-like surfaces when polished, and usually the ability to conduct heat and electricity well. A few, however, have no resemblance whatever to the substances we think of commonly as "metallic." These are called in chemistry "nonmetals."

Of course, all the gaseous elements are nonmetals, and of the liquid elements, although mercury is metallic, bromine is not. The solid nonmetals are boron (B), carbon (C), silicon (Si), phosphorus (P), arsenic (As), sulfur (S), selenium (Se), tellurium (Te), iodine (I), and astatine (At). Some of these have some metallic properties.

Boron you may never have seen in the free state, which does not occur in nature. It is a very hard, black substance. Combined with oxygen and hydrogen, it makes boric acid, commonly used in weak solution as an eye wash. Borax washing powder is a compound of boron with sodium, oxygen, and hydrogen. Combined mainly with hydrogen, boron forms fuels whose burning produces a very large amount of energy per pound of fuel, and which are therefore very interesting as possible special purpose fuels, as for rockets and similar devices.

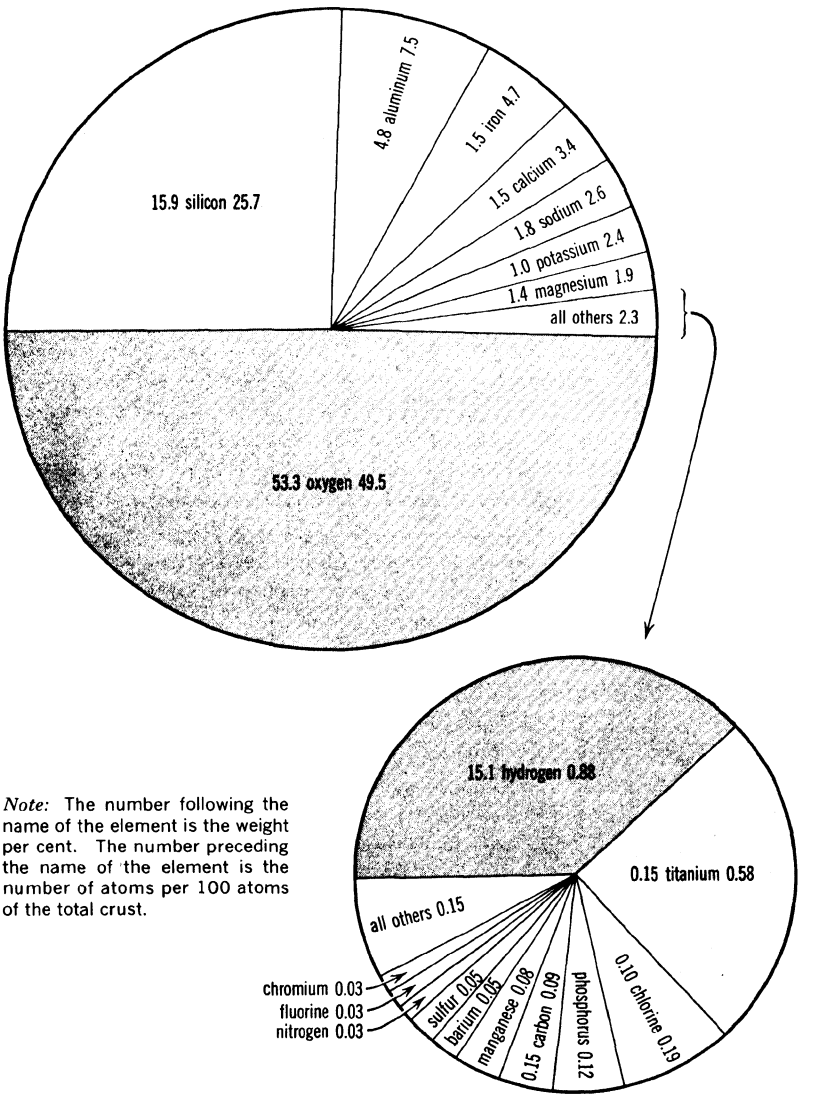
Carbon you have seen in various forms. Charcoal is chiefly the element carbon, as is the ink on this very page, and if you were to char the page itself thoroughly little would be left of it but carbon. Coal and graphite are also carbon, the former with appreciable amounts of other elements. Pencil "lead" is not lead at all, but a mixture of clay and graphite. That sparkling gem on the lady's left hand, third finger, is only a lump of carbon, too, and would burn just as well as a lump of coal. Compounds of carbon are among the most important and the most familiar to you. With oxygen, of course, carbon forms the well-known gases carbon dioxide and carbon monoxide. Combined with oxygen and various metals, carbon forms many compounds called "carbonates," of which "sodium carbonate" is household washing soda, and "sodium bicarbonate," containing also hydrogen, is household baking soda. With hydrogen, as already mentioned, carbon forms the natural gas in your cookstove and furnace, the gasoline and lubricating oil in your car, the rubber in its tires, and the asphalt beneath them. With hydrogen, oxygen, and a few other elements such as sulfur, nitrogen, and phosphorus, carbon forms even more important substances; for example, you. Enough carbon is in you to make a diamond twice the size of the Koh-i-Nor, with two shovelsful of coke left over. Nearly a million different compounds of carbon have been identified.

Silicon, next to oxygen, is the most abundant of the elements, making up about one-fourth of the earth's crust. It is a grey-black, metallic-appearing solid, occurring in immense quantities but only in the form of its compounds. Isolated from such compounds, silicon is useful in electrical devices such as transistors. Melted together with various metals it gives them desirable special properties, for example, making iron very resistant to corrosion by acids. In combination with oxygen alone it forms quartz and sand. In combination with oxygen and various metals it forms most of the rocks and minerals on the surface of the earth.

Phosphorus is a curious element, existing in several different forms with widely different appearance and properties. These forms, however, do not occur as such in nature, for phosphorus is always combined with other elements unless deliberately separated by man. A red form is part of the red-brown coating on the folders of safety matches, where it aids ignition when the match head is dragged across it. A white form is so reactive that it causes terrible burns on the body when it comes in contact with the skin, is extremely poisonous, and catches fire so readily that it is used in tracer bullets and incendiary shells and bombs. In the form chiefly of phosphates, phosphorus combined with oxygen and various metals is very useful and needed as plant food. There is within

you, in fact, enough phosphorus to make five or six pounds of "superphosphate" fertilizer.

Arsenic, too, exists in various forms, a steely, grey, metallic-appearing form, and yellow, grey, and brown nonmetallic-appearing forms. It is



Note: The number following the name of the element is the weight per cent. The number preceding the name of the element is the number of atoms per 100 atoms of the total crust.

Figure 2. Composition (weight percentage) of earth's crust (includes upper 10 miles: land, sea, and air).

quite notorious for its toxicity in both free state and combined. Some of the compounds are well known. For example, arsenic combined with oxygen and lead forms lead arsenate, a valuable insecticide. Combined with carbon and hydrogen, arsenic forms a large number of compounds, some of which have medicinal application.

Sulfur is the element often sold as "flowers of sulfur," or in "sulfur candles" for fumigation. It is a yellow solid occurring in the free state in rich deposits underground. If you have passed near a sulfuric acid manufacturing plant you may have seen a huge pile of yellow solid out in the open; this was undoubtedly sulfur. Sulfur combines with oxygen to form sulfur dioxide, a suffocating gas, or sulfur trioxide, a choking, fuming gas that combines with water to form sulfuric acid. Combined with hydrogen, sulfur contributes notoriously to the odor of rotten eggs (hydrogen sulfide). Combined with hydrogen and carbon, sulfur gives confidence to the skunk and warning to the housewife whose gas stove is on while the flame is out. You yourself contain enough combined sulfur to make nearly a quart of sulfuric acid, or almost five cubic feet of pure hydrogen sulfide gas.

Selenium you have probably not seen, but it is used in glass to give that familiar red color to the traffic light. Perhaps you have heard of its use in photoelectric cells. Tellurium is a rather rare, grey, metallic-appearing solid having little practical application, as yet, either free or in compounds.

Iodine is a common household element because of the antiseptic qualities of its solutions. Free iodine is a dark, purplish or brownish-grey solid with a slight metallic luster. In solution in alcohol, forming the familiar "tincture of iodine," it has a red-brown color, but in some other liquids the color is a deep purple. Iodine is essential to the diet, being needed for the proper functioning of the thyroid gland, but it is a poison in the free state. It is taken as a dietary essential chiefly as its compound with sodium, called "sodium iodide."

Astatine is a very unstable, artificially created element not known in nature either free or combined with other elements. It bears some resemblance to iodine, but is made only in extremely small quantities. The properties are very incompletely known.

SOLID ELEMENTS AND SOME OF THEIR COMPOUNDS: METALS

All the rest of the elements are metallic, and many of them are quite familiar to you.

One group, called the alkali metals, is composed of elements so reactive that you may not have seen them in their free metallic state.

These are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). All are very light in weight and, except lithium, so soft that they can easily be cut with a knife; in fact, cesium is as soft as beeswax. They are too easily corroded by air and moisture to find much practical application as metals. Some of them will even catch fire when exposed to air, or to water and air. Sodium and potassium are by far the most common and abundant, but none occurs in the free state in nature. Sodium, if it is protected against air, moisture, and other corrosive agents, has found some application as a molten metal having good heat conductivity. For example, certain bronze aircraft engine exhaust valves have centers of sodium to help prevent overheating. Also, liquid sodium has been used as a heat-transfer medium in atomic power plants.

Combined with chlorine, sodium occurs in enormous quantities as ordinary salt. It also occurs in many other compounds that are familiar to you, such as washing soda, baking soda, soap, and lye. Enough sodium is in you yourself to make over a pound of table salt. Potassium likewise occurs in widely distributed and common compounds. Combined with oxygen, silicon, and certain other metals, chiefly aluminum (Al), it is a component of many clays and other mineral substances. It is also an essential to plant growth, and in combination with other elements, such as with carbon and oxygen (in potash), it is used in fertilizers. Enough potassium is in you to make about three quarts of liquid soap.

Copper (Cu), silver (Ag), and gold (Au), are three more of the metallic elements, and from one of their most common uses are frequently called the "coinage metals." They are not easily corroded by air or water. Copper and silver are common enough to have found wide practical application, while gold is uncommon enough to have been the root, through the ages, of a very substantial quantity of evil. In general, properties of the metallic elements can be varied and often improved by mixing two or more metals under various conditions to form new metallic materials called "alloys." Thus, although pure copper is extensively used for electrical wire, other metals are alloyed with it to give greater rigidity and strength for construction. Silver and gold are seldom used in the pure form, since they are too soft. You probably think of a dime as being silver because it looks like silver, but actually it also contains about 10 per cent copper. Pure gold, which is "24 carat," is too soft to be suitable for use in jewelry, but it is improved by adding copper, silver, or other metals. Ordinary 14 carat gold is an alloy containing 14 parts by weight of gold and 10 parts by weight of other metals.

Compounds of copper have numerous applications. One of the more familiar is as fungicide. In combination with sulfur and oxygen, copper forms copper sulfate, which water dissolves to a blue solution that is toxic to certain forms of vegetation, depending on the concentration of the solution. Such solutions can be used to kill the rootlets that thirstily worm their way into home sewers if trees are nearby. Copper compounds in extremely small quantities apparently have some function in the human body, and in certain forms of marine life they are all important. For example, you have undoubtedly heard of the importance of iron in human blood; the blood of oysters contains copper, instead.

Compounds of silver (Ag) are chiefly known in photography, where the combination of silver with bromine is especially important (silver bromide). Medicinal applications also occur; the solution dropped into the eyes of newborn infants to insure that infection does not cause blindness contains a compound of silver with oxygen and nitrogen, called "silver nitrate."

Gold (Au) forms relatively few compounds. These are generally quite unstable, and therefore few have practical use. Gold is found and used primarily in the free state.

Beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are all silvery metals. Beryllium is not commonly encountered uncombined, and never occurs free in nature. In its compounds, for example with oxygen, it is extremely poisonous, whether absorbed through cuts in the skin, inhaled as a dust, or ingested accidentally with food. It can cause very slowly healing sores or serious lung difficulties. Its compounds were used as part of the coating of the inside of fluorescent lighting tubes until the danger from breakage of worn-out tubes was recognized.

Magnesium (Mg) is a strong metal, especially when alloyed with small amounts of other metals. Most metals are from 6 to 20 times as dense as water, but magnesium is less than twice as dense. It is being used more and more as a light-weight structural material for airplanes, ladders, wheelbarrows, and many other products. In the form of its compounds magnesium is very common, and there is a high enough concentration in sea water to make the production of metallic magnesium from this source profitable. Combined with oxygen, it contributes high-heat stability to such materials as high-temperature cements and fire brick. If the complete magnesium content of your body were to be extracted in the free state, it would make a cube of the metal about one inch on a side. If pulverized as a flashlight powder, this would make an extremely bright flash.

Calcium (Ca) is somewhat similar to magnesium but, being much

softer and more easily corroded, is of no important value as a structural material. In its compounds, calcium is very abundant and common. Combined with carbon and oxygen, it forms limestone and marble, and probably also the "hard water" deposit on the family drinking glass. Combined with oxygen alone it is "quicklime," which adds water to form "slaked lime" used in plaster. Calcium combined with oxygen, silicon, and aluminum, is contained in "Portland cement." Combined with chlorine, calcium forms "calcium chloride," which has wide application as a dehumidifying agent because it can extract water vapor from the air. Enough calcium is in you, chiefly in your bones and teeth, to make about four pounds of plaster.

Strontium (Sr) is very similar to calcium but much less common. You have perhaps heard of "radioactive strontium" as a major hazard contained in the "fallout" from the explosion of nuclear weapons. This is a special form of strontium that may result from such explosions. The dangers arise from the facts that (*a*) such strontium, like calcium, can become part of the structure of the bones when taken in with food or inhaled as dust, and (*b*) it continues for a very long time to emit radiation that is harmful to the surrounding cells of the body, and may eventually cause leukemia or other insidious ailments. The ordinary strontium found in nature, however, has no tendency to emit radiation, and is therefore not dangerous. Compounds of strontium have limited use, but you have undoubtedly seen the beautiful red light emitted in signal flares and fireworks that results from heating strontium compounds, especially the combination of strontium with nitrogen and oxygen, called "strontium nitrate."

Barium (Ba) is also similar to calcium and strontium, but more reactive. Furthermore, it and its compounds are poisonous. In preparation for a series of x-ray pictures of the gastrointestinal (GI) region, one is usually requested to drink a chalky slurry of a compound of barium, sulfur, and oxygen, called "barium sulfate." This, although hardly nourishing, is not toxic because the barium sulfate is too insoluble to be absorbed by the body. The purpose depends on the ability of the barium to block X rays, although they penetrate all around the barium to the film. Thus is delineated on the film the exact shape of the container that is filled with the barium sulfate slurry. Perhaps your only other acquaintance with barium compounds would be, again, related to their use in signal flares and fireworks, wherein barium, especially in combination with nitrogen and oxygen as "barium nitrate," imparts a green color.

Radium (Ra) is perhaps too scarce for you to be familiar with its appearance, but you are undoubtedly well aware of its unusual radiation

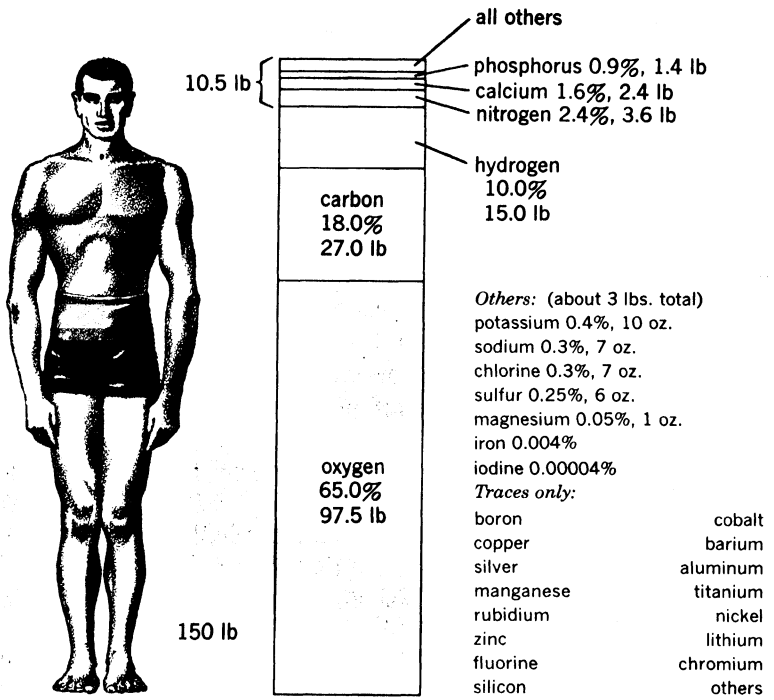


Figure 3. Elemental composition of human body (weight per cent).

properties. These are shown quite satisfactorily by radium in its compounds with other elements, and it may be used, for example, in its combination with chlorine, as "radium chloride." Radiation from radium is destructive to all living cells, but more so to the especially rapidly growing cells that characterize malignancies.

Zinc (Zn) is a common element of commerce. Your garbage can does not rust away rapidly despite the fact that it is mostly iron and that the conditions both inside and out are usually very favorable for rusting. The reason lies in the coating of zinc that protects the iron. The process of protecting iron in this manner is called "galvanizing." Cadmium (Cd) is similar to zinc, but denser, and sometimes tools are coated with cadmium to prevent rust. It seems unlikely that you would have encountered many compounds of these two metals. An important exception is the compound of zinc with oxygen, "zinc oxide," commonly used in ointment. This same compound mixed in rubber helps to prevent overheating and therefore deterioration of heavy-duty tires.

Aluminum (Al) is of course very familiar to you as the material of which most of your cooking utensils are made. It has also found wide use as a light-weight structural material, especially when alloyed with small amounts of other metals which improve its strength. Various compounds of aluminum with other elements have the property of inhibiting the production of sweat, and are therefore the chief active ingredients in personal deodorants. In combination with silicon, oxygen, and other metals, aluminum is a component of clays and numerous minerals.

Related to aluminum are some much less common metals: scandium (Sc), yttrium (Y), lanthanum (La), actinium (Ac), gallium (Ga), indium (In), and thallium (Tl). Neither in the free state nor in any of their compounds are these metals likely to be familiar to you. If you have read the label on certain household ant poisons, you may have observed that one active ingredient is a compound of thallium.

Another group of related metals is composed of: germanium (Ge), tin (Sn), and lead (Pb). Germanium is a very scarce and unfamiliar element, but it has received much attention because of the electrical properties shown by very pure germanium containing impurities in very carefully controlled traces. It is a grey-black solid, not too metallic in nature, but having an important use in transistors, which take the place of vacuum tubes in electronics. You will probably not have had occasion to know compounds of germanium, which are uncommon and without practical application at present. Tin, an element well known from early times, has been a boon, especially before the days of frozen foods and well-stocked freezers, to the busy housewife, for it kept her purchased containers of ready-prepared food from rusting on the shelves. Tin cans, it should be pointed out, are mostly iron, but they have a very thin plate of tin to prevent rusting. Compounds of tin are sometimes used to weight silks and other fabrics, and alloys of tin and lead are useful as solder. Lead is also a well-known element, and was once used in water pipes and even cooking vessels before its poisonous nature was recognized. Lead has many important industrial applications, as the metal and also in alloys and in compounds, some of which are doubtless familiar to you. "White lead," for example, a compound of lead with carbon, oxygen, and hydrogen, is a useful paint pigment, but hardly safe for toys for teething infants. "Red lead," a vermilion powder used in coating on steel to prevent corrosion, is a compound of lead with oxygen. The use of lead arsenate as an insecticide has already been mentioned. "Leaded" gasoline contains "lead tetraethyl," a compound of lead with carbon and hydrogen (from which the term "ethyl gasoline" is derived). This compound helps to control the combustion of the gasoline in a way that prevents or at least reduces

"knock" and produces greater power. And, of course, your automobile would be difficult to start without that storage battery, which contains lead, a compound of lead with sulfur and oxygen (lead sulfate), and a compound of lead and oxygen (lead dioxide).

A somewhat similar group of metals is formed by the elements titanium (Ti), zirconium (Zr), and hafnium (Hf). As improvements are made in the production of titanium from its naturally occurring compounds, it is likely to become very important as a light-weight structural metal and as a valuable ingredient of special alloys. The compound of titanium and oxygen called "titanium dioxide" can be prepared. Its pure white color and high reflecting power make it invaluable as a pigment in non-darkening white paint. The remaining two metals are quite rare, and have only very special applications.

Vanadium (V) may be unfamiliar, although a little of it may be mixed with the steel of your axe to give extra toughness. Niobium (Nb) and tantalum (Ta) may also be unfamiliar, although the latter sometimes is used to reinforce or replace part of people's bones, since it is one of the few materials that can resist the corrosive action of the internal fluids of the body. Antimony (Sb) and bismuth (Bi) are two more elements which do not find much application in the pure form, but they are very useful in alloys with other metals, where they impart special properties. Thus, antimony is contained in the lead of your automobile battery and in any bearings made of babbitt metal, as well as in type metal. Bismuth is a constituent of the low-melting alloys used as fusible plugs in automatic sprinkler systems and other fire-prevention apparatus. Compounds of none of these elements are very familiar, although a compound of antimony and sulfur (antimony pentasulfide) is used to make red rubber.

One of the most spectacularly glittering metallic elements is chromium (Cr), used as a plating metal because of its resistance to tarnish. Stainless steels are usually alloys containing chiefly iron and chromium. Molybdenum (Mo) is a related metal, unfamiliar but commonly used to impart special qualities to steel. Tungsten (W), one of the heaviest and strongest of the metals, is used as electric light filaments and in tool steels. Manganese (Mn) is another element used chiefly in steel, imparting extra toughness. Technetium (Tc) and rhenium (Re) are related to manganese but extremely rare. Again, none of the compounds of these elements are likely to be known to you, although an external first aid application to snake bites is sometimes a compound of manganese with potassium and oxygen called "potassium permanganate."

Now comes a group of metals which includes some of the most

familiar ones, and also some of the most expensive ones. They are: iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). Iron, of course, is the chief component of steel, having mixed therein only small percentages of carbon and of other metals. Nickel you know best as a coinage metal and as a plating material. It is also a component of Nichrome wire, used in electrical heating elements, and in alloy steels nickel imparts high resistance to corrosion. The nickel coin is an alloy containing actually only about one-fourth nickel; the rest is copper. Platinum you know chiefly as used in jewelry, and your fountain pen may be tipped with an alloy of iridium. The other metals of this group are much less familiar, except cobalt which is very useful in certain alloys, among them "Alnico" (aluminum-nickel-cobalt), which makes very powerful permanent magnets. Relatively few compounds of these elements are familiar substances. All too familiar is that sinister enemy of iron and steel called "rust," a compound of iron with oxygen. Compounds of iron with other elements are sometimes used in blue ink pigments. Iron is a component of the complex compound, the hemoglobin of the blood, but the total amount of iron in your body would be only enough to make one small nail.

Finally, the following metals are for the most part little known, but they complete the list of the known elementary substances of which all matter is composed: polonium, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium. You will recognize uranium (U) as being an element widely sought as a fuel for nuclear energy production. Although you will probably not recognize the names of most of the other metals listed above, a mixture of some of them is the material that gives off sparks to ignite the fuel of your cigarette lighter. All the elements from neptunium on are entirely man made, in the sense that they have not been found in nature. Most of them have become available only on such a small scale that relatively little is known about their compounds, although the amount of information is amazingly great considering the difficulties involved. Compounds of any of the above metals are certainly not familiar substances to the ordinary household today, although in the horse and buggy days certain of their compounds with oxygen helped to produce brighter light from gas mantles.

Up to this point, we have gone through the complete list, as far as they are known at this time of writing, of all the 103 basic components

of matter (of which only 88 are found in nature). As you will see later, one can be reasonably certain that no others will ever be discovered to be a significant part of the surface of the earth. Do not be alarmed about the number of unfamiliar elements, with their strange-sounding names. Most of them are relatively unimportant, especially to students beginning the study of chemistry. In fact, many successful professional chemists could not tell you much about most of the elements in the last group listed, or possibly about some of the others.

The important point is that you have some familiarity, if not always a speaking acquaintance, with a considerable proportion of these elements and their important compounds. The fact that you may never before have had formal instruction in chemistry by no means implies that you enter the field now totally uninformed and inexperienced. Chemistry is so inextricably interwoven with your daily living that you cannot have lived this long without acquiring some practical knowledge of it, even though you might not always have recognized this knowledge as "chemistry." The purpose of this book from here on is to help you *extend* the learning of chemistry, in which you have already become acquainted with many important facts.

SPECIAL HELP

The best help that can be given you at this point is some encouragement and advice.

The encouragement is that, if you have assimilated the fundamental facts presented in this chapter, if you have become convinced that you do indeed begin the study of chemistry with a background of pertinent and useful information about familiar substances, you have already made important progress toward an understanding of chemistry. You are not expected to learn the names and symbols of all the elements. They were mentioned only to show you that they include many substances already familiar to you, and so that you may at least recall having seen the names when you meet them again. The elements that are most important in introductory chemistry you will meet many times in this book, giving you ample opportunity to become well acquainted with them. The others need not worry you.

The advice, unfortunately, is of the kind that is best appreciated when it is too late to follow it. Chemistry can be a fascinating subject, but, as is true of plays, you must come in at the beginning to understand it. Please do not make chemistry unnecessarily difficult for yourself by

neglecting these preliminary studies. If you will make the necessary effort to learn each part of chemistry as it comes along, you will find it progressively easier and more interesting. But, unless you are exceptional indeed, you will not learn chemistry just by remaining wakeful during lectures. What comes in easily by one ear may depart from the other with equal ease, and possibly less pain. You will find it helpful to study this text in advance of the lectures, and then again after the lectures. Taking good notes during lectures will also be helpful, even though the material may also be found in the book, for it will require you to pay very concentrated attention and will open up another possible avenue by which some chemistry may reach your brain. Every path helps.

But however you do it, do keep up from day to day. If, instead, you wait to study until the night before each test, your study of chemistry will become progressively more difficult and much less interesting, and it might even be better to stop now. An understanding of chemistry can be most rewarding, but the reward comes only to those who are willing to work.

3

Atomic Structure

ALL ORDINARY MATTER is composed of atoms. These are particles at least roughly spherical in shape, only a few one-hundred-millionths of an inch in diameter. Their structure is quite complex, but in this structure lies the key to understanding the behavior of atoms and thus to understanding chemistry. It is therefore worthwhile to examine what is known about atomic structure at once, before trying to describe its consequences in chemical properties.

FUNDAMENTAL PARTICLES

Physicists have listed about thirty different particles of matter that are "subatomic," which means "smaller than atoms," but fortunately only three of these appear to be essential components of atoms from the viewpoint of explaining chemistry. These are called "**neutrons,**" "**electrons,**" and "**protons.**" They are roughly alike in order of magnitude, about one hundred-thousandth to one ten-thousandth of an atom

in diameter. Protons and neutrons are nearly equal in mass, but electrons weigh only about $\frac{1}{1840}$ as much. As indicated by their name, neutrons are electrically neutral, but electrons and protons bear electrical charge.

The properties of electrical charge are quite thoroughly known but its fundamental nature is still, and perhaps will always remain, a mystery. The properties of electrical charge most interesting in chemistry are three in number:

(1) It is discontinuous, occurring in packets or particles that are always whole number multiples of the same irreducible minimum quantity.

(2) It is of two kinds, of such opposite nature that they mutually mask each other's effects, that is, neutralize one another when placed in the same position in equal quantity. Charges of the same kind repel one another and charges of opposite kind attract one another, the forces becoming larger with increasing amount of charge and increasing closeness of approach.

(3) Electrical charge in motion produces magnetism.

The minimum possible quantity of one kind of electrical charge, called "**negative**" charge, appears to be the charge on one electron. This minimum charge is one of the "truly fundamental" constants of physics. It is equal to 4.8×10^{-10} electrostatic unit. All electrons are equal in charge; they appear to be the fundamental units of negative electricity. The minimum possible quantity of the other kind of electrical charge, the "**positive**" charge, appears to be the charge on a proton. The charge on one electron is exactly equal in magnitude but opposite in sign to the charge on one proton.

Both the electron and the proton appear capable of stable isolated existence. Not so the neutron. This particle shows a marked tendency to explode without provocation and with great violence (great release of energy) relative to its tiny size. If billions of neutrons were observed over a period of time, their spontaneous disintegration would be found to follow a rate law such that at the end of about fourteen minutes half would have disintegrated, at the end of about another fourteen minutes half of the remainder would have disintegrated, and so on. The period of about fourteen minutes is called the "**half-life**" of the neutron. The exact nature of this decomposition is not understood. It suggests, however (and this is pure speculation), that the neutron itself is constantly undergoing entirely random changes in structure or orientation of components, and that one or more of the many possible configurations are unstable. Whether the neutron explodes now, one second from now, ten minutes from now, or a million years from

now seems to depend on the pure chance of its acquiring an unstable configuration. One might consider the analogy of a can containing a marble, and a hole exactly the size to permit escape of the marble if it strikes the hole exactly straight. One might then shake the can in a random manner. The marble, bouncing around inside, might happen to strike the hole and fly out within the first few shakes. It might, on the other hand, not hit the hole in thousands of shakes. But if we had billions of such cans with marbles in motion, a steady outflow of marbles would be observed, and a half-life of the marble in the can could be evaluated.

When a neutron disintegrates, it forms one proton and one electron, at the same time releasing a large amount of energy.

The three component particles of which all atoms are made are summarized in the following table.

PARTICLE	RELATIVE MASS	CHARGE	STABILITY
electron	$\frac{1}{1840}$	−1	stable
proton	1	1	stable
neutron	1	0	unstable

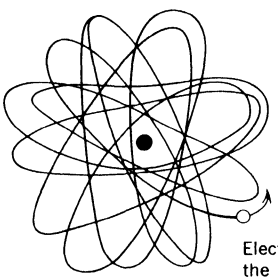
THE GROSS STRUCTURE OF ATOMS

An important natural principle is that, when a process is capable of occurring in both directions, backwards and forwards, if energy is given out in one direction the opposite direction will require absorption of energy. For example, if a ball can give up energy by rolling downhill, energy must be supplied to move the ball back uphill. This principle must be borne in mind when the question is considered, what would happen if an electron and a proton should come together? From the fact that these particles are oppositely charged, one might expect them to come together strongly, perhaps forming a neutron, since they would neutralize each other's charge. But we have just seen that a neutron decomposes spontaneously, with the release of much energy, to form a proton and an electron. According to the above principle the reverse process, joining a proton and an electron to form a neutron, would require input of a relatively large amount of energy. Therefore we cannot expect an electron and a proton to form a neutron.

Then what does happen when an electron and a proton come near to one another? They rotate around one another, since they cannot coincide, and the result on the charge is essentially the same: the center of

negative charge and the center of positive charge do coincide. If you were to throw a straight stick of uniform diameter end over end into the air, it would rotate about its center of gravity which would be close to its center. If you were to throw a hammer end over end into the air, you would observe the handle to rotate around the head much more than the head around the handle. The rotation again would be about the center of gravity, which this time is much closer to the head. When the rotating system consists of an electron and a proton, with the proton weighing nearly two thousand times as much as the electron, the center of gravity almost coincides with the center of the proton. We may therefore for practical purposes describe this system as consisting of an electron rotating around a proton, although in reality both are rotating about their mutual center of gravity.

This combination of electron and proton whirling around one another at the most stable average distance is an atom. It is the simplest of all



Electron travels around proton (nucleus) so rapidly that the effect is to create a cloud of negative electricity around the nucleus.

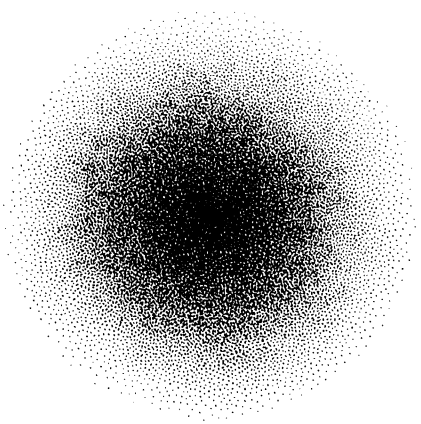


Figure 4. Hydrogen atom—a representation.

atoms, an atom of hydrogen. Since this is the prototype of all atoms, let us consider it in more detail. The speed of the electron is so great, and the distance it travels so relatively small per trip, that the number of revolutions is close to six billion in one-millionth of a second. In effect, then, the electron is everywhere at once around the proton, and one may picture it as composing a cloud of negative electricity with the proton at the center. Relative to the proton, this cloud is extremely nebulous, bearing only an insignificant part of the mass of the atom. Yet the size of the cloud, which is, of course, the effective size of the atom, is such that most of the atom is vacant space. Indeed, if the proton were a baseball the electron might be another baseball travelling at distances up to nearly half a mile from the proton. Yet the great void in between is effectively filled by the electron because of its terrific speed.

The central particle of the hydrogen atom, the proton, contains all the positive charge and practically all the mass of the atom. We call this central particle in an atom the "**nucleus.**" The electron cloud contains all the negative charge, exactly enough to neutralize the positive charge of the proton, with the result that the atom as a whole is electrically neutral. Formerly, the electron was likened to a planet revolving around the sun and called a "planetary" electron. All atoms that contain but a single proton in the nucleus and a single electron to balance it are called hydrogen atoms. Hydrogen is one of the chemical elements. Its chemical symbol is H.

Now, suppose two protons are put together. According to Coulomb's law these, having like charge, should repel one another with a force increasing with decreasing distance. A combination of two protons in close proximity should be exceedingly unstable. Evidently, however, protons can be held together somehow, in a way not yet understood, through the agency of neutrons. At the same time the stability of the neutrons is somehow increased. A stable particle can therefore exist, consisting of a combination of two protons and two neutrons. Such a particle is called an "**alpha particle.**" As will be described in Chapter 27, alpha particles were first identified as being ejected from certain substances as part of the process called "**radioactivity.**"

Suppose an electron is brought toward an alpha particle. Since they are oppositely charged particles, one might expect considerable attraction between them. Indeed there is, up to a point. But, just as in the case of the hydrogen atom, when a certain average distance is reached the electron can go no closer but instead goes into orbit around the alpha particle. A second electron does likewise, and there are now two electrons whirling around the alpha particle, with its positive charge of the two protons exactly balancing the negative charge of the electrons.

This is another atom, that of helium. All atoms that contain two protons in the nucleus, and two electrons in the cloud, are atoms of the element helium, symbolized by He.

In a similar manner, addition of neutrons to the nucleus permits addition of more and more protons, and electrons will go into orbit around the nucleus in the correct number to balance the nuclear charge due to the protons. There can thus be atoms with three protons in the nucleus and three electrons in the cloud, or four nuclear protons and four electrons, or any other whole number up to at least 103.

Atomic Number

All atoms ordinarily are electrically neutral. This requires that the number of electrons per atom must equal the number of protons. This number, an extremely significant one in chemistry, is called the **"atomic number."** All atoms having the same atomic number behave identically, or nearly so, and are the basic components of the species of matter known as a chemical element. Each different atomic number represents a different chemical element. All chemical elements are now known, from atomic number 1 to atomic number 103, consecutively. As already pointed out, hydrogen is the element of atomic number 1, and helium of atomic number 2. To cite some other familiar examples, 6 is carbon (C), 7 is nitrogen (N), 8 oxygen (O), 11 sodium (Na), 12 magnesium (Mg), 13 aluminum (Al), 14 silicon (Si), 15 phosphorus (P), 16 sulfur (S), 17 chlorine (Cl), 20 calcium (Ca), 24 chromium (Cr), 26 iron (Fe), 29 copper (Cu), 30 zinc (Zn), 33 arsenic (As), 47 silver (Ag), 50 tin (Sn), 79 gold (Au), 80 mercury (Hg), 82 lead (Pb), and 92 is uranium (U). The familiar differences in the properties of these elements are, it will be demonstrated, a logical and inevitable outcome of differences in their atomic number.

General Structure

All atoms, whatever their atomic numbers, are similar in the general features of their structure. Each atom has a relatively compact central core called the nucleus, consisting of the **"nucleons"**—all the protons and neutrons—and therefore bearing positive charges numerically equal to the atomic number. Consequently the nucleus contains practically all the mass of the atom, since electrons are so much lighter. Surrounding this nucleus, in a very nebulous, or attenuated, cloud, are all the elec-

trons. As indicated previously, both electrons and nucleons are much tinier than atoms. Thus most of the space actually occupied by an atom must be empty, but the electron cloud effectively fills this space by virtue of the high velocity with which the electrons are traveling around the nucleus. Since electrons repel one another, the size of a more-than-one electron cloud must represent a balance between these repulsive forces and the attraction exerted between them and the nucleus.

ISOTOPES AND ATOMIC WEIGHTS

The atomic number absolutely identifies the chemical element. All atoms of the same element must have the same atomic number—the same number of electrons in the cloud around the nucleus and the same number of protons in the nucleus. The number of neutrons, however, may vary. That is, different atoms of the same element may not all contain the same number of neutrons. For example, most chlorine atoms contain 17 protons and 18 neutrons per nucleus, but some contain 17 protons and 20 neutrons. Such differences require the term **"isotope,"** which means it is the same element but has a different number of neutrons. The first chlorine isotope just mentioned has two fewer neutrons per nucleus than the second isotope. Obviously atoms of the second isotope are heavier than those of the first, because of the additional neutrons. Isotopes therefore always differ in the weights of the atoms, never in atomic number.

The weights of individual atoms are so tiny as to be meaningless to us. Yet relative to one another these weights are very important. Chemists have devised a relative atomic weight scale, until recently based on oxygen, but now based on the carbon isotope which has 6 neutrons per atom, to which the weight of 12 is assigned. All other elements are assigned atomic weights relative to 12 for this carbon isotope. For example, hydrogen atoms weigh only $\frac{1}{12}$ as much as the carbon atoms and therefore have atomic weight 1. Helium atoms are $\frac{1}{3}$ as heavy as the carbon atoms; the atomic weight of helium is 4. Sulfur atoms are $2\frac{2}{3}$ as heavy as carbon atoms; atomic weight 32. Since these are relative numbers and dimensionless, they have been named "atomic mass units," abbreviated "a.m.u."

Now consider the significance of the atomic weight of 1 for hydrogen. A hydrogen atom contains only one proton and one electron. The weight of the electron is only $\frac{1}{1840}$ that of the proton. This means that the proton weighs $\frac{1839}{1840}$, or practically all, of a hydrogen atom. The **"atomic weight"** of a proton is therefore essentially 1. It was earlier

stated that neutrons have nearly the same mass as protons. Thus the "atomic weight" of a neutron can also be taken as one. Since even 100 electrons weigh only $\frac{100}{1840}$ of an atomic weight unit, or about 0.06 unit, we may for most purposes neglect the contribution that electrons make to the mass of an atom and consider that the atomic weight equals the sum of the protons and neutrons. Thus oxygen has atomic weight 16, which means 16 nucleons (protons and neutrons) per atom. Its atomic number is 8. Subtracting the 8 from the 16 leaves 8 for the mass contribution, and therefore number, of neutrons.

In general, one can find the average number of neutrons per atom by subtracting the atomic number from the atomic weight. This method works unquestionably well when the atomic weight of the element is practically a whole number, but for many of the elements the atomic weight is not near to a whole number. For example, the atomic weight of chlorine is 35.45. One can see the cause of this by recalling that some chlorine atoms have 18 neutrons per atomic nucleus and some have 20. The atomic weight for each isotope would then be close to 35 for the first and 37 for the second. The value of 35.457 is the value for the average atom in a mixture of isotopes. It would correspond approximately to a mixture of about three 35-mass atoms to one 37-mass atom. No matter what the source of the chlorine in nature, whether from salt water of the tropical seas or underground deposits in Michigan, the atomic weight always comes out to be 35.457. In other words, the relative abundance of the isotopes remains generally constant. With but few exceptions, this is true for most chemical elements as they are found in nature. For this reason, one may accept the atomic weight determination as significant, even though for most of the chemical elements it represents only the average of all the atoms and not the exact relative weight of any one isotope. When the isotopes have significantly different properties it is usual to distinguish among them by their mass number. For example, uranium 238 (U^{238}) refers to the most abundant isotope of uranium, and uranium 235 (U^{235}) to the isotope having three fewer neutrons per nucleus. For hydrogen, the isotopes are actually assigned special names. Ordinary hydrogen atoms have only a proton in the nucleus. Some hydrogen atoms have a neutron per nucleus, as well, and this is an isotope called "deuterium" (H^2). Still rarer are hydrogen atoms having two neutrons per nucleus (H^3); this isotope is called "tritium."

If the atomic weight of an element is an average of the isotopes present in the element as it is found in nature, then what about oxygen, the previous standard? When the weight of 16.0000 was originally chosen as that of oxygen, and the whole atomic weight scale was set up with this value as basis, isotopes of oxygen were unknown. It has

since been discovered that natural oxygen is mostly composed of atoms having 8 protons and 8 neutrons in the nucleus, but also contains small traces of isotopes having 8 protons and 9 neutrons (O^{17}) and 8 protons and 10 neutrons (O^{18}). If one takes as standard the major isotope as having atomic weight 16, natural oxygen has an atomic weight slightly higher than this. Physicists have taken the O^{16} isotope as the standard, and based their atomic weight scale on it. Chemists, however, have been reasonably content to stay with 16.0000 as representing natural oxygen with its mixture of isotopes, since the revision would be confusing, and since there is actually little difference between the two scales—a negligible difference from most viewpoints. An atomic weight unit on the chemist's scale equalled 1.000275 atomic weight unit of the physicist's scale. Since the chemist's units were larger, the relative atomic weights were smaller on the chemist's scale.

To eliminate such discrepancies, the atomic weight standard has been shifted from natural oxygen to the carbon isotope of mass 12.00. This change has had a practically negligible effect on the atomic weight table, individual values remaining almost the same as when oxygen was the standard. Natural oxygen itself, for example, is changed from 16.0000 to 15.999.

The Mole

Since atoms are so tiny and atomic weight units represent mass units far too small for any practical scale of measurement, chemists use much larger units which keep the same relationship among the elements. They call these "moles." A mole may be defined here as that quantity of an element weighing the number of grams equal to its atomic weight. A mole of an element is sometimes called its "gram-atomic weight." Thus, the atomic weight of magnesium is 24; one mole is 24 grams. The atomic weight of helium is 4; one mole is 4 grams. One mole of magnesium is 6 times heavier than one mole of helium, just as one atom of magnesium is 6 times heavier than one atom of helium. One can correctly infer that if the weights of samples of two elements are in the same ratio as their atomic weights, the two samples must contain identical numbers of atoms. The number of atoms in a mole of atoms is 6.02×10^{23}. This holds for all elements. Chemists find the mole a very valuable unit, for, by working with moles, they know how many atoms they are dealing with. The concept is commonly expanded to include moles of molecules, moles of compounds, and moles of electrons, as will be described in later chapters.

SUMMARY

All matter is composed of atoms, which in turn are made up of electrons, protons, and neutrons. Neutrons and protons are nearly alike in mass, which is about one-twelfth that of an atom of carbon. Neutrons differ from protons in having no electrical charge, and in being unstable when isolated, breaking into an electron and a proton, with a large release of energy. The proton bears a positive charge, equal and opposite to that of the negative electron. The electron weighs only about $\frac{1}{1840}$ as much as a proton or neutron. Since the latter each weigh about one atomic weight unit, the atomic weight of the electron is about 0.0006.

Every atom consists of a relatively compact center of mass and positive charge called the "nucleus," imbedded in a relatively very thin cloud of electrons, larger in diameter than the nucleus by a factor between ten thousand and one hundred thousand. The nucleus contains all the protons and all the neutrons. Somehow, the neutrons appear to make it possible for the mutually repelling protons to be held together closely yet stably, and the protons appear to make the neutrons relatively stable in most nuclei.

The number of electrons per atom is exactly equal to the number of protons. This number is called the "**atomic number.**" The atomic number is one of the most significant numbers in chemistry, for it designates exactly the identity of each chemical element. The chemical elements, basic substances of which all ordinary matter is composed, are now known for each atomic number from 1 to 103. All of the atoms of any given element must be alike in atomic number, but they may differ in number of neutrons and therefore in atomic weight. Such different kinds of atoms of the same element are called "**isotopes.**"

ELECTRONIC STRUCTURE OF ATOMS

One of the most fascinating facts about chemistry is that all the myriad forms of matter on earth are composed of one or more of the same, relatively few, chemical elements. The elements are evidently able to combine with one another, according to certain rules and restrictions, to form compound substances having properties entirely different from those of the component elements in the uncombined state. Yet the identity of each atom, although concealed in the compound, is never permanently destroyed by such a change. By appropriate means, the individual elements may be recovered again from the compound. Chemistry is largely the science of combination, recombination, and separation of atoms, for it is by these processes that materials

Table 1 Symbols, Atomic Numbers, and Atomic Weights of the Chemical Elements

NAME	NO.	SYMB.	AT. WT.	NAME	NO.	SYMB.	AT. WT.
hydrogen	1	H	1.008	tellurium	52	Te	127.60
helium	2	He	4.003	iodine	53	I	126.904
lithium	3	Li	6.939	xenon	54	Xe	131.30
beryllium	4	Be	9.012	cesium	55	Cs	132.905
boron	5	B	10.811	barium	56	Ba	137.34
carbon	6	C	12.011	lanthanum	57	La	138.91
nitrogen	7	N	14.007	cerium	58	Ce	140.12
oxygen	8	O	15.999	praseodymium	59	Pr	140.907
fluorine	9	F	18.998	neodymium	60	Nd	144.24
neon	10	Ne	20.183	promethium	61	Pm	147
sodium	11	Na	22.990	samarium	62	Sm	150.35
magnesium	12	Mg	24.312	europium	63	Eu	151.96
aluminum	13	Al	26.982	gadolinium	64	Gd	157.25
silicon	14	Si	28.086	terbium	65	Tb	158.924
phosphorus	15	P	30.974	dysprosium	66	Dy	162.50
sulfur	16	S	32.064	holmium	67	Ho	164.930
chlorine	17	Cl	35.453	erbium	68	Er	167.26
argon	18	Ar	39.948	thulium	69	Tm	168.934
potassium	19	K	39.102	ytterbium	70	Yb	173.04
calcium	20	Ca	40.08	lutetium	71	Lu	174.97
scandium	21	Sc	44.956	hafnium	72	Hf	178.49
titanium	22	Ti	47.90	tantalum	73	Ta	180.948
vanadium	23	V	50.942	tungsten	74	W	183.85
chromium	24	Cr	51.996	rhenium	75	Re	186.2
manganese	25	Mn	54.938	osmium	76	Os	190.2
iron	26	Fe	55.847	iridium	77	Ir	192.2
cobalt	27	Co	58.933	platinum	78	Pt	195.09
nickel	28	Ni	58.71	gold	79	Au	196.967
copper	29	Cu	63.54	mercury	80	Hg	200.59
zinc	30	Zn	65.37	thallium	81	Tl	204.37
gallium	31	Ga	69.72	lead	82	Pb	207.19
germanium	32	Ge	72.59	bismuth	83	Bi	208.980
arsenic	33	As	74.922	polonium	84	Po	210
selenium	34	Se	78.96	astatine	85	At	210
bromine	35	Br	79.909	radon	86	Rn	222
krypton	36	Kr	83.80	francium	87	Fr	223
rubidium	37	Rb	85.47	radium	88	Ra	226
strontium	38	Sr	87.62	actinium	89	Ac	227
yttrium	39	Y	88.905	thorium	90	Th	232.038
zirconium	40	Zr	91.22	protactinium	91	Pa	231
niobium	41	Nb	92.906	uranium	92	U	238.04
molybdenum	42	Mo	95.94	neptunium	93	Np	237
technetium	43	Tc	99	plutonium	94	Pu	242
ruthenium	44	Ru	101.07	americium	95	Am	243
rhodium	45	Rh	102.905	curium	96	Cm	247
palladium	46	Pd	106.4	berkelium	97	Bk	247
silver	47	Ag	107.870	californium	98	Cf	251
cadmium	48	Cd	112.40	einsteinium	99	Es	254
indium	49	In	114.82	fermium	100	Fm	253
tin	50	Sn	118.69	mendelevium	101	Md	256
antimony	51	Sb	121.75	nobelium	102	No	254
				lawrencium	103	Lm	

valuable to man are obtained and all substances, whether at present valuable to man or not, are created or changed. Also, these changes always involve energy changes, and many, like the burning of coal or gasoline, can be applied to the practical production of energy to do man's work. In order to acquire some understanding of chemistry, one must try to understand the nature of properties and of chemical combination.

Consider what must happen if two or more atoms are to combine. The first requirement is that they must come together. There can be no joining together without proximity. Now remember that each atom is outwardly a cloud of electrons, held within limits by a positively charged nucleus in the interior. Such clouds can only repel one another. No interaction of an attractive nature can occur unless some other factors can exert influence. We know that some kinds of atoms come together and do not stick together, but some other kinds do. In the former case, we can account for the observed result in terms of the repulsion among electron clouds of the separate atoms. In the latter instance, we must recognize that some other force must exceed the repulsion among electron clouds. The simplest or most obvious "other force" would be significant if each atomic nucleus could attract the electrons of another atom. In other words, if the electron cloud about an atomic nucleus can shield this nucleus effectively from the attractions exerted by outside electrons two atoms will repel one another, but if the electron cloud cannot shield the nucleus completely from the attractions exerted by outside electrons the two atoms may attract one another. It follows that since atoms must come in contact through their exteriors, if sometimes this contact has one result and sometimes the opposite atomic exteriors cannot be all alike. From this, it should be clear that one must seek further knowledge of these electron clouds before he can begin to understand the interactions of atoms.

Atomic Spectra

The minuteness of atoms prevents them from being seen, and any information concerning their structure must of course be acquired indirectly. Probably the most valuable source of such information has been the study of the reactions of atoms when outside energy has been applied to them. When substances are subjected to electrical discharge, heat, or light under certain conditions, they give off light. When this light is examined by separating its component frequencies, using a diffraction grating (a refined device for producing the spectrum, as does

a prism), the light is found to be discontinuous, only certain frequencies being emitted, with dark areas in between. Furthermore, the particular frequencies emitted are found to be characteristic of the particular elements, which can thereby be identified. Immediately this has practical significance, for it permits the study of atomic spectra, as the separated frequencies of the emitted light are called, to be the basis of spectroscopy as an analytical tool. Spectroscopes have been designed to detect all the elements present in a given substance, even when they are present only in traces, and even to measure their concentrations quantitatively. An element found to be "spectroscopically pure" is very pure indeed.

The differences among the spectra emitted by different elements can even be perceived visually, without a spectroscope, for some of the elements. For example, compounds of lithium impart a crimson color to the flame. Boron and copper color the flame different hues of green. Calcium gives an orange-red color, potassium violet, and sodium

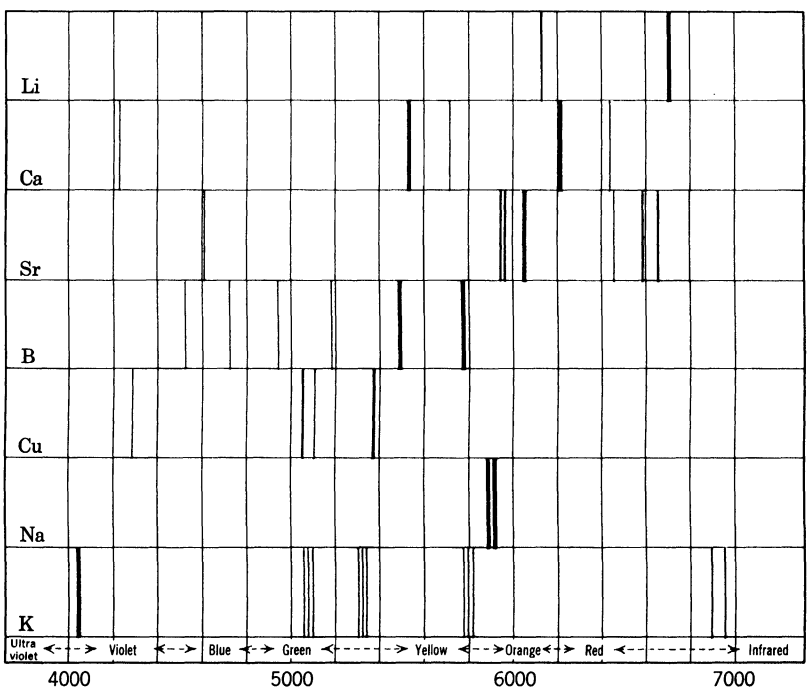


Figure 5. Portions of emission spectra of some elements identifiable by flame tests (wavelengths given in Angstrom units (Å): 1 Å = 10^{-8} cm).

an intense pale yellow. All these are the result of one or more frequencies of light that are emitted especially strongly in a particular part of the visible spectrum.

To understand the above phenomena, one wants to know how light is emitted from atoms under the described conditions and why the frequencies of the lines of the spectra depend on the kind of atom. Surely the simplest spectrum should be that emitted by hydrogen, since these atoms are undoubtedly simplest of all. Nearly a century ago, a man named Balmer studied especially that part of the hydrogen spectrum which occurs in the visible violet and near ultra-violet portion of the frequency range. He found that a series of lines occur, whose frequencies are related to one another by the following simple but empirical formula:

$$\lambda_n = B\frac{n^2}{n^2 - m^2}$$

λ_n is the wavelength, B is a constant, and n and m are integers, m having the value 2 and n, values of 3, 4, 5. . . . Later, other series of lines were found, and a physicist named Rydberg found that the Balmer formula could be generalized to account for each of these series:

$$\bar{\nu}_n = \bar{\nu}_\infty - \frac{R}{(n - A)^2}$$

In this equation $\bar{\nu}_n$ is the "wave number," the number of waves per cm or $1/\lambda$, $\bar{\nu}_\infty$ and A are constants depending on the particular series, and n can be any integer. R is a general constant for all series, called the Rydberg constant.

Obviously, something very fundamental was involved here. The great problem was, what in the nature of an atom could cause it to emit such spectral lines? Of what significance is their frequency?

The Bohr Theory

A great answer came from a brilliant young Danish physicist, Neils Bohr. Bohr assumed that an electron could occupy only certain discrete energy states about the nucleus of an atom, one of which, called the "ground state," would be most stable and therefore preferentially occupied. As long as an electron revolves about the nucleus in the ground state, or in any specific energy state, no energy is absorbed or emitted. But since these energy states differ, any transition from one state to another must involve an absorption or emission of energy

in quantity exactly equal to the energy difference between the two states. When a hydrogen atom is exposed to a sufficient source of energy, then, its electron may absorb enough energy to jump to a higher energy state from the ground state. In this higher state, however, it is very unstable, and in a tiny fraction of a second, the electron jumps back to a more stable state. When this jump occurs, Bohr postulated, the difference in energy between the two states is released in the form of light of a certain frequency, and one line of the spectrum is created. If E_2 is the energy of the higher state (called an "excited" state), and E_1 the energy of the lower state, then the frequency of the light is given by $E_2 - E_1 = h\nu$, where h is Planck's constant and ν is the frequency.

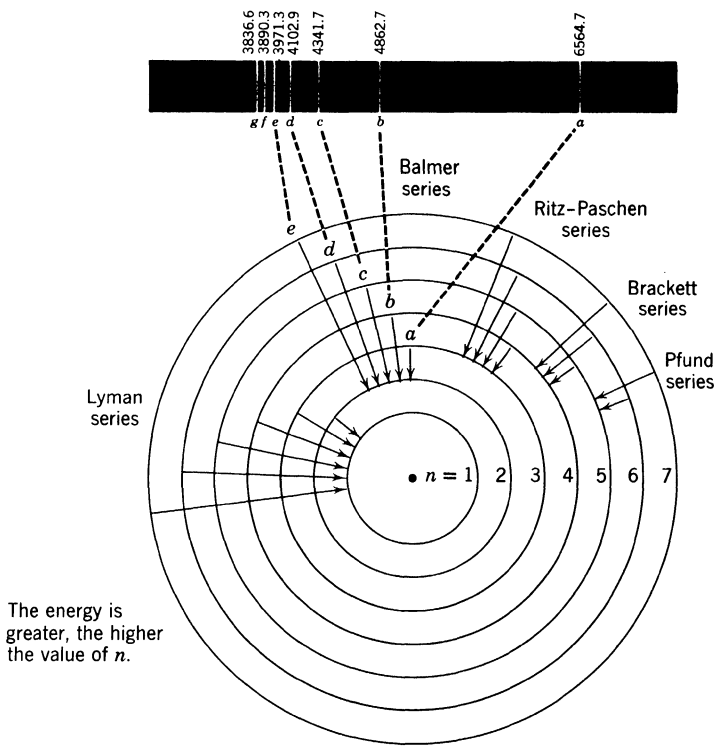


Figure 6. Schematic representation of Bohr energy levels in hydrogen atom; origin of spectral lines. Notice especially the correspondence between the lines of the spectrum and the electron jumps, shown for part of the Balmer series. Each jump shown, as well as others, corresponds also to a line in the hydrogen spectrum. Notice also that the longer the jump, the more energy released and the shorter the wavelength (higher frequency).

In other words, the energy of an electron in an atom is quantized—which means that, like energy in general, it cannot be transmitted continuously but is discontinuous, and can have only certain discrete values. This fact was discovered by Max Planck. Bohr pictured the hydrogen atom as consisting of the nucleus at the center of circular orbits, differing in radius. These orbits he designated as principal quantum levels, with integral principal quantum numbers $n = 1$, for the stablest, or smallest, 2 for the next stablest, and so on. When a hydrogen atom is excited, the electron may be raised to an energy level several steps above the ground state. Its return to the ground state may then have several alternatives. It may jump back all at once, by single steps, or by any possible combination of steps downward in energy. Each jump corresponds to emission of a particular line of the hydrogen spectrum. It was observed that the Balmer series corresponds to jumps from various higher levels to the $n = 2$ level. Similarly, the Lyman series, in the ultraviolet, corresponds to jumps from any higher level to the $n = 1$ level, other series result from jumps to the $n = 3$ and $n = 4$ levels, and so on. By taking into account the electrostatic attraction between electron and proton and the angular momentum of the electron in orbit, Bohr was able actually to calculate the Rydberg constant, R, and thence the individual spectral frequencies of the hydrogen with extraordinary success.

Wave Mechanics of the Atom

Similar calculations could be made for hydrogen-like atoms—that is, heavier atoms from which all but one electron have first been removed. But unfortunately even for helium, of atomic number two, the Bohr theory ran into difficulties. It was apparent that the general mechanism of absorption of energy by atoms and its almost immediate emission in the form of light must be essentially correct, yet other factors evidently were not being taken adequately into account. The quantum picture originated by Bohr became known as the "older quantum mechanics" of the atom when, more than a decade later, it was displaced by the "newer quantum mechanics, or wave mechanics." The essential difference arose from the recognition by DeBroglie that particles in motion have wave characteristics. Unless these characteristics are taken into account, the energy of an electron in an atom cannot be evaluated. Yet the mathematical treatment becomes enormously more complex, and the physical picture of an atom becomes much more nebulous. As a consequence, one can no longer point out definite orbits occupied by electrons, but only consider them in terms of proba-

bilities. The individual electron becomes in a sense a cloud, occupying a region within which one can only say that the electron has greatest probability of being. Here we must stop at the borderline, accepting the futility of trying to understand, at this stage of instruction, the mathematical complexities that are now considered to represent reality more accurately. We can, nevertheless, also accept certain useful parts of the modern quantum theory that can help us at once toward a practical understanding of chemistry.

Quantum Numbers. The most important knowledge from this source is that the condition of each electron of an atom can be fully designated in terms of four quantum numbers. An exact physical picture of the significance of each quantum number is not available, but very roughly the meanings are indicated as follows:

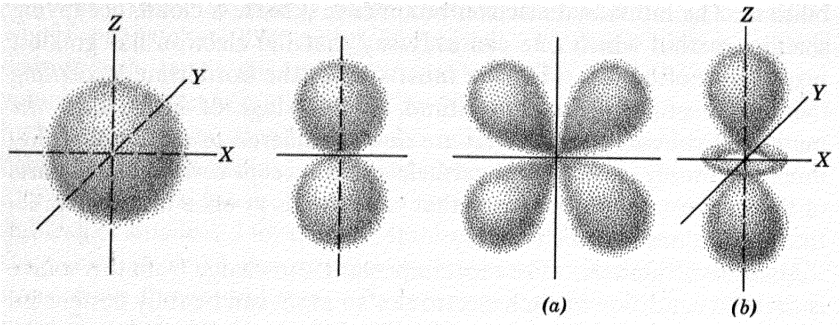
(1) **Principal** quantum number, $n = 1, 2, 3, 4 \ldots$ designates the average distance of the electron from the nucleus. If one considers that the electrons around the nucleus are arranged in concentric spheres of energy increasing with radius, then the nearest sphere to the nucleus is referred to as the first principal quantum level, or $n = 1$, the next sphere is the second principal quantum level, or $n = 2$, and so on.

(2) **Orbital** quantum number, $l = 0, 1, 2$, up to $n - 1$. This designates the individual regions within the principal quantum levels. Each such region is the modern version of the older "orbit" and is called an "orbital." Each orbital can accommodate a maximum of two electrons. The l values designate different shapes of the orbitals. These orbitals are called s orbitals if $l = 0$, p orbitals if $l = 1$, d orbitals if $l = 2$, and f orbitals if $l = 3$. No higher l values are important in ordinary chemistry. (This designation by letter comes from spectroscopy, where different series of lines in the same spectrum are observed to be "sharp," "principal," "diffuse," and "fundamental," whence the $s, p, d,$ and f.)

(3) **Orbital magnetic** quantum number, $m_l = 0$ to $\pm l$. The electron travelling in its orbital is a moving charge and therefore has associated with it a magnetic field. This magnetic field can have various orientations in an external magnetic field, which are quantized. According to the limits given for the values which this number can have, an s orbital may have only one orientation ($m_l = 0$); a p orbital may have one of three orientations ($m_l = 0, 1, -1$); a d orbital may have one of five orientations ($m_l = 0, 1, 2, -1, -2$); an f orbital may have one of seven orientations ($m_l = 0, 1, 2, 3, -1, -2, -3$).

(4) **Spin magnetic** quantum number, $m_s = +1/2, -1/2$. Each electron appears to be a tiny magnet, and thus is described as having spin. The direction of spin determines the orientation of the magnet.

Now, every electron in an atom can be designated in terms of a



s orbital, 1, spherically symmetrical about the origin (nucleus).

p orbitals, 3, one directed along each axis (*X*, *Y*, and *Z*). Taken together, the 3 *p* orbitals are spherically symmetrical about the origin (nucleus).

d orbitals, 5, 4 shaped like *a*, the fifth like *b*. Three are between axes (*X*-*Y*, *X*-*Z*, *Y*-*Z*) in their plane, as shown. The fourth is directed along the *X* and *Y* axes. The fifth, as shown, extends along the *Z* axis. A doughnut-shaped ring is perpendicular to its center, in the *X*-*Y* plane. Taken together, the 5 *d* orbitals are spherically symmetrical about the origin (nucleus).

Figure 7. Shapes of atomic orbitals.

combination of these four quantum numbers, subject to the restrictions placed above on their possible numerical values, and subject to an important empirical principle of quantum mechanics called the "Pauli Exclusion Principle." This may be stated: **no two electrons within the same atom may have the same four quantum numbers.**

It may easily be seen that this principle, together with the numerical restrictions listed above, limit the electron capacity of the principal quantum levels. Thus in the first level, where $n = 1$, there can only be one l value, which is 0, and therefore but the single orbital designated as the 1*s* orbital. This can have no variations in magnetic orientation. The two electrons which it can accommodate can only be held if their spin magnetic quantum numbers are of opposite sign—in other words, if their magnetic poles are opposed. The capacity of the first principal quantum shell is therefore two electrons. Their quantum numbers are given as follows:

ELECTRON NUMBER	n	l	m_l	m_s
1	1	0	0	$+\frac{1}{2}$
2	1	0	0	$-\frac{1}{2}$

A third electron in this shell would have to duplicate one of these sets of four quantum numbers—in effect, it would have to coincide with an electron already there. This is impossible.

Similarly, in the second principal quantum level, or shell, where $n = 2$, there may be an s orbital, just as in the first shell, which would now be called the $2s$ orbital. In addition, l can now have also the value 1. For this value, three orientations in a magnetic field are permissible, which correspond to the m_l values of 0, $+1$, and -1. Thus for $l = 1$, three orbitals are possible, the $2p$ orbitals. As before, each of these can accommodate only two electrons, and these only if their m_s values are of opposed sign. In summary, the second principal quantum level can contain electrons in one $2s$ orbital, or 2 electrons, plus three $2p$ orbitals, or 6 electrons, totaling 8 electrons for the capacity of this level. The combinations of quantum numbers for the individual electrons at this level are as follows:

ELECTRON NUMBER	n	l	m_l	m_s	NAME OF ORBITAL
1	2	0	0	$+\frac{1}{2}$	$2s$
2	2	0	0	$-\frac{1}{2}$	$2s$
3	2	1	0	$+\frac{1}{2}$	$2p$
4	2	1	0	$-\frac{1}{2}$	$2p$
5	2	1	1	$+\frac{1}{2}$	$2p$
6	2	1	1	$-\frac{1}{2}$	$2p$
7	2	1	-1	$+\frac{1}{2}$	$2p$
8	2	1	-1	$-\frac{1}{2}$	$2p$

In a similar manner, it can easily be shown that the third principal quantum level, $n = 3$, can have 8 electrons similar to the s and p electrons tabulated above, plus the additional electrons wherein $l = 2$. There are five d orbitals with $l = 2$: where $m_l = 0, 1, 2, -1, -2$. Each of these can contain two electrons, so this adds 10 more electrons, for a grand total of 18 electrons as the capacity of this third principal quantum shell. Likewise, the fourth and all higher shells can have all these 18 combinations of quantum numbers, plus the ones added by the l value of 3, which leads to seven f orbitals, where $m_l = 0, 1, 2, 3, -1, -2, -3$. These f orbitals can of course contain 14 electrons, bringing the total capacity to 32. In none of the elements are we concerned with shells containing more than 32 electrons, no matter how high the principal quantum number of the shell.

A number of interesting conclusions may be drawn here. One is that the number of each kind of orbital in a given principal quantum level is *odd,* beginning with one: one *s* orbital, three *p* orbitals, five *d* orbitals, and seven *f* orbitals. Another is that the number of kinds of orbitals within any given principal quantum level equals the principal quantum number of that level, up to 4, that is, the level where $n = 1$ can contain only one kind of orbital, *s*. Where $n = 2$, two kinds of orbitals, *s* and *p*, occur. Where $n = 3$, three kinds of orbitals, *s*, *p*, and *d*, occur. Finally, where $n = 4$ or more, four kinds of orbitals are present: *s*, *p*, *d*, and *f*. Furthermore, whereas the number of *kinds* of orbitals equals the principal quantum number, the number of *orbitals* in total within a given principal quantum level is given by the *square* of the principal quantum number, or n^2. Thus where $n = 1$, only one orbital is present; where $n = 2$, four orbitals (one *s* and three *p*) are present; where $n = 3$, nine orbitals (one *s*, three *p*, and five *d*) are present; and where $n = 4$ (or higher), 16 orbitals are present (one *s*, three *p*, five *d*, and seven *f*). Since each orbital can accommodate two electrons only, the capacity of each principal quantum level is therefore given by $2n^2$. Thus the first shell can hold only two electrons, the next 8, the third 18, the fourth 32. The fifth, in principle, could hold 50, but no existing atom has more than 32.

Electronic Configurations

The electronic structures of the atoms of the different elements can now be assigned, if one more principle is recognized. This is the logical "**aufbau**" principle, according to which, in the addition of electrons one by one to a given nucleus, each successive electron goes into the most stable position available to it. Each successive atomic number, with only minor exceptions, corresponds to the identical configuration of the atom immediately preceding it in atomic number, with one electron added.

It is found that *within* a given principal quantum level, the sequence of diminishing stability is *always s-p-d-f*. Hence electrons never begin filling *p* orbitals until the *s* orbital is filled, or *d* orbitals until both the *s* and three *p* orbitals are full, or *f* orbitals until *s*, *p*, and *d* orbitals are already filled.

With just these rules, assigning to the elements their correct electronic configurations would be very straightforward and simple. Unfortunately, the problem is not that simple, because the principal quantum

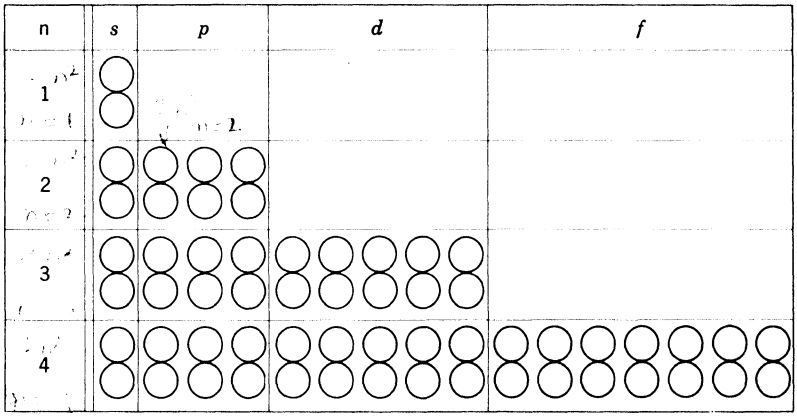
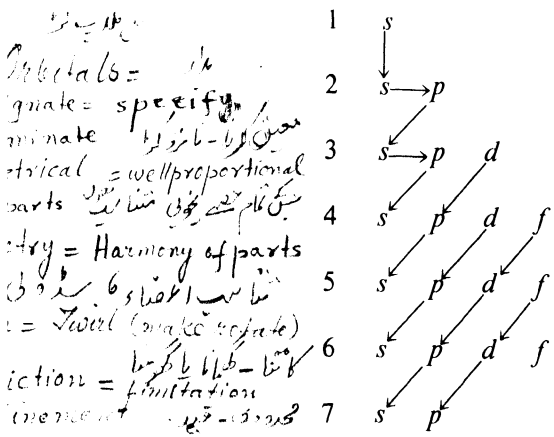


Figure 8. Orbitals available in principal quantum levels (capacity, two electrons per orbital).

levels overlap. That is, not all of a given shell is more stable than the most stable part of the next higher shell. This leads to complications, but they are not beyond our understanding. In general, the order of filling of orbitals is represented by the following chart:



The complete electronic configurations of the chemical elements are shown in Figure 9. The physical and chemical properties of the elements are the logical and inevitable result of these electronic configurations, as will become increasingly apparent in the discussions to follow.

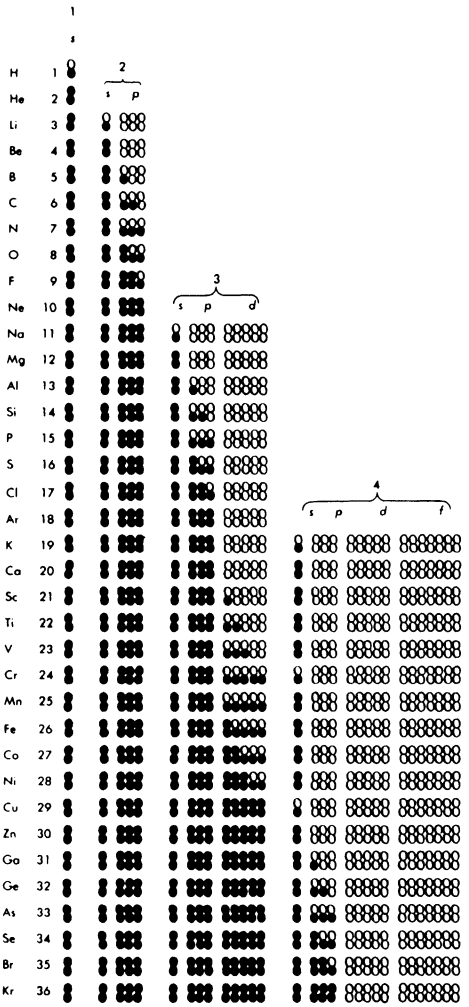


Figure 9. Electronic configurations of the elements. (Note: Exact arrangement in "lanthanides" and "actinides" is uncertain.) With permission, from *Chemical Periodicity,* by R. T. Sanderson, Reinhold Publishing Corp., 1960.

SPECIAL HELP

Here and at the end of each succeeding chapter, three kinds of aid are provided to help you to learn. First, the most important facts of the chapter are indicated by questions to test your memory. Second, if new applications of mathematics are introduced in the chapter, or if

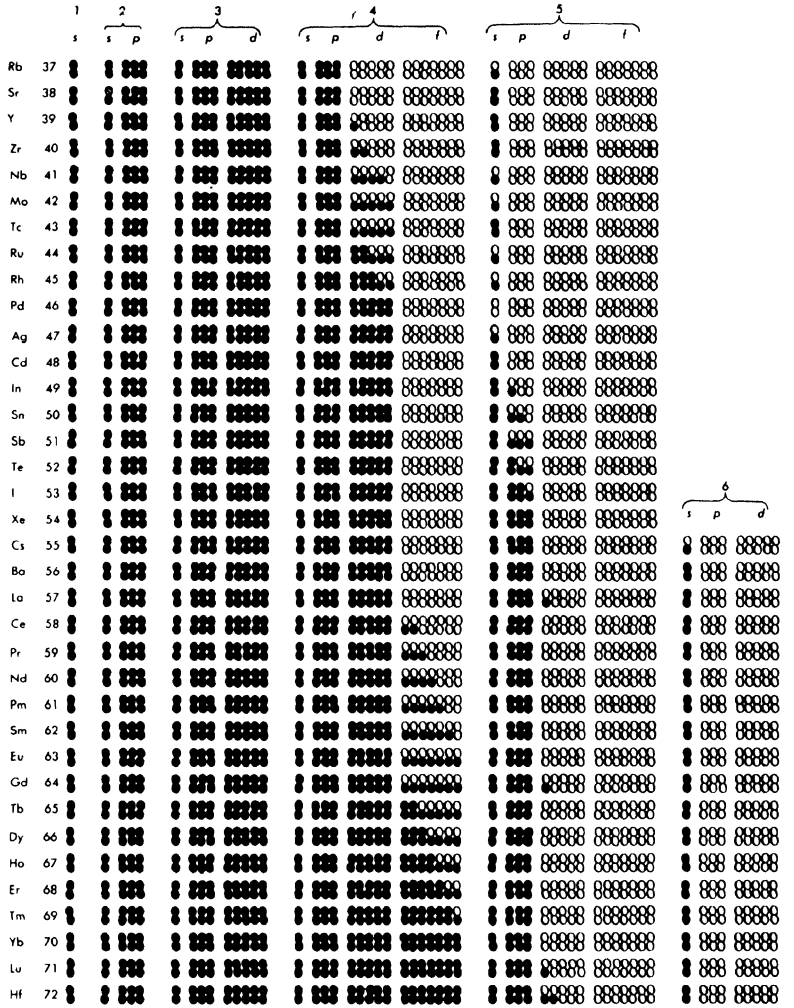


Figure 9 (*Cont.*)

review would be especially useful, a number of representative practice problems are given. Third, a number of questions designed to test your understanding are provided. Answers to some of the mathematical problems and all of the questions of Test Your Understanding are in the Appendix, beginning on page 567. *You are urged to give close attention to all these aids, to get maximum benefit from them.*

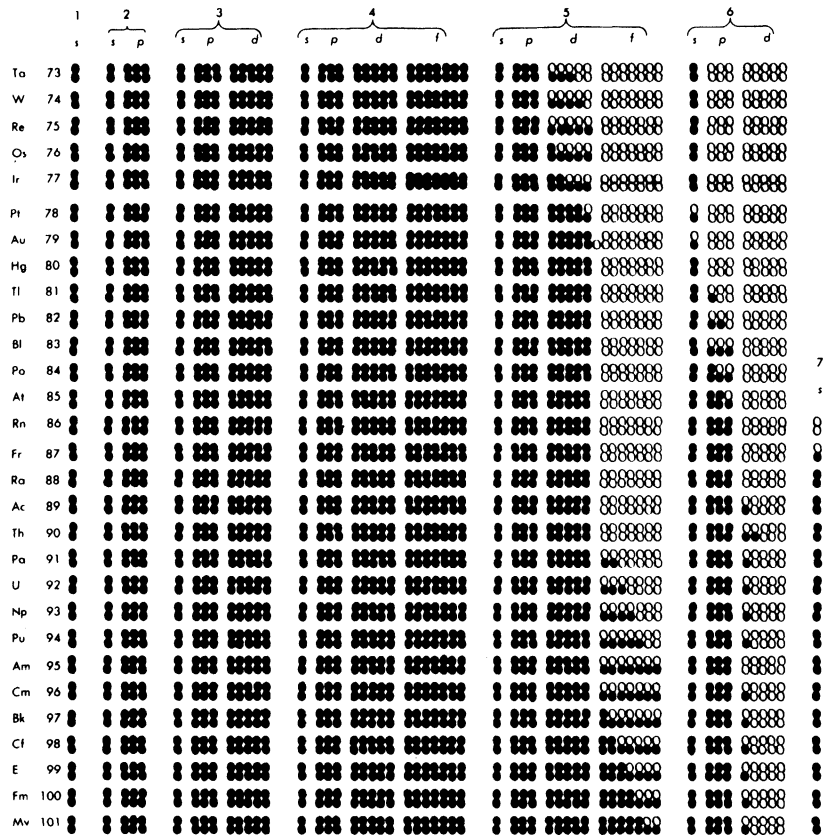


Figure 9 (*Cont.*)

Test Your Memory

1. Name the three component particles of atoms.
2. How do these particles compare in mass and charge?
3. What is "atomic number"?
4. What is meant by "nuclear atom"?
5. In what fundamental respect do isotopes of any given element differ from one another?
6. Name the four quantum numbers and tell what each represents.
7. What numerical values can each type of quantum number have?
8. State the Pauli Exclusion Principle.
9. What is meant by "orbital"?
10. How many kinds of orbital are there?

11. What are these orbitals named?
12. How many of each kind are there?
13. How many orbitals, and which kinds, are in each of the first six principal quantum levels?
14. What is the order of decreasing stability of different kinds of orbitals within a given quantum level?
15. How many orbitals and how many electrons can be accommodated in each of the first four principal quantum levels?
16. State the "aufbau" principle.

Test Your Math

1. What is the atomic weight of an atom having 10 neutrons and 8 protons in the nucleus?
2. What is the approximate percentage of each isotope in boron, atomic weight 10.82, if the isotopes contain 5 and 6 neutrons?
3. What is the atomic number of an element of atomic weight 60 that has 33 neutrons per atom?
4. What is the distribution of electrons among orbitals in a principal quantum level containing 15 electrons? 7 electrons? 23 electrons?
5. How many *d* electrons are present in an atom of atomic number 37? (Determine by the aufbau principle; then check with Figure 9).
6. How many grams of aluminum would be required to contain the same number of atoms as in 8 grams of magnesium?

Test Your Understanding

1. How can rotation of a negative charge around a positive charge create the same effect as if the charges coincided?
2. Why does changing the mass of an atom, by changing the number of neutrons in its nucleus, not change the nature of the element?
3. Why do electrons refrain from pairing until each orbital of the same kind has one electron?
4. In the filling in of orbitals around a nucleus of charge +19 (K), the nineteenth electron enters a 4*s* orbital. When the nuclear charge is +21 (Sc), however, the nineteenth electron enters a 3*d* orbital. What is the reason for this difference?
5. Why, as shown in Figure 9, does one of an outermost *s* electron pair sometimes drop back to an underlying *d* orbital? For example, see the configuration of Cr 24.

4

Chemical Bonding in the Elements

BEFORE UNDERTAKING a detailed study of the combination of *different* elements to form chemical *compounds,* we should consider the fact that when atoms of the *same* element have no atoms of different elements with which to combine, they usually combine with one another. As a result, most elements in the "free state" are composed of like atoms held together in polyatomic units, or aggregates, with sufficient strength that considerable energy must be absorbed before these atoms can become separated. In Figure 10, the **"heat of atomization,"** the energy needed to separate these atoms from each other at 25°C, is plotted against the atomic number. It will be observed that only in a few elements, namely, helium, neon, argon, krypton, xenon, and radon, is the heat of atomization zero. In most elements it is quite high.

STRUCTURE AND THE EXISTENCE OF BONDS

The forces that must be overcome in order to separate the atoms of stable aggregates are called **"chemical bonds."** The heat of atomization is a general measure of the strength of bonding through a mass of sub-

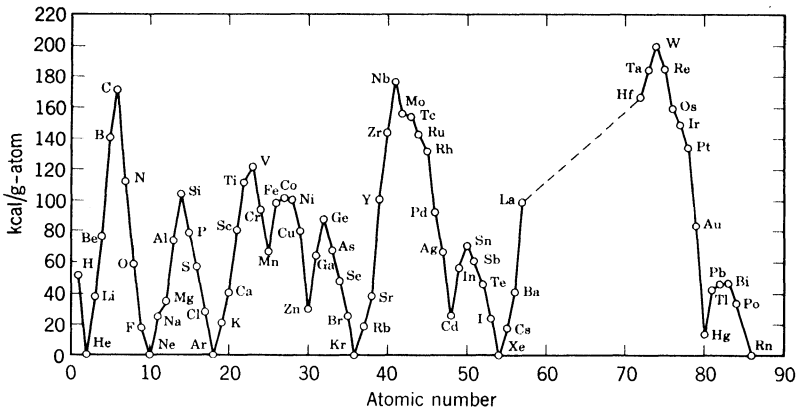


Figure 10. Heats of atomization of elements at 25°C.

stance, but of itself tells us nothing about the number and strength of the individual bonds. Before we can begin to understand the causes and nature of bonding, we need information about the arrangement of the individual atoms in an aggregate. In other words, what bonds are formed? The assumption is made that definite bonds exist only between adjacent atoms that are closest neighbors. Other atoms, either adjacent but farther away, or not adjacent, are considered not to be joined to a given atom by definite bonds. We need to know, then, what neighbors an atom has.

Fortunately, this information is available to us from experimental measurements involving such physical methods as X-ray diffraction, electron diffraction, microwave spectroscopy, and others. For example, when X rays are directed at crystalline substances, they are reflected back at definite angles and in measurable relative intensities that can be revealed as patterns on photographic film. Mathematical analysis of these patterns can disclose what atomic arrangement was necessary to cause them. In general, these methods supply quantitative information, often very accurate, concerning the spatial arrangements of the atomic nuclei. They tell us how many neighbors each nucleus has, and how (at what angles and at what distances) they are distributed around it. One may determine, from the distances between adjacent atoms, which atoms are directly in closest contact and which are not. From this information, one can usually judge where the bonds between atoms are located, and how many atoms are directly attached to a given atom. One is then prepared to compare the number and direction of the bonds formed by an atom, with its electronic configuration, to see whether any relationship can be recognized.

By such means, coupled with studies of chemical properties of the elements and the physical properties of their compounds, hydrogen atoms have been found to form but one bond each and fluorine, chlorine, bromine, and iodine atoms likewise. But in the diamond, each carbon atom is evidently bonded to four neighbors, and silicon atoms similarly form four bonds each. Phosphorus atoms form three bonds, and sulfur atoms, two. Sodium atoms have eight closest neighbors, but magnesium atoms have twelve, as do atoms of iron and silver. On the other hand, helium, neon, argon, krypton, xenon, and radon form no bonds at all. How can these bonding properties, and differences in bonding properties, be explained?

FUNDAMENTAL FORCES IN BONDING

Calculations of the gravitational forces that would exist between particles of atomic and/or subatomic mass, separated by atomic distances, show them to be insignificantly small compared to the forces known to exist between atoms in aggregates of the elements. Neither is the magnetic attraction between two electrons of opposed spins appreciable, in comparison with the electrostatic repulsion. Fundamentally, then, the forces among the atoms must be electrical in nature, arising from the fact that all atoms contain positively charged nuclei and negatively charged electron clouds surrounding these nuclei.

When two atoms approach one another, electrostatic interactions to be expected are threefold: (1) repulsion between electronic clouds; (2) repulsion between the nuclei; and (3) attraction between each nucleus and the electronic cloud of the other atom. In the inert elements, helium, neon, argon, krypton, xenon, and radon, the lack of evidence of interatomic attractions suggests strongly that repulsions are dominant. In the active elements, which includes all the rest, the existence of strong attractions demonstrates the dominance of the attractive forces. We may therefore conclude, tentatively at least, that chemical bonds result when the attraction between each nucleus and the electronic cloud of the other atom is significantly higher than the total internuclear and interelectronic repulsions. This attraction is higher in the active elements, but repulsions are higher in the inert elements. Why?

THE SIGNIFICANCE OF THE INERT ELEMENTS

To find an answer to this vital question, we must examine the electronic configurations of the atoms. In particular, we must study the

outermost portion of the electronic clouds, since this portion comes most directly in contact when two atoms come together. Especially, we need to be concerned with any differences between atoms that do form bonds and atoms that do not.

It may be helpful to begin with the inert elements, which, as shown by the zero heats of atomization, form no bonds. Their atomic structures are included in Figure 9, pages 54–56. For convenient reference, they are repeated in the following table:

n	1	2	3	4	5	6
He	2					
Ne	2	8				
Ar	2	8	8			
Kr	2	8	18	8		
Xe	2	8	18	18	8	
Rn	2	8	18	32	18	8

Notice that helium has only two outermost electrons, but this is all that can be accommodated in the first principal quantum shell. All the others have 8 electrons per outermost shell. *No other elements have atoms with 8 electrons in the outermost shell.* In fact, the atoms of all other elements have *fewer* than 8 electrons in the outermost shell (or fewer than 2 when the outermost shell can hold only 2). In other words, in atoms of all the active, bond-forming elements, vacancies occur in the outermost shell, in which electrons from some other atom might be accommodated. In atoms of the inactive, non-bond-forming elements, no stable vacancies exist.

If we accept the basic assumption that bonding must be caused by significant net attractions between the nucleus of each atom and the electrons of the other atom, we must conclude that significant net attractions can occur only when vacancies exist. Atoms of the inert elements cannot join together because they lack such vacancies. This suggests that an electron outside of an atom cannot be attracted to the nucleus unless a vacancy exists in an available orbital of the atom, in which that electron can be accommodated. In a sense, then, we may look upon an outermost shell of 8 electrons (or 2 if it is the first shell) as a coat of armor effectively shielding the nucleus from any electron outside of the atom. We may look upon a vacancy in the outermost shell as a hole in the electronic armor that surrounds the nucleus, a hole through which the electrostatic attraction of the nuclear positive charge can be substantially felt by an electron outside the atom.

A simple, qualitative explanation of the difference between atoms that can form bonds and atoms that cannot form bonds is thus available to us. It is an extremely useful concept even though the complete explanation of bonding would need to be much more complex. But with this concept, we have only begun to understand. Next, we need to know why atoms of some elements can form only one bond, others more than one.

COVALENCE

We have been discussing the attraction of the nucleus of an atom for an electron outside the atom, implying, without specifically stating, that this outside electron is part of the other atom forming the bond. Now let us consider the two complete atoms. For example, two hydrogen atoms. With only one electron in its only shell, which has the capacity for two, a hydrogen atom contains also one outermost shell vacancy. When two hydrogen atoms are brought together, the electron of each must repel the electron of the other and the proton at the nucleus of each must repel the proton of the other. The electron of each and the proton of the other, however, are potentially mutually attractive. This attraction can be significantly large because each atom has one vacancy capable of accommodating the electron of the other. Each atom has, to use our earlier crude picture, a hole in its electronic armor through which the attractive force of the nucleus can be felt by the electron of the other atom. The electron of each therefore *is* accommodated by the orbital of the other, and the two atoms become bonded together through the attractions of the two nuclei for the two electrons. The bond so formed is very stable, resisting rupture up to very high temperatures. It is called a "**covalent** bond," the word covalent meaning, "sharing together." This is the simplest example of a covalent bond.

From this example, the requisites for the formation of a covalent bond can be specified. Each atom must supply each of the following: (1) an outermost electron that is unpaired and available to be shared by another atom; and (2) an outermost orbital vacancy that can accommodate an electron from the other atom. Both these requisites are implied if it is specified that each atom must have one half-filled orbital in its outermost shell. They are mentioned separately because the vacancy is just as important as the electron. The word "unpaired" is used in requisite (1) because if the electron is paired with another it can have no vacancy associated with it.

Theoretical chemists prefer to describe such a bond in one of two ways. (1) They may speak of the "**atomic orbitals,**" one on each atom,

overlapping so that the two electron clouds occupy a region in common between the two nuclei. (2) They may regard the two atomic orbitals as somehow coalescing to form a new single orbital, involved with both nuclei, called a "**molecular orbital.**" We do not need at this point to be concerned with trying to give this bonding an exact mathematical description. For our purposes, it is quite satisfactory merely to recognize the requisites for bonding, and to know that however the bond may be described it arises fundamentally from a mutual attraction between the nucleus of each and electron(s) of the other.

The two hydrogen atoms, held together by this stable covalent bond, constitute a unit which is called a "molecule." Since the molecule contains but two atoms, it is called "diatomic." The **formula** for this molecule is H_2. Why should this molecule exist as a unit? Why does not further combination with other hydrogen atoms occur? When two hydrogen atoms have each formed one covalent bond, then neither of them retains any further bonding capacity. Neither has any longer an unpaired electron, and neither has a vacancy. A hydrogen atom that has formed a covalent bond with another hydrogen atom is therefore finished, so far as bonding is concerned. The only way in which a hydrogen atom that is part of a H_2 molecule can possibly form any other bond is first to break loose from its union with the second hydrogen atom. "**Valence**" is a somewhat unprecise term meaning "combining

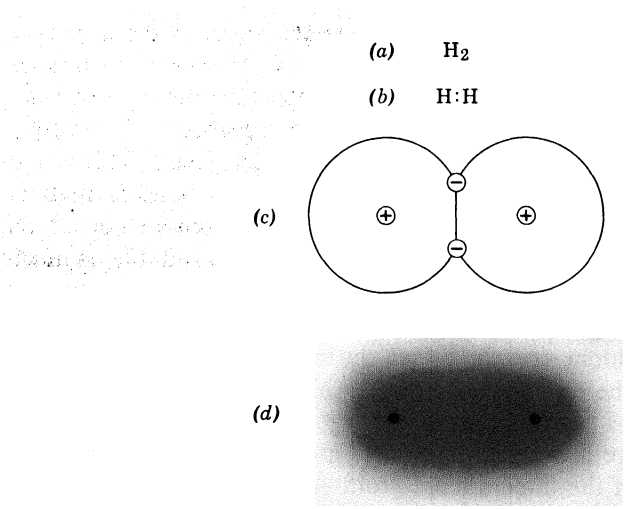


Figure 11. Some representations of the hydrogen molecule. (*a*) Formula; (*b*) electronic formula; (*c*) schematic drawing showing the single covalent bond; (*d*) approximate representation of the electronic cloud around the two nuclei of the molecule.

power." Hydrogen is described as having a valence of one, because it can form but one single covalent bond per atom.

In the hydrogen molecule, the electrons that are mutually shared by the two nuclei are believed, and reasonably so, to spend most of their time in the region between the two nuclei. We may speak of the "bonding electrons" or "valence electrons" of a covalent bond in general as being "**localized**" between the two atoms. This designation is very important, especially since we shall later see that the bonding electrons are not localized in some other elements.

Based on the requisites for covalent bond formation listed above, we can now recognize that atoms of other elements may be able to form more than one covalent bond if they possess more than one half-filled outermost orbital. Indeed, one can determine exactly how many covalent bonds an atom can form, by counting the number of electron-and-vacancy combinations that could be produced in the outermost shells by distributing their electrons, as far as possible, one to an orbital. What is the meaning of this last phrase, "distributing their electrons . . . one to an orbital"?

Valence-State Structure

Electrons of the same type of orbital become distributed more stably, one to an orbital, not doubling up until no empty orbital of the same type remains. This is shown in Figure 9, pages 54–56. However, in an outer shell consisting of one *s* and three *p* orbitals, the *s* orbital is sufficiently more stable than a *p* orbital that electrons pair together in the *s* before any enters a *p* orbital of the same principal quantum level. This would appear to remove the *s* orbital from the possibility of bond formation. However, it does not. The energy required to promote one of an *s* pair out to a vacant *p* orbital, if such an orbital is available, is much smaller than the energy released by the formation of the two additional covalent bonds that would thus become possible. Hence a pair of outer *s* electrons will seldom remain intact during bonding if a *p* orbital is vacant. One of the *s* electrons practically always goes to an otherwise vacant *p* orbital.

We must therefore distinguish between "**ground-state**" structure—the most stable state of the uncombined atom—and "**valence-state**" structure, which represents the atom ready for combination. In the free elements, this distinction only exists for the outer shell arrangements shown in Figure 12. For all other structures, ground and valence states are the same.

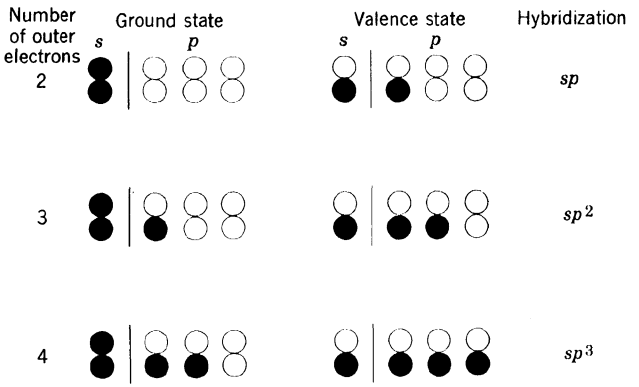
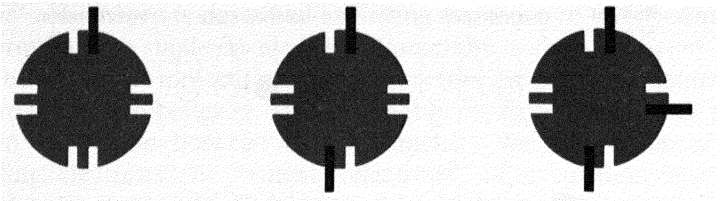


Figure 12. Electronic distinction between ground and valence state structures. (Ground state and valence state are identical when the number of outermost electrons is 1, 5, 6, or 7.)

Valence, or Number of Covalent Bonds per Atom

An atom of fluorine or one of chlorine contains seven outermost electrons, leaving only one vacancy. Such an atom can form but one covalent bond. An atom of oxygen or one of sulfur contains six outermost electrons, and therefore only two vacancies. The number of covalent bonds that can be formed is limited by the number of vacancies to only two, even though the number of outermost electrons is much greater. An atom of nitrogen or one of phosphorus has five outermost electrons, but consequently only three vacancies. The number of covalent bonds these can form is therefore three. An atom of carbon or one of silicon has four outermost electrons and four vacancies. The ground state would have two of these electrons in the *s* orbital and only two single *p* electrons available for bonding, with one *p* orbital completely empty. In the valence state, however, one of the *s* electrons would be promoted to the remaining *p* orbital, giving the total capacity to form four covalent bonds.

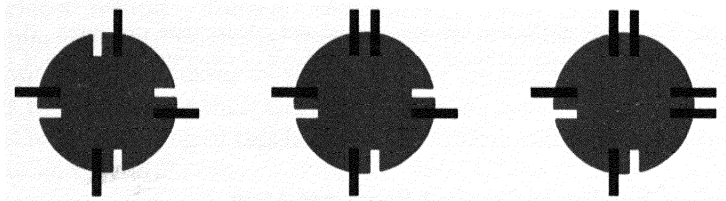
It should be apparent that four bonds is the maximum number any atom can form using the four outermost orbitals. If the number of electrons is less than four, the number of bonds is limited by the number of *electrons* although the number of vacancies is more than enough. If the number of electrons is more than four, pairing has begun, and the number of bonds is limited by the number of *vacancies*. When each orbital is half filled, the bonding capacity is at the maximum.



With one outer electron, this atom can form only one covalent bond, even though vacancies are plentiful.

Two covalent bonds are expected. The number of bonds is limited by the number of electrons.

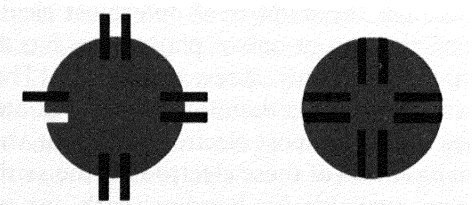
With 5 vacancies but only 3 electrons, 3 covalent bonds can form.



Each of the 4 outer orbitals is now half full, permitting 4 covalent bonds to form.

Although 5 outer electrons are here, only 3 vacancies exist. The bonding is thus limited not by the number of electrons but by the number of vacancies.

Because only 2 vacancies occur, only 2 covalent bonds can form, despite the 6 electrons.



Only one vacancy here (one half-filled orbital) means the ability to form but one covalent bond.

With no unpaired electrons and no vacancies, this atom must remain inert.

Figure 13. Valence structure types. This kind of schematic representation of atoms, being restricted to two dimensions, cannot show the geometric arrangement of the orbitals. Each orbital is represented as a pair of wells in the atomic circle. A black bar represents an electron. The "valence" of each type of atom—number of covalent bonds it can form—is easily predicted and understood from this knowledge of the external shell structure. Keep in mind, however, that these are only crude, static representations of the infinitely more complex, dynamic structures of real atoms.

As a general rule, atoms seem inclined to form *all the bonds of which they are capable.* If an atom can form three covalent bonds, for example, using three electron-and-vacancy combinations, it will seldom if ever use fewer than three of these combinations in its bonding. A consideration of the electronic configurations of the atoms of the elements therefore does not merely tell us how many covalent bonds are *possible,* but also how many are *highly probable.*

Hybridization

The promotion of an outer *s* electron to an otherwise vacant *p* orbital would seem to permit two additional bonds, but since *s* orbitals differ in shape from *p* orbitals these bonds would be expected to be somewhat unlike. In fact, however, the bonds are not unlike. It appears that *new* orbitals form, partaking of the nature of each of the original orbitals. For example, the outer shell of a magnesium atom in the ground state contains only two electrons, both in the *s* orbital. The three *p* orbitals are empty. In this state, magnesium would be unable to form any covalent bonds, whereas actually it can form two. In the valence state, one of these *s* electrons goes into one of the otherwise empty *p* orbitals, giving the atom the ability to form two covalent bonds. But these bonds are found to be exactly alike, which could not be true if one bond were made with an *s* orbital and the other bond with a *p* orbital. Evidently the two bonding orbitals have somehow become equalized.

This equalization process is called **"hybridization."** The bonds formed by magnesium are called "*sp*" hybrid bonds. Similarly, boron with three outer electrons forms three "sp^2" hybrid bonds, all alike. Carbon, with four outer electrons, forms four "sp^3" hybrid bonds. Other types of hybridization will be encountered when chemical compounds are studied.

Bond Angles

Before the structural consequences of these different bonding abilities of the atoms can be described adequately, it is necessary to consider another property of the covalent bond. This is direction. Unlike the all-directional fields around a point electrical charge, covalent bonds are directional, the orbitals forming definite angles with one another. Some very sophisticated explanations of these directional properties have been derived from wave mechanical calculations, which indicate the

general shape and orientation of the orbital wave-clouds in space. For the present purposes, however, the knowledge that like charges repel one another is sufficient. One needs merely to picture pairs of electrons, whether shared with other atoms or not, as being distributed over the surface of the atomic sphere in the most stable positions possible in view of their mutual repulsions. In other words, these electron pairs, or filled orbitals, will tend to be as far apart from one another as they possibly can.

If there are only two pairs, the farthest apart these can be is at opposite sides of the sphere, making an angle of 180° between the two bonds. If there are only three pairs, the farthest apart these can be is at the corners of an equilateral triangle with the atomic nucleus at its center. In other words, the angles between any two bonds must be 120° and the bonds are all in the same plane. If there are four pairs, their maximum distance apart is found at the corners of a regular tetrahedron with the nucleus at its center. The bond angles in such a figure are 109°28′.

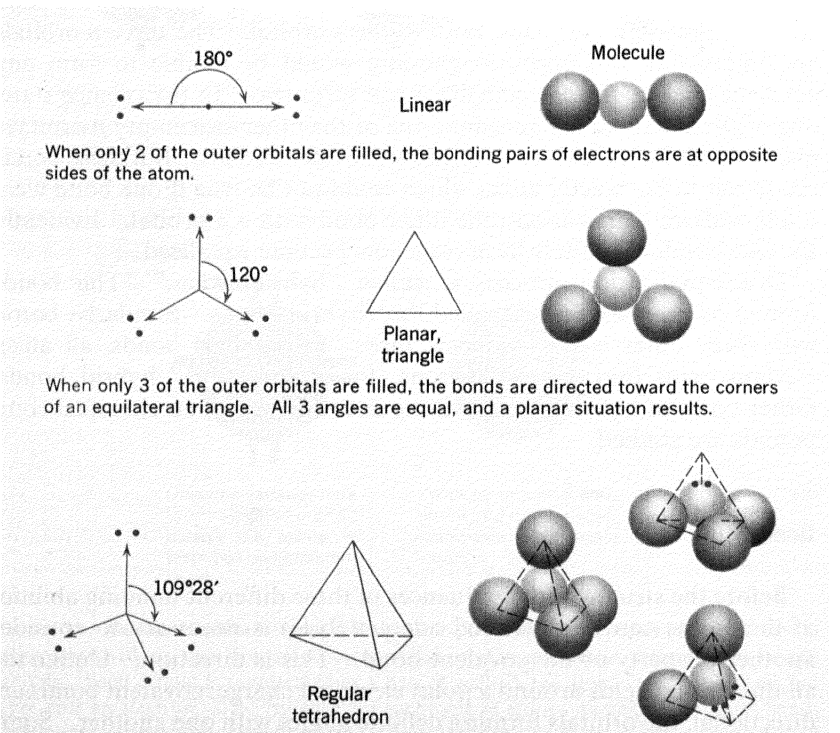


Figure 14. Bond angles.

Bond Multiplicity

One other property of covalent bonds that needs to be considered in the study of the structure of the free elements is related to the directional properties of the bonding orbitals. Especially when the shell beneath the outermost shell has only two electrons, as in carbon, nitrogen, and oxygen, two atoms can come together so that more than one orbital from each atom overlaps with an orbital of the other. In other words, more than one electron from each atom can be shared. To state it still differently, more than one covalent bond can form between the same two atoms. When two covalent bonds are formed, the result is called a "**double bond.**" When three covalent bonds are formed, the result is called a "**triple bond.**" Four covalent bonds cannot possibly be formed between the same two atoms, because when three bonds form between these atoms the fourth orbital of each projects outward at the opposite side of the atom. Because of the directional nature of the orbitals and the difficulty of concentrating additional negative charge between the same two atoms, a double bond, although stronger than a single bond, cannot be twice as strong. Similarly, a triple bond is stronger than a double bond, but not three times as strong as a single bond. Multiple bonds are shorter than single bonds; closer interaction of the two atoms is necessary for their formation. Such closeness of interaction is evidently possible when the underlying shell contains but two electrons, but an underlying shell of eight electrons on each atom seems to prevent, through mutual repulsion, two such atoms from approaching closely enough to form multiple bonds of the type described. The significance of this difference will shortly become apparent.

STRUCTURES OF NONMETALS

With these qualities of covalence in mind, one can proceed rather easily to account for the observed structures of the nonmetallic elements. First, consider carbon. With its capacity to form four covalent bonds, directed toward the corners of a regular tetrahedron, it does just this, and the structure of the **diamond** results. For a diamond crystal consists simply of a three-dimensional array of carbon atoms, each interior atom being surrounded by four others, and joined to each of them by a single covalent bond. This is not the most stable way in which carbon atoms can join together, however, and consequently the diamond form of carbon is relatively rare. A little more stable is the form called "**graphite.**" In this form, carbon atoms occur in layers composed of condensed hexagonal rings, with each carbon atom joined directly

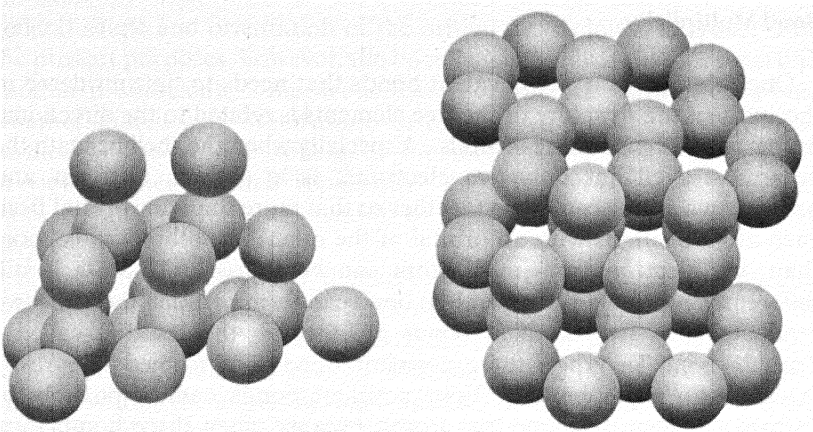


Figure 15. Structure of diamond (left) and graphite (right), both containing carbon atoms only, but very different in physical properties.

to three close neighbors by bonds equal in strength but shorter and stronger than a carbon-carbon single covalent bond. These layers are planar and the bond angles are 120°—just what one would predict if all four outermost electrons of each atom were involved almost completely in but three bonds. Here one encounters a familiar phenomenon in chemistry—an instance where bonds intermediate between single and double appear to exist—bonds of non-integral multiplicity.

In order for a carbon atom to use all four valence electrons and bonding orbitals in three bonds, one bond would seem necessarily to be double and the other two single. However if, as in graphite, all interior carbon atoms seem to be in exactly identical positions, why should the double bond lie between a given carbon and any particular one of its three neighbors, rather than either of the other two? There is no reason. The double bond might equally well be in any of the three possible positions. An important principle of bonding is involved here. Whenever a situation such as this exists, in which bonds might be in more than one position but not all at the same time because enough electrons or vacancies are not available, the electrons or vacancies tend to contribute to all the possibilities at once partially, rather than one completely. This appears to impart greater stability. The phenomenon is called **"resonance."** It will be met again later in this chapter, and considered in more detail in Chapter 9.

The bonds between carbon atoms in graphite thus appear to involve $2\frac{2}{3}$ electrons per bond instead of two, as though each bond were one and one-third of a covalent bond. The separate layers are held together by

much weaker residual attractions of the nature of "**van der Waals forces,**" to be described in the following chapter.

The element having the next higher atomic number is nitrogen. With five outermost electrons but only three vacancies, a nitrogen atom is able to form three covalent bonds, and a pair of electrons not involved in the bonding remains. Having underlying shells of only two electrons, two nitrogen atoms are able to join through a triple bond. Evidently this results in much greater stability than would be possible if the atoms could form a continuous network joined together by single bonds, or chains joined by alternate single and double bonds. The result, then, is diatomic molecules of formula N_2, which are held together as a unit by one of the strongest of known chemical bonds. Six electrons are mutually shared by the two nitrogen nuclei. In addition, each atom has a pair of electrons not involved in the bonding, and these pairs are at opposite ends of the molecule.

In phosphorus atoms, the electronic arrangement of the outermost shell closely resembles that of nitrogen atoms. However, here the underlying shell is of eight electrons, in contrast to the two of nitrogen. Consequently, the closeness of approach permissible for two nitrogen atoms is not apparently possible for two phosphorus atoms. Instead of forming diatomic molecules held together by triple bonds, phosphorus atoms join together by single covalent bonds. The simplest aggregate obtainable, in which each phosphorus atom forms three single bonds, would be an aggregate of four atoms, a tetrahedron with each phosphorus atom joined to each of the other three. The bond angles, considering the three bonds together with the pair of electrons uninvolved in the bonding, should be tetrahedral, or 109°, except that then the tetrahedral grouping of the atoms would be impossible, for in this grouping the bond angles must be only 60°. Yet phosphorus does exist in tetrahedral clusters of four atoms each, with formula P_4. In this form it is known as "white phosphorus." This is not very stable, and changes readily to other, more stable forms in which each atom again forms three single bonds to other phosphorus atoms but the bond angles are no longer strained. These forms include the more familiar "red phosphorus."

Oxygen atoms, each with the capacity of forming two single covalent bonds, might join together in long chains, but they do not. Instead, two atoms join by double bonds, about which more will be said later (page 223). Having done so, they have reached their valence capacity, and the oxygen remains as diatomic molecules of formula O_2.

Sulfur atoms, instead of having only two electrons in the principal quantum level underlying the outermost, as in oxygen, have eight. The closeness of approach needed for double bonding is therefore much

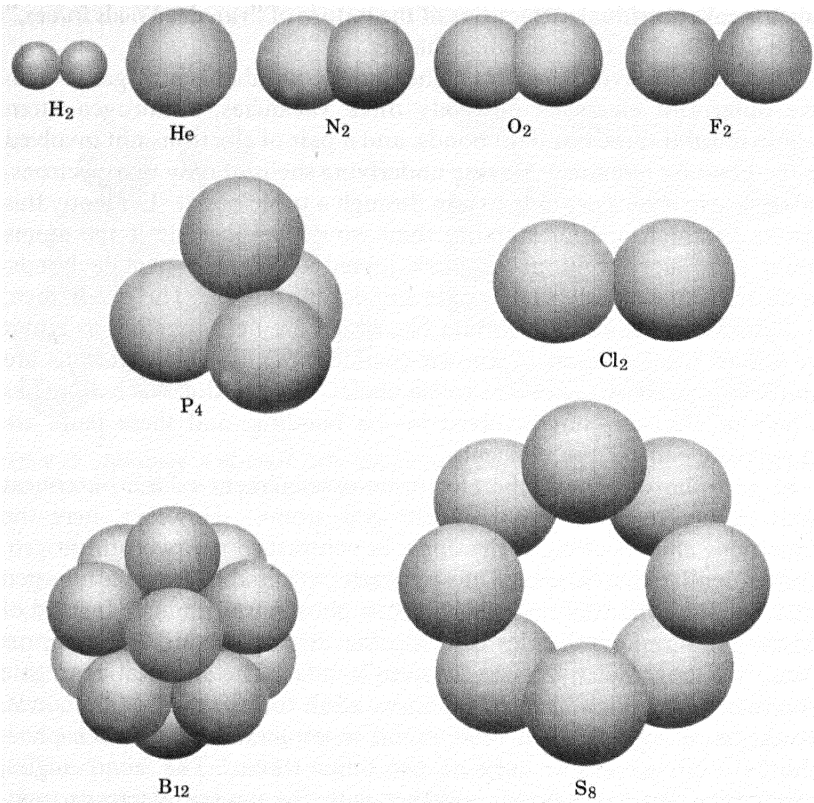


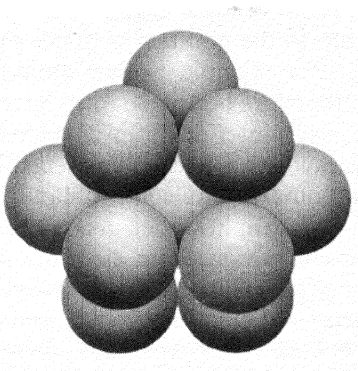
Figure 16. States of aggregation of some nonmetallic elements. (For carbon, see Figure 15.)

more difficult, and at ordinary temperatures sulfur atoms do not form diatomic molecules. Instead they form, by single bonds, two to each atom as would be predicted, closed 8-membered rings. These are staggered rather than planar, for the latter would require distortion of the bond angles. It is not easy to explain why the 8-membered ring is more stable than some other ring or than long chains of sulfur atoms. Such chains do form at higher temperatures.

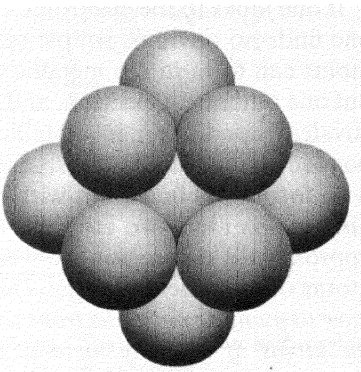
The "**halogens,**" fluorine, chlorine, bromine, and iodine, resemble one another in that they all have atoms with 7 outermost electrons. This leaves one vacancy per atom, and therefore the capacity to form but one single covalent bond. When two atoms have come together, as in hydrogen, the covalent bonding ability is completely used. The halogens all occur as diatomic molecules held together by single covalent bonds: F_2, Cl_2, Br_2, and I_2.

METALS

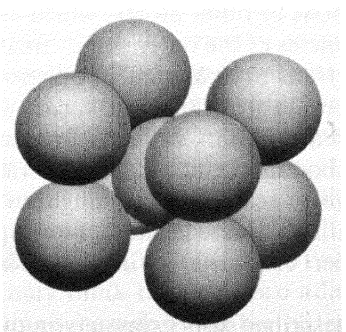
A survey of all the elements discloses that most of them are metals. By this term, everyone understands them to be characterized by certain physical properties not ordinarily possessed by other compositions of matter. They have peculiar reflective power familiarly referred to as "metallic luster," they feel cold to the touch as a result of their rapid conduction of heat away from one's skin, they conduct electric



Hexagonal closest packing: The top triangle rests on a hexagon of atoms about the central atom. The 2 atoms showing at the bottom are part of a second triangle beneath the hexagon. Thus the central atom has 3 + 6 + 3 or 12 atoms attached to it. Each interior atom of the crystal is similarly at the center of a cluster of 12.



Cubic closest packing (face-centered cubic): The central atom has 4 other close neighbors directly behind the top square shown above. Thus 12 atoms are directly in contact with the central atom. Each interior atom of the crystal is similarly at the center of a cluster of 12. This situation differs from the hexagonal only by the orientation of the bottom triangle, of which only one atom shows above. Each central atom is also at the center of a cube face, formed by the 4 outermost atoms shown above.



Body-centered cubic: Each interior atom of the crystal is in direct contact with 8 other atoms, at the corners of a cube surrounding it. In addition, the 6 atoms at the centers of the 6 adjacent cubes are only 15% farther away from the central atom.

Figure 17. Structure of metals. Most of the metallic elements crystallize in one or more of the above forms, or in a form very similar.

current, and most of them are strong yet ductile and malleable. Structurally, their atoms are usually very closely packed. In most, the packing is the closest possible for spheres of equal size, with each interior atom in contact with twelve closest neighbors. In some, each interior atom is at the center of a cube of 8 atoms, and hence has 8 closest neighbors at the cube corners, plus 6 more, one at the center of each of the 6 adjacent cubes, about 15 per cent farther away. In most metals, the forces of interattraction are quite high, as shown in Figure 10, page 59. The question is, what holds these atoms so tightly together?

If one looks to the electronic configurations of these metallic elements, one finds no obvious, simple relationship to the number of bonds their atoms can form in the metallic crystal. For example, a silver atom has but one outermost electron, and should therefore be able to form but one covalent bond. Yet in metallic silver, each interior atom is evidently bonded equally to 12 others. Similarly, each atom in calcium metal likewise forms 12 bonds, but with only two outermost electrons should be able to form but two covalent bonds. We can, however, recognize an approximate distinction between atoms of nonmetallic elements and atoms of metallic elements: *The atoms of typically nonmetallic elements have as many or more electrons as vacancies in the outermost shell, whereas the atoms of typically metallic elements have fewer outermost electrons than vacancies.*

Metallic Bonding

By thinking of metal atoms as atoms having outer shell vacancies in excess, we can gain some understanding of the nature of the bonding in metals, and why it differs from that in nonmetals. For, being relatively unshielded by outermost electrons, the nuclei of metal atoms are able to exert a substantial attraction for electrons of other atoms, which can be accommodated within the orbital vacancies of the outer shell. But there are more vacancies than there are electrons to be shared, and there is no reason why the electrons should be more stably held in one vacancy than in another. It is believed that in such a situation, instead of remaining localized between two atoms, as in the bonding of nonmetals, the valence electrons move about through all possible vacancies, becoming thus nonlocalized, or at least relatively nonlocalized. Here is another example of the phenomenon of *resonance,* earlier encountered in the structure of graphite.

Indeed, bonding in metals can be described approximately in quite a satisfactory manner in terms of the concept that the outermost electrons

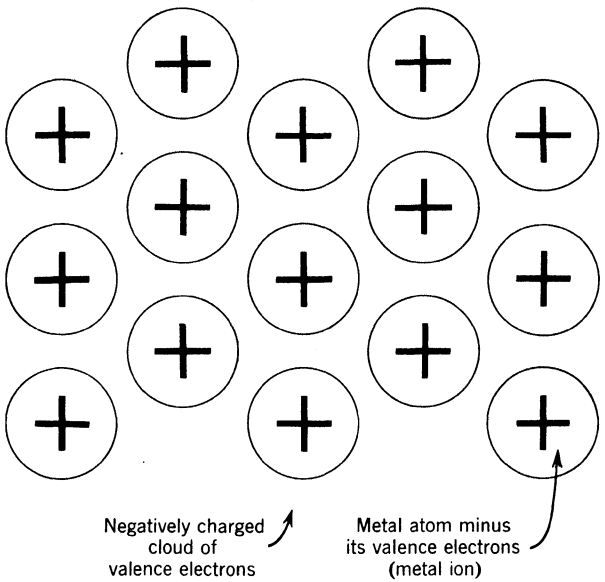


Figure 18. Simplified representation of metallic bonding. The metal ions are held together by their attractions for the negative cloud in which they are imbedded.

are relatively nonlocalized, being relatively free to move about. With an excess of low energy orbital vacancies, these electrons may rather readily move from near certain nuclei to near other nuclei where their positions would be indistinguishable from the first. Crudely, a metal thus can be pictured as a collection of positively charged atoms imbedded in a fluid of valence electrons which serves as a kind of electrostatic glue to hold the positively charged atoms together in the metallic crystal. The strength of this glue must of course depend on the number of outermost electrons per atom, on the atomic radii, on the nature of the orbitals involved (*s*, *p*, *d*, or *f*), and on other factors. In general, the force holding the atoms together results from an electrostatic attraction between relatively nonlocalized outermost, or valence, electrons and the nuclei of the atoms. Such attraction is called "metallic bonding." It is not necessary to imagine a specific bond between two neighboring atoms in a metallic crystal, as though the two atoms directly attracted one another. One may think rather of two adjacent atoms remaining in contact and resisting separation because of their mutual attraction for the nonlocalized outermost electrons.

The Relation of Bonding to the Structure of Metals

Although no simple explanation of structural differences among metals is available, we can understand the general nature of metallic packing as the logical result of the kind of bonding. The number of neighbors is not restricted by the number of bonding electrons available, and therefore tends to become as great as the packing of spheres will permit. For this reason, metals commonly exhibit structures in which each interior atom has twelve closest neighbors, for this is the closest packing possible for spherical atoms of equal size. When there are certainly no bonds at all, as among tennis balls, or among atoms of neon or argon in the solid state (which exists only at extremely low temperatures), the packing is similar to that observed for most metals.

In the following chapter, the significance of the structures resulting from chemical bonding in the elements will be examined and the differences between metals and nonmetals more clearly detailed.

SPECIAL HELP

Test Your Memory

1. What is meant by "heat of atomization"?
2. In metals, how is the number of outer electrons related to the number of vacancies?
3. What kinds of electrostatic interactions occur when two atoms approach one another?
4. What feature of the outer electronic structure of an atom appears essential to a strong attraction between that atom and outside electrons?
5. What is the crude electrostatic picture of a metal?
6. State the fundamental requirements for the formation of a single covalent bond.
7. Under what conditions does the ground state differ from the valence state?
8. What is a hybrid bond?
9. What is meant by "bond angle"?
10. How can bond angles be explained most simply?
11. What is a double bond? A triple bond?
12. How does bond multiplicity affect bond length?
13. How do the "diamond" and "graphite" structures differ?

14. How are the diamond structure and the atomic structure of carbon related?
15. How can the diatomic molecules of nitrogen be explained?
16. What is the molecular structure of white phosphorus, and how can it result from the known structure of phosphorus atoms?
17. Explain the diatomic nature of the halogens.

Test Your Understanding

1. Why does beryllium, with two electrons in the outer shell, not resemble helium, which also has two electrons in the outer shell?
2. When atoms are individually electrically neutral, with the center of negative charge coincident with the center of positive charge, how can an electrostatic attraction exist between them?
3. Why does the nature of bonding change from nonlocalized to localized electron sharing as the ratio of outer vacancies to electrons in the outer shell decreases?
4. What makes an atom tend to form as many covalent bonds as it can, instead of fewer?

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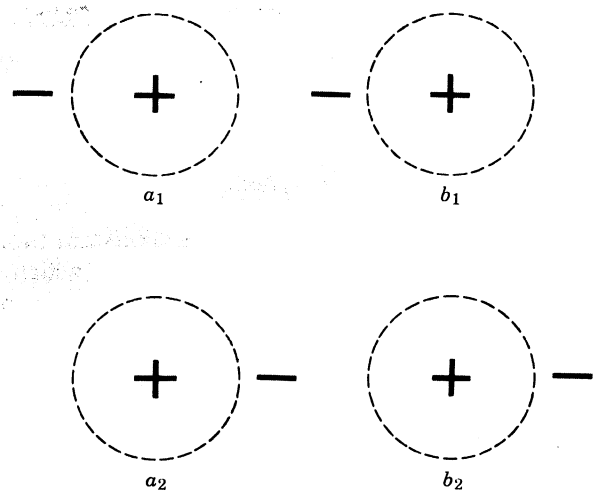
The Physical States and Physical Properties of the Elements

THE "FREE" ELEMENTS themselves illustrate three radically different states or forms of matter, states commonly known to everyone as solid, liquid, and gas. We know, for instance, that hydrogen and oxygen are gaseous, that mercury is liquid, and that carbon and iron are solid. Why are some elements solid, some liquid, some gaseous? We also know that if iron is heated very hot it melts, that if oxygen is cooled to a very low temperature it becomes a liquid, and that mercury is not suitable for thermometers at very low temperatures because it changes to solid. Yet the identity of the element does not change. Liquid iron is just as truly iron as is the more familiar solid, and liquid oxygen is just as truly oxygen as is the more familiar gas. Why do these different states of matter exist, and why and how are they interchangeable?

VAN DER WAALS FORCES

Before answering these questions, one must consider forces additional to those included in the preceding discussion of chemical bonds. When two or more atoms have combined through bond formation by the

sharing of electrons, to form an individual molecule in which all the covalent bonding capacity of the component atoms is completely used up, does this mean that two such molecules cannot attract one another? Experimental observation that definite and significant attractions do occur is abundant. For example, a lump of sulfur has some hardness and strength, despite the fact that it is merely a collection of individual molecules each of formula S_8. Where does it derive this hardness and strength, unless from attractions among the separate molecules? Then what is the nature of these attractions? Such attractive forces were first studied in detail by a physicist named van der Waals, and have become known as "van der Waals forces." Presumably they originate with the polarizability of electron clouds, which means simply that these clouds can be deformed (polarized—the center of negative charge shifted away from the center of positive charge) under the stress of an external electrical field. Given the facts that atoms and molecules are deformable, and that like charges repel one another but unlike charges attract one another, there is no logical difficulty in imagining how mutual deformation by two molecules could result in like charges moving a little farther away and unlike charges moving a little closer, resulting in a net attractive force. In other words, by their proximity two atoms



Atoms a and b, although electrically symmetrical when isolated, can be distorted (polarized) into forms a_1, a_2 and b_1, b_2 under the influence of each other. Two such atoms can exert a continuous electrical attraction for one another through such alternating induced "dipoles" (forms in which the centers of positive charge and centers of negative charge do not coincide as they do in the isolated atoms).

Figure 19. Representation of van der Waals forces.

or molecules can deform one another so that electrons of one are attracted by the nucleus or nuclei of another. Especially if the two atoms or molecules are alike, there need be little difference between the state where the positive charge of one attracts the negative charge of the other and the state where the negative charge of the first attracts the positive charge of the second. Rapid interchange between such states may therefore occur, still resulting in a net attractive force.

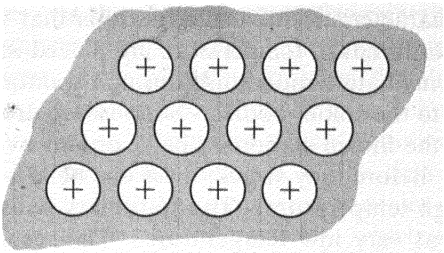
Van der Waals forces appear to be greater, the larger the number of electrons involved. Larger atoms and larger molecules in general tend to cling together more strongly.

COHESIVE FORCES: SUMMARY

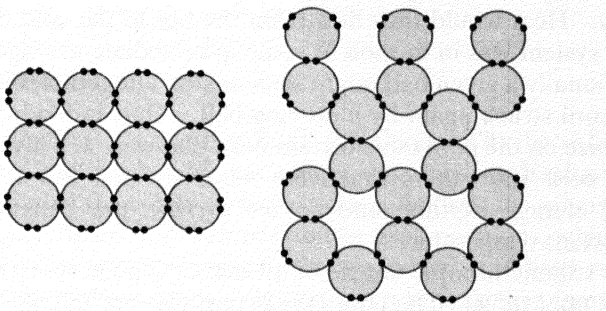
We have seen that some of the elements consist of atoms held together through the sharing of nonlocalized electrons, a process known as metallic bonding. Others of the elements consist of atoms held together through the sharing of localized electrons, known as covalent bonding. Sometimes this covalent bonding extends indefinitely through three dimensions, linking together all the atoms in a given gross fragment of the element. Sometimes it extends only to relatively few atoms in a group, leading to molecules which are then able to be held together through van der Waals forces. Finally, sometimes there is no bonding at all, only van der Waals forces between the individual atoms being in any way effective.

TEMPERATURE

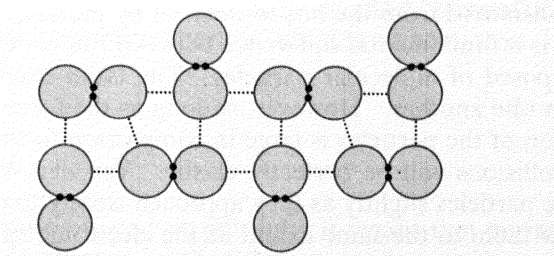
In all matter the component particles are in constant motion. The vigor of this motion is measured by the temperature, which can therefore be taken as an index of the kinetic energy (energy of motion) of the particles. If you strike the cue ball a straight blow, directing it toward the triangle of 15 stationary balls at the other end of a pool table, the cue ball receives kinetic energy which the others do not possess. When the cue ball strikes the group of other balls, however, they all nearly simultaneously acquire kinetic energy from it. The cue ball slows down, and the fifteen other balls depart in various directions. Thus, through bodily collision, energy is transferred from one ball to others. If all collisions were completely elastic, occurring with no total loss of energy, including both inter-ball collisions and ball-cushion collisions, and if all friction between balls and table surface could be eliminated, all sixteen balls would keep on moving indefinitely.



Metallic bonding: Metal cations imbedded in "glue" of valence electrons.



Giant molecule: All atoms held together in two-dimensional sheets or three-dimensional aggregates by covalent bonds between all pairs of closest neighbors.



Covalent molecules: Atoms joined in molecules by covalent bonds, but molecules joined only by van der Waals forces (dotted lines).

Figure 20. Summary of types of cohesive forces in elements.

Any given ball would change speed and direction many times, on collision with one or more other balls, but no energy would be lost to the system of balls, and the *average energy* per ball would remain constant. It would be one-sixteenth of the energy initially transferred from cue to cue ball.

One of the characteristics of temperature is that when two or more bodies initially different in temperature are placed in contact, they will acquire an intermediate temperature through spontaneous flow of heat from the hotter to the colder bodies. Suppose we drove fifteen cue balls at once toward the fifteen stationary balls, on our hypothetical frictionless pool table. Before they struck, these cue balls would be equivalent to a body at high temperature. The stationary balls would be equivalent to a body at very low temperature. The result of the collisions would be to distribute the energies such that all the cue balls would on the average lose a considerable part of their initial kinetic energy and the initially stationary balls would gain this same amount of kinetic energy. Heat would thus flow from the hot to the cold body, until the whole system was in motion at some intermediate average temperature. Occasionally a given ball might slow or stop altogether, but not for long, only until struck again by a moving ball. Thus individually one might recognize on the pool table certain balls that were at a given instant relatively cold and others that were relatively hot, but these situations would change rapidly, and *on the average* the balls would remain at constant temperature.

The submicroscopic nature of all matter is something like these balls on the pool table. The component particles are in constant motion at all temperatures except "absolute zero," where they are motionless. The temperature will inevitably change whenever this matter comes in contact with other matter which is at different temperature, energy being transmitted from the hot to the cold by particle collision.

There is a fundamental difference between the pool ball system and one composed of molecular particles. The latter exert van der Waals forces on one another. However, so long as the force associated with the motion of the particles is large in comparison to the van der Waals forces, collisions will be perfectly elastic. Van der Waals forces may speed the particles slightly as they approach closely to one another, but they slow them to the same extent as the electronic spheres recoil and bounce.

COHESION VERSUS DISRUPTION

Opposed to the static configurations of matter in bulk, which would result in all cases if inter-particle forces were the sole factor, is the kinetic energy of the particles. The question of whether a given substance is solid, liquid, or gas is determined by a combination of influences: (1) the inter-particle attractive forces, and (2) the kinetic energy as measured

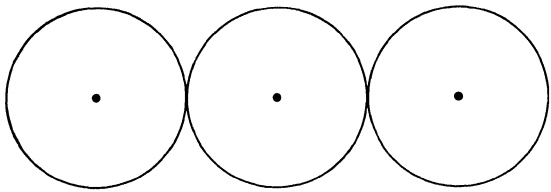
by the temperature. At the absolute zero of temperature, never quite attainable, all substances must be solid. The only possible exception is helium, whose atoms exert so little attraction for one another that external pressure must be applied to cause it to solidify. Whenever possible, particles collect in aggregates which represent the minimum energy content. Commonly this involves a high degree of symmetry. When, as in the free elements, the component particles are all alike, this results in a very regular array of particles, which is characteristic of crystalline solids. The particles are arranged, in the most stable form, so that the attraction which they exert upon one another is at a maximum.

Thermal Expansion

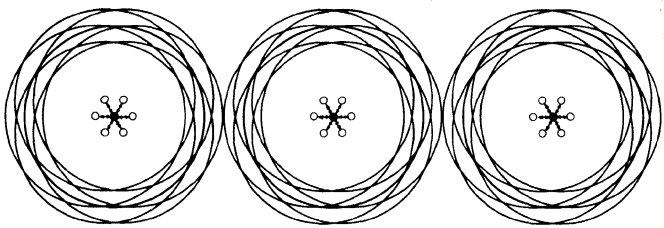
Let us imagine that we begin with all the elements in the solid state at absolute zero, and slowly add heat energy—in other words, slowly give energy of motion to the component particles. At first, the atoms begin to move back and forth over their previously fixed positions, which now become only the average positions of particles in back-and-forth motion. This cannot occur without forcing the particles a little farther apart, since in effect the moving particles require more space than when they were stationary. Thus there are now fewer particles per unit volume, which means that the density (mass per unit volume) is lower. This expansion resulting from an increase in kinetic energy is called **"thermal expansion."** The first thing that happens after the addition of heat, then, is thermal expansion.

Melting

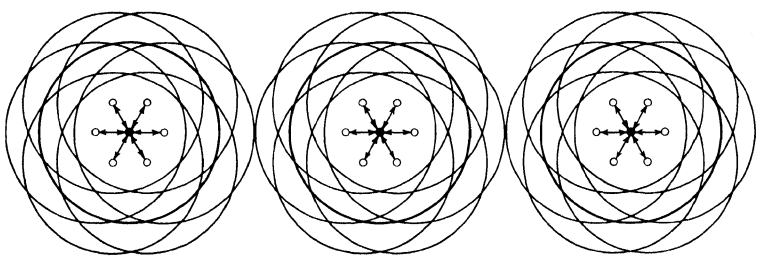
Thermal expansion is very significant. It means that on the average the particles are farther apart than they were when stationary. In the stationary state they were as close together as the attractive forces could hold them. When they are moved farther apart, they become fundamentally no less able to attract one another, but since all such forces diminish with increasing distance the attractions become, on the average, weaker. Sooner or later, with all elements, a point is reached where the thermal motion of the component particles is sufficiently great that the attractive forces are no longer capable of holding the crystal together, with the positions relatively rigidly fixed with respect to one another. In any substantial quantity of an element, the propor-



Lacking thermal energy, atoms or molecules in a crystal would occupy fixed positions as shown above.



An increase in temperature is shown by increasing the motion of the individual atoms or molecules around their average fixed positions. These larger orbits require the particles to push one another apart to make room for their individual motion, thus weakening the attractive forces, which must now operate over larger average distances.



Still further increase in thermal energy causes still greater expansion and thus further weakening of the attractions. When these attractions are no longer adequate to maintain the components particles in their fixed average positions, the crystal lattice breaks down (smelts).

Figure 21. Representation of thermal expansion.

tion of surface particles to interior particles is extremely small. Since the interior particles, because of the symmetry of the crystal, are in positions equivalent to one another (held together by the same amounts of force), the temperature is reached where practically all particles at once have enough energy to overcome the attractive forces, and the crystal breaks down. This temperature, actually a small range of

temperature covering only a small fraction of a degree, is called the **"melting point."** It is the temperature at which the kinetic energy of the component particles becomes high enough to overcome the effect of the attractive forces which held them in relatively fixed positions. The component particles are moving just a little too vigorously to be held as in a crystal. However, the attractive forces are not completely overcome at this temperature, and the particles still hold together. The chief difference is that now the particles are able to move about relative to one another. Whereas in the solid state the aggregation effectively held its shape despite the force of gravity, in the new state it cannot. Now the element flows under gravity to fill any container, whatever its shape, but maintains a level surface at the top. This is the liquid state of matter. The melting point is the lowest temperature at which solid changes to liquid.

Starting with absolute zero and adding heat slowly to all the elements in the solid state would result first in the melting of helium. Absolute zero, as will be discussed later (page 119), is about 273° centigrade below the freezing point of water, the zero point of the centigrade scale. Since the centigrade scale should be more meaningful, at present, it is used here. The next solid element to melt would be hydrogen, at −259.2°C. Next would be neon, at −249.6°. Following close together would be fluorine, then oxygen, then nitrogen, then argon, krypton, xenon, and chlorine (at −101°). Why should these elements be the first to melt? The explanation is to be found in the nature of the aggregation of the atoms—the nature and amount of attractive forces in the crystals. In helium, neon, argon, krypton, and xenon are no covalent bonds, only van der Waals forces which are here especially weak. Their weakness results because the very stable configurations of the electronic clouds about these atoms make them less easily deformed (polarized) than any other kinds of atoms. Hydrogen, fluorine, oxygen, nitrogen, and chlorine all consist of diatomic molecules held together by single or multiple covalent bonds which are strong, but the separate molecules are very symmetrical and can attract one another only weakly by van der Waals forces. Rupture of the covalent bonds is not necessary for the breaking down of the crystals of these elements, for only the intermolecular forces need be overcome.

The reason, then, that these elements are first to melt as the temperature is raised is that the attractive forces operative in their crystalline state are weakest of all the elements. All the elements at any given temperature are alike in the average kinetic energy of their component particles, but some become liquid while others remain solid because of differences in the attractions among particles.

The next lowest melting element is radon, at −71°C. This again consists only of single atoms unable to become covalently bonded to one another and exerting only van der Waals attractions for one another. Just as neon melts at a higher temperature than helium, argon higher than neon, krypton higher than argon, and xenon higher than krypton, so radon melts highest of all these, because its atoms contain more electrons (86) and therefore are more deformable (polarizable), with van der Waals forces correspondingly higher.

Next come mercury, at −38.87°, and bromine, at −7.2°. Why these, which, incidentally, are the only two elements normally liquid under ordinary conditions? Mercury is a metal, but, as will be seen later also, the heavy metals, mercury, thallium, lead, and bismuth seem for some reason very reluctant to use their outermost *s* electrons in bonding. Since all that mercury atoms have in the outermost shell is their two *s* electrons, and these are not readily available for sharing in a nonlocalized manner with other atoms, the metallic bonding is relatively weak. Consequently a lower temperature is required to melt it than is needed for any other metal. In bromine the situation is quite different. Here, diatomic molecules occur, the atoms held together fairly strongly by single covalent bonds. In the crystal, these diatomic molecules retain their individuality and are held together only by van der Waals forces. Although these are weak, they are stronger than those in chlorine because of the greater number of electrons per molecule (70) compared to chlorine (34). The forces become too weak to hold the molecules in relatively fixed positions when the temperature has not yet reached "room temperature" (assumed to be about 25°C), so bromine is familiarly known as a liquid.

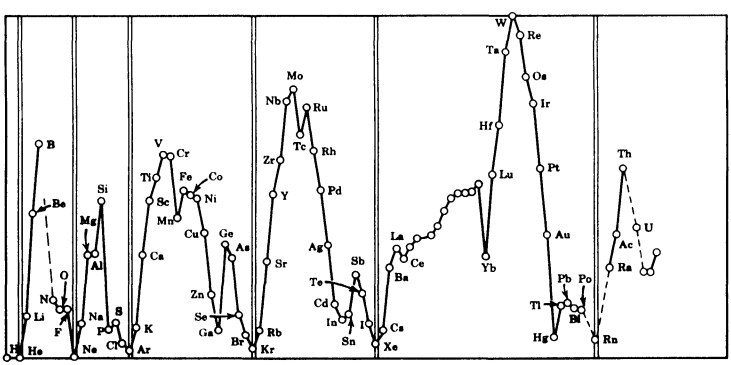
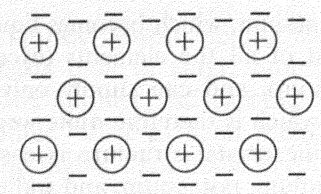


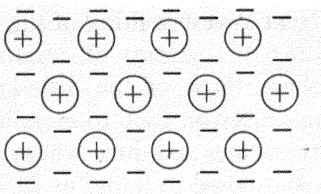
Figure 22. Melting points of the elements in relation to their atomic numbers.

Next lowest melting of the elements is cesium, which becomes liquid at 28.6°C. Atoms of cesium are largest of all the elements (except perhaps those of the little-known francium), and can supply only a single electron each to metallic bonding, which is therefore quite weak. Next comes gallium, whose weak metallic crystal structure is easily broken down to liquid at 29.78°C. Rubidium, potassium, and sodium follow, each consisting of relatively large atoms with but a single electron apiece to contribute to the metallic bonding. Between rubidium and potassium should come phosphorus, in its white modification. Here is the first instance of an element having more than one form of aggregation. Each form, naturally, is of different stability and therefore melts at a different temperature, even though the individual atoms in each modification are identical. White phosphorus consists of P_4 molecules, which persist in the melt. In other words, all that is necessary to change this element from solid to liquid is to overcome the relatively weak attractive forces among the separate P_4 molecules, the covalent bonds within the molecules remaining intact. Following sodium are the two nonmetals iodine and sulfur. Both of these elements exist in polyatomic molecules. Iodine forms diatomic molecules, I_2, in which the atoms are held together by single covalent bonds. Sulfur exists as molecules of formula S_8, also apparently held together by single covalent bonds which form a ring of sulfur atoms. Again, the melting process requires the breaking, not of these covalent bonds, but rather of only the van der Waals forces among the molecules.

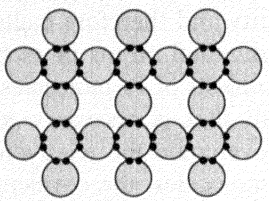
Almost all the other elements are metals. Their melting involves overcoming metallic bonding at least enough to break down the crystal. The highest melting metallic element appears to be tungsten, which melts at 3380°C, showing the great strength of its metallic bonding. Among the few nonmetals not yet mentioned are carbon and silicon. Carbon tends to change directly to vapor without melting, and its exact melting temperature is not known. However, the temperature is certainly well over 3000°C. Why? Both in graphite and in diamond, carbon atoms are held together by strong covalent bonds extending throughout the crystal. Here melting is not merely a matter of overcoming weak van der Waals forces among molecules, or of weakening the all-directional metallic bonding enough to give the atoms greater freedom of relative movement. It requires the breaking of covalent bonds, at least to the extent that relatively small aggregates are formed. In silicon, the structure closely resembles that of the diamond, but the covalent bonds are somewhat weaker, corresponding to the larger size of the silicon atoms. Enough of these bonds are broken to melt the crystal at 1423°C.



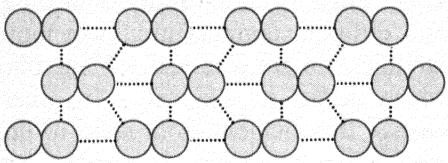
Metal: inner *d* orbitals used in bonding —high bond strength—high melting: e.g. titanium, chromium, tungsten.



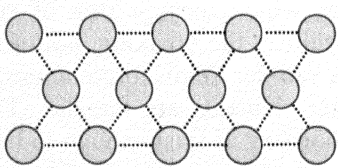
Metal: inner *d* orbitals not available for bonding—lower bond strength—relatively low melting: e.g. sodium, aluminum, zinc.



Giant molecule: continuous network of covalent bonds, which must be broken (at least some) before melting can occur—high melting: e.g. carbon, silicon.



Molecular crystal: small polyatomic molecules, held together only by relatively weak van der Waals forces —tend to be low melting: e.g. hydrogen, nitrogen, phosphorus (P_4).



Monatomic molecular crystal: very weak van der Waals forces—very low melting: e.g. helium, neon, argon.

Figure 23. Relation of an element's melting point to its state of aggregation.

In summary thus far, the chemical elements change from solid to liquid as the temperature is increased, in accordance with their state of aggregation and the nature of the forces which must be overcome to effect this change in state. The existence of an element as solid or liquid, at the temperatures most familiar to us, depends on the relationship between the attractive forces and the disrupting force of kinetic energy. The structure of the individual atoms determines the nature of the aggregate, but it is the nature of the aggregate that determines the physical properties.

Physical Equilibrium at the Melting Point

Up to this point, we have been considering only what happens to a solid element as its temperature increases. We have noted that when it reaches a certain temperature the solid changes to liquid, a process called melting, or fusion. The temperature can also be diminished, and we might equally well consider what happens when an element in the liquid state is cooled. When it reaches a certain temperature, it solidifies. This temperature is called the "**freezing point.**" For a given substance, the freezing point and the melting point are the same temperature. In other words, at this particular temperature, the substance can change both from solid to liquid and from liquid to solid. If a mixture of the liquid and the solid exists at this temperature, both processes occur at the same time. If the temperature were increased, the rate of melting would increase rapidly and the rate of freezing would decrease rapidly. If the temperature were decreased, the rate of freezing would increase rapidly and the rate of melting would decrease rapidly. But at the melting temperature, if no heat is added or withdrawn from the system, the rates of freezing and melting must become equal.

When two exactly opposite processes are occurring together at exactly the same rate of speed, the system is said to be "at **equilibrium.**" This particular equilibrium is called "**dynamic** equilibrium" because action is occurring, in contrast to the "**static** equilibrium" of a man standing on his head, for example. Also, since it involves physical change, it is called "**physical** equilibrium."

The melting or freezing point can now be defined as the temperature at which solid and liquid are in equilibrium. More will be said about this equilibrium, and physical equilibria in general, later in this chapter.

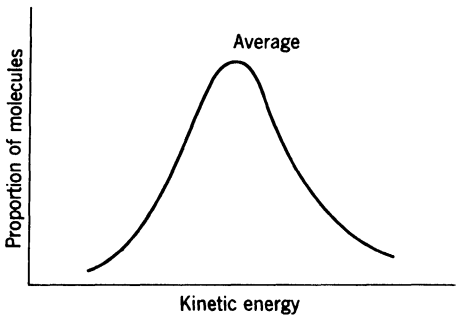
VAPORS AND GASES

Although the temperature of a body of matter represents the *average* kinetic energy of its component particles, individually the particles may vary up and down from this average to a significant extent. This variance will not necessarily last long for any one particle, but rather change rapidly from one particle to another. Even in a very symmetrical crystalline solid, therefore, although nearly all of the particles may possess too little kinetic energy to overcome the attractive forces enough to form liquid, a very few may at any given moment have much higher

Temperature measures the average energy, which can be transmitted by collision, of all the molecules.

However, at any one moment all the molecules are not equal in energy.

The distribution of energies looks something like this:
Some molecules have more than average energy.
Some have less.



In a mass of liquid or solid, the molecules are close enough for large attractive forces to be effective. Only the molecules of highest energy can overcome these forces and escape by evaporation.

If the total energy of all the molecules remains unchanged, and the molecules of highest energy escape, the average energy of the remaining molecules must be less.

This is why evaporation is a cooling process.
The hottest molecules escape.

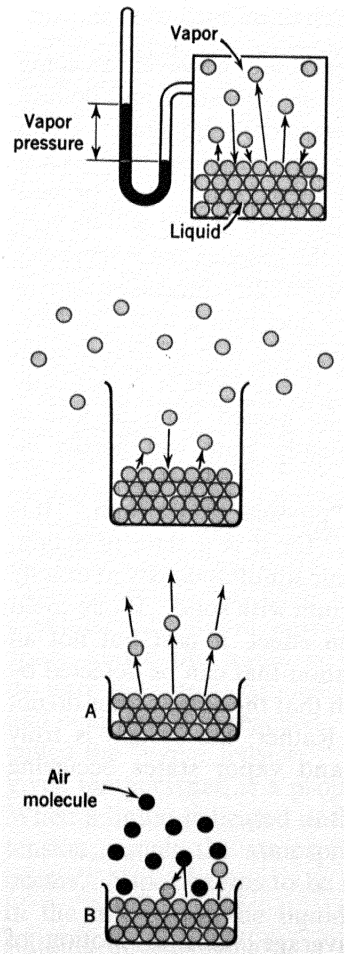
Figure 24. Approximate distribution of kinetic energies.

energy than this. If one of these should happen to be close to the surface and propelled outward by collision from beneath, it might escape from that surface into the space surrounding it. Two such particles, having escaped with so much energy, might come in contact by colliding, reaching such proximity that the attractive forces could be effective. However, being possessed of too much energy to remain together, the particles must bounce apart with perfect elasticity. Such a state of matter is the gaseous state, wherein the kinetic energy has overcome completely the attractive forces in solid and liquid.

When a portion of a certain element is in the gaseous state but much of it remains as solid or liquid, the part in the gaseous state is called "**vapor.**" When the kinetic energy of all of the element is too high for the attractive forces to be effective, the element is said to be a "**gas,**" or to be in the "**gaseous state.**" Clearly all vapors are gases, but all gases are not customarily called vapors. For example, liquid oxygen cannot exist at ordinary atmospheric conditions, so oxygen is called a gas, in the air, and never a vapor. On the other hand, liquid water does exist

under ordinary conditions, but some of it easily vaporizes to the gaseous state. The custom is to refer to that part of the water that is in the gaseous state as "water vapor," and seldom if ever as "gas," even though it is.

When certain of the most energetic particles of a given solid element escape into the space around it, these "hottest" particles no longer contribute to the average kinetic energy in the solid. Therefore, this average must go down. If the hottest particles escape, the temperature of the remaining particles must be lower. The escape of the hottest



I. In a limited space at a fixed temperature, the rate of escape of molecules from liquid to vapor soon is equaled by the rate of return to liquid. The pressure of the vapor is then the equilibrium vapor pressure. The amount of liquid remains unchanged.

II. In an unlimited space at the same fixed temperature, the rate of escape of molecules from liquid to vapor is the same, but the concentration of vapor never builds up to where the rate of return is equal because molecules are now able to escape from the environment of the liquid. The liquid eventually "dries up."

III. Evaporation into a vacuum (*A*) is much faster than into air (*B*), because when escaping vapor molecules collide with O_2 or N_2 molecules of the air they may bounce back into the liquid again.

Figure 25. Vaporization of a liquid.

particles is called "**vaporization,**" and one can understand readily why vaporization is always a cooling process. If the space around the solid is in no way restricted, the escaped particles may well depart from the region of the solid and never find their way back. Even moving molecules obey the laws of mechanics that deal with bodies in motion. Such bodies continue at constant velocity in a straight line until interfered with by some outside influence. If the body of solid is maintained at a constant temperature, which is sufficient to permit the escape of some vapor, then eventually it will all evaporate and disappear.

Physical Equilibrium during Vaporization

If the space around the body of solid is enclosed, however, escaping particles eventually collide with the walls of the container and bounce away again. Some of these will rebound toward the solid again. Upon striking the solid surface, some of the particles may lose their excess energy to other particles and therefore stick to the solid. This process is called "**condensation.**" The rate of condensation at first will be very slow, but as the concentration of particles in the gaseous space increases through evaporation from the solid, the probability increases that in their motion, made erratic by collisions, they may return to the surface. Presently a steady state is reached, in which the rate of evaporation exactly equals the rate of condensation. If the system is perfectly insulated so that no kinetic energy can be gained from or lost to the outside environment, this dynamic steady state will persist indefinitely.

This is another example of what is called "physical equilibrium." It is also an example of "dynamic equilibrium," for it is a state of action, involving two opposite processes which occur simultaneously at exactly the same rate of speed. Vapor is in equilibrium with solid. If one could label individual atoms (as can be done, in effect, if part but not all of the atoms are radioactive, emitting radiation that can be detected by physical instruments), one would soon learn that the same atoms do not remain in the vapor state all the time. Rather, the system is truly dynamic, with exchange between solid and vapor states occurring rapidly and constantly.

Boiling

Since the temperature indicates the average vigor of motion of the molecules or other particles, for each particular temperature a particular concentration of vapor will exist over the solid at equilib-

rium. As will be explained in detail on page 116, the concentration of a vapor or gas can be measured quantitatively in terms of the pressure exerted by the collision of the particles against the walls of the container. The pressure of the vapor in equilibrium with the solid at a given temperature is called the "**vapor tension**" of that solid. As the average kinetic energy is increased, the proportion of the total particles having sufficient energy to escape from the surface of the solid likewise increases. Therefore vapor tension always increases with increasing temperature. Furthermore, vapor tension is a property characteristic of any pure substance, and no two substances are likely to be exactly alike in vapor tension. As far as the different elements are concerned, their vapor tensions vary over an extremely wide range for any given temperature.

The pressure due to molecules of air in the atmosphere is called the atmospheric pressure. When a solid changes directly to vapor without first melting, the process of evaporation is called "**sublimation.**" It is convenient to compare sublimation of different substances by comparing the temperatures at which their equilibrium sublimation pressures equal one atmosphere, the same as the pressure of the air at sea level on a fair day. Below this temperature, evaporation of a solid into the air is impeded seriously by collisions of escaping particles with the molecules of the air. Above this temperature, evaporation can be much more rapid because the particles are escaping rapidly enough to knock most of the air molecules out of the way.

As solids can evaporate directly, so can liquids. Again, the molecules that are able to escape from the surface must be those which have enough energy at the time they happen to be near the surface. The escape of the fastest moving molecules leaves the remaining molecules moving at a lower average rate than before, and the evaporation is therefore a cooling process. If the space above a liquid is unlimited, the vapor molecules may never find their way back to the liquid surface, and eventually the liquid evaporates completely, or dries up. But if the space above the liquid is enclosed, the vapor concentration builds up until the rate of condensation again equals the rate of vaporization, and equilibrium is reached. The vapor pressure at equilibrium is again called the "vapor tension." The vapor tension of a pure liquid, at any given temperature, is a property uniquely characteristic of that liquid. When a liquid is heated until the equilibrium vapor pressure, or vapor tension, equals the atmospheric pressure, an interesting phenomenon occurs. Vapor begins to be released not merely at the surface but also in the interior of the liquid, where bubbles are formed around any suitable nucleus such as a speck of dust, an unevenness in the wall of the container, or any porous solid present. These bubbles, being naturally much less dense than the liquid, rise rapidly to the surface and

the vapor escapes into the space above it. This process is called "**boiling.**" The temperature at which it begins is called the "**boiling point.**" For a given substance, the boiling point might be anywhere within a wide range of temperatures, depending on the pressure of the atmosphere over the surface. A liquid boils at any temperature at which its vapor tension equals the pressure of the atmosphere. Scientists have established a standard atmospheric pressure, however, and unless otherwise specified the boiling point is given as the temperature at which the vapor tension equals that standard pressure.

Now consider what vaporization requires. It requires not merely that the attractive forces among component particles be overcome, to the extent of allowing relative freedom of motion as in a liquid, but that they be completely overcome, giving the component particles almost complete freedom of motion. The existence of a substance, such as a chemical element, in the gaseous state under ordinary conditions, then, is an indication that the attractive forces are not very strong. In general, the attractive forces that interfere with melting are essentially the same as those that interfere with vaporization. One therefore finds a rough parallelism between melting and boiling points, when comparing all the chemical elements. Helium boils lowest, at −268.9°C. Next comes hydrogen, at −252.8°. Then come neon, nitrogen, fluorine, argon, oxygen, krypton, xenon, radon, and chlorine—all consisting either of monatomic molecules or diatomic molecules, exerting only very small van der Waals forces of attraction for one another. No other elements boil below 0°C. Above this temperature, first come the elements whose molecules are still fairly small but whose van der Waals forces are somewhat larger: bromine at 58.2°, iodine at 184.5°, white phosphorus at 280°, astatine at about 380°, sulfur at 444.60°—all

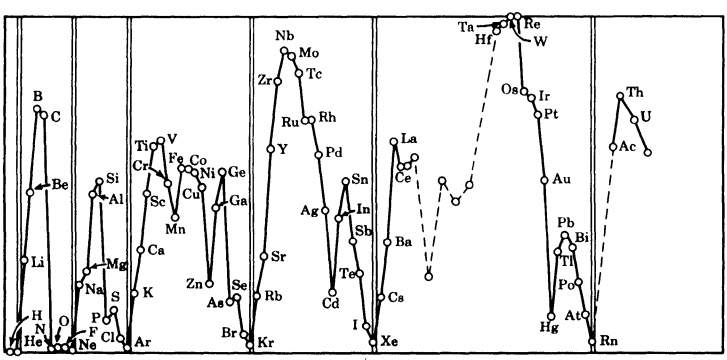
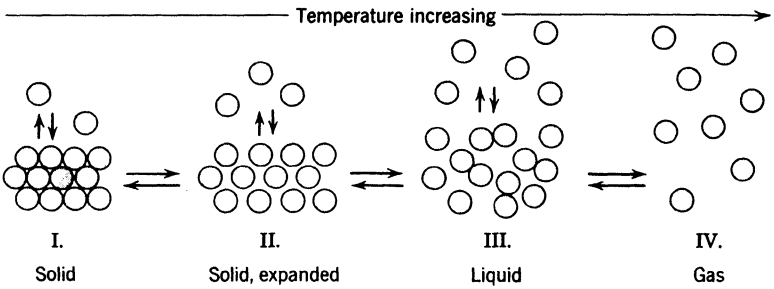


Figure 26. Boiling points of the elements in relation to their atomic numbers.



I. Crystalline solid. An occasional surface molecule receives enough energy to escape as vapor (sublimation energy).

II. When the solid is heated, the increased molecular motion forces the molecules farther apart (thermal expansion). In addition, more molecules receive enough energy to vaporize.

III. When enough heat is added (heat of fusion), the solid breaks up to a liquid, whose molecules are relatively free to move independently. The proportion of molecules vaporizing is increased.

IV. When enough heat is added so that all the molecules can overcome the attractive forces (heat of vaporization), the molecules are now wholly in the vapor or gas state.

Decreasing the temperature reverses these processes.

Figure 27. Relation of temperature to physical states.

nonmetals; and mercury, the lowest boiling metal, at 356.57°C. Beyond that come the somewhat metallic arsenic, which sublimes rather than boils, at 613°, and selenium, which boils at 688°. Of the solid metals, the lowest boiling is the same as the lowest melting, cesium at 685°. From here on, with metallic bonding in most of the remaining elements, boiling temperatures rise to a maximum for rhenium, 5630°, not far above tungsten, which boils at 5530°, and melts highest of all the elements. The persistence of some covalent bonds in the liquid state of silicon is shown by the high boiling point of 2680°. Carbon is one of the few elements whose vapor tension reaches one atmosphere pressure before it is hot enough to melt. This sublimation point is 3800°—again demonstrating the strength of the covalent bonds that must be broken to permit vaporization.

Thus, in boiling point as well as melting point, the relationship between state of aggregation and forces that must be overcome, to effect a change in state from solid to liquid to gas, is readily apparent. Gross physical properties of the chemical elements, such as melting and boiling points, are clearly the result of their states of aggregation. Thus definitely, but nevertheless indirectly, these physical properties can be explained on the basis of atomic structure. They are not mysterious peculiarities of the individual elements.

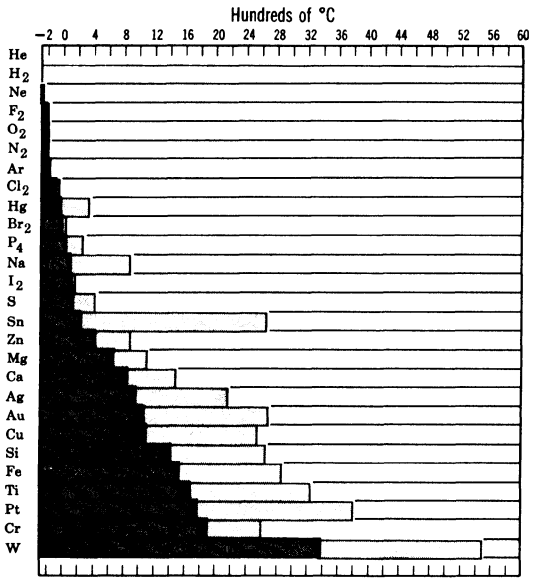


Figure 28. Solid-liquid-gas temperature range of some elements.

ENTHALPY DIFFERENCES AMONG PHYSICAL STATES

If one begins to add heat energy to a sample of an element at absolute zero, he finds that as the temperature rises heat is absorbed. For each substance, the amount of heat that must be absorbed per unit of weight, to raise the temperature by one degree C, is called the "**heat capacity.**" The heat capacity of a given substance varies somewhat with temperature; in other words, the quantity of heat needed to raise the temperature of a gram of the substance from 7 to 8° above absolute zero is not equal to the quantity needed to raise the temperature from 20 to 21°C. The total quantity of heat absorbed in raising the temperature of a sample of substance from absolute zero to some higher value is called the "**enthalpy**" or "**heat content**" of that sample at that temperature.

Heat of Fusion

Suppose a sample of an element is heated until dynamic equilibrium is reached at the melting point. Indeed, the melting point is defined as the temperature at which solid and liquid phases are in equilibrium. The system of solid and liquid is now kept perfectly insulated, so that

no heat can either enter or escape. The element is assumed to consist of molecules, which, constantly changing in energy of motion, are constantly exchanging places between solid and liquid. The temperature under these equilibrium conditions must remain constant, and be identical in solid and in liquid. How can this be true, when obviously heat needs to be added to the solid to produce the liquid? Do the molecules of liquid possess greater energy than the molecules of solid, on the average, or don't they? If they do, how can they be at the same temperature? If they do not, how is the liquid distinguishable from the solid?

The answer is not immediately obvious, for clearly no system can be at equilibrium if one part remains at a temperature different from that of another part. Therefore both solid and liquid must have the same temperature. The answer lies in making a distinction between energy associated with motion—*kinetic* energy—and energy associated with position—*potential* energy. Temperature measures only the kinetic energy, and in this the solid and liquid are alike. But because of the attractive forces, which are stronger in the solid than in the liquid, the molecules of the liquid possess greater potential energy—energy as the result of the fact that the molecules are farther apart—energy that

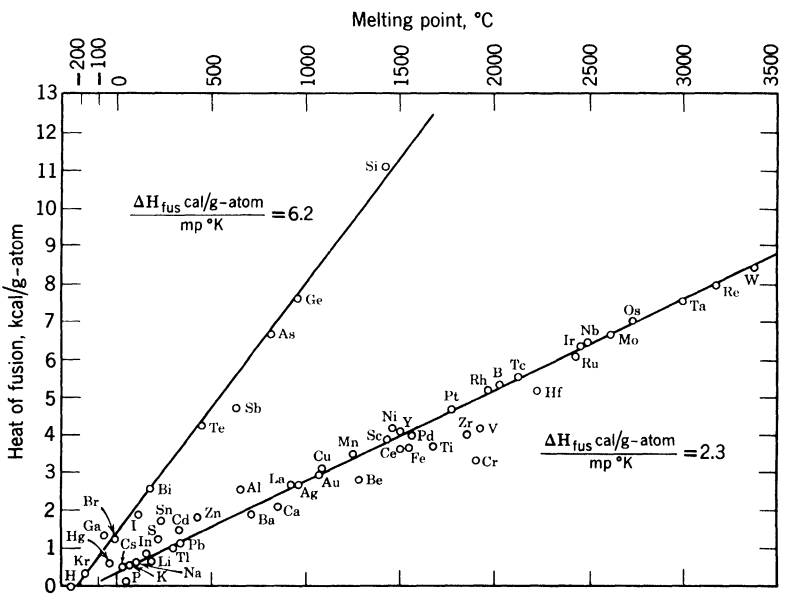


Figure 29. Melting points of the elements compared with their heats of fusion.

is given up when they come closer together. We describe this difference by saying that the average molecule in the liquid has greater potential energy than the average molecule in the solid, and therefore greater total energy. This difference in potential energy is a difference in heat content or enthalpy. It is called the "**heat of melting**" or "**heat of fusion.**" Referred to one gram of substance, it is called the "**specific heat of fusion.**" Referred to one mole of substance, it is called the "**molar heat of fusion.**"

In general, substances whose crystalline states are so easily broken down to liquid that they have very low melting points have correspondingly low heats of fusion, and vice versa. For example, the heat of fusion per gram atom of helium is only 0.005 kcal, but the heat of fusion of tungsten is 8.42, and that of silicon, whose covalent bonds must be broken, is 11.1. (A kilocalorie, abbreviated "kcal," is 1000 calories, or enough heat to raise the temperature of 1 liter—1000g—of water by one degree Centigrade.)

Heat of Vaporization

Similarly, let us imagine an enclosed space containing nothing but a liquid in equilibrium with its vapor, at a temperature where the vapor pressure is equal to one atmosphere—in other words, at the standard or normal boiling point. Here again, the temperature is identical for liquid and vapor, from which one must conclude that molecules in both states on the average have equal vigor of motion, equal kinetic energy. But the molecules in the vapor are much farther apart than in the liquid—moved to an average separation where the attractive forces are completely overcome. Obviously these vapor molecules, by virtue of their wide separation, possess potential energy not present in the liquid molecules. In fact, one would predict that this energy difference between the two states should be much greater than it is between solid and liquid phases. One could also predict that where the forces of attraction require high temperatures to be overcome completely, there also will be found the higher energy differences.

This difference in potential energy, the difference in heat content or enthalpy, between a liquid and its vapor in equilibrium with it at the normal boiling point, is called the "**heat of vaporization.**" As with heats of fusion, "**molar heat of vaporization**" refers to one mole.

To test the prediction that heat of vaporization should greatly exceed heat of fusion for the same element, consider the heat of vaporization of helium, only 0.02 kcal per mole but four times as great as the heat

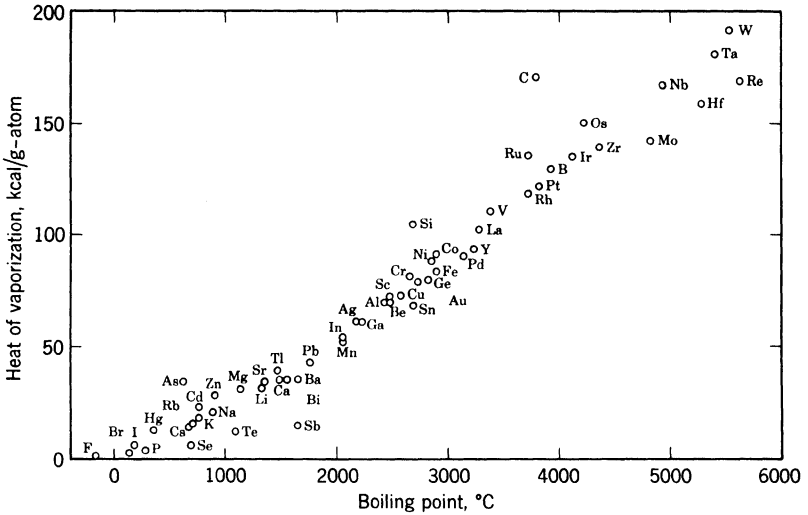


Figure 30. Boiling points of the elements compared with their heats of vaporization.

of fusion. The heat of fusion of tungsten is 8.42 but the heat of vaporization is 191, greater by a factor of more than twenty.

To test the prediction that boiling points and heats of vaporization should tend to go together, consider that the lowest boiling element, helium, has also the lowest heat of vaporization. For rhenium and tungsten, whose boiling points are 5630 and 5530°, the heats of vaporization are 169 and 191 kcal per mole.

In summary, the enthalpy of any substance in the gas state exceeds that of the same substance at the same temperature in the liquid state by an amount equal to the heat of vaporization. The enthalpy of any substance in the liquid state exceeds that of the same substance at the same temperature in the solid state by an amount equal to the heat of fusion. Similarly, the enthalpy of any substance in the gas state exceeds that of the same substance in the solid state at the same temperature by an amount equal to the heat of sublimation.

THE PRINCIPLE OF LE CHATELIER

A French scientist named Le Chatelier made an observation concerning systems at dynamic equilibrium that serves very usefully as a practical rule for predicting their behavior under stress. The rule may be stated: *When a system at equilibrium is subjected to a stress which*

tends to disturb this equilibrium, the equilibrium changes in a manner which opposes or reduces that stress.

This seems to imply a certain inherent contrariness in nature, which of course does not exist. Actually, its application is logical when one understands how it works. It simply means that changes in forces acting on the system cause a realignment of the forces acting within the system. The principle is best understood from examples.

Consider a solid in equilibrium with liquid at the melting point. Not only is the rate of melting equal to the rate of freezing, but also heat is being absorbed as fast as it is being evolved. If one tries to change the temperature, to raise it by supplying heat, the added heat cannot raise the temperature as long as any solid remains. Instead, it is absorbed by the melting process. For if the added heat did momentarily raise the temperature, this would now lie above the melting point where no solid phase could exist. The solid would melt rapidly, and freezing would cease. Thus heat would be absorbed much faster than evolved, and the temperature would go down to the melting point once more. It could not go lower, without causing freezing to occur much more rapidly than melting. Since freezing is exothermic, heat would be evolved, restoring the melting temperature. Built into the equilibrium system, then, is the capacity to adjust to small stress. Obviously, if a large enough quantity of heat is added to melt all the solid, equilibrium is permanently destroyed. It cannot be regained without external aid. But if the quantity of heat is smaller, the equilibrium is upset only enough to melt part of the solid. This melting restores equilibrium, which now exists with the relative quantity of solid smaller than it was originally.

The effect of adding heat would normally be to raise the temperature. The system at equilibrium adjusts to keep the temperature constant. In general, the reaction that absorbs heat (here, melting) is the one favored by the addition of heat.

Similarly, the withdrawal of heat from any system tends to lower its temperature. If a quantity of heat is withdrawn from a system at the melting equilibrium, however, the system adjusts to keep the temperature from decreasing. Enough of the liquid phase solidifies to give out heat equal to the quantity withdrawn. The temperature remains at the melting point, and a new equilibrium is reached in which there is relatively more solid and less liquid than there was initially.

If the densities of the liquid and solid are equal at the melting point, increasing pressure on the system at equilibrium should have no effect. But suppose the solid is more dense—has its atoms closer together. Increasing pressure should then favor freezing, for by this means pres-

sure can be relieved. This should raise the melting temperature, since freezing gives out heat. This is reasonable, since atoms held together under pressure cannot break loose from their crystalline symmetry as easily and therefore must have higher kinetic energy. Similarly, if the solid is less dense than the liquid, increase in pressure should favor melting, which in turn should result in a lower melting point.

Another example of physical equilibrium is that between vapor and liquid. Le Chatelier's principle tells us that an attempt to raise the temperature by adding heat will result in vaporization occurring momentarily more rapidly than condensation, since vaporization is endothermic. But in a closed system the vapor pressure cannot be increased without increasing the concentration of vapor and therefore the rate of condensation, which soon again equals the rate of vaporization. But a new equilibrium, with higher vapor tension, cannot be reached unless the temperature of the system is raised. In such a system, the effect of adding heat cannot be opposed successfully, but the system does change in the direction of counteracting the temperature rise by becoming proportionately greater in amount of vapor and less in amount of liquid.

An attempt to increase the pressure on such a system will similarly be met by a corresponding reduction in pressure, by condensation of vapor. If the pressure increase is not too great it will merely cause a new equilibrium to be reached, for which the proportionate amount of space devoted to vapor is smaller.

Le Chatelier's principle applies even more usefully to systems in which opposite chemical reactions are occurring simultaneously at equal rates. Chemical equilibrium will be discussed first in Chapter 15.

SOME ADDITIONAL PHYSICAL PROPERTIES OF THE ELEMENTS

Between the two broad classes of metals and nonmetals, certain other properties have been recognized as having distinctive differences dependent on the state of aggregation. Perhaps those of greatest interest are electrical conductivity, thermal conductivity, and mechanical properties.

Electrical and thermal conductivity appear to be closely associated from the viewpoint of fundamental structure. Both appear to depend largely on the relative freedom of relatively nonlocalized electrons that are characteristic of metallic bonding. There are wide differences among the different metallic elements and their alloys, but as a class metals are able to conduct an electric current well, and nonmetals are essentially nonconductors. An electric current is a flow of electrons.

Electrons cannot flow like water through a pipe, but must travel from one atom to another. Electrons repel one another and therefore tend to move as far apart from one another as possible. If a battery or generator or other source of electrons delivers electrons to one point on a metallic conductor, their mutual repulsion forces them to spread through the conductor instantly and thus reach the other end. In a metal, relatively little energy is required to shift electrons through the lattice, since this does not require removal but only displacement of electrons by other identical electrons. In a solid nonmetal, the crystal is held together either by covalent bonds or by van der Waals forces which hold together molecules that in turn are held together by covalent bonds. In all cases, the electrons involved in the bonding, as well as any electron pairs not directly involved in the bonding, are localized, and can only be removed by the expenditure of considerable energy. Consequently, external electrons cannot displace those already in position, and the elements are nonconductors, or "insulators."

The transfer of heat from one atom to its neighbor seems also to involve relative freedom of motion, or delocalization, of electrons. Metals commonly conduct heat well, but nonmetals are thermal insulators.

Three elements stand out as being far superior to all others in both electrical and thermal conductivity. These are copper, silver, and gold. Doubtless these properties are a reflection of their special electronic configurations, as will be mentioned again in discussing their chemistry.

Metals also differ widely in mechanical properties, such as toughness, malleability, ductility, and general structural strength, but as a class they are quite distinct from nonmetals. In metals, the nonlocalization of the bonds makes it possible for layers of atoms to slide over one another without any bond breaking. Under stress such as a hammer blow, therefore, most metals tend to change shape, to flow away from the point of stress. This they can do without destroying the crystal strength. A solid nonmetal, however, such as sulfur, held together by covalent bonds and van der Waals forces, can endure no such stress because the bonds are localized between specific atoms, and the relative positions of the atoms in the molecules cannot be changed without breaking these bonds. The intermolecular forces are relatively weak. Nonmetals therefore tend to be brittle and easily crumbled, or else very hard and brittle, but almost never very ductile or malleable. Furthermore, in reaction to a straight as opposed to a shearing force, metallic bonding is commonly strong enough to offer powerful resistance. The close packing of the atoms gives much greater strength to the solid than is usual in nonmetallic solids, where the atoms cannot be so closely packed and the forces may not be as strong.

Further discussion of physical properties can be deferred until more kinds of matter have been described, except for the properties of the gaseous state which will be essentially the same for all kinds of matter. Since several of the chemical elements occur in the gaseous state, a consideration of its special qualities will be appropriate in the next chapter.

THE COLLOIDAL STATE

The Nature of Surfaces

Surfaces of liquids and solids are especially important for two reasons: (1) Their atoms are the only atoms available for chemical reaction with exterior substances, because without contact no reaction is possible, and all interior atoms are shielded from such contact. (2) Their atoms are not so stably located as those on the interior and exert attractive forces out into the space outside as well as toward interior atoms.

As a consequence of (1), the proportion of available surface influences the potential reactivity.

As a consequence of (2), outside substances that happen to come in contact with the surface are held there. This is a universal phenomenon, the extent and nature of which vary widely depending on substances and conditions. Sometimes the attraction is weak and fleeting, sometimes

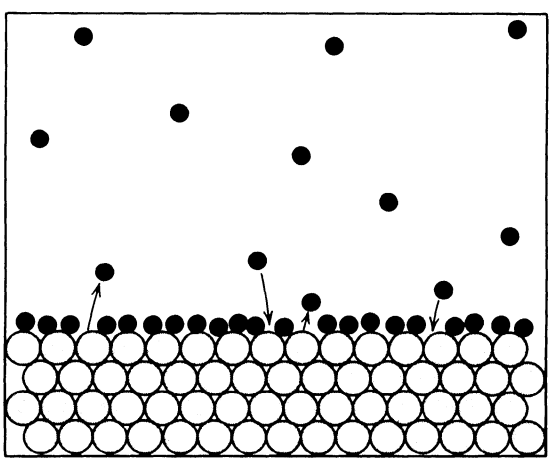


Figure 31. Sorption of gas on a solid surface. At equilibrium, molecules of gas leave and join the surface at the same rate.

strong and effective chemical bonding. Attempts are made to distinguish between these as "**physical sorption**" and "**chemisorption,**" but often no clear distinction can be made. Also, sometimes a foreign substance seems to "soak in," and is called "*ab*sorption," in contrast to "purely surface" attraction, called "*ad*sorption." Here again, distinction is often impossible. All such phenomena may safely be classified, however, as "**sorption.**"

Any surface exposed to a gas, such as the atmosphere, will hold some of that gas sorbed on it. In general, the less polar, less easily condensed gases, such as O_2 and N_2, will be held less strongly. Polar gases, e.g. CO_2 and H_2O, especially the nearer they are to their condensation points, will be held much more strongly. In the steady presence of an external gas, equilibrium tends to be set up, with a layer of sorbed gas, one or two molecules thick, more or less, remaining on the surface. Individual gas molecules, however, are constantly changing places with sorbed molecules. Similarly, liquids are also sorbed on solid surfaces in contact with them. When subjected to a vacuum, surfaces lose most of their volatile sorbed gases and liquids rather promptly. However, the last traces often leave extremely slowly unless their departure is encouraged by elevation of the temperature.

In practice, two metal surfaces placed in contact will not stick together, partly because really close contact is prevented by surface irregularities but mainly because both surfaces are contaminated by oxide film and by sorbed impurities. In principle, two highly polished surfaces in a high vacuum should become bonded together on contact. The potential bonding capacity is there—the metal nuclei to attract and the electrons to be attracted. Equal or lesser forces are potentially available at every unprotected surface.

Colloids

Ordinarily, only in a gas are the component particles accessible to chemical attack on all sides. In a liquid, only the surface molecules can come in contact with other substances unless these substances dissolve, in which case the situation somewhat resembles that in a gas, in that each particle is vulnerable on all sides. A solid is usually much less penetrable than a liquid, and normally only the exterior layer of component particles is accessible. Most commonly, the proportion of the total number of atoms at the surface in a liquid or solid is extremely small. For example, assuming 2Å(2×10^{-8} cm) diameter per atom, a perfect cube 1 cm on a side would contain 5×10^7 atoms on an edge.

If packed as tiny cubes, these atoms would number 1.25×10^{23} in the cubic-centimeter cube. Of these, 25×10^{14} are in one face, so six faces would contain about 150×10^{14} or 1.5×10^{16} surface atoms. The ratio of total atoms to surface atoms is $1.25 \times 10^{23}/1.5 \times 10^{16} = 8.3 \times 10^{6}$. In other words, for every surface atom about 8 million atoms are on the interior. Or, only one in 8 million of the atoms is in a position where it is possible for it to come in contact with an outside atom. Only one in 8 million is immediately in a position to react chemically.

Furthermore, among these relatively few surface atoms one can recognize differences in position which should also affect potential reactivity. At each corner of the large cube rests one atom which, as a cube, has three exposed faces. Along each of the six edges the atoms each have two exposed faces. Within the faces of the large cube the atoms have but one exposed face each. The corner atoms should therefore be more reactive than the edge atoms, which in turn should be more reactive than the face atoms.

If one cuts this 1-cc cube into smaller cubes, each successive dissection, by creating two new faces, must result in (1) increasing the proportion of surface atoms, and (2) increasing the proportion of corner and edge atoms among the surface atoms. Both effects would enhance the reactivity of the solid.

The proportion of surface atoms could be increased in yet another way. Among three-dimensional rectangular faced geometric figures, the cube has the highest proportion of interior atoms—in other words, maximum volume for the amount of surface. If a cube is flattened, the amount of surface increases. One might imagine a cube flattened to a very thin sheet, giving two large dimensions and one very small. If the

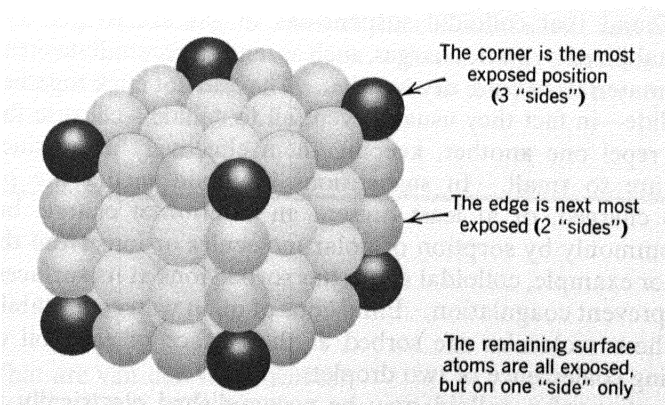


Figure 32. Cube of exposed atoms.

1-cm cube were flattened to a layer one atom thick, the area would be 5×10^7 sq cm, equivalent to a square 7,000 cm on a side (more than one acre). In this form, *all* of the atoms would be surface atoms, and hence potentially very reactive.

In summary, the proportion of surface atoms is very low in ordinary liquid or solid matter, and becomes significantly increased when the matter is either (1) very finely divided or (2) spread out in a very thin film. The reactivity of matter in these forms is so greatly enhanced as to bear little resemblance to the same matter in common bulk form. For this reason, the state of having a relatively high ratio of surface to interior atoms is conveniently studied as a special state of matter, supplementary to the three conventional states of solid, liquid, and vapor. It is called the "**colloidal state.**"

Stabilization and Precipitation of Colloids. The colloidal state in liquids and solids is represented by thin films and by finely dispersed liquid droplets or tiny solid particles. The medium in which these droplets or solid particles are dispersed may be gas, liquid, or even, though less commonly and less significantly, solid. A **colloidal dispersion** of liquid in gas is a "fog," or "mist." In another liquid it is an "emulsion." A colloidal dispersion of solid in gas is a "smoke" or "dust." In a liquid it is often called a "colloidal solution," although it is not at all a true solution, as we shall see later. Since all these dispersed particles, liquid or solid, have in common a relatively large proportion of surface atoms, one would expect them to tend to cling together when they come in contact, through residual bonding or at least van der Waals attractions. The fact that often such dispersions appear to be very stable and show no tendency to coalesce or coagulate therefore needs special explanation.

It is found that colloidal suspensions in gas are frequently if not always stabilized by static charges, such as tend to accumulate on nonconducting materials in cold, dry weather. They do not stick together when they collide—in fact they usually even fail to collide—because their like charges repel one another, keeping them effectively apart since their masses are so small. In suspensions in liquid media the particles are also charged, or at least present an exterior of charge, but here more commonly by sorption of polar molecules or ions from the solution. For example, colloidal sulfur has sorbed ions at its surfaces which tend to prevent coagulation. Emulsions of oil in water are stabilized by soap, whose molecules are sorbed at the surface of each oil droplet, preventing coalescence of two droplets.

Destruction of a colloid may be accomplished electrically, by discharging the particles so they will not repel one another but stick together when they meet. When a smoke or dust cloud, for example,

is passed between charged plates, the electrostatic charge is removed, and the solid settles. A device to accomplish this is called an "electrostatic precipitator." A colloidal suspension of solid in liquid can often be "**flocculated**"—caused to form larger particles which settle out—by addition of a salt having highly charged ions. These ions are attracted to the particles and neutralize their stabilizing charge.

Properties of Colloidal Suspensions. All degrees of dispersion and subdivision are possible, so that no exact definition of a colloidal particle exists. In general, however, the term colloidal is applied mainly to particles so small that they are prevented from settling out by the kinetic activity of the molecules of the liquid medium in which they are suspended, as well as by their electrical charge. Thus they exhibit "Brownian movement," an intermittant zig-zag random motion, visible when properly illuminated against a dark background. Such particles are not retained by any ordinary laboratory filter. They are usually individually invisible, but reflect light so that a bright beam directed through the suspension is visible at the sides. This is called the "**Tyndal effect.**" Colloidal particles permit chemical reactivity at a speed second only to that in true solutions.

Importance of Colloid Chemistry. Life processes depend much on interactions between surfaces and between substances in colloidal suspension, of which blood is a good example. The chemistry of soils and their function in agriculture is largely colloidal. Substances of high surface activity, such as charcoal, are invaluable in purifying by sorption of impurities and for promoting many chemical reactions which occur most easily when the reagents are condensed together on a surface. Hardly an area of chemistry exists in which colloids or films of matter do not play a vital role. For these reasons, many thousands of scientists have concentrated on studies of the colloidal state, and hundreds of books on the subject have been written. All that can possibly be accomplished in a book of this scope is to tell you in a very general way what a colloid is and why.

SPECIAL HELP

Test Your Memory

1. What are van der Waals forces?
2. List the kinds of cohesive forces that may hold elementary substances together.
3. What is meant by "temperature"?

4. How is "kinetic energy" related to temperature?
5. How is heat transferred in a gas?
6. What two factors determine the physical state of an element?
7. How do the liquid and solid states of an element differ?
8. Explain the physical nature of the elements which are gases at ordinary temperatures. Why are they gaseous?
9. How are melting point and state of aggregation of the elements related?
10. Define the melting point in terms of an equilibrium process.
11. What is the fundamental difference between liquid and vapor?
12. Why is vaporization a cooling process?
13. Define "vapor tension."
14. How are volatility and state of aggregation of the elements related?
15. Define the "enthalpy" of melting and of vaporization.
16. State the principle of Le Chatelier.
17. What is the special nature of surface atoms or molecules?
18. What distinguishes the colloidal state of matter from other states?
19. Name several kinds of colloidal system.
20. How are colloidal suspensions stabilized, and how caused to flocculate?

Test Your Understanding

1. Why does cooling never convert a pure solid substance to a liquid or a gas, or a pure liquid substance to a gas?
2. What causes van der Waals forces to diminish, as a rule, when temperature is increased?
3. How can two samples of water be at the same temperature yet have different enthalpy?
4. Since it would be a practical impossibility to insulate the contents of a container perfectly, how can they be kept at a constant temperature?
5. How could you distill sulfur without heating it to its normal boiling point?
6. What would you conclude about the state of aggregation and/or atomic number of an element whose melting point is extremely low?
7. What does a very high melting point of an element signify?
8. How can the vapor tension and vapor pressure of the same substance at the same temperature be different?
9. How and why can finely divided charcoal remove chlorine from air containing it?

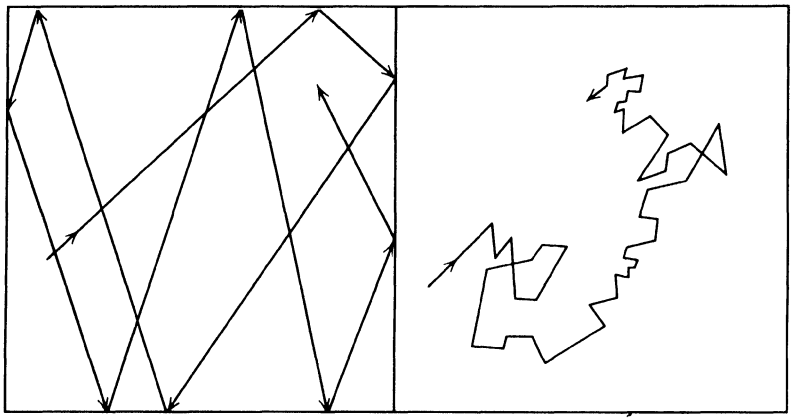
6

Some Properties of Gases

THE GENERAL PICTURE of a gas has already been described: It is matter in a state where the kinetic energy of the component particles is sufficient to overcome quite completely the attractive forces which would otherwise tend to hold them together in liquid or solid form. The elements that are gaseous at ordinary temperatures are the elements whose monatomic or diatomic molecules are held together in the condensed states only by weak van der Waals forces: helium, neon, argon, krypton, xenon, radon, hydrogen, nitrogen, oxygen, fluorine, chlorine. These elements, and many gaseous compound substances as well, have in common a number of interesting physical characteristics.

DIFFUSION

Perhaps the first and most important such characteristic is that of "diffusion." The molecules of a gas are in constant motion. If this were not so, they would condense and the gas would change to liquid or solid. This motion obeys the laws of mechanics regarding moving



In a vacuum

Straight line motion changed only by collision with walls of container.

In a gas

Innumerable changes in direction result from collisions with other molecules. The average distance between collisions is called the "mean free path."

Figure 33. Path of a single gas molecule.

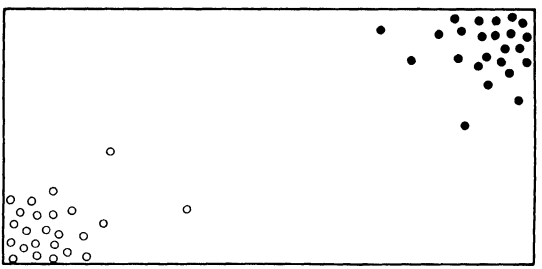
bodies. That is, each molecule has, as a consequence of its motion, the kinetic energy, $\frac{1}{2}mv^2$, where m is its mass and v its velocity. Also, each molecule moves at a constant speed in a straight line path until acted upon by some outside force. Consider a huge empty space, and imagine that, at its center, a large number of molecules of a gas are liberated simultaneously, in a single cluster. Molecules on the outside of this cluster may happen to be moving in any direction at all at the time of release. Those that are moving outward from the cluster will encounter nothing whatever to impede their straight line progress, and will continue to travel to the limits of the space. Those that are on the outside of this cluster but moving inward, will almost certainly encounter inner molecules, and bounce away in a different direction. But if they meet no inner molecules, they will pass right through the cluster and travel to the limits of space in that particular direction. Inner molecules are more likely to have collisions and consequent changes of direction, but on the average such collisions are most probable in the direction of the greater concentration of molecules. The result is that, on the average, the molecules will tend to spread out from one another. They will occupy eventually, as effectively as their number and motion permit, the entire space into which they were liberated.

If now we suppose that some distance away a second cluster of molecules is liberated at the same time as the first, these too will tend

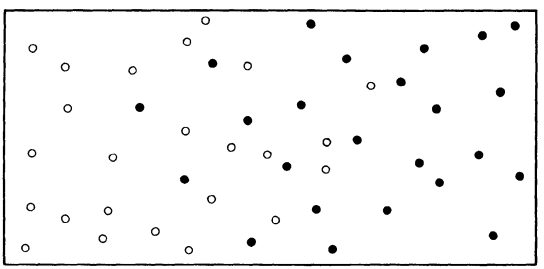
to spread out, and soon some of them will be colliding with some of the molecules of the first cluster. Before long, both clusters will occupy the entire space and be thoroughly mixed with one another.

This phenomenon of spontaneously spreading through the entire space available to it, even when it means becoming mixed with another gas, is characteristic of a gas and is called "**diffusion.**"

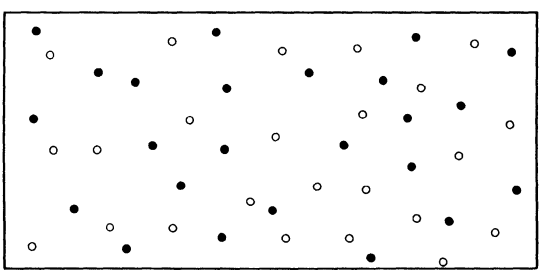
The energy of a gas molecule at ordinary temperatures is relatively large, and the mass is small. This means, from the expression for kinetic



1. Gases released at opposite ends of evacuated container.



2. A tiny fraction of a second later.



3. Same, a little or a lot later.
Each now exerts a pressure on the walls wholly independent of the other.

Figure 34. Diffusion of two gases into evacuated space.

energy, that the velocity is relatively large. At 25°, the average molecule of air travels at about 700 miles per hour. Consequently, diffusion occurs rapidly. Diffusion into a vacuum—a space where there are no other molecules—occurs most rapidly because there is nothing to impede it. Diffusion of one gas into another occurs more slowly because it is impeded by intermolecular collisions, which obstruct and change the direction of the straight-line motion of the molecules. In air under ordinary conditions, molecules only travel about 300 molecular diameters on the average before colliding. At 700 miles per hour, this means about 3×10^9 collisions per second, or one every three-billionth of a second, for each molecule.

Since all molecules, on the average, possess the same amount of kinetic energy at the same temperature, and this is equal to $\frac{1}{2}mv^2$, obviously the larger the mass the smaller the velocity, and therefore the slower the diffusion. Assume that one gas has mass m_1 and velocity v_1, and a second gas has mass m_2 and velocity v_2. At the same temperature, they have the same kinetic energy: $E_1 = E_2$. These can therefore be equated:

$$E_1 = \tfrac{1}{2}m_1v_1^2 = \tfrac{1}{2}m_2v_2^2 = E_2$$

Cancelling the coefficients $\frac{1}{2}$ and rearranging:

$$\frac{m_1}{m_2} = \frac{v_2^2}{v_1^2}$$

or

$$\frac{v_2}{v_1} = \sqrt{\frac{m_1}{m_2}}$$

Since, in the above ratio, the molecular weights can be expressed in the atomic weight scale, we can write:

$$\frac{v_2}{v_1} = \sqrt{\frac{M_1}{M_2}}$$

where M_1 is the molecular weight of the molecule of mass m_1, and M_2 is the molecular weight of the molecule of mass m_2. This is a mathematical expression of "Graham's law": *The rate of diffusion of a gas is inversely proportional to the square root of its molecular weight.*

How, for example, would the rates of diffusion of helium and argon compare? The molecules of both these elements are single atoms. The atomic weight of helium is 4, and the atomic weight of argon is about 40. The ratio of the rate of diffusion of helium to that of argon is therefore equal to the square root of the ratio of the molecular weight of argon to that of helium, or $\frac{40}{4} = 10$. The square root of 10 is

3.16. Helium would diffuse 3.16 times as fast as argon. Suppose a fifty-fifty mixture of helium and argon were placed in a container having a porous plug through which gas could leak. With the helium initially leaking more than three times as fast as the argon, you can see that the gas coming out would be richer in helium, and the gas left behind would become richer in argon. This is very important, because it gives a means of separating gaseous substances that might be separable in no other way. For example, in the production of nuclear energy, uranium of mass 235 must be separated from a much larger quantity of uranium 238. Chemically these isotopes are practically identical, but a volatile compound of uranium can be made in which six fluorine atoms become attached to one uranium, giving two kinds of "uranium hexafluoride." One consists of molecules of mass 352, the other of molecules of mass 349. Not a very large difference, to be sure, but a highly significant one. The compound can be completely vaporized at 56° and one atmosphere pressure. In the vapor or gaseous state, the species having mass 349 diffuses just a little more rapidly, but it is enough to permit, eventually, separation of the uranium 235 isotope in quantities useful in the production of nuclear energy.

A much greater difference in diffusion rate is shown by helium and nitrogen, the latter having a molecular weight of 28, seven times that of helium. Persons with respiratory difficulties find it easier to breathe synthetic air, composed of mixtures of oxygen with helium, than ordinary air, which is four-fifths nitrogen.

The diffusion of vapors and gases has important practical application in scientific laboratories, where it serves as the basis of elegant techniques for the manipulation of very small quantities of volatile materials, which may be highly toxic, explosively reactive with air or water, or by reason of their small quantities difficult to handle. The volatile materials are introduced into all-glass systems where they need never come in contact with anything but glass, which is chemically quite unreactive, or mercury, also fairly unreactive. The fundamental principle is that the vapors diffuse rapidly through a vacuum—a space where there are no molecules to impede their flow. The glass apparatus is pumped out until relatively few air molecules are left; not enough to interfere seriously with the desired studies or with the diffusion of gases through the apparatus. Any volatile material introduced into this apparatus will then almost immediately diffuse throughout the entire apparatus. Now, to persuade this material to move quantitatively to one particular part of the apparatus, a refrigerant is placed in contact with this part—some substance such as dry ice or liquid nitrogen, to cool it down. If the refrigerant is cold enough to remove most of the kinetic energy of the

molecules which strike this part, they will then be unable to move, but remain in a condensed liquid or solid phase. This condensation decreases the pressure in this part of the apparatus. The gas or vapor diffuses from the rest of the apparatus to it, until all has been condensed. The entire transfer takes only a few seconds. It works because the kinetic energy of the molecules moves them all eventually into the cooled zone, which removes this kinetic energy, preventing them from moving away again.

Clearly one of the most important jobs, in using these techniques successfully, is to produce the vacuum inside the apparatus first. Here again, diffusion of gases is vitally important. A pump can only be connected to the glass system at one point—it cannot have contact with the system as a whole. It certainly cannot reach into the apparatus and scoop out the molecules until the apparatus is empty. Yet it can function very effectively to remove them. All the pump does is to take molecules which of their own kinetic energy happen to diffuse into it, and sweep them out in such a way that they cannot get back inside. But as the pump does this, more molecules continually diffuse from the apparatus into the pump, until finally most of the gas from the apparatus has been given one-way passage into the outer atmosphere. From the necessity of first removing gases from inside the apparatus, the techniques are called "high vacuum techniques." They constitute one of the most useful practical applications of gaseous diffusion in the scientific laboratory.

PRESSURE

Let us now consider a gas contained inside an enclosed space. Its molecules have spread throughout the space and are still in constant rapid motion in a variety of directions, frequently colliding with one another. The fact that they remain within the enclosed space means that they must also collide with the atoms of the substance that composes the container. All these collisions must be perfectly elastic. That is, on the average there can be no loss or gain of energy through these collisions. As long as the container walls are maintained at the same temperature as that of the gas, the collisions must be elastic. If energy were gained, the gas would spontaneously heat up. If energy were lost the gas would cool, and eventually the molecules would "run down" and move so slowly that they would become stuck to one another in a condensed liquid or solid phase. We know that heat flows spontaneously from a body of higher temperature to one of lower temperature in contact with

it, but within the gas itself, unless some profound change can occur within the molecules, no mechanism exists by which energy can be given out or absorbed without outside help. Individually, molecules of gas can indeed be slowed in some of their collisions, speeded up in others. The temperature of the gas only indicates, as in the case of liquids and solids, the *average* kinetic energy of the molecules.

We know that the motion of the gas molecules would lead to the spreading out, or diffusion, of the gas indefinitely, were it not for the confining walls of the container. Each molecule of gas is so small in mass that, even though its speed may be great, it can hardly exert a very significant push on the wall when it hits. Nevertheless, here we are not dealing with one individual molecule, but with billions and trillions of molecules. Thus, instead of the intermittent force that would be exerted by a single molecule bouncing back and forth from wall to wall, a steady pressure on the wall results from a constant succession of billions of impacts. And instead of a tiny insignificant force of one collision, the wall feels the net force of trillions of collisions. This force, the total effect of the bombardment by enormous numbers of molecules, is called the "pressure." It is the pressure of the gas; it is the pressure exerted by the gas; it is the pressure exerted by the wall to restrain the gas.

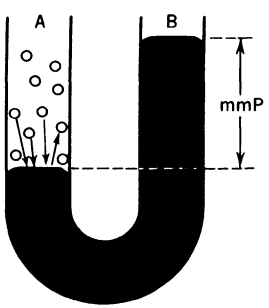
The Measurement of Pressure

Torricelli, an Italian physicist, discovered that when a long tube closed at one end was filled with mercury and then inverted with the open end beneath the surface of mercury in a dish, the mercury always ran out of the tube down to a certain level and then stopped. The space vacated by the mercury at the closed end of the tube must have been a vacuum since there was no opportunity for anything to replace the mercury originally present there. The mercury column thus invisibly supported in the tube extended about 76 cm above the surface of mercury in the open dish. Evidently the pressure of the atmosphere on the mercury surface was the force holding up the mercury column in the tube. The atmospheric pressure did not restrain the mercury from running partly down from the closed end because it was not strong enough. One could then take the height of the mercury column supported by the atmosphere as a measure of the atmospheric pressure. From the density of mercury, about 13.5 times that of water, one can calculate that a column 76 cm high represents an atmospheric pressure of about 15 pounds per square inch. This is the pressure at sea level on a

fair day. In the mountains, or during stormy weather, the pressure is appreciably less, as shown by the reduction in the height of the mercury column that the atmosphere can support. This simple device thus has become useful as a barometer, to be used in predicting and describing the weather. It can similarly be used for the measurement of any pressure of a confined gas, and is called a "**manometer.**" In recognition of small variations in the fair weather pressure at sea level, a standard of 760 mm has been adopted, which is defined as "one atmosphere" of pressure. The 760 mm is called "standard pressure"; implied but unsaid is that this is the height of the column of mercury supported by the gas under measurement. Actually, then, "760 mm of mercury" would be more complete, but it is customary in scientific measurement to omit the "of mercury," leaving it clearly understood.

When pressures in excess of one atmosphere are evaluated, the unit used to express them is usually "atmospheres": e.g., 10 atmospheres (about 150 pounds per square inch). Pressures near to or less than 1 atmosphere are almost always measured in mm (of mercury). If mercury is in a U-tube, closed at one end and open at the other, and if the space above the mercury in the closed end is a vacuum, the pressure exerted by gas at the open end is shown by the difference in heights of mercury in the two arms of the U-tube—in other words, by the height of the mercury supported by the gas. If the space above the mercury is open to the outside atmosphere at one end and to some other gas at the other, then the difference in heights of the mercury will show the pressure difference between the atmosphere and the other gas. Various devices based on the similar principles are used in experimental studies of gases. All are "manometers."

In *A*: molecules striking mercury surface push on it and exert pressure.

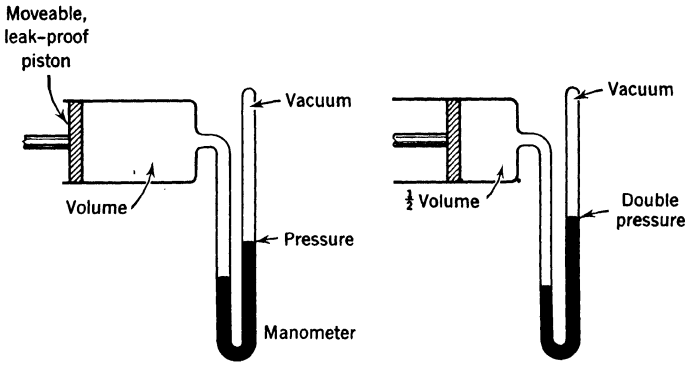


In *B*: vacuum, practically no molecules striking mercury surface. No push by gas molecules, no pressure.

Pressure exerted by gas molecules in A must be balanced by pressure of extra mercury in B.

Hence pressure is measured in terms of the height of the mercury column, in millimeters, supported by the gas.

Figure 35. Measurement of pressure.



I. Volume $= V$
Pressure $= P$

II. Volume $= V' = \frac{V}{2}$
Pressure $= P' = 2P$

Boyle's Law: $P \times V = \text{Constant} = P' \times V'$

$$PV = \frac{2PV}{2} = PV$$

Figure 36. Boyle's law.

BOYLE'S LAW

If a container encloses a sample of gas which exerts a certain pressure on its walls within a certain volume, and if the volume of the container is varied, perhaps by sliding a piston, keeping temperature constant, the pressure of the gas is found to change. The same sample of gas is involved—no molecules are added or taken away. But if the volume occupied by the gas is reduced to half, each unit volume of the space must now contain on the average twice as many molecules of gas as it did before. Therefore, the number of collisions per unit area of the wall must be twice as great. Since the pressure exerted by the gas is the result of these molecular collisions, it is obvious that increasing the frequency of the collisions must increase the pressure in direct proportion. The volume was cut in half and the pressure doubled. Now, if the volume of the original sample is increased instead, for example, to twice the original value, with only the same number of molecules, only half as many molecules can occupy each unit of volume. This means that the frequency of collisions with a given area unit of the wall must drop to half, which results in decrease of the pressure to half its original value. The volume was doubled and the pressure decreased to half.

The behavior of gas samples when volume is changed at constant temperature was studied by Robert Boyle, one of the earliest of the scientific chemists. He discovered that no matter what the gas, its volume and pressure were interrelated by the following simple expression:

$$PV = k$$

The constant k is determined by the quantity of gas. If a sample of gas occupying volume V_1, wherein it exerts a pressure of P_1, is changed to a volume V_2, therein it will exert a new pressure P_2. According to Boyle's law,

$$P_1V_1 = k = P_2V_2$$

Therefore, if any three of these values are known, the fourth can easily be calculated.

EXAMPLES. 1. A sample of nitrogen occupying 10 liters at atmospheric pressure is forced into a volume of 1 ml. What pressure does it exert?

Let P and V be the initial pressure and volume and P' and V' the final pressure and volume. Then, $P = 1$ atm, $V = 10$ liters, $V' = 10^{-3}$ liter, and P' must be determined.

$$PV = P'V'$$
$$1 \times 10 = P' \times 10^{-3}$$
$$P' = \frac{1 \times 10}{10^{-3}} = 1 \times 10 \times 10^3 = 10^4, \text{ or } 10{,}000 \text{ atm} \quad \text{ANS.}$$

2. In a bulb having a volume of 150 ml, the pressure of a sample of chlorine gas is found to be 100 mm. What volume would this gas occupy at 1 atmosphere pressure?

One atmosphere is 760 mm. V is 150 ml, P is 100 mm, P' is 760 mm, and V' remains to be determined.

$$PV = P'V'$$
$$100 \times 150 = 760V'$$
$$V' = \frac{100 \times 150}{760} = \frac{15{,}000}{760} = 19.7 \text{ ml} \quad \text{ANS.}$$

3. The Boyle's law constant for a given sample of hydrogen is 3600, when pressure is in mm and volume in ml. Prepare data for a graph of P vs V for this sample.

Here, $PV = 3600$. By assigning arbitrarily the values of either P or

V, we can calculate the others. For example, when $P = 1$, $V = 3600$. When $P = 2$, $V = 3600/2 = 1800$. When $P = 3$, $V = 3600/3 = 1200$. Thus a table of data to be plotted graphically can be assembled:

P	V
1	3600
2	1800
3	1200

CHARLES' LAW

Boyle's law holds only when the temperature is kept constant. The French scientist Charles, and later Gay-Lussac, investigated the behavior of gases when temperature is changed. They found that when a sample of gas is cooled, with the pressure kept constant, its volume contracts by 1/273 of its volume at 0°C for every degree decrease in temperature. If this could be continued far enough, the gas would disappear at 273° below 0°C. In practice, as we have already seen, intermolecular attractions become effective before this point is reached, and the gas condenses to liquid and solid. But this temperature of −273°C is the "absolute zero" which was described earlier as the point where all kinetic energy had been removed. On this temperature is based a temperature scale in which the individual degrees are of exactly the same magnitude as degrees of the Centigrade scale, only the entire scale is set 273 degrees lower. It is called the "**absolute**" or the "**Kelvin**" temperature scale, abbreviated either "A" or "K," and the relationship to the Centigrade scale is simply this:

$$°K = °C + 273$$

Charles discovered that, at constant pressure, the expansion of gases when heated is directly proportional to their *absolute* temperature. When the absolute temperature is T, Charles' law can be expressed:

$$\frac{V}{T} = k$$

Thus if a given sample of gas of volume V_1 is at temperature T_1, and the temperature is raised to T_2, the sample must expand, if pressure is kept constant, to V_2, such that:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

A knowledge of any three of these values, of course, makes it easy to calculate the fourth.

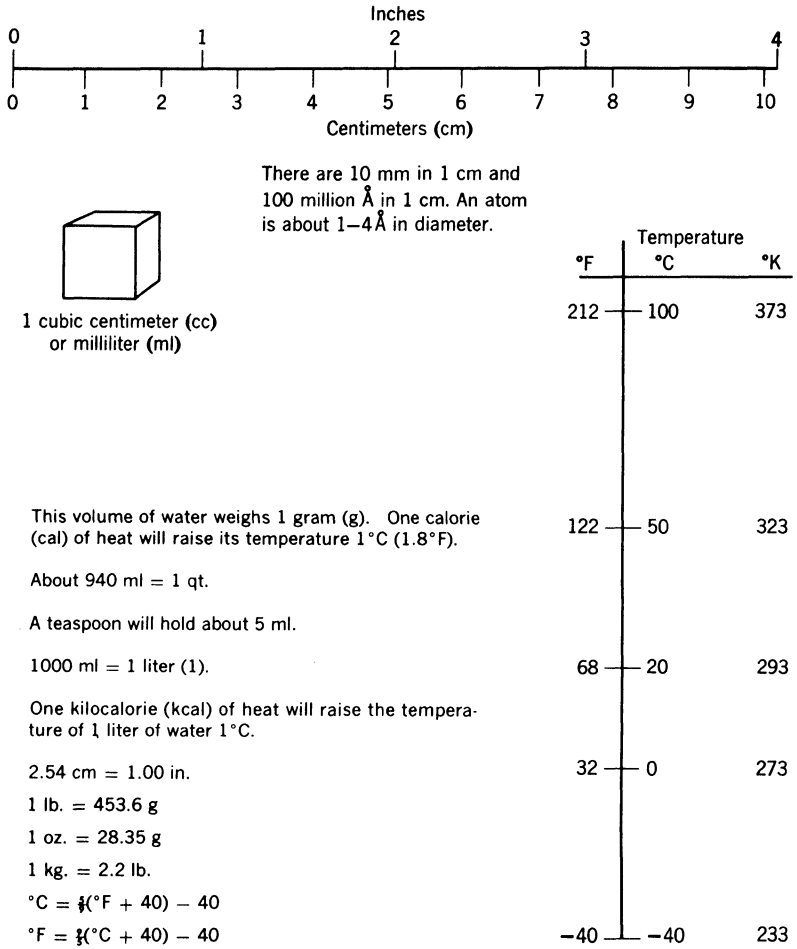


Figure 37. Some units of measurement.

EXAMPLE. Nitrogen, 5 liters at 25°C, is heated at constant pressure to 50°C. What is its final volume?

First: ALWAYS convert centigrade to Kelvin temperature if necessary.

$25°C = 25 + 273 = 298°K$
$50°C = 50 + 273 = 323°K$

Then: $5/298 = V/323$ or $323(5/298) = V = 5.3$ liters ANS.

The explanation of Charles' law lies in the fact that as the kinetic energy of the molecules of a gas is increased, they strike the walls of the container with greater force, *and* they strike the walls more frequently because they are moving faster. Both these effects would increase the pressure if the volume were kept constant. However, if the pressure is kept constant the volume must be increased, so that although the molecules individually are striking more often and harder there are fewer of them striking per unit time per unit of wall area.

THE EFFECT OF TEMPERATURE ON GAS PRESSURE

More common than volume changes at constant pressure are pressure changes at constant volume. For example, if one heats a sample of gas within an enclosed container, assuming that the expansion of the container is negligible, the volume will remain essentially unchanged. Still confined to the same space, the molecules will strike harder and more frequently, resulting in an increase in pressure. The same effect is noticed in an auto tire, which keeps the air within it at nearly constant volume, but through flexing of the rubber, and perhaps with the help of the sun's heat on the pavement, becomes much warmer when a car is driven at high speed for some time. This builds up the pressure within the tire, enhancing the possibility of blowouts. The wise motorist will have this pressure periodically checked and adjusted.

From Boyle's law and Charles' law, it is not surprising that when volume is kept constant pressure is found to be directly proportional also to absolute temperature:

$$\frac{P}{T} = k$$

THE COMBINED GAS LAWS

Since both P and V are directly proportional to T, and PV is constant for any fixed value of T, the above three gas law expressions may easily be brought together in the following form:

$$\frac{PV}{T} = k$$

Obviously, if T is kept constant it becomes part of k, and Boyle's law results. If P is kept constant, Charles' law results. If V is kept constant, the third law above (sometimes ascribed to Gay-Lussac but not so

called because of another law of Gay-Lussac to be discussed presently) results. Using a given sample of gas, one can convert its volume at one pressure and one temperature to the volume it would occupy at any other pressure and any other temperature:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Rather than memorize and use this equation as such, it will be much more instructive to you to form the habit of reasoning out conversions of this type. By a simple rearrangement of the above equation, the new volume, V_2, of a sample of gas will be the old volume, V_1, multiplied by a pressure factor and by a temperature factor:

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

It is not necessary to memorize in this expression which is P_1 and which P_2, or which T_1 and which T_2. One merely, as before, first converts °C to °K, and then looks at the initial and the final pressure. What if the final pressure is higher? This means that the effect of the pressure change must be to reduce the volume, because increased pressure pushes the molecules closer together. What if the final pressure is lower? Then obviously the molecules must be farther apart, which means the volume must be greater. You have two pressures to work with. If you decide that the effect of pressure is to *reduce* the volume, then the pressure factor must be less than unity, and you place the larger pressure as the denominator and the smaller pressure as the numerator of the pressure factor. If you decide that the effect of pressure change is to *increase* the volume, then the pressure factor must be greater than unity, and you simply make the larger pressure the numerator in the pressure factor.

Similarly, you consider the effect of temperature. Is the final temperature higher or lower than the initial temperature? If it is higher, the gas is warmer and must expand. Therefore the temperature factor must be greater than one, and you make the larger temperature the numerator. If the final temperature is lower, the gas must contract, and the temperature factor must be smaller than one. The higher temperature then becomes the denominator of the factor, and the lower temperature its numerator.

By thus considering, as independent effects, first the pressure effect and then the temperature effect, you can confidently complete the necessary calculations, knowing that they are reasoned calculations and not meaningless memorizations.

STANDARD CONDITIONS

One atmosphere, or 760 mm (of mercury), has already been given as a standard pressure for the measurement of gases. A standard temperature is also useful, for only when two gas volumes are compared at the same temperature *and* pressure is the comparison meaningful. For a standard of temperature, the melting point of ice, or 0°C, has been established. Unless otherwise specified, a given volume of gas is understood to be the volume which that quantity of gas would occupy under **standard conditions** of pressure and temperature. Standard conditions are sometimes abbreviated as **SC**, or they are sometimes referred to as **"normal temperature and pressure, NTP"**; the former seems preferable.

EXAMPLE. A sample of argon, labeled A, is found to occupy 200 ml at 10°C and 300 mm. A second sample, B, of argon occupies 250 ml at 100°C and 200 mm. Which sample is larger?

In order to compare different samples of gas by volume, we must be sure that these volumes correspond to identical pressure and temperature. The above data must therefore be converted to comparable conditions. For example, we might convert the volumes to standard conditions (0°C, 760 mm).

Sample A:

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

$$V = V'\left(\frac{P'}{P}\right)\left(\frac{T}{T'}\right) = 200\left(\frac{P'}{P}\right)\left(\frac{T}{T'}\right)$$

The pressures are 300 and 760. Since 300 is the initial value, and 760 the final, the pressure is being increased. According to Boyle's law, this must correspond to a decrease in volume. Thus the pressure factor must be less than one, or 300/760 rather than 760/300.

The initial temperature is 10° and the final is 0°. This means cooling, with the consequent reduction of volume predictable by Charles' law. Hence the temperature factor must also be less than one, since cooling brings contraction of the gas. But we must always remember to use the Kelvin scale: 10 + 273 = 283°; 0 + 273 = 273°.

$$V = 200\left(\frac{300}{760}\right)\left(\frac{273}{283}\right) = 76.2 \text{ ml at SC}$$

Sample B: Here we find the pressure being increased and the temperature decreased. Thus the pressure factor must be less than one, since

higher pressure means lower volume. The temperature factor must be less than one, because cooling the gas causes contraction of the volume.

$$273 + 100 = 373°$$

$$V = 250 \left(\frac{200}{760}\right) \left(\frac{273}{373}\right) = 48.2 \text{ ml at SC}$$

Only by making such calculations can we be sure which sample (A) is actually larger. We could, however, have compared the two samples under any other set of conditions we wished. For example, it would have saved work, in this particular problem, to convert one sample to conditions like those of the other. We could calculate directly what volume B would occupy at 10°C and 300 mm:

$$V = 250 \left(\frac{200}{300}\right) \left(\frac{283}{373}\right) = 126.5 \text{ ml}$$

The volume of A under these same conditions was 200 ml.

REAL GASES

Gas Law Deviations

The laws of Boyle and Charles and their combination hold strictly only for the "**ideal**" or "perfect" gas. This is a hypothetical gas whose molecules are "point masses" having no volume and no interattraction. Under all conditions, collisions among molecules are perfectly elastic. All **real** gases, of course, consist of molecules that do individually occupy space and do attract one another at close range. The ideal gas laws therefore are applicable with reasonable accuracy to real gases only within a range of temperatures and pressures where the factors of molecular volume and attraction are relatively ineffective. This means temperatures well above the condensation point, giving the molecules ample kinetic energy to overcome the "drag" of interattraction. It means also pressures well below those which bring the molecules to within relatively few molecular diameters of one another, where their size and interattractions gain significance. For, under high pressure, the space actually occupied by the molecules becomes a significant part of the total volume, which is therefore larger than otherwise would be calculated. At close intermolecular distances, the interattractive forces pull the molecules closer than would otherwise be calculated, making the volume less and the pressure seem greater. Deviations from the ideal gas laws are therefore commonly observed, especially at high pressures and low temperatures. However, the laws are reasonably exact for

real gases at pressures up to a few atmospheres and at temperatures well above the boiling point.

Critical Temperature and Pressure

Often when the molecules of a gas are forced together by an external pressure until they are quite close, intermolecular attractions are thus made effective enough for the gas to change to liquid. For each gas, however, there is a certain temperature above which no amount of pressure can liquefy it. The gas simply becomes increasingly denser until it is visible, but at no time does the phase separation occur that characterizes condensation to the liquid state. This temperature is called the "**critical temperature,**" and the pressure required for liquefaction at that temperature is the "**critical pressure.**"

Some gaseous elements and their critical temperatures are listed in Table 2. From this information one could predict, for example, that chlorine could be liquefied and confined in a strong cylinder at ordinary temperatures, but hydrogen, oxygen, and nitrogen could not. These must be cooled below their critical temperatures before any amount of pressure can liquefy them.

Table 2 Critical Temperatures and Pressures of Gaseous Elements

	T_c °C	P_c(atm)
He	−267.9	2.26
H_2	−239.9	12.8
N_2	−147.1	33.5
O_2	−118.8	49.7
Cl_2	144	76.1

At critical temperature, or higher, not just a fraction of the total molecules but essentially all of them have enough kinetic energy to overcome the intermolecular attractions.

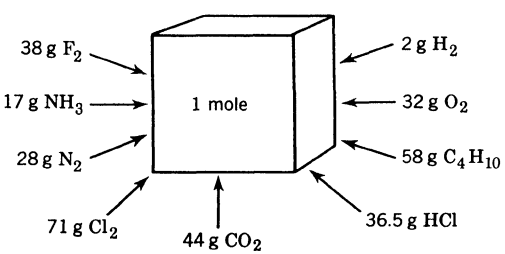
AVOGADRO'S LAW

An Italian physicist, named Avogadro, studied many data accumulated from experiments with gases, especially those dealing with chemical reactions of gases and described by Gay-Lussac's law (see page 130). He concluded that the properties of gases were consistent with the hypothesis that under equal conditions of temperature and pressure, equal volumes of all gases must contain equal numbers of molecules. This

hypothesis became eventually so well accepted and well established by experiment that it is now classed as a law. It is a very important law, for it permits one to calculate the weight of a sample of known gas from its volume, temperature, and pressure.

Let us come back to the concept of a mole. If the molecular weight of hydrogen, H_2, is 2, and the molecular weight of oxygen, O_2, is 32, then the ratio of the weight of one oxygen molecule to the weight of one hydrogen molecule is $32/2 = 16$. It follows that the ratio of the weight of twenty oxygen molecules to the weight of twenty hydrogen molecules would likewise be 16, as would be the ratio of the weight of one thousand oxygen molecules to one thousand hydrogen molecules, or one billion to one billion. From this, since one mole of oxygen weighs 32 grams, by definition of a mole, and one mole of hydrogen weighs 2 grams, the ratio is the same as for the single molecules, and therefore one mole of oxygen must contain the same number of molecules as one mole of hydrogen. This is true for a mole of any substance.

The number of molecules in a mole is called "**Avogadro's number.**" This number has been determined by a variety of experimental methods to be about 6.02×10^{23}. If equal volumes of different gases contain the same number of molecules, and equal numbers of molecules are contained in one mole each of different gases, it follows that a mole of any gas should occupy the same volume under standard conditions. This volume, occupied by a mole of any gas at 0°C and 760 mm, is approximately 22.4 liters. It is called the "gram-molecular volume," and should be committed to memory without fail. It is extremely useful, for if one knows the identity and therefore the molecular weight of a gas he can know what volume will be occupied by a given weight of the gas under given conditions. If he knows the volume of a sample of gas under given conditions, he can easily calculate its molecular weight from the weight



At the same temperature and pressure, equal volumes of different gases contain the same number of molecules.

At ordinary temperature and pressure, 1 mole of any gas occupies approximately 1 cu ft of space (22.4 liters at 0°C, 760 mm).

Figure 38. Avogadro's law and standard conditions.

of this sample. Small samples of gas are much easier to measure by volume than by weight, and if the identity is known the weight can easily be calculated from the volume measurement. On the other hand, if both weight and volume are known the molecular weight can easily be calculated. This method is an invaluable aid in the identification of unknown molecular species.

EXAMPLES. 1. To determine the molecular weight of bromine, a sample of its vapor was weighed and its volume measured. The volume was 200 ml at 27°C and 35 mm. The sample weighed 0.0597 g.

First, it was necessary to convert the volume to standard conditions:

$$V = 200\left(\frac{35}{760}\right)\left(\frac{273}{27 + 273}\right) = 8.38 \text{ ml}$$

Then, knowing that one mole of bromine, as of any other gas or vapor, must occupy 22.4 liters at standard conditions, one determines what fraction of a mole this sample of 7.94 ml is:

$$\frac{8.38}{22{,}412} = 0.000374 \text{ mole}$$

The molecular weight is then:

$$\frac{0.0597 \text{ g}}{0.000374 \text{ mole}} = 160$$

Knowing the atomic weight of bromine to be 80, we can easily determine the association to be dimeric, and thus the formula of the vapor, Br_2.

ANS.

2. A scientist had a sample of neon in a tube where he could observe its volume, pressure, and temperature, but his need was to know its weight. It would have been very difficult to weigh this sample accurately, but, knowing it to be pure neon, he could calculate the weight more accurately than he could have measured it directly. How? He found the volume to be 15.0 ml at 284 mm and 25°C. First, he converted this to standard conditions:

$$V = 15\left(\frac{284}{760}\right)\left(\frac{273}{298}\right) = 5.18 \text{ ml}$$

He knew this to be 5.18/22,412 mole, and one mole to weigh 20.18 g (since 20.18 is the atomic weight of neon). Therefore the weight of his sample was:

$$\frac{5.18 \times 20.18}{22{,}412} = 0.0047 \text{ g neon}$$

ANS.

3. Iodine is a solid but easily vaporized. We wish to know what pressure would be exerted by 10 g of I_2 vapor at a temperature of 400°C, inside a one-liter flask.

The atomic weight of iodine is 127, making the molecular weight 254. One mole of vapor at SC would weigh 254 g and occupy 22.4 liters. Ten grams at SC would occupy 10/254 x 22.4 liters = 0.88 liter. Our problem is now simply to convert this volume to the new conditions of 1 liter and 400°C(= 673°K).

$$\frac{PV}{T} = \frac{P'V'}{T'}; \quad P = P'\left(\frac{V'}{V}\right)\left(\frac{T}{T'}\right)$$

$$P = 760\left(\frac{V'}{V}\right)\left(\frac{T}{T'}\right)$$

Here the volume factor must be less than one, since increase in volume leads to decrease in pressure. But higher temperature means higher pressure.

$$P = 760\left(\frac{0.88}{1}\right)\left(\frac{673}{273}\right) = 1649 \text{ mm} \qquad \text{ANS.}$$

SPECIAL HELP

Test Your Memory

1. What is meant by "diffusion"?
2. State Graham's law.
3. What is the high-vacuum technique for manipulating volatile materials?
4. What is the cause of gas pressure?
5. State Boyle's law in words.
6. Why does Boyle's law describe the behavior of gases?
7. State and explain Charles' law.
8. What is the absolute temperature scale?
9. How does temperature affect pressure, and why?
10. State standard conditions. What is their use?
11. What is the ideal gas law?
12. What is Avogadro's number? What does it represent?
13. What is the standard volume of a mole of gas?
14. How is vapor density used to determine molecular weight?

Test Your Math

1. Assuming no reaction with the rubber, in what order of preference would you use the following gases to keep a leaky tire inflated until you could drive to a service station? H_2, Cl_2, F_2, Ar, N_2, O_2, Xe.
2. A skunk expresses his annoyance at a hunter in the form of a substance having a molecular weight of 89. The hunter, a chemist, releases an equimolar quantity of chlorine at exactly the same time. They are 100 feet apart and there is no wind. Assuming that the skunk dislikes the chlorine as much as the hunter dislikes the skunk odor, who will retreat first? Why?
3. Assuming constant temperature, what pressure would result from liberation of 20 liters of gas (at 1 atm) into a volume of 5 ml?
4. What volume would be occupied by 10 ml of oxygen (at SC) held at a pressure of 10^{-3} mm?
5. What volume would be occupied by a liter of helium at SC if, at constant pressure, the temperature were increased to 5000°C?
6. Assuming no stretching of a tire, if it is filled to 28 lbs per sq in at 20°C, what pressure will it contain when warmed to 50°C?
7. What is the weight of oxygen that you would take up each day if you breathed 12 times per minute, three liters each breath, and absorbed 5 per cent of the oxygen (which totals 20 per cent of the air)? The temperature is 20°, and the atmospheric pressure is 760 mm.
8. How many times per minute would you have to breathe to take in the same quantity of oxygen at 10°?
9. What is the weight of krypton contained in a cylindrical tube 10 cm long and 1 sq cm cross section in which it exerts a pressure of 0.1 mm at 20°?
10. What is the maximum weight of chlorine gas you could carry in a one-liter container at 25° that can safely hold a maximum pressure of 5 atm?
11. Which would have the greater buoyant force, hydrogen at 0° and 500 mm or helium at 50° and 760 mm?

Test Your Understanding

1. In a mixture of gases, what would you expect to be the effect of each individual gas on the total pressure?
2. Why do not nitrogen molecules in air get in the way of oxygen molecules, and vice versa, preventing their striking the container surface so frequently and thus reducing the pressure?

3. Why does not the kinetic activity of gas cause all the atmosphere to spread throughout the high vacuum of outer space?
4. Then why should two gases of different molecular weights diffuse evenly through one another to form a homogeneous mixture? Why does not the heavier gas become concentrated near the bottom of the container?
5. In reading a mercury manometer, why is it unnecessary to correct for the vapor tension of mercury in the "Torricellian vacuum"?
6. If the thermal expansion of mercury is enough to give it usefulness in thermometers, what precautions should be taken in determining pressures by mercury manometers?
7. Gay-Lussac made an important observation about gas reactions, which became known as Gay-Lussac's law: Gases react chemically in a volume ratio of small whole numbers. For example, three volumes of hydrogen combine with one volume of nitrogen, forming two volumes of ammonia. Avogadro explained this phenomenon. How would you do this, using Avogadro's law?
8. How would you justify the statement that the density of a gas, at specified conditions, is directly proportional to its molecular weight?

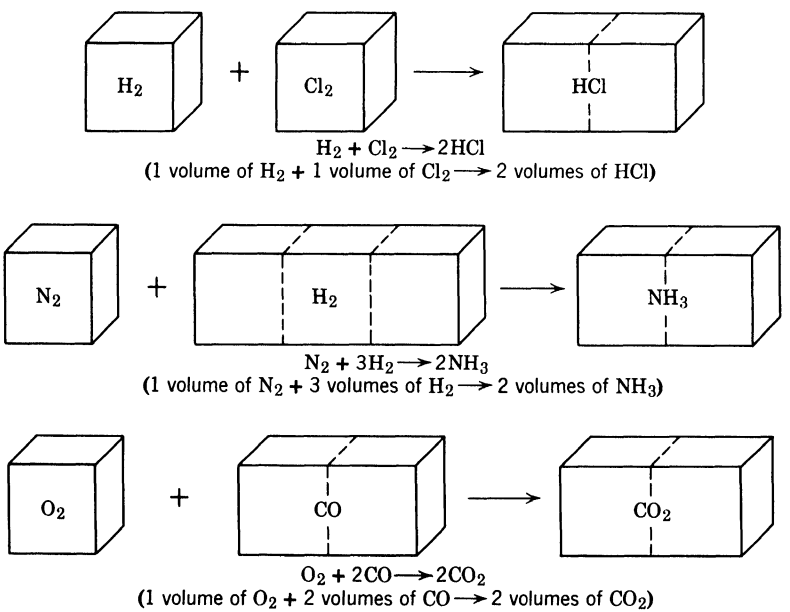


Figure 39. Gay-Lussac's law of combining volumes.

7

Introduction to the Periodic Table

PLEASE CONSIDER carefully now the way in which the structure of the atoms changes with increasing atomic number. Pay special attention to the exterior shells. Therein lie differences among the elements that are highly significant, for these shells largely determine the influence the atom can exert on its environment, and vice versa.

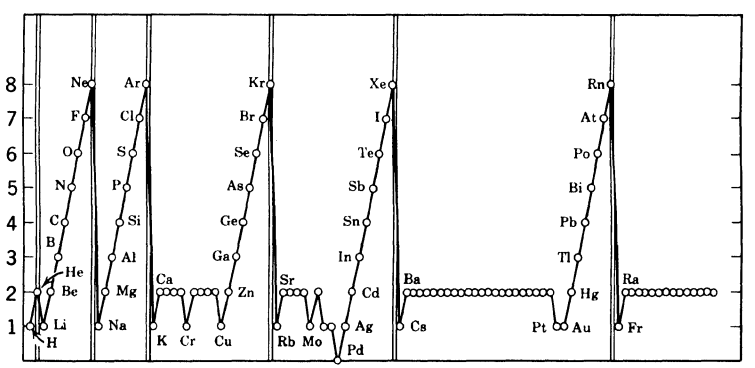
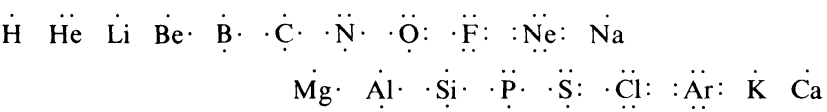


Figure 40. Variation in number of outer electrons per atom, with atomic number.

Notice (Figure 9, p. 54) that in hydrogen, atomic number 1, the first shell begins to fill, and is already full at helium, atomic number 2. Then the third electron, in lithium, must begin a new shell. Successive electrons add to this shell as the atomic number increases, until with neon, the shell is filled to capacity at 8. The eleventh electron must therefore begin the third shell, in sodium, Na. The next element, magnesium (Mg) has 2 electrons in this shell, the next, aluminum (Al) 3, and so on, until this shell also reaches 8, with argon. The nineteenth electron, in potassium, K, begins a fourth shell, and a second electron enters this shell in the next element, calcium, Ca, atomic number 20.

Let us represent these atoms by their symbols, with dots surrounding them to show only the outermost electrons. Study them, as aligned in order of increasing atomic number:



If only the numbers of outermost electrons are listed, the following sequence is obtained:

1–2–1–2–3–4–5–6–7–8–1–2–3–4–5–6–7–8–1–2–

Such a series may be described as "periodic," because of its cyclic or recurrent nature. The number of outermost electrons, at least for the first 20 elements, is thus a "**periodic function** of," or "varies periodically with," the atomic number. A period here may be defined as beginning with an element having 1 outermost electron per atom and continuing up to, but not including, the next element having 1 outermost electron per atom.

Suppose we place these periods next to one another so that their corresponding parts are adjacent. Almost at once the question arises concerning helium: Should it be placed next to other elements that also have 2 outermost electrons or next to other elements that end the periods? As will become apparent later, a great difference exists between 2 electrons that fill a principal quantum shell and 2 electrons that only begin to fill the shell. In fact we have already observed that helium remains monatomic whereas beryllium, also with 2 outermost electrons, packs its atoms together in a tight metallic lattice. Furthermore, a close similarity exists between an element with a filled outermost shell of 2 (helium) and an element with an outermost shell of 8 (all the other inert, monatomic gases).

By our definition of a period, the first period begins with hydrogen and ends with helium. Here are only two elements, and the next period has 8. How shall they be compared? Even when we place helium above

neon in the second period, the question persists, what shall be done with hydrogen? By our definition hydrogen begins the period, and ought to be placed over lithium, which begins the second period. On the other hand, hydrogen also comes next to ending the period, and ought to be placed over fluorine, which in the second period comes next to the end of the period. The past has been filled with arguments as to whether hydrogen should be grouped with lithium or fluorine, but one logical point has been overlooked. By virtue of being almost the only element of its period, hydrogen both begins and ends it, and therefore even more logically can be regarded as occupying the middle position. Hydrogen can therefore be placed near carbon in the second period. Although the number of outermost electrons is not the same in hydrogen as in carbon, in fact they resemble one another in several ways. The placement of hydrogen at the center of the period actually seems more useful than any other placement that has been suggested. We cannot ignore the fact, however, that electronically hydrogen stands alone.

When the several periods are placed in juxtaposition as suggested above, the following arrangement results:

I	II	III	IV	V	VI	VII	0
			(1 H)				2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca						

Here is the beginning of what is called the **"Periodic Table."** It is an arbitrary arrangement of the chemical elements designed to display the periodic changes, and also to group together elements of similar electronic structure. Thus, in the above tabulation, Li, Na, and K atoms all have a single outermost electron, Be, Mg, and Ca 2 electrons, B and Al 3 electrons, C and Si 4 electrons, N and P 5, O and S 6, F and Cl 7, and Ne and Ar 8. The above table may be repeated, giving the electronic configurations by principal quantum levels instead of just the atomic number:

I	II	III	IV	V	VI	VII	O
			(H)				He
			1				2
Li	Be	B	C	N	O	F	Ne
2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8
Na	Mg	Al	Si	P	S	Cl	Ar
2-8-1	2-8-2	2-8-3	2-8-4	2-8-5	2-8-6	2-8-7	2-8-8
K	Ca						
2-8-8-1	2-8-8-2						

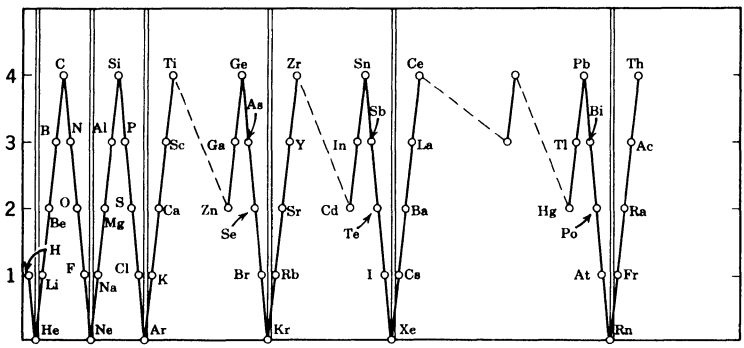


Figure 41. Variation in number of covalent bonds possible per atom (excluding use of outer *d* orbitals), with atomic number.

If only these structural trends and similarities were observable, a periodic table would be relatively useless. However, the physical and chemical properties of the elements are found to depend very significantly on the atomic structure—and more specifically on the outer shell electrons. As we have already seen, the outer-shell electron arrangement determines the number of covalent bonds that an atom can form. Thus, placed in the same vertical group of the periodic table, designated by Roman numerals, are the elements having the same valence. The trend from left to right across a period is a trend of first increasing, then decreasing, valence. Also, as we have already seen, elements in which the outer electron-to-vacancy ratio is small are metallic, and as this ratio increases they tend toward nonmetallic properties. In the periodic table, then, the trend from left to right across a period is from metal to nonmetal. Trends in other, physical properties are shown in Figures 10, 22, 26, 42, and 43.

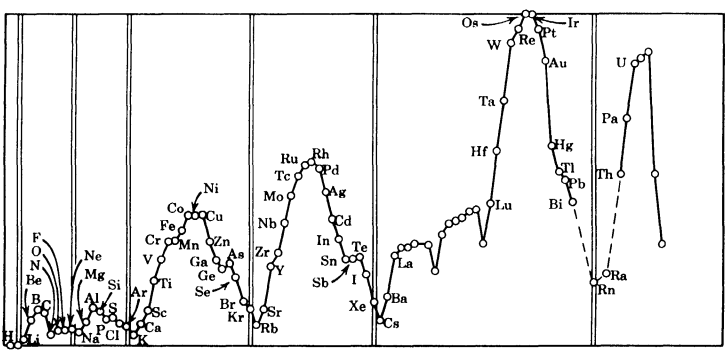


Figure 42. Variation of density with atomic number of element.

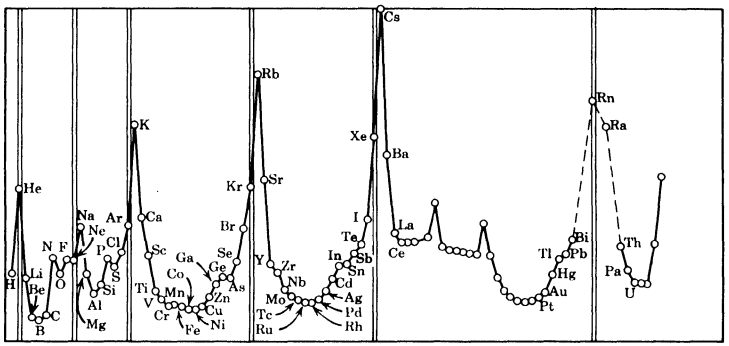


Figure 43. Variation of atomic volume (ml/g-atom) of the elements with atomic number.

The above discussion purposely was limited to the first twenty elements because thereafter complications arise. Beginning with scandium, element number 21, the 3*d* orbitals are filled in, up to zinc, number 30. The electronic difference between calcium, number 20, and zinc, number 30, is shown by their configurations: Ca 2–8–8–2, and Zn 2–8–18–2. In calcium the five 3*d* orbitals are vacant; in zinc they are filled. In between calcium and zinc, the 3*d* orbitals are partly but incompletely filled. Under these conditions, they participate in bonding, giving bonding characteristics different from those imparted by *s* and *p* orbitals. These differences are important enough to justify setting these intermediate elements in a class by themselves, and thus to group them in the periodic table by themselves. Elements in which the *d* orbitals underlying the outermost or valence shell are partly but incompletely filled are called the "**transition elements.**" (Zinc, cadmium, and mercury are commonly included, for want of a better place, but as will be discussed presently, are not typically "transition.") They are all metals, having as a class from fairly high to high density, strong metallic bonding leading to high melting and boiling points, good corrosion resistance, and very desirable and useful mechanical properties.

A similar series of transition elements begins with yttrium, atomic number 39, and extends to cadmium, atomic number 48. These correspond to the successive filling of 4*d* orbitals. A third such series begins with lanthanum, atomic number 57, continuing to mercury, atomic number 80. But this is not ten elements; it is 24. We shall return to this point in a moment. Included within this 24, however, are a series of 10 elements corresponding to the successive filling of 5*d* orbitals. Placement of these three series in vertical order, with atomic number increasing from top to bottom as well as from left to right, forms 10 groups of the periodic table in addition to the 8 shown in the begin-

ning fragment of the periodic table. To distinguish these groups from the first mentioned, they are called "**subgroups,**" whereas the first are called "**major groups.**"

You will observe that in the simplified introduction to the foregoing table, the group of elements whose atoms contain one electron beyond the inert element is called I, with two electrons beyond the inert element, II, with three electrons beyond the inert element, III, and so on across the table. These group numbers thus indicate the number of electrons beyond the inert element. For the transition metal subgroups, the number of electrons beyond the inert element is also indicated by the group number. Here the electrons beyond the inert element structure are not *s* and *p* electrons as before, but *d* and *s* electrons. For example, aluminum, atomic number 13, has 3 electrons beyond the inert element, neon, and these three electrons are *s* and *p*. Scandium, atomic number 21, has 3 electrons beyond the inert element argon, but these three electrons are *d* and *s*. In order to differentiate between these two kinds of element, the major groups are called "A" elements and the subgroups are called "B" elements. Aluminum is in Group IIIA. Scandium is in Group IIIB.

Beyond calcium, strontium, and barium—elements 20, 38, and 56—we may then insert between Group IIA and Group IIIA in the periodic table the following subgroups, for which atomic numbers and electronic configurations are also given so that the relationships may be more easily recognized. As we shall see later on, when the chemistry of these elements is discussed, a shell of 18 electrons underlying the outermost shell is never broken into for bond formation when the number of outer-

IIIB	IVB	VB	VIB	VIIB
21-Sc	22-Ti	23-V	24-Cr	25-Mn
2-8-9-2	2-8-10-2	2-8-11-2	2-8-13-1	2-8-13-2
39-Y	40-Zr	41-Nb	42-Mo	43-Tc
2-8-18-9-2	2-8-18-10-2	2-8-18-11-2	2-8-18-13-1	2-8-18-13-2
57-La	72-Hf	73-Ta	74-W	75-Re
2-8-18-18-9-2	2-8-18-32-10-2	2-8-18-32-11-2	2-8-18-32-12-2	2-8-18-32-13-2

VIIIB-a	VIIIB-b	VIIIB-c	IB	IIB
26-Fe	27-Co	28-Ni	29-Cu	30-Zn
2-8-14-2	2-8-15-2	2-8-16-2	2-8-18-1	2-8-18-2
44-Ru	45-Rh	46-Pd	47-Ag	48-Cd
2-8-18-15-1	2-8-18-16-1	2-8-18-18	2-8-18-18-1	2-8-18-18-2
76-Os	77-Ir	78-Pt	79-Au	80-Hg
2-8-18-32-14-2	2-8-18-32-15-2	2-8-18-32-17-1	2-8-18-32-18-1	2-8-18-32-18-2

most electrons is two or more, but it can be broken into when the ground state configuration indicates only one outermost electron, as in the IB elements. In other words, of the above groups, all fit the specification of using underlying *d* electrons and orbitals in their bonding except the elements of IIB, which never do. Zinc, cadmium, and mercury are therefore *not* typical transition elements and ought not to be so classified, for they use outer *s* and *p* orbitals in bonding just the way the major group elements do. However, there is no appropriate place in the table for them, except to include them at the end of the transition subgroups. The major group IIA, for which they might qualify by virtue of their two outermost electrons and their exclusive use of outermost orbitals in bonding, is already occupied by the elements, calcium, strontium, and barium.

You may well wonder why three transition groups are labelled VIIIB-a, VIIIB-b, and VIIIB-c. Ordinarily, these three vertical groups are included under the single heading, VIII or VIIIB. No logical justification exists, for reasonable consistency would demand that they be designated VIIIB, IXB, and XB. Unfortunately, however, these elements seemed to be superfluous when the first periodic tables were arranged, and so they were all included together as one group. Also, more than ordinary resemblance was noted between iron, cobalt, and nickel, which suggested that they might be located together in the table. Now that we know the fundamental basis for the periodic table, which is the electronic configurations of the elements, we realize that the VIII classification was ignorant, but it is so well established in the chemical literature that a change might prove more confusing than advantageous.

Please refer now to the electronic configurations indicated in the facing table of transition subgroups, and compare lanthanum, 57, to hafnium, 72. Fourteen elements are evidently missing: 58 to 71. What are these? Remember that although the capacity of the fourth principal quantum shell is 32, all earlier elements stop the filling of this shell at 18. The 4*f* orbitals, seven in number and thus having a capacity of 14 electrons, are unoccupied. These are of higher energy than the *s*, *p*, and *d* orbitals of this shell, and thus are not filled until the nuclear charge becomes high enough, which happens beginning with atomic number 58. The fourteen missing elements thus constitute a series in which the 4*f* orbitals are being successively filled. This series is a transition within a transition, since the third transition has already begun with lanthanum, 57. It is called, therefore, an "inner transition" series. The elements are all metals, and generally similar to transition metals. Because they were earlier believed to be much less abundant than some of them actually are, and occurred in oxides called "earths," their oxides have been called

"rare earths," and the elements themselves either the "rare earth elements" or sometimes loosely referred to as simply the "**rare earths.**" Because they begin at lanthanum—actually just beyond lanthanum—they are called also the "lanthanides" or "**lanthanons.**" Because they resemble one another quite closely, they are often regarded as occupying the same space in IIIB with lanthanum.

A fourth transition series appears to begin with atomic number 89, actinium, which follows radium, of IIA. But this series is again interrupted, just as the transition series following lanthanum, by the filling of *f* orbitals, in the second from outermost shell, this time, the 5*f* orbitals. Another inner transition series appears to occur, which includes uranium and the transuranium elements (those having higher atomic number than uranium, 92). This series is called, after actinium, the "**actinide**" series. Even for the "lanthanides," the exact electronic configurations are somewhat controversial because of the closeness in energy level between 4*f* and 5*d* orbitals. In the "actinides," the uncertainty is greater because of even closer 5*f* and 6*d* orbitals. These elements are often considered to occupy the same space in IIIB with actinium itself.

In order to show each individual element, however, it is unsatisfactory to group the inner transition elements into the two spaces of lanthanum and actinium. They should more accurately be represented as a second interruption in the filling of the outermost shell, and inserted between IIIB and IVB in the periodic table. This would make a very awkward spread in the table, however, which is already made awkward enough by the insertion of the transition groups, and usually the inner transition elements are shown in separate series below the main part of the periodic table.

When the atoms have been built up electronically until the underlying *d* orbitals, and later also the *f* orbitals, are filled, resumption of the filling of the outer four orbitals occurs. Thus, beyond zinc the next electron, in gallium, goes in an outermost *p* orbital; similarly for indium beyond cadmium, and thallium beyond mercury. In this respect, these elements resemble those of the major groups. That is, these elements, like the major group elements, use only outermost shell orbitals in valence, and are thus distinct from the transition elements which also use underlying *d* orbitals. This similarity to the major group elements is taken to justify including the elements from gallium, indium, and thallium to the next higher inert elements, krypton, xenon, and radon, in the major groups. The periodic table is therefore extended downward, giving the following major groups:

IA	IIA	IIIA	IVA	VA	VIA	VIIA	O
3-Li 2-1	4-Be 2-2	5-B 2-3	6-C 2-4	7-N 2-5	8-O 2-6	9-F 2-7	10-Ne 2-8
11-Na 2-8-1	12-Mg 2-8-2	13-Al 2-8-3	14-Si 2-8-4	15-P 2-8-5	16-S 2-8-6	17-Cl 2-8-7	18-Ar 2-8-8
19-K 2-8-8-1	20-Ca 2-8-8-2	31-Ga 2-8-18-3	32-Ge 2-8-18-4	33-As 2-8-18-5	34-Se 2-8-18-6	35-Br 2-8-18-7	36-Kr 2-8-18-8
37-Rb 2-8-18-8-1	38-Sr 2-8-18-8-2	49-In 2-8-18-18-3	50-Sn 2-8-18-18-4	51-Sb 2-8-18-18-5	52-Te 2-8-18-18-6	53-I 2-8-18-18-7	54-Xe 2-8-18-18-8
55-Cs 2-8-18-18-8-1	56-Ba 2-8-18-18-8-2	81-Tl 2-8-18-32-18-3	82-Pb 2-8-18-32-18-4	83-Bi 2-8-18-32-18-5	84-Po 2-8-18-32-18-6	85-At 2-8-18-32-18-7	86-Rn 2-8-18-32-18-8
87-Fr 2-8-18-32-18-8-1	88-Ra 2-8-18-32-18-8-2						

It is important to keep in mind, however, that the elements having inert element configurations underlying their outermost shell differ from elements having a shell of 18 electrons underlying the outermost shell. Therefore from IIIA on, until the inert element structures are attained, the elements within each group are not as similar electronically as they are in Groups IA and IIA. The change from underlying structure like that of an inert element to an underlying shell of 18 electrons, occurring within the same group, brings with it significant changes in properties.

The assembly of the three parts of a periodic table discussed above, the major groups, the transition groups, and the inner transition series, into a unified whole is usually accomplished as shown in Figure 44, which represents the most commonly used form of the periodic table. However, by folding the periodic table in appropriate locations, one can demonstrate the complete table and show how the trends from left to right are interrupted by the filling of *d* and *f* orbitals. One of the most important lessons to be derived from such a table is that the separation, in Figure 44, between IIA and IIIA elements, Be and B, and Mg and Al, is purely mechanical and has no fundamental significance whatever. In the trend of properties from left to right across the periodic table, there is no gap corresponding to the physical space gap in the long form of the periodic table.

Hundreds of modifications of the periodic table have been proposed, and the form most commonly used (Figure 44) has no fundamental superiority that makes it unquestionably the best. It is good enough to be reasonably satisfactory, and has the special advantage of being relatively simple. The periodic table itself is not fundamental. What is very fundamental is the **"Periodic Law"** on which it is based. This law is usually stated: *"The properties of the chemical elements vary periodically with atomic number."* We might better state it this way: **"The electronic configurations of the elements vary periodically with atomic number. Properties of the elements that depend on their electronic configurations therefore also vary periodically with atomic number."** Various physical properties of the elements are plotted against their atomic number in Figures 10, 22, 26, 42, and 43; you will observe that the fact of periodicity is amply demonstrated.

The periodicity of the chemical elements was first observed about a century ago by the French geologist, de Chancourtois, and the English chemist, John Newlands. A few years later it was established on a more thorough and convincing basis by Lothar Meyer in Germany and Dmitri Mendeleev in Russia, independently, who set up periodic tables much like those in use today. When we realize that these men knew nothing of atomic structure, basing their ideas solely on the then known

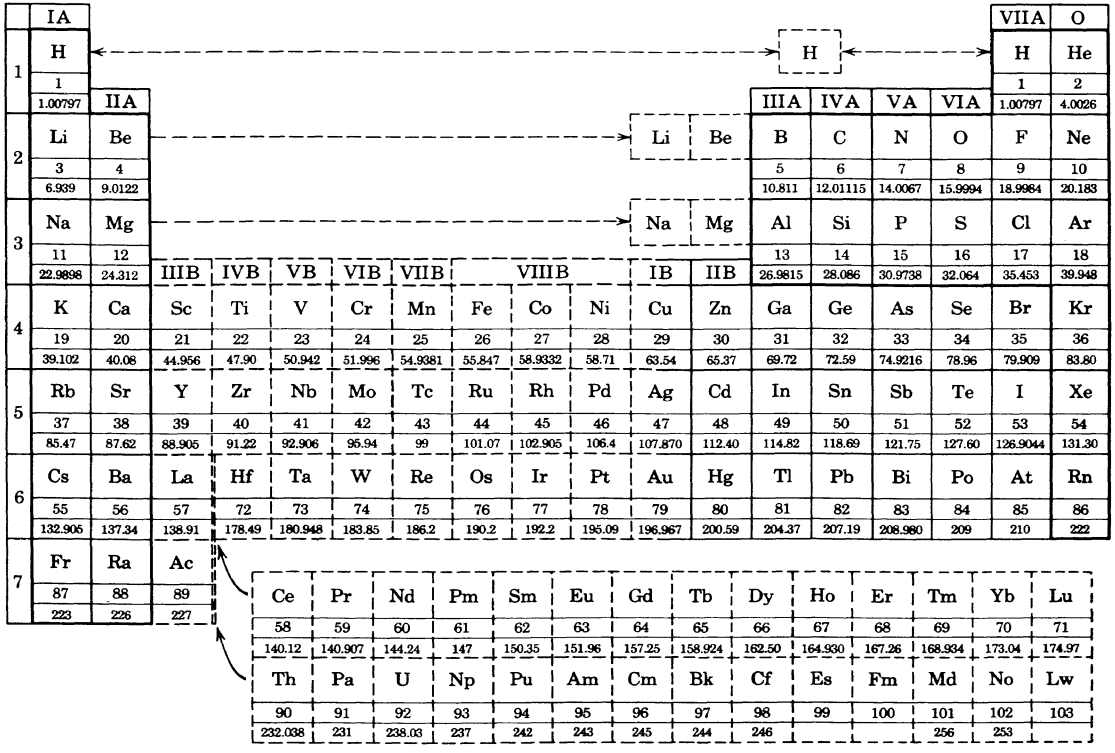


Figure 44. Modified Standard "Long Form" of Periodic Table. Heavy lines designate inert and inert-shell elements, thin lines 18-shell elements, and broken lines the transition elements.

properties of only the fifty-odd elements then recognized, we can better appreciate the quality of their contribution. For although the fundamental basis of the Periodic Law was not developed for half a century, the periodic table became promptly both a guide to and the framework of systematic chemistry. It has remained so ever since. Although we now know enough about the atoms of each individual element to begin to understand its properties independently of its position in the periodic table, the periodic law will remain one of the most useful generalizations in chemistry.

The Nature of the Periodic Table: A Summary

Now that we have a periodic table, what can we do with it? What is it good for? In fact, just exactly what is it?

To answer the last question first, a periodic table is an arbitrary method of organizing the chemical elements in an orderly and systematic manner so that the relationships among the elements can be studied and remembered and understood. In the form discussed herein, elements having greatest electronic similarity, particularly with reference to the bonding characteristics, are grouped vertically together, their atomic numbers increasing from top to bottom. Such elements show general similarities within groups, which permit reasonable predictions of the properties of one from a knowledge of the properties of another. The groups are placed side by side in such a way that horizontally they bring to adjacent positions elements differing in atomic number by one, and with steady increase in atomic number from left to right. A series of elements from left to right begins with an element just beyond an inert element in atomic number, and proceeds to the next higher inert element, which ends the series. Such a series is called a "**period.**"

Four electronic types of atoms may be distinguished. (1) The **inert elements,** except helium, are alike in exterior shell of 8; the helium shell is filled at 2. (2) The "**inert shell**" elements have inert element structures underlying the outermost shell. (3) The "**18-shell**" elements have a penultimate shell (immediately below the outermost) of 18 electrons. (4) The **transition** and **inner transition** elements have a penultimate shell incompletely filled with *d* electrons, and thus ordinarily containing more than 8 but fewer than 18 electrons. Types (2) and (3) are alike in using only the outermost shell for valence, and are classified as major group or Group A elements. Type (4) elements use both the outermost and the penultimate shell in bonding, and are classified as subgroup or Group B elements.

In order to preserve the sequence of increasing atomic number of the

elements, the subgroups are inserted between major groups IIA and IIIA. The result is that the periodic table begins at the top with a short period of two elements, hydrogen and helium, followed by two periods of 8 elements each, from lithium to neon, and from sodium to argon. The periods are numbered from the top, so the fourth period begins with potassium. This and the next period consist of 18 elements each. The sixth period contains both transition and inner transition series, and has thus $8 + 10 + 14 = 32$ elements. The seventh period is incomplete, but presumably resembles the sixth, and should come to an end at atomic number 118, the hypothetical next inert element beyond radon, 86. There is reason to believe that it would be so highly unstable that it may never be made. In summary, the periods contain the following numbers of elements: 2, 8, 8, 18, 18, 32, 17 (incomplete).

What is a periodic table good for? Earlier, it was extremely useful as a guide to the discovery of new elements, although now of course we believe that all possible elements have been discovered, up through atomic number 103. It still serves as an invaluable framework upon which to organize and systematize the myriad facts of chemistry. From the viewpoint of physical properties, we can note a tendency toward increasing metallic nature going down a group, and a tendency toward decreasing metallic nature and increasing nonmetallic nature going from left to right across a period. We can predict with some confidence that elements in the same group will have numerous similarities, and thus if we know the properties of one or two members we can guess reasonably well about the other members. We can predict with somewhat greater confidence that any element in a period will in most respects be intermediate between its left-hand and right-hand neighbors. Thus, if we know something of the neighbors, we can guess with some justification about the properties of any given element. You can learn much about these interrelationships from a study of Figure 44.

The greatest use of the periodic table, however, is in application to chemical properties. This application will be discussed in Chapters 11, 12, 13, 25, and 26.

SPECIAL HELP

Test Your Memory

1. What are the four types of element, on the basis of electronic structure?
2. Which of these are in major groups? Which in subgroups?

3. Across a period, how does electronic configuration of the outer shell change?
4. Across a period, how do the elements change in metallic nature?
5. How does the covalent radius change with the filling in of the outermost shell with electrons?
6. Within a major group of the periodic table, how do the elements differ electronically from one another? How, within a subgroup?
7. How does the covalence change, both down a major group and across a period?
8. State the Periodic Law.
9. What is the fundamental basis of the periodic table?

Test Your Understanding

1. Why are the elements placed in groups based on their outer-shell electronic structure?
2. Why are transition elements grouped separately instead of with major group elements having the same number of outermost shell electrons?
3. Why is it unsatisfactory to group hydrogen with Group IA elements, although it, like them, contains but one outermost electron per atom?
4. Why is it unsatisfactory to group hydrogen with Group VIIA, whose atoms, like hydrogen atoms, have but one outermost vacancy?
5. How do we know that some presently unknown low atomic number element may not yet be discovered?

PART TWO

Chemical Compounds

8

Formulas, Weights, and Equations

THE ASSIGNMENT of symbols to designate the chemical elements has previously been discussed. It has also been pointed out that polyatomic molecules of the elements can be represented as symbols with subscripts to tell the number of atoms per molecule. Symbols representing polyatomic aggregates are called "**formulas**" or "**chemical formulas.**" For example, H_2 is the formula for hydrogen molecule, in contrast to H which represents merely the element, hydrogen, or a single atom of hydrogen. The existence of white phosphorus as molecules containing four atoms each is represented by P_4, the molecular formula.

FORMULAS OF COMPOUNDS

Chemical compounds, containing two or more elements, are represented in a similar way. The symbol for each element is given, followed immediately by a subscript giving the number of atoms of that element

in each unit of the compound. For example, the chemical compound, water, consists of individual molecules each containing two hydrogen atoms and one oxygen atom. A molecule, and therefore the compound, is represented by the chemical formula, H_2O. Each molecule of sugar, a compound called "sucrose," contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. The chemical formula is $C_{12}H_{22}O_{11}$.

As will be detailed presently, however, not all chemical compounds exist as collections of individual molecules. For example, when sodium unites with chlorine, the compound contains one atom of sodium per atom of chlorine, but it is crystalline, with each sodium surrounded at equal distances by six chlorines and each chlorine by six sodiums. No individual molecules can be distinguished in such a crystal; indeed, there is no way of knowing which sodium might originally have reacted with which chlorine. Consequently, the compound is represented simply as NaCl.

A chemical formula thus may have one of two meanings. It may represent the actual composition of a molecule of a compound, or it may only represent the composition of the compound, without regard to whether it exists as separate molecules or not. When it has the first meaning, as when applied to water (H_2O), it is called the "**molecular formula.**" When it has the second meaning, as when applied to sodium chloride (NaCl), it is called an "**empirical formula,**" and is always reduced to its simplest possible form, giving the smallest whole numbers of atoms. Practically all gaseous and liquid compounds, and many also that are solids, are molecular in nature, and are represented by molecular formulas. Many solid compounds, however, are not molecular in nature, and are represented by empirical formulas, or by more informative formulas when appropriate.

Sometimes more than just the molecular or empirical composition of a compound is known. Sometimes also something is known of the way in which the atoms are grouped together. Frequently, in such cases, the formula can be written to include this extra information. For example, a blue crystalline solid known as "copper sulfate" has the empirical formula, $CuH_{10}O_9S$. However, it is known that this is obtained from copper sulfate, $CuSO_4$, and water, so the formula is never written as above, but rather as $CuSO_4 \cdot 5H_2O$. This tells us that five molecules of water are chemically combined as such, with one $CuSO_4$. Further study of the nature of this crystalline material has disclosed that four of the water molecules are attached directly to the copper. This would justify using the formula $Cu(H_2O)_4SO_4 \cdot H_2O$ which now gives as much information about this compound as it is possible

for the formula alone to give. Incidentally, the sulfate group, SO_4, is one that occurs in many combinations. Such a group is called a "**radical**" and written as a unit in chemical formulas. Some common radicals are listed in Table 3. For example, aluminum sulfate has three sulfate radicals to two aluminum atoms. Its formula is therefore written $Al_2(SO_4)_3$. Practically never is it written $Al_2S_3O_{12}$, although this would also be correct, because the first tells more about the compound. When a group of symbols is included within parentheses, the subscript following the parentheses applies to *each* element inside. Thus, $(SO_4)_3$ means S_3O_{12}.

Table 3 Some Common Radical Ions and Radicals

NH_4^+	ammonium	NO_2^-	nitrite
CN^-	cyanide	NO_3^-	nitrate
$CO_3^=$	carbonate	$SO_3^=$	sulfite
HCO_3^-	bicarbonate	HSO_3^-	bisulfite
OH^-	hydroxide	$SO_4^=$	sulfate
—OH	hydroxyl	HSO_4^-	bisulfate
$—CH_3$	methyl	$PO_4^{\equiv}$	phosphate
$—C_2H_5$	ethyl	ClO^-	hypochlorite
—COOH	carboxyl	ClO_3^-	chlorate
$S_2O_3^=$	thiosulfate	ClO_4^-	perchlorate

To answer the inevitable question of what determines the order of elements as written in a chemical formula, we must anticipate some of the information of the following chapter. There, some chemical compounds are described as composed of oppositely charged ions and others as having uneven electron sharing, which causes one element to be partially positive and another partially negative, the bond being called "**polar.**" The custom is to write the positive ion first and the negative ion second, if an ionic compound is involved. Usually this custom is followed for polar compounds in general, the more positive element being written first and the more negative element after. For example, one writes NaCl but not ClNa, and H_2O but not OH_2. However, there are exceptions, some very common, such as the formula for ammonia, NH_3, in which the nitrogen is partially negative and the hydrogen partially positive. Following the usual custom would lead to writing H_3N for ammonia, but this is almost never used. You will, as you continue your study of chemistry, develop an intuitive feeling for the writing of formulas. There is no need to worry about them here, especially since an unconventional order of writing is not actually incorrect.

MOLECULAR AND FORMULA WEIGHTS

The "**molecular weight**" of a compound is simply the sum of the atomic weights of all the atoms in the molecule and hence in the molecular formula. The "**formula weight**" is the sum of the atomic weights of all the atoms in the empirical formula. Sometimes the empirical formula and the molecular formula are identical, but sometimes the empirical formula is smaller than the molecular formula. Of course, the empirical formula is always used when the compound does not exist as molecules. Often the terms "molecular weight" and "formula weight" are used as though they were synonymous. Although strictly speaking they are not, usually there is little ambiguity. For example, one might refer to the "molecular weight" of sodium chloride, actually meaning the "formula weight."

EXAMPLES. 1. What is the molecular weight of sulfuric acid, H_2SO_4?

Atomic weight of H = 1, × 2 = 2
S = 32, × 1 = 32
O = 16, × 4 = 64
98 is molecular weight of H_2SO_4 ANS.

2. What is the formula weight of washing soda, $Na_2CO_3 \cdot 10H_2O$?

Atomic weight of Na = 23, × 2 = 46
C = 12, × 1 = 12
O = 16, × 13 = 208
H = 1, × 20 = 20
286 is formula weight. ANS.

COMPOSITION BY WEIGHT: THE MOLE

The concept of the mole has already been introduced (p. 41, 126) in its application to the elements in their free states. It is equally applicable to compounds, where it has the similar meaning of the weight in grams equal numerically to the molecular or to the formula weight. In other words, it is an amount of a substance that contains Avogadro's number (6.02×10^{23}) of molecules, or the same number of "formula units." For example, the molecular weight of water, H_2O,

is 18; one mole of water weighs 18 g. The formula weight of sodium chloride, NaCl, is about 58.5; one mole of NaCl weighs 58.5 g.

A chemical formula can tell us not merely the relative number of atoms of each element in the compound, but also the relative weights. For each element of a compound contributes to the total weight in proportion to the number of its atoms per molecule or formula and in proportion to the atomic weight. For example, the molecular weight of water, 18, is the sum of the atomic weight of hydrogen taken twice, because there are two atoms, and the atomic weight of oxygen taken once: $1 + 1 + 16 = 18$. Thus hydrogen contributes $\frac{2}{18}$ of the weight of water, and oxygen contributes $\frac{16}{18}$ of the weight. This is true no matter how much water is involved. If there is one mole of water, 18 g, this must contain 2 g of hydrogen and 16 g of oxygen. If there is a quantity of 100 tons of water, this must contain $\frac{2}{18}$ of 100, or 11.11 tons of hydrogen, and $\frac{16}{18}$ of 100, or 88.89 tons of oxygen. The composition of water by weight is 11.11 per cent hydrogen and 88.89 per cent oxygen.

In a similar manner, the weight percentage composition of any compound can be computed from its chemical formula. The weight per cent of any element in the compound is the weight contribution made by that element to the molecular or formula weight of the compound divided by the total molecular or formula weight.

EXAMPLE. What is the weight percentage composition of sugar?

The formula is $C_{12}H_{22}O_{11}$, from which the molecular weight is computed:

$$\begin{aligned} \text{C, } 12 \times 12 &= 144 \\ \text{H, } 22 \times 1 &= 22 \\ \text{O, } 11 \times 16 &= 176 \\ &\overline{} \\ &342 \text{ is the molecular weight} \end{aligned}$$

Then the percentage by weight of carbon is 144/342 (times 100)
$= 42.11\%$

For hydrogen, 22/342 (times 100) = 6.43%
For oxygen, 176/342 (times 100) = 51.46% ANS.

One could hardly overemphasize the importance of such weight relationships. They permit calculation of how much of an element or compound is needed to make a given quantity of another compound. This kind of calculation is used in chemical manufacturing. Equally important, if the weight percentage composition can be calculated

from a chemical formula the formula can be calculated from the weight percentage composition. Indeed, this is how nearly all chemical formulas have actually been determined, as will be shown presently.

Perhaps the most important conversions involving moles are those between number of moles and weight in grams. These two rules should be memorized:

(1) The number of moles equals the total weight in grams divided by the weight of one mole.

(2) The total weight in grams equals the number of moles multiplied by the weight of one mole.

EXAMPLES. 1. How many moles in 1800 g of water?

Water is H_2O, with molecular weight $2 + 16 = 18$; 18 g is 1 mole.

$$\text{No. moles} = \frac{\text{total weight}}{\text{weight of 1 mole}} = \frac{1800}{18} = 100 \text{ moles} \qquad \text{ANS.}$$

2. How many grams of carbon dioxide, CO_2, in 6 moles?

One mole of CO_2 (mol. wt. $12 + 2 \times 16 = 44$) is 44 g

No. grams = no. moles $\times$ wt of 1 mole $= 6 \times 44 = 264$ g ANS.

INTRODUCTION TO THE CONCEPT OF CHEMICAL EQUIVALENCE

As we shall be able to see more clearly later, chemical substances react with one another to form compounds of definite composition. Since atoms must combine as whole atoms, the molecules or other component units of these compounds must contain whole numbers of atoms of each component element. Likewise, in order to form compounds of such composition, whole numbers of atoms or molecules must also be involved in the reactions that produce these compounds. We therefore find that 1, 2, 3, 4, 5 . . . moles of A are needed to react with 1, 2, 3, 4, 5 . . . moles of B, forming 1, 2, 3, 4, 5 . . . moles of each product.

It is convenient to reduce, if possible, these often different numbers of moles to a common basis. This is done by introducing the concept of **"chemical equivalence."** An **"equivalent weight"** of a substance is the exact amount of it needed to react with an equivalent weight of another substance. The common basis is one mole, or Avogadro's

number, of hydrogen atoms (H, not H_2), which, by definition, is one gram of hydrogen. An equivalent weight of a substance is that quantity in grams which will react with one gram of hydrogen, or which will react with that amount of another substance which in turn will react with one gram of hydrogen. For example, chlorine atoms can form but one covalent bond, and hydrogen atoms can form but one covalent bond. Coming together, these elements can only unite one to one (forming hydrogen chloride, HCl). Since 1 g of H contains Avogadro's number of atoms, the same number of Cl atoms will be required, or 35.5 g, since the atomic weight of chlorine is 35.5. One equivalent weight of chlorine is therefore 35.5 g.

One mole of chlorine atoms is 35.5 g and is thus an equivalent weight. However, as we have already learned, elementary chlorine gas consists of Cl_2 molecules. One mole of Cl_2 molecules would therefore weigh 71 g and contain *two* equivalent weights. Similarly, hydrogen gas consists of H_2 molecules, one mole therefore containing two equivalent weights.

An oxygen atom can form two covalent bonds and will combine with two atoms of hydrogen (forming the compound, water, H_2O). One mole of oxygen atoms will thus react with two moles of hydrogen atoms. Only half a mole of oxygen atoms is therefore enough to react with one mole, or an equivalent weight, of hydrogen atoms. Since one mole of oxygen atoms would weigh 16 g, half a mole or 8 g is an equivalent weight of oxygen.

We have already learned that elementary oxygen gas consists of diatomic molecules, O_2. One mole of oxygen gas would therefore weigh 32 g, containing four equivalent weights of oxygen.

An aluminum atom can form three covalent bonds. Therefore it can combine with three hydrogen atoms. The atomic weight of aluminum is 27, and one mole is 27 g. Since this unites with 3 g of hydrogen, the amount of aluminum necessary to unite with 1 g of hydrogen is $\frac{27}{3} =$ 9 g. This is the equivalent weight of aluminum.

The significance of equivalent weights can be illustrated by the following table of relative quantities of elements needed for reaction.

1 equivalent wt	+	1 equivalent wt	forms
H_2 (1 g)	+	Cl_2 (35.5 g)	HCl
H_2 (1 g)	+	O_2 (8 g)	H_2O
H_2 (1 g)	+	Al (9 g)	AlH_3
Cl_2 (35.5 g)	+	O_2 (8 g)	Cl_2O
Cl_2 (35.5 g)	+	Al (9 g)	$AlCl_3$
O_2 (8 g)	+	Al (9 g)	Al_2O_3

In contrast, we can use moles instead of equivalent weights:

moles of element	+	moles of element	forms
1 H_2	+	1 Cl_2	HCl
2 H_2	+	1 O_2	H_2O
3 H_2	+	2 Al	AlH_3
2 Cl_2	+	1 O_2	Cl_2O
3 Cl_2	+	2 Al	$AlCl_3$
3 O_2	+	4 Al	Al_2O_3

Any given number of equivalent weights of any substance is exactly the right amount to react completely with the same number of equivalent weights of any other substance. The concept of chemical equivalence has rather limited applicability, largely because in some cases it becomes quite ambiguous, but in certain applications it is very useful. We shall meet it again in discussing solutions (Chapter 16) and in studying chemical effects of electricity (Chapter 20).

EMPIRICAL FORMULAS

When a chemist has isolated a new, or at least unrecognized, substance, and determined that it is a chemical individual and not a mixture of compounds, he then carries out two types of test. First, he runs chemical tests which serve to show him what elements are present in the compound. This procedure is called "**qualitative analysis.**" He then carries out careful quantitative experiments to measure how much of each element is present. This is called "**quantitative analysis.**" The data he obtains in this way are like those you might calculate in determining the weight percentage composition.

Having determined by analysis what the relative weights of the component elements are, he then wishes to know the relative numbers of atoms of each element. Since a mole of any element contains exactly the same number of atoms, he can divide the weight percentage by the atomic weight (weight, in grams, of 1 mole) and come out with a relative number of atoms (number of moles) of the element. For example, he might have discovered that his compound consisted of 11.11 per cent hydrogen and 88.89 per cent oxygen. He would then divide the 11.11 (which is really parts by weight out of a total of 100 parts by weight) by the atomic weight of hydrogen, 1. This would of course give 11.11. He would then divide the 88.89 by the atomic weight of oxygen, 16. This would give 5.56. He has thus learned that in his compound there must be 11.11 atoms of hydrogen for every 5.56 atoms of oxygen. But

he knows that the atoms must occur whole, and therefore he must reduce these decimals to whole numbers. The simplest procedure is to begin by dividing each by the smaller. Dividing 11.11 by 5.56, he obtains 2.00. Dividing 5.56 by 5.56, of course, gives 1.00, so he now knows that the compound has two hydrogen atoms to each oxygen atom. He can then write the empirical formula, which must be the smallest possible formula containing whole numbers of the atoms, as H_2O.

He does not yet know whether this is a molecular formula or not. He must next, if he wishes to know the correct or true molecular formula, determine the molecular weight of the compound. If he does this, he finds that it is 18. Since the empirical formula weight is also 18, he knows that the empirical formula and the molecular formula are, for this particular compound, identical.

Suppose he had found the molecular weight to be 54, instead. He would have divided this by the empirical formula weight, 18, obtaining 3. This would let him know that the empirical formula must be multiplied by 3 to give the true or molecular formula: $3 \times H_2O = H_6O_3$. The true or molecular formula is always equal to the empirical formula or a multiple of it by some small (usually) whole number.

In some instances, the initial division of the weight percentage by the atomic weight of each element will not result in numbers that are reducible to small whole numbers by dividing through by the smallest. One can usually determine by inspection that multiplication of each by a small whole number will change the relative numbers of atoms to small whole numbers. For example, one might divide through by the smallest value and obtain the following relative numbers of atoms: 1.0, 2.0, 3.5. It would be obvious that these elements occur in relative numbers of atoms obtained by multiplying by 2, =2, 4, and 7.

EXAMPLES. 1. A sample of a pure compound is analyzed. It contains Na 32.4%, S 22.5%, O 45.0%. What is its empirical formula? First, divide each percentage by the atomic weight, to find the relative number of atoms. Then divide each by the smallest:

$$\text{Na}\ \frac{32.4}{23} = 1.41; \frac{1.41}{0.70} = 2.01$$

$$\text{S}\ \frac{22.5}{32} = 0.70; \frac{0.70}{0.70} = 1.00$$

$$\text{O}\ \frac{45.0}{16} = 2.81; \frac{2.81}{0.70} = 4.01$$

The empirical formula is therefore $Na_{2.01}S_{1.00}O_{4.01}$, or, Na_2SO_4. **ANS.**

2. A gaseous compound is analyzed and found to contain B 22.1% and F 77.9%. A sample weighing 0.0433 g occupies 128 ml at 64 mm and 23°C. What is the true molecular formula?

First, find the empirical formula as above.

$$\text{B}\ \frac{22.1}{10.8} = 2.05; \frac{2.05}{2.05} = 1.00$$

$$\text{F}\ \frac{77.9}{19} = 4.10; \frac{4.10}{2.05} = 2.00$$

The empirical formula is BF_2. Now we must find the volume of the sample at standard conditions.

$$V = 128 \frac{64}{760} \frac{273}{296} = 9.94 \text{ ml}, = 0.0433 \text{ g}$$

$$1 \text{ mole is } \frac{22412}{9.94} \times 0.0433 \text{ g} = 97.6 \text{ g}$$

For empirical formula BF_2, the formula weight is B 10.8 + F 2 × 19.0 = 48.8. Dividing 97.6 by 48.8 gives 2.00. Thus, the molecular formula is found to be double the empirical formula, or B_2F_4.

CHEMICAL EQUATIONS

A **chemical equation** is a collection of symbols and/or formulas which indicate the reactants and the products of a chemical reaction. For example, hydrogen gas burns in air or oxygen to form water. We know that this burning is a chemical reaction between hydrogen and oxygen, both of which occur as diatomic molecules. We therefore know the correct formulas for these elements as well as that of water, and can write:

hydrogen plus oxygen forms water

or, $H_2 + O_2 \rightarrow H_2O$

But the word "equation" implies equality, and as written this is not an equation because the same number of atoms of each element does not appear on each side of the arrow. Since no atoms may be created or destroyed in such a reaction, the expression needs further adjustment. In its present form, it is often called an "unbalanced" equation. It is said to need "balancing," but this is not an apt term because if it is truly an equation, it *is* balanced. It seems better to speak of *completing* the equation. How?

We observe that since oxygen occurs in diatomic molecules, the smallest amount of oxygen that could possibly participate in this reaction would be one molecule, which contains two atoms. But a molecule of water only contains one atom of oxygen. If an atom of oxygen is not to become lost during this reaction, which is impossible, then it must be accounted for in the product(s). Clearly, two water molecules are needed to account for the two atoms of oxygen in one O_2 molecule. In this way, are determined correct relative amounts of water and oxygen. But two molecules of H_2O, which is the minimum possible to be formed in this reaction, obviously contain two molecules of hydrogen, or four hydrogen atoms. Therefore the initial amount of hydrogen must be doubled. We then have,

$$2H_2 + O_2 \rightarrow 2H_2O$$

This equation is "complete" and "balanced." The test of this is that the total number of atoms of each element involved must appear on both sides of the arrow—in the reactants and in the products. Here hydrogen and oxygen are termed the reactants, and water is the sole product. The number of hydrogen atoms in the reactants, four, is the same as the number in the product. The number of oxygen atoms in the reactants, two, is the same as the number in the product.

What do we need to know, then, to write a complete chemical equation? First, we must know the identity of all reacting materials. Second, we must know the identity of all products. This means that we must know the correct chemical formulas of each of these substances. Then, to write the equation, we first write down the formulas of the reactants and the formulas of the products. Next, by observation, we decide what must be the coefficients of each reactant and each product, in order to produce the correct balance so that the expression becomes a complete equation. The coefficients must be whole numbers, because only whole atoms or molecules can be among the reactants or products. Finally, we make sure that the equation is reduced to its lowest possible coefficients. For example, $4H_2 + 2O_2 \rightarrow 4H_2O$ is a complete equation, but since each coefficient can be divided by two to give a whole number, this equation is not reduced to its lowest terms.

What does a chemical equation tell us? It tells that certain specified substances react with one another to form certain specified products. It also tells us the relative number of moles of each substance involved in the reaction. From this, we can easily calculate the relative quantities by weight, and this is of extreme practical importance. All we need is the exact quantity of one reagent (reactant) or of one product, and from these and the chemical equation we can calculate the exact amounts of all other substances included in the equation.

EXAMPLE. Limestone, or calcium carbonate, $CaCO_3$, can be decomposed by heat to liberate carbon dioxide, CO_2, and leave behind quicklime, calcium oxide, CaO. The chemical equation is $CaCO_3 \rightarrow CO_2 + CaO$

The formula weight of $CaCO_3$ is Ca 40 + C 12 + 3 O 48 = 100
The formula weight of CO_2 is C 12 + 2 O 32 = 44
The formula weight of CaO is Ca 40 + O 16 = 56

Just as no atoms can be created or destroyed in any ordinary chemical change, so there can be no change in weight between reactants and products. Therefore the sum of the weights of the reactants must always equal the sum of the weights of the products. On the mole basis, 100 g $CaCO_3$ = 44 g CO_2 + 56 g CaO. We know that 100 g of limestone will produce 44 g of carbon dioxide and 56 g of lime. From this, we know how to calculate from any amount of one substance the corresponding amounts of the other two substances. For instance, from 10 tons of limestone how much products?

This is simple enough to solve by inspection. Obviously, 10 tons of limestone will produce 4.4 tons of carbon dioxide and 5.6 tons of lime.

Suppose we began with 10 tons of lime. How much limestone would be needed to produce it? For every 56 parts of lime, 100 parts of limestone would be required. Then 100/56 times 10 tons CaO = 1000/56 or 17.86 tons of $CaCO_3$. How much carbon dioxide would be formed? This is simply the difference in weight between the limestone and the lime: 17.86 − 10 = 7.86 tons of CO_2.

Alternatively, we could have observed that for every 56 parts of lime, 44 parts of carbon dioxide are produced. Therefore, 44/56 times 10 tons CaO = 440/56 = 7.86 tons of carbon dioxide.

Suppose 10 tons of CO_2 were produced. How much limestone would be needed? From the equation, we note that 100 parts of limestone produces 44 parts by weight of carbon dioxide. Hence 100/44 times 10 tons CO_2 = 1000/44 = 22.73 tons of $CaCO_3$.

Such weight relationships as these help to make chemistry a quantitative science. Their importance can hardly be overestimated. You should practice working numerical problems such as those above, until their working comes almost as second nature to you.

We shall see later that many chemical reactions are reversible—the products can form reactants as well as reactants form products. Equations for such reactions use either a double-headed arrow ($\longleftrightarrow$) or opposing arrows ($\rightleftharpoons$). The latter is adopted in this book.

SPECIAL HELP

Test Your Memory

1. Define "chemical formula."
2. Distinguish between "molecular weight" and "formula weight."
3. What is the difference between a "balanced" and an "unbalanced" chemical equation?
4. Write chemical formulas for each of the following radicals: sulfate, nitrate, carbonate, nitrite, sulfite, phosphate, ammonium, acetate.

Test Your Math

1. How many atoms of oxygen are in a mole of $Al_2(SO_4)_3 \cdot 12H_2O$?
2. How many moles are in 100 g of each of the following? NaCN, NH_3, K_2SO_4, AgCl, $C_{10}H_{22}$, O_2.
3. How many grams of each of the following are in 5 moles? $AgNO_3$, NaCl, H_2O, HCl, CH_4.
4. Sulfur is burned in air to form SO_2. This dissolves in water containing $Ca(OH)_2$, forming a solution of $Ca(HSO_3)_2$, which is used in paper pulp treatment. From one ton of sulfur, how much $Ca(HSO_3)_2$ could be formed?
5. How much limestone would be needed to make the $Ca(OH)_2$ needed in problem (4)?
6. In the reaction $4HCl + MnO_2 \rightarrow Cl_2 + MnCl_2 + 2H_2O$, assume 100 g of (*a*) HCl, (*b*) MnO_2, (*c*) Cl_2, (*d*) $MnCl_2$, and (*e*) H_2O. For each one, calculate the corresponding weights of each of the other substances.
7. Calculate the weight percentage composition of each of the following: (*a*) Na_2SO_4, (*b*) HNO_3, (*c*) $Ca(H_2PO_4)_2$.
8. Given the following weight percentage compositions, find the empirical formulas: (*a*) O 38.1, K 26.6, Cr 35.3, (*b*) S 32.7, O 49.0, Al 18.3.
9. A sample of hydrocarbon is burned completely to carbon dioxide and water. The hydrocarbon, 0.54 g, produced 2181 ml of carbon dioxide at 24°C and 316 mm, and 0.86 g of water. Another sample of this hydrocarbon weighing 0.58 g was found as a vapor to occupy 492 ml at 380 mm and 27°C. What is the true formula of this hydrocarbon?

10. A man did a favor for a wealthy maharajah, in return for which he was given a choice of a pound of gold or as much gold as could be obtained from $AuCl_3$ prepared by use of all the chlorine in a pound of table salt. Assuming that he wished to profit as much as possible, what should have been his choice?
11. What weight of coke would be required to reduce a ton of iron ore containing 80 weight per cent Fe_2O_3, if the coke contains 85% carbon and the reactions are:

$$2C + O_2 \rightarrow 2CO$$
$$3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$$

12. What volume of CO_2 measured at 700°C and 780 mm, would be produced?
13. What weight of iron would be produced?

Test Your Understanding

1. If necessary or otherwise desirable (conventional), change the following empirical formulas to their proper form: ONa_2, H_6N_2, $MgCl_2$, Al_4O_6.
2. Write chemical formulas for the following compounds: (*a*) one atom of fluorine to one atom of potassium, (*b*) two atoms of oxygen to one atom of titanium, (*c*) one atom of beryllium to two atoms of chlorine, hydrated by four molecules of water.
3. Why is it incorrect to write equations showing reactions of such gases as chlorine, hydrogen, or oxygen representing them by the symbols Cl, H, or O?
4. Why are solid elements in the free state represented in equations as the symbol without indicating that the atoms are joined together?
5. Why must the number of atoms of each element in the reactants exactly equal the number in the products, and thus be shown by the complete chemical equation?

9

Inter-Element Bonding

THE CHEMICAL ELEMENTS in the free state account for only about 89 kinds of matter, but hundreds of thousands of kinds of matter have been recognized. Since all these must also consist only of some of these same elements they must be composed of mixtures or combinations of the elements. Mixtures are of course possible, but what elements could you mix to obtain water, for instance? Clearly, something more profound than mere physical mixing must be involved.

A hint as to what is involved can be found in the nature of the elements themselves. We have seen that with the exception of the inert elements (helium, neon, argon, krypton, xenon, radon) all elements consist normally of atoms joined together by bonds. If like atoms can thus join together, what about unlike atoms? These also can join together. The most fascinating fact about such combining is that in the process each element loses completely its outward characteristics, and the combination has new properties uniquely its own. And yet, fascinating though this is, it is not too surprising when one recalls that even in combination with like atoms, carbon may be either colorless, hard diamond or black, soft graphite; phosphorus may be white and highly reactive, or red and much less reactive, and so on.

In their simpler combinations, unlike atoms join to one another by bonds of essentially the same kind as those between like atoms in the free elements. A review of these bonds and the requirements for their formation should be useful here. Let it be understood that bonds may have all degrees of strength. If the bonds are strong enough that the aggregate of atoms is stable enough to be treated as a unit, and if more than one element is included, the combination is called a "chemical compound." A more precise definition is not available, for although definite and invariable composition is a common quality of chemical compounds, there are some solid compounds whose composition is somewhat variable. In general, however, a compound has a sufficiently fixed and definite composition that it can be represented reasonably well by a chemical formula containing whole numbers of atoms of each element. All molecular compounds, whether gaseous, liquid, or solid, can be represented *exactly* by such a formula. Only certain solids deviate, and usually only to a small extent.

THE NATURE OF CHEMICAL BONDS IN COMPOUNDS

Metal to Metal Bonding

When two or more metallic elements come together, they may or may not form "intermetallic compounds." In such compounds as do form, which are numerous indeed, the relative numbers of atoms of each element involved (in keeping with the nonlocalization of bonding electrons that characterizes metallic bonding) appear to depend more on the relative sizes of atoms and on other factors associated with stability of the metallic lattice than on the number of outermost electrons and vacancies. Therefore, it is much more difficult to understand the composition of intermetallic compounds, and impossible to predict it solely from knowledge of the potential covalence of each metal. Fortunately, such compounds are relatively unimportant in elementary chemistry, and there will be little need to say more about them herein.

Nonmetal to Nonmetal Bonding

The nonmetals, on the other hand, combine in the free element by covalent bond formation. The nature and number of these bonds is much more clearly related to the electronic configurations of the atoms. Remember that in the atoms beyond helium, the outermost shell ordi-

narily contains 4 stable orbitals, able to hold a maximum of 8 electrons. To form a covalent bond, each atom must provide (1) an outermost unpaired electron to be shared with the other atom and (2) an outermost single vacancy, capable of accommodating an electron from the other atom. In other words, an atom can form a single covalent bond for each electron-plus-vacancy combination (half-filled orbital). Any combination of nonmetal atoms of different elements is, in principle, possible if it utilizes all the covalent capacity of each atom.

In addition, although only *s* and *p* orbitals are included in the outermost four usually involved in valence, sometimes outer *d* orbitals, less stable than the *s* and *p*, can be used. If an atom has fewer outer vacancies than electrons, and therefore possesses one or more filled orbitals—pairs of outer electrons—sometimes one or more of these pairs can be used for single bonds by promoting *one* out of the pair into an outer *d* orbital. Observe that this creates simultaneously the capacity to form *two* additional covalent bonds. This procedure is sometimes called "expanding the valence octet." For example, the number of outermost electrons on an atom of phosphorus is 5. Since there is room for only 8 in the *s* and *p* orbitals, this means that there can be but 3 vacancies or, in other words, 3 electron-plus-vacancy combinations, leaving one filled orbital or outer electron pair. Normally one would expect the phosphorus atom, therefore, to form 3 single covalent bonds. This expectation is realized, we have already seen, in elemental phosphorus. In an atom of fluorine, on the other hand, there are 7 outermost electrons, leaving but 1 vacancy, and therefore the capacity to form but 1 covalent bond. We have recognized the full utilization of this capacity in the F_2 molecule. It is therefore possible for 1 phosphorus atom to unite with 3 fluorine atoms, to form a compound whose molecules are represented by the chemical formula PF_3. However, it is also possible for one of the paired electrons not directly involved in the bonding in PF_3 to be promoted into an outer *d* orbital, there being 5 of these 3*d* orbitals around the phosphorus atom. This creates simultaneously the capacity to form 2 new bonds, and 2 more fluorine atoms can join here. This results in a different compound, with molecular formula PF_5, which indicates that 5 fluorine atoms are joined to the same phosphorus atom. Now each of the 5 outermost electrons of the phosphorus atom is utilized in forming a single covalent bond. There is no possibility of combining additional fluorine atoms with the phosphorus.

Another possible illustration of "expanding the valence octet" is the recently reported xenon tetrafluoride, XeF_4. For more than half a century the "inert" elements have been universally recognized as forming no covalent bonds, and XeF_4 (and a more complex $XePtF_6$) have been

the first exceptions discovered. With its outer 8 electrons, the xenon atom normally lacks the requisites for bonding. If it is heated with fluorine, however, one electron from each of two pairs seems to be promoted to outer *d* orbitals, creating at once four half-filled orbitals and thus the possibility of four covalent bonds. The surprising result is then a stable crystalline material, XeF_4. There is also evidence of a XeF_2, which presumably would be the result of promotion of just one electron from the xenon octet to an outer *d* orbital, thus forming the requisites for two covalent bonds. Similar compounds evidently form also with radon and krypton.

Metal to Nonmetal Bonding

A possibility not quite like that in any pure element exists when two or more elements are combined, that at least one may be a metal and at least one other, a nonmetal. Many combinations of this kind are known. Invariably, at least so far as the outermost valence octet is involved, the bonds are covalent, the number of bonds that each atom can form being determined by the conventional requirements for covalence. For example, an atom of sodium contains but a single outermost electron. This means that it can form but one covalent bond. We have just seen that an atom of fluorine can also form but one covalent bond, although here the reason is that there is only one vacancy. Consequently, sodium and fluorine combine, one atom to one atom. Similarly, an atom of aluminum has 3 outermost electrons, which leaves 5 vacancies, but only 3 covalent bonds can be formed. With fluorine, an atom of aluminum would join to 3 atoms of fluorine, the resulting compound having the formula AlF_3.

COVALENT BONDING IN GENERAL

Since they follow the same general rules, the bonding between two different nonmetals and the bonding between metal and nonmetal may conveniently be considered together. Let us then begin a detailed study of chemical compounds by first classifying the elements according to their bonding characteristics and then considering one class at a time.

The most useful classification is perhaps one which distinguishes between the types of orbitals used in the bonding. Thus far, only outermost *s*, *p*, and occasionally *d* orbitals have been mentioned. Also to be considered are those elements whose electronic configurations are

characterized by having underlying *d* orbitals partly but incompletely filled. These are the elements known as "transition" elements. Incompletely filled underlying *d* orbitals can also become involved in bonding, and in some respects this bonding differs significantly from that in which only *s*, *p*, or possibly outer *d* orbitals are involved. These differences serve as a basis for distinguishing two major types of elements. One type, the "major group" elements, uses only outermost *s*, *p*, and possibly *d* orbitals in bonding. The other type, the "transition" or "subgroup" elements, uses underlying *d* orbitals as well as outermost *s* and *p* orbitals in bonding.

Major Group Elements

This class of elements consists of atoms having shells immediately underlying the outermost shell, containing 2, 8, or 18 electrons. In other words, either no underlying *d* electrons are present or else all 10 of them are present. These elements, which constitute the major groups of the periodic table as discussed earlier, are arranged in periodic table form together with their summarized electronic configurations on page 139. Notice that the group numbers, in Roman numerals at the top of each column, are in all cases equal to the number of outermost electrons in the atom. The number of covalent bonds that can be formed by each atom, without any promotion to outermost *d* orbitals, is then determined by the number of electrons up to and including four, and thereafter, going from left to right, by the number of vacancies. Excepting compounds between two metals, you can easily determine the possible or most probable formula of a compound between any two nonmetals or between any metal and any nonmetal, in terms of the covalent bonding possibilities. For example, any of the metals in Group IA, whose atoms all have but a single outermost electron, will combine with any of the nonmetals in Group VIIA, whose atoms all have but a single outermost vacancy, one to one. With any of the nonmetals in Group VIA, whose atoms all have two outermost vacancies, they will combine two to one. If asked, for example, the formula for a compound of strontium and tellurium, although you might never have heard of either one of them, from the table you could predict with assurance that since strontium atoms have two outermost electrons and tellurium atoms two outermost vacancies they would combine one to one, SrTe. What if gallium were to unite with sulfur? Each gallium atom has three outermost electrons, and each sulfur atom has two outermost vacancies—how can they combine evenly? The simplest ratio would be, two gallium atoms to three sulfur atoms, Ga_2S_3.

This simple procedure permits the prediction of a large number of correct formulas, but other formulas are possible, too, and involve somewhat greater complexity. For example, the formation of a compound, PF_5, has already been described. A familiar compound is sulfur dioxide, SO_2—how can this formula be arrived at? One might predict that since oxygen atoms can form two single covalent bonds and sulfur atoms can form two single covalent bonds, they would unite one to one, the formula being SO. Actually, however, no such compound is known. When one sulfur atom has joined to one oxygen atom, both bonding electrons of each may be involved, with the result that a double covalent bond holds them together. A second oxygen can become attached to the sulfur only if one of the two pairs of electrons on the sulfur can be promoted to an outer *d* orbital. This permits the formation of two additional single bonds, or their equivalent, one double bond, to the second oxygen. Still another pair of electrons exists on the sulfur, and if one of these could be promoted to still another outer *d* orbital, a third oxygen atom could be accommodated by a double bond. Indeed, SO_3 is another well-known compound of sulfur and oxygen.

Transition or Subgroup Elements

As stated earlier, subgroup elements cannot form bonds exactly as do the major group elements, but there is a general similarity in that the basic requirements are the same. That is, the number of bonds that can be formed is equal to the number of electron-plus-vacancy combinations that can occur. Here, however, underlying *d* orbitals can also have such combinations and enter into bond formation. These elements are all metals, and their valence is characterized by variability. We cannot therefore predict the formulas of their compounds with nonmetals with such easy assurance as we can for the major group elements, but at least we can predict what the maximum number of bonds can be. This does not mean that compounds in which these atoms form fewer bonds are not also possible. Indeed, sometimes they are much more stable than those in which the maximum number of bonds is formed. This is quite in contrast to the major group elements, which tend to form all the covalent bonds of which they are capable.

The subgroup elements can be represented electronically as in the fragment of the periodic table given on page 136. With minor exceptions to be discussed later, these all have two outermost electrons per atom. The maximum number of bonds that can be formed includes these two, and one in each of the underlying five *d* orbitals. Rarely, in other words, can more than seven bonds form. When the number of electrons

in the underlying *d* orbitals is less than five, of course, correspondingly fewer bonds can form. When the number of *d* electrons is more than five pairing has begun, and the bonding is restricted to the number of vacancies left. For example, consider titanium, with 10 electrons in the penultimate shell and 2 in the outermost. We know at once that of the 10, 8 are very stably located in filled *s* and *p* orbitals and cannot possibly be pressed into service to form bonds. Subtracting this 8 from the 10 leaves 2 electrons that must be the underlying *d* electrons, and these must be in separate orbitals, giving possibilities for two covalent bonds. The two outermost electrons can also form two covalent bonds, with the result that an atom of titanium can form a total of four covalent bonds. (It can also form only three, or two, but this could not be predicted from the electronic configuration except from the general knowledge that the transition metal atoms do not always use all the *d* electron possibilities for bonding that may exist.) Since oxygen can form two bonds, an expected compound of titanium with oxygen would have the formula, TiO_2. This compound is well known as the white pigment in nonyellowing paints. Since chlorine can form but one bond per atom, an expected compound of titanium with chlorine would have the formula $TiCl_4$. This compound is also well known.

Another example is manganese, which has two outermost electrons per atom and 13 in the penultimate shell. Again subtracting the 8 which we know must be in the very stable filled *s* and *p* orbitals, we find that 5 *d* electrons are present. These, distributed one in each *d* orbital, contribute the possibility of five bonds, and the outer two electrons contribute two more, making a total maximum of seven bonds which might be formed by a manganese atom. In fact, not many compounds of this nature are known, and those known are not very stable, but there is an oxygen compound having the formula Mn_2O_7, as we could predict. What we could not predict from this knowledge, but what would be reasonable possibilities also, are the known compounds of formula MnO, Mn_2O_3, and MnO_2.

Again the group number may be observed to be the same as the number of electrons beyond the closed shell (with the exception of the VIIIB-b and VIIIB-c elements), but this time the number includes not only the outermost electrons but also the underlying *d* electrons.

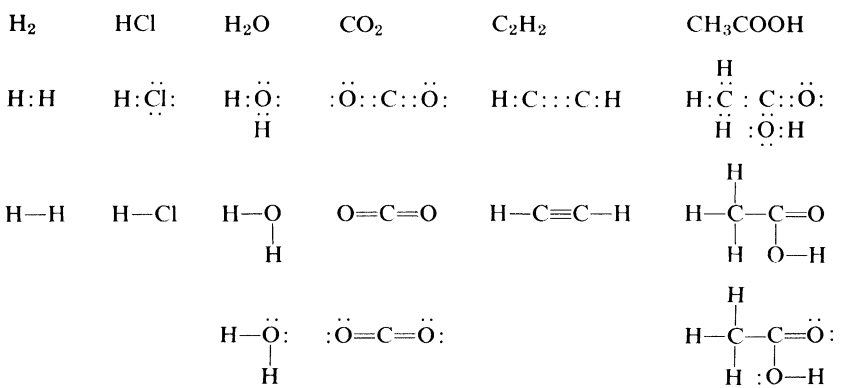
Electronic and Structural Formulas

Ordinary chemical formulas frequently fail to disclose how the atoms are attached to one another. We cannot expect to gain from any two-dimensional representation a completely realistic perception of molecular

structure, but at least it should be possible to show which atoms are attached to which, and how many electrons are involved in the bonding. Two equivalent types of representation are electronic and structural formulas.

Electronic formulas give the outer-shell electrons as dots around the symbol representing each atom. If two electrons are shared, as in ordinary or coordinate covalence, a pair of dots is placed between the symbols. A double bond is represented by two pairs of dots, and a triple bond by three. Such formulas also show structure to the extent of indicating how the atoms are linked, but cannot, of course, show the actual arrangement in space, especially if the structure is nonplanar.

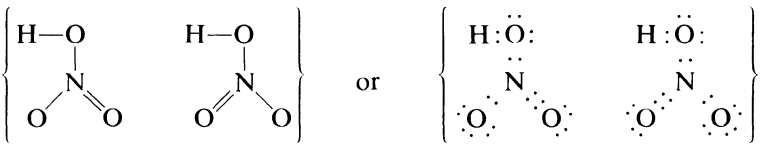
Structural formulas simply substitute a straight line for each pair of dots showing covalence, and either omit the unshared outer electrons or show them as dots. Examples are given below:



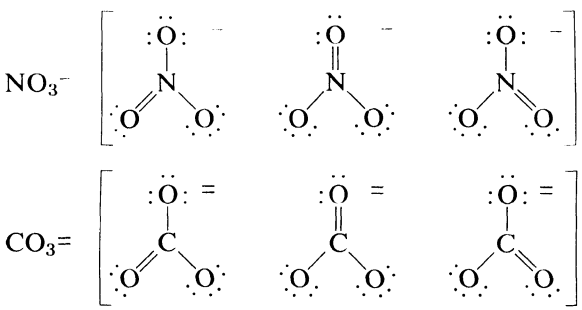
Resonance

As suggested in Chapter 4 in connection with the bonding in graphite, many compounds occur in which the bonds cannot be adequately represented as integral multiples of a covalent bond. For example, nitric acid, HNO_3, has two lone oxygens and one hydroxy oxygen joined to the nitrogen at corners of a triangle. The hydroxy oxygen seems fairly adequately described as joined to nitrogen by the second covalent bond of the oxygen, the first being O—H. This uses one bonding orbital, with one electron, of the nitrogen. Four electrons remain available on the nitrogen, but only three orbitals, for bonding to the two lone oxygens, which are found to occupy exactly equivalent positions. Bond lengths here are found to be short, indicating multiple bonds. But there are not enough orbitals for two double bonds at a time. The only possible explanation seems to be that each of these two bonds

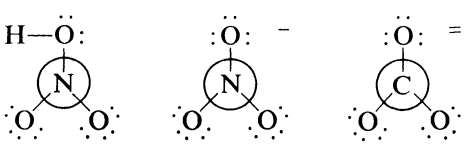
is part single and part double. Since this could not be represented by a single structural formula, the molecule is shown by several conventional structures, equivalent to one another, and said to be a "resonance hybrid" of these "contributing structures." This term is intended to convey the concept that the actual structure is neither one, but something in between. Contributing structures are written in braces.



Other very common examples are the nitrate ion, NO_3^-, and the carbonate ion, $CO_3^=$. In each, the oxygens are all in equivalent positions and closer to the central atom than expected for single bonds, yet too few orbitals are available for double bonds. Six orbitals would be required on the nitrogen and six on the carbon, yet only four are available on each. The structures are represented, therefore, as resonance structures:



It has been suggested that since these are actually single-structured ions, they ought more appropriately to be represented by a single diagram. To do this, the structure is represented first as of single bonds, with all other outer electron pairs shown. Then the available extra orbitals are represented as circles around their atoms. It is to be understood that if two or more atoms, each adjacent to the one with a vacant orbital, have pairs of electrons that might be used in bonding, no one pair monopolizes the orbital, but all use it partially.



Resonance appears to be a general phenomenon in chemical bonding. We have seen it demonstrated earlier, in metals, where rather than use only the minimum of orbitals the valence electrons use all that they can. When an orbital is equally available (or nearly so) to more than one electron pair, it tends to accommodate all pairs partially, rather than one pair exclusively. When an outer electron pair is equally available (or nearly so) to more than one outer orbital, it tends to occupy all orbitals partially rather than one orbital exclusively. By following these rules, atoms find their most stable positions in aggregates, because the maximum use is thereby made of available attractive interactions.

THE PROPERTY OF ELECTRONEGATIVITY

But this is not all that needs to be known about compounds. Knowing their formulas and structures is important, but one also needs to know, or at least should wish to know, why the compounds form and why they have the properties that they do. To approach an understanding of these things, we must study the nature of the individual atoms more closely than we have by examining their electronic configurations and counting the number of outermost electrons and vacancies.

Combining the fact of the inertness of the elements whose atoms have 2 or 8 electrons in the outermost shell—their usual reluctance to form covalent bonds—together with the bond-forming ability of elements whose atoms have fewer than 2 or 8 outermost electrons, one can infer that atoms can attract the electrons of other atoms strongly enough to form chemical bonds only when each atom has single electrons to share and outermost vacancies to accommodate electrons of other atoms.

What is the nature of the attraction that holds two atoms together by a covalent bond? Electrostatic attraction, exerted between nuclei and shared electrons, is of course the simplest fundamental explanation. But no two elements are alike in atomic number and hence in nuclear charge on the atoms. Do not these differences have some effect on the bonding? Then, too, no two elements are exactly alike in electronic configuration of the atoms. Some have many electrons underlying the valence level, some have few. Some have valence electrons in one kind of orbital, some in another. Do not these differences also influence the bonding?

Certainly *any* differences between atoms must affect their bonding, for an atom's inherent electrical nature makes it impossible for two or more atoms to be close to one another without also adjusting to one

another. Such adjustment is at least approximately equivalent for all interior atoms of a sample of pure element, and may more or less be taken for granted in considering covalent bonds between atoms of the same kind. But in compounds, which involve bonding between unlike atoms, the degree and kind of adjustment by each atom require special study if the properties of the compound are to be understood. An atom of a given element adjusts differently in different combinations, and thus contributes differently to the properties of the compound. The nature of this adjustment is doubtless far too complex to treat in an exact and, at the same time, readily comprehensible manner. Fortunately, however, a concept that seems qualitatively sound, although quantitatively somewhat elusive, can be used to approach a practical understanding.

Consider two atoms sharing two electrons. If the atoms are alike, each will attract the electron pair equally. The bond is then electrically symmetrical. Such bonds are called "**nonpolar.**" But if the atoms are unlike, the chances are excellent that among their differences will be a difference in their attraction for the bonding pair of electrons. If one atom attracts these electrons more strongly than the other, the electrons must as a result favor an average location more closely associated with the first atom than with the second. Since the atoms were initially neutral, and the two bonding electrons came one from each atom, the atom finally having more than half of the shared electrons must, in effect, acquire a negative charge, leaving behind on the other atom a corresponding positive charge. The bond is thus electrically unsymmetrical. Such a bond is called "**polar.**"

The quality of an atom that determines its *relative* attraction for the electrons when it unites with another atom forming a covalent bond, is called "**electronegativity.**" Literally, as used in this connection, it means "*relative tendency to become negatively charged—i.e., to gain electrons.*" It does *not* mean "quality of *being* negatively charged" (although this is probably the original meaning of the word).

If the atoms that form a covalent bond are initially different in electronegativity, more than a half share of the bonding electrons is taken by the atom of initially higher electronegativity. The bond is polar to the extent indicated by the relative electronegativities.

How can electronegativities be determined?

Several approaches, of varying utility and reliability, have been proposed, and with reasonably good success. But electronegativity is an elusive quality, in that its effects are easily noticed but not so easily evaluated quantitatively. Its nature is easier to understand in terms of certain measurable properties of individual atoms.

Ionization Potential

One property of an atom that can be determined experimentally and usually with high accuracy is the energy required to remove an electron from it. The removal of an electron from a neutral atom leaves it with excess positive charge, because the nucleus remains unchanged. A charged atom, one in which the nuclear charge is not equalled by the number of electrons, is called an "**ion.**" The process by which an ion is produced is called "**ionization.**" As the energy required to remove an electron is often recorded in volts, it is commonly called the "**ionization potential.**" However, more consistent with chemical energies is the unit called "**kilocalorie.**" One volt in ionization potential is equivalent to 23.06 kcal per mole for the removal of an electron from each of Avogadro's number of atoms. The energy will be expressed herein as "**ionization energy**" in kcal/mole.

Electrons can be removed successively from the same atom if succes-

Table 4 First Ionization Energies of the Elements

(kcal/g-atom)

				H				He
				313				567
Li	Be		B	C	N	O	F	Ne
124	215		191	260	336	314	402	497
Na	Mg		Al	Si	P	S	Cl	Ar
119	176		138	188	254	239	300	363
K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
100	141	216	138	187	231	225	273	323
Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe
96	131	207	133	169	199	208	241	280
Cs	Ba	Hg	Tl	Pb	Bi			Rn
90	120	241	141	171	185			248
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
151	158	156	156	171	182	181	176	178
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
152	160	156	166	167	173	178	192	175
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
129	127	138	184	182	201	212	207	213

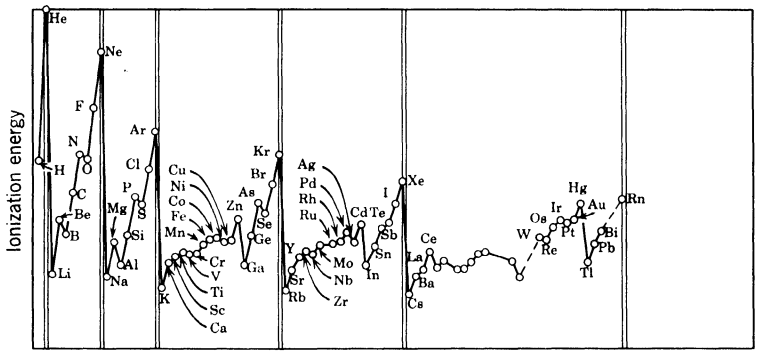


Figure 45. First ionization energy: variation with atomic number.

sively higher quantities of energy are employed. If E is an atom of any element having several electrons, then the energy for $E \rightarrow E^+ + e^-$ is called the "**first ionization energy.**" For $E^+ \rightarrow E^{++} + e^-$, the energy is called the "**second ionization energy,**" and so on.

The ionization energy of an atom is of course not the same as the electronegativity, but surely there must be a fairly close relationship between the attraction for electrons exerted by an atom and the energy required to take an electron away from the atom. The first ionization energies of the elements are listed in Table 4, and their relation to atomic number is shown in Figure 45. Notice especially the following facts:

1. In each period, the element having highest ionization energy is the inert element, which terminates the period.

2. In each period, the trend from left to right is from lowest to highest, but deviations occur from Groups IIA to IIIA, and VA to VIA, where decreases are observed. From IIA to IIIA, the difference arises from the fact that in IIA the electron removed is one of a pair of *s* electrons, but in IIIA it is a less tightly held *p* electron. From VA to VIA is a change evidencing a special stability when a set of similar orbitals has one electron in each. In nitrogen, for example, removal of one electron must disrupt the special stability of the three half-filled *p* orbitals. In oxygen, the electron removed is only a *p* electron that is paired, and its removal leaves the stable set of one in each of three *p* orbitals.

3. The trend downward in a periodic group is downward in ionization energy, except usually when the atom type changes from inert shell to eighteen shell.

Electron Affinity

Another atomic property of interest in relation to the electronegativity is the energy released when an atom acquires an electron, forming a negative ion:

$$E + e^- \rightarrow E^- + \text{energy}$$

This energy is called the "electron affinity." Unfortunately, for only a few elements can this be measured by direct experiment. Indirect experiment suggests values for others, and empirical extrapolations produce others, but very few truly reliable values are available. One might at first think that this quantity would be almost identical with the electronegativity, but there is a significant difference between acquiring an electron completely and merely exerting an attraction for a shared pair. Nevertheless, the two properties seem logically related.

Table 5 Electron Affinities of Some Elements

(kcal/g-atom)

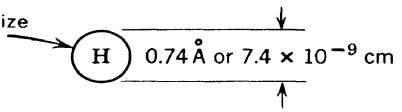
H	16.1	Cl	87.9
F	83.3	Br	81.4
O	34.0	I	74.5

Atomic Radius

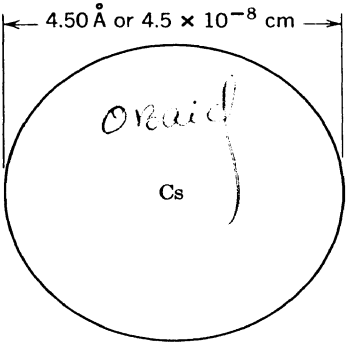
The size of an atom is difficult to define because its electronic cloud is so nebulous and deformable. In general, however, one can consider the electrons to be held within certain bounds, despite their mutual repulsion, by the attraction of the nucleus. If one could compare the radii of atoms of different elements, one would have an indirect measure of the relative effectiveness of this nuclear attraction.

Atomic radii can only be measured experimentally in terms of internuclear distances when the atoms come together, because although nuclei are relatively massive and can be located rather precisely, electronic clouds are not and cannot. Two kinds of internuclear distance can be recognized. One is the distance between neighbors not held together by a covalent bond. The other, substantially shorter, is the distance between bonded atoms, called the **"bond length."** In either case, if the two atoms are alike half the internuclear distance is defined as the atomic radius. Half the nonbonded distance is called the van der

The atoms of the elements vary in size from those of hydrogen, like this:

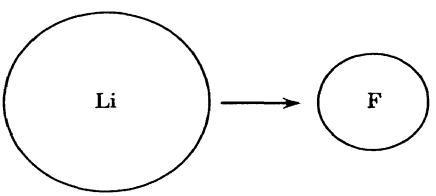


to those of cesium, like this:

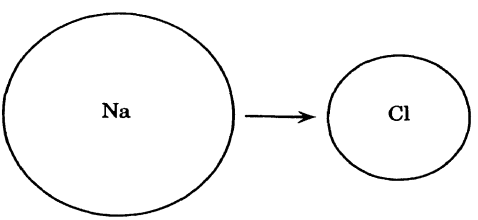


All other elements have atoms intermediate in size (except the little-known element, francium, whose atoms may be slightly larger).

When electrons are added to the same principal energy level (simultaneously increasing the nucleus charge), the atoms become smaller. Thus, the increase in the 2 shell from 1 electron (Li) to 7 electrons (F) is accompanied by the decrease in size shown.



Similarly, the increase in the 3 shell from 1 electron (Na) to 7 electrons (Cl) is accompanied by the decrease in size shown.



Completion of a shell from 7 to 8 (or 17 to 18) is believed to cause an increase in size, and beginning a new shell also causes an increase. Thus, the neon atom is thought to be intermediate between a fluorine atom and a sodium atom.

Figure 46. Relative sizes of atoms.

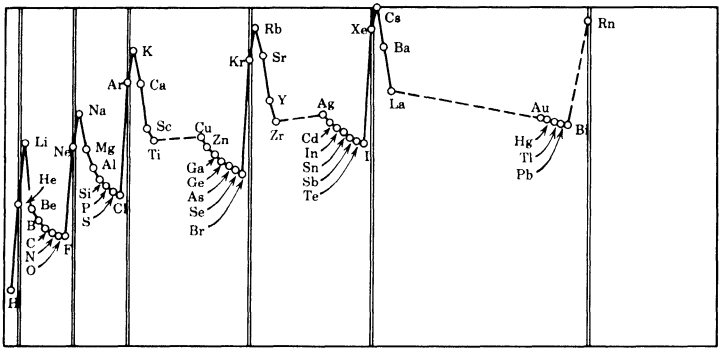


Figure 47. Variation of nonpolar covalent radius with atomic number.

Waals radius. Half the bond length, if the bond is nonpolar and the atoms alike, is the "**covalent radius,**" or, more strictly, the "nonpolar covalent radius." Van der Waals radii are too variable and uncertain in most instances to be evaluated accurately for useful tabulation. Many nonpolar covalent radii, on the other hand, can be measured accurately, and others determined reasonably reliably from less direct evidence. These radii, together with hypothetical values for the inert elements which usually form no covalent bonds, vary with atomic number as shown in Figure 47.

Notice especially that the trend from IA to VIIA is always down, the atoms being smaller with increased number of outermost electrons, consistent with the higher nuclear charge and despite the increase in interelectron repulsion. Notice that a similar change, though much less pronounced, seems to accompany the addition of inner *d* and even *f* electrons. Also, notice that extension of the cloud of electrons to the next higher principal quantum level always results in an increase in radius, with the result that radius increases down each group, except where the *f* electron contraction has intervened.

Evaluations of Electronegativity

An atom engaged in sharing a pair of electrons in covalent bonding may be regarded as doing simultaneously these two things: (1) attracting an electron from the other atom, and (2) resisting the removal of its own electron by the other atom. If the first can be represented by the electron affinity and the second by the ionization energy, an average of these might be considered a fair representation of electronega-

tivity. (A related suggestion has been that the electronegativity is the rate of change of energy with charge, obtained as the slope at the origin, of a curve of ionization energy and electron affinity versus charge.) Both yield values that for the most part agree reasonably well with what is known about the polarity of bonds, but both depend on electron affinities, which are mostly either uncertain or unavailable.

Another approach is based on the observation that polar bonds appear usually to be stronger. Therefore heats of formation of compounds, yielding bond energies, have served as the basis for evaluating electronegativity. Other methods have involved calculating the potential at the surface of an atom—in other words, the extent to which the nuclear charge is effective at the surface. This requires difficult and not always reliable estimates of the "shielding" power exerted by each electron, which depends in part on the nature of the orbitals. Nevertheless, all these methods give reasonable values of electronegativity that are in generally good agreement with one another.

The use of covalent radii to suggest relative attractions of atoms for electrons can be greatly improved and extended by applying them to estimation of atomic compactness. That is, the "*average* electronic density" of an atom can be calculated in number of electrons per unit volume (cubic Angstrom unit) of the atom:

$$D = \frac{Z}{4\pi r^3/3} = \frac{3Z}{4\pi r^3}$$

where D is the average number of electrons per cubic angstrom unit, Z the atomic number, and $4\pi r^3/3$ the volume of the atom in cubic angstrom units, calculated from the covalent radius, r. If such "densities" are corrected for variations with atomic number that have nothing to

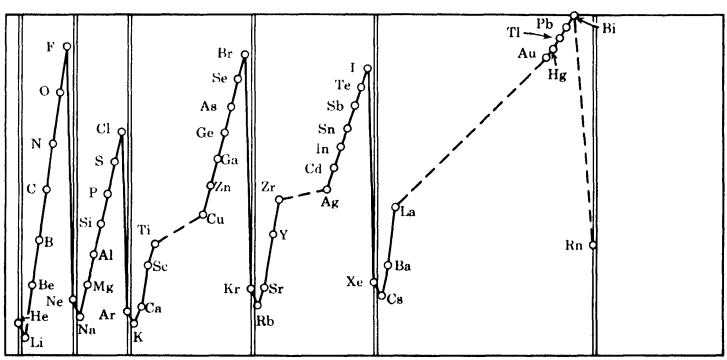


Figure 48. Average electronic densities of the elements: variation with atomic number.

Table 6 Electronegativities of the Elements

				H			
				2.31			
Li	Be		B	C	N	O	F
0.86	1.37		1.88	2.47	2.93	3.46	3.92
Na	Mg		Al	Si	P	S	Cl
0.85	1.21		1.39	1.74	2.16	2.66	3.28
K	Ca	Zn	Ga	Ge	As	Se	Br
0.80	1.06	1.86	2.10	2.31	2.53	2.76	2.96
Rb	Sc	Cd	In	Sn	Sb	Te	I
0.77	1.00	1.73	1.88	2.02	2.19	2.34	2.50
Cs	Ba	Hg	Tl	Pb	Bi		
0.76	0.96	1.92	1.96	2.01	2.06		

do with electronegativity, as shown by their occurrence in the inert elements, a value S, the electronegativity, is obtained, which can be termed the "relative compactness" of an atom. When converted to the usual arbitrary scale of electronegativity, these S values agree closely, for most elements, with electronegativity values obtained by other methods. These are the values to be used in this book. They are tabulated in Table 6, and their periodic variation with atomic number is shown in Figure 49.

The relationship between the relative compactness of an atom and its electronegativity can be understood qualitatively by the following simple reasoning. If an atom cannot hold even its own electrons closely, as shown by lack of compactness of its electronic cloud, then it can

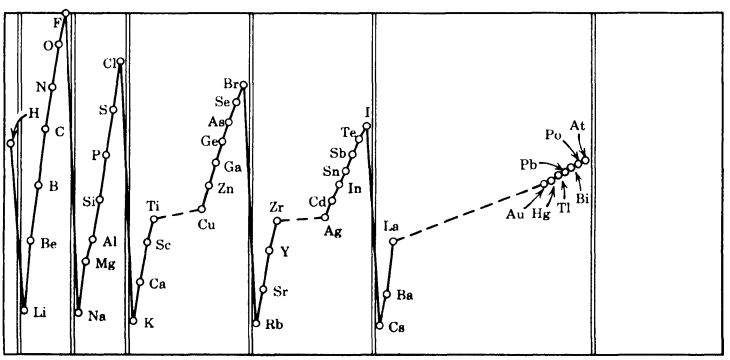


Figure 49. Variation of electronegativity with atomic number.

hardly be expected to attract outside electrons strongly. Sodium atoms, for instance, are very low in electronic compactness and also very low in electronegativity. But if an atom holds its own electrons closely, despite their mutual repulsion, then, if it has outer vacancies, it should be able to attract outside electrons strongly. Atoms of fluorine are about seven times more compact than those of sodium (have, on the average, seven times as many electrons per unit volume), and are also very high in electronegativity.

Electronegativity seems to be a quality of atoms rather than a fundamental quantity capable of exact determination. Therefore we perhaps will never be able to judge the accuracy of the numerical values selected by any of the proposed methods, except in respect to their consistency with chemical knowledge in general and their usefulness in correlating such knowledge.

The Use of Electronegativity

The significance of electronegativity values is simply this: a covalent bond in a diatomic molecule is nonpolar if the electronegativities are alike and polar if they are different, the polarity increasing with greater electronegativity difference. The element initially more electronegative becomes partially negative, leaving the other partly positive. By what mechanism can this happen, and what determines these charges?

Picture two atoms joining together through a covalent bond. Each provides one electron to be shared by the other. Each provides one space to accommodate the electron of the other. If the two atoms are initially unlike in electronegativity, which is almost always the case unless they are atoms of the same element, one will attract the shared pair more strongly than the other. Naturally the pair, being free to shift, will become more closely associated with the atom attracting it more strongly. We do not know how to describe the result in a simple pictorial manner, because the electrons are presumably in constant rapid motion, and all we can say of their exact location is that the probability is highest that they will be found between the two atomic nuclei. We can say, however, that on a time-average basis the electrons will spend more than half the time more closely associated with the one atom than with the other. Think what effect this must have on the electronegativities of the two atoms. The atom that acquires more than a half share can no longer be as electronegative as it was before the bond was formed, for its attraction for electrons must diminish as it succeeds in gaining negative charge. The atom left with less than a

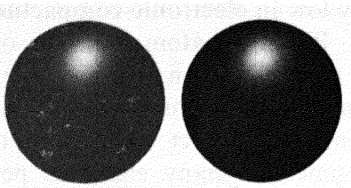
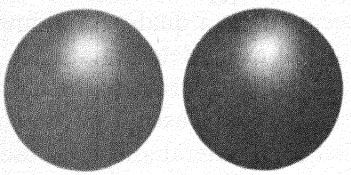
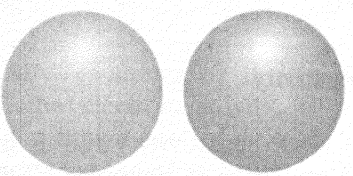
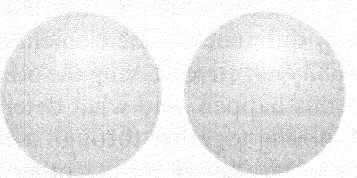
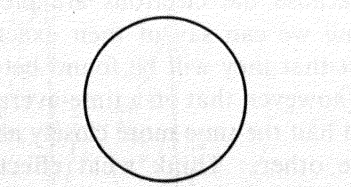
Electro-negativity	Partial charge		Electro-negativity	Partial charge
0.8	0.40 and greater		3.61 to 3.9	−0.40 and greater
0.91 to 1.2	0.22 to 0.40		3.31 to 3.6	−0.22 to −0.40
1.21 to 1.5	0.13 to 0.21		3.01 to 3.3	−0.13 to −0.21
1.51 to 1.8	0.08 to 0.12		2.71 to 3.0	−0.08 to −0.12
1.81 to 2.1	0.03 to 0.07		2.41 to 2.7	−0.03 to −0.07
			2.11 to 2.4	0 to ±0.029

Figure 50. Color scale for electronegativity and partial charge.

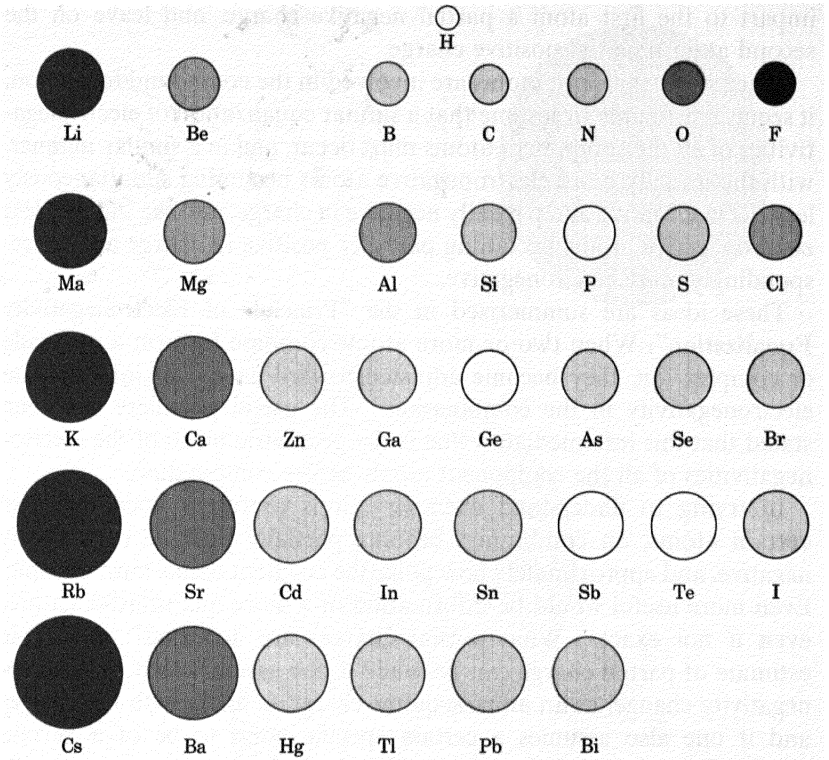


Figure 51. Relative covalent radii and electronegativities of major group elements. (See color key, facing.) Transition elements are similar to one another and would have electronegativity resembling Mg on color scale.

half share must now become more electronegative than it was initially, for added to its initial attraction for electrons is the increased energy to be released if it can regain what it has lost. We may thus think of the two atoms as initially different in their attraction for the shared electrons, but the one diminishing in its attraction for the electrons and the other gaining in its attraction for the electrons. The only logical point for this adjustment of the two atoms to cease seems to be when the electrons are shared equally by the two atoms—in other words, when the electronegativities have become equalized. By spending more than half the time more closely associated with the initially more electronegative atom, and less than half the time with the initially less electronegative atom, the shared electrons reach an energy situation corresponding to final equal attraction by the two atoms. In so doing, however, they

impart to the first atom a partial negative charge, and leave on the second atom a partial positive charge.

When more than two atoms are involved in the compound formation, it seems reasonable to assume that a similar equalization of electronegativities of all the component atoms must occur, and in a similar manner, with the initially more electronegative atoms becoming simultaneously less electronegative and partially negative in charge, and the initially less electronegative atoms becoming partially positive in charge and correspondingly more electronegative.

These ideas are summarized in the **"Principle of Electronegativity Equalization"**: When two or more atoms combine to form a molecule or complex ion, they become adjusted toward an equal, intermediate electronegativity in the combination. The useful postulate has been stated that this intermediate value is the geometric mean of the electronegativities of all the component atoms before combination.

In trying to understand chemistry, it is useful to know whether certain atoms, on combining, become partially positive or partially negative, and approximately how polar the covalent bonds must become. Even more useful would be information of a more quantitative nature, even if not exact. What partial charges are acquired? A simple estimate of partial charge can be made if one assumes that the electronegativity change, as an atom acquires charge, is linear with the charge, and if one also assumes a certain specific bond to be of a certain percentage polarity or "ionicity." By guessing that a gaseous molecule of sodium fluoride would be 75 per cent ionic—in other words, that the sodium atom would have a partial charge of 0.75 (electron) and the fluorine atom would have a partial charge of -0.75 (electron)—one can then calculate the change in electronegativity corresponding to complete loss or gain of one electron. Starting with sodium and fluorine, one can then calculate this change for the other elements. Details are outside the scope of this textbook, but the result is not, for it is very useful in helping to describe chemical bonds and the properties of compounds. The result is that the partial charge on a combined atom is the ratio of the change in electronegativity which accompanied the act of combination to the change in electronegativity which would have occurred had unit charge been acquired.

For example, the electronegativity of hydrogen is 3.55* and that of oxygen 5.21. The intermediate electronegativity resulting when hydrogen and oxygen combine to form water is the geometric mean of

*A different electronegativity scale is used here only, for the calculation, because the method has been developed only for this scale.

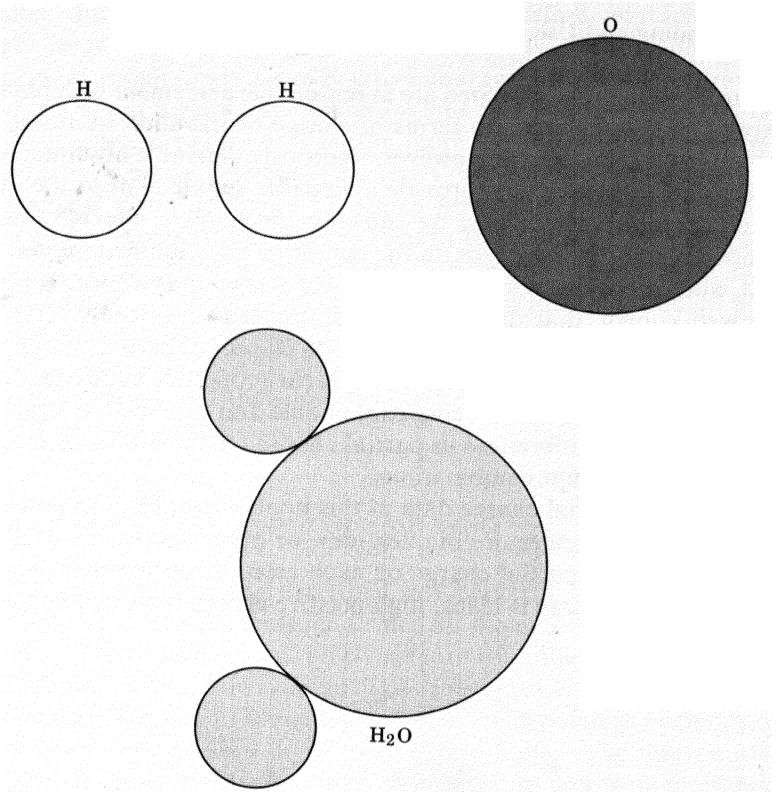


Figure 52. Equalization of electronegativities. Originally the oxygen is more electronegative than the hydrogen. When they combine to form water, the oxygen becomes less electronegative and the hydrogen more electronegative until both are equal in the molecule.

the electronegativities of the component atoms before combination, which is the cube root of the product of $3.55 \times 3.55 \times 5.21 = 4.03$. Thus the hydrogen atoms have gained in electronegativity by forming water, in the amount $4.03 - 3.55 = 0.48$. Had they lost an electron completely, they would have gained in electronegativity by 3.92. The partial charge on hydrogen in the water molecule is then taken as the ratio $0.48/3.92 = 0.124$. Similarly, the oxygen atom lost electronegativity by the amount $5.21 - 4.03 = 1.18$. Had it gained an electron completely, it would have lost in electronegativity by 4.75. Therefore, the partial charge on oxygen in the water molecule is taken as the ratio $1.18/4.75 = -0.248$. The sum of the charges on hydrogen and oxygen of course is zero, for the electrically neutral water molecule.

The Meaning and Use of Partial Charge Data

Partial charges so estimated are in reasonable agreement with physical experiments interpreted in terms of charge distribution in atoms and molecules. They are not, however, rigorously derivable absolute quantities. Nevertheless, they provide a valuable supplement to the utility of electronegativity values, by showing the relative effects of initial electronegativity differences on the condition of combined atoms. We find, when these charges are calculated for compounds whose properties are well known, that these properties appear to be closely related to the condition of the combined atoms with respect to partial charge. We find that the same element imparts different properties in different combinations, the differences being explainable and predictable largely on the basis of the differences in partial charge on the atoms of that element in the different combinations.

One use of partial charge data in this book is graphic. In numerous drawings of molecules or complex ions, or other aggregates of atoms, the approximate partial charge on each atom is represented by color. High negative charge is black, high positive charge blue, and neutrality,

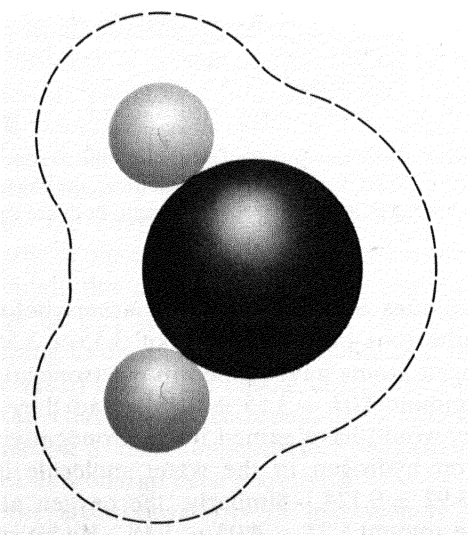


Figure 53. Water molecule, showing partial charge on atoms. (See color scale, page 180.) The circles represent covalent radii. The broken line surrounding the molecule represents the approximate closest approach of other nonbonding atoms or molecules, or the van der Waals radius. It will be omitted from all subsequent drawings in this book, with the understanding that it is assumed.

white. Increasingly dark shades of grey therefore represent increasingly large negative charges, and increasingly dark shades of blue represent increasingly large positive charges. From these drawings, one can see at a glance the direction and approximate extent of bond polarity, and recognize at least the more significant differences in the condition of a given element in a series of different combinations. An example is given in Figure 53, which represents a molecule of water. The circles represent the relative sizes of the atoms in covalent radii—van der Waals radii would extend farther out, as suggested by the dotted lines. A single covalent bond is therefore represented as two atoms in tangential contact. The bond angle is that observed for water, 104.5°. The pale blue of the hydrogen atoms represents their partial positive charge, and the somewhat less pale grey of the oxygen atom represents its negative charge.

POLAR COVALENCE AND IONIC BONDING

The covalent bonding described in Chapter 4, page 58, is that occurring in the free elements, and since all the atoms are alike it is nonpolar. The existence of electronegativity differences among the different elements, however, suggests that most chemical compounds have bonds that are to some degree polar. The polarity, evidently, can vary from none or very slight to relatively high. The unevenness of sharing, in other words, may vary from none to complete unevenness. Complete unevenness is that state reached when the two electrons, spending more and more of their time around one atom as the bond polarity increases, spend finally *all* of their time around the atom that was initially more electronegative and *none* of their time around the other. This is obviously the extreme of polar covalence—this is as polar as bonds can become. Through the bond becoming so polar, one atom actually acquires completely the electron supplied to the bonding by the other atom, while retaining completely its own bonding electron. It becomes a negative ion. The other atom is left completely without its own electron and without any share in the one originally supplied by the first atom, and thus it becomes a positive ion. No longer, in this extreme, are the two atoms held together by a mutual sharing of a pair of electrons. They are, however, charged particles and, being of opposite charge, attract one another just as any two electrostatic charges of opposite nature attract one another. This force of attraction is usually quite strong, with the result that the atoms are firmly held together in a chemical bond called an "**ionic bond.**"

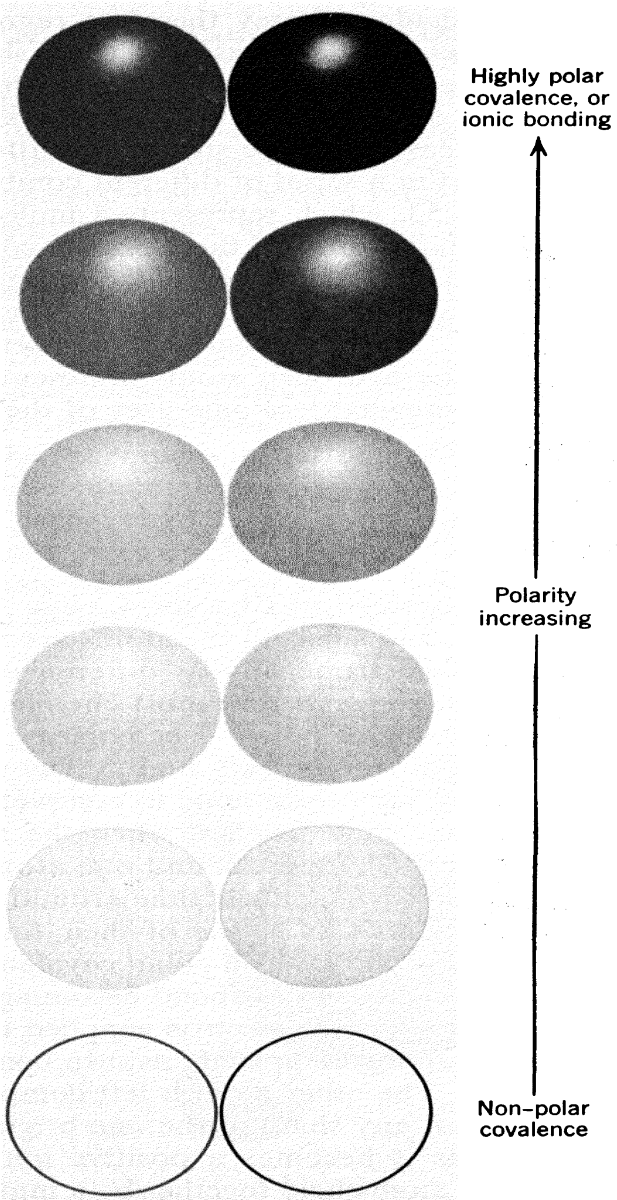


Figure 54. Representation of bond polarity.

Remember that covalent bonds are directional in nature. This directional nature can be described most easily as the result of repulsion among the outer electrons, such that their orbitals tend to point in directions as far removed from one another as possible. Polar covalent bonds likewise have these directional characteristics, but as the polarity approaches the extreme of forming a pair of ions these directional properties change. A charged particle extends its electrostatic field in all directions equally. Association through ionic bonding therefore cannot be expected to be limited to the formation of a pair of oppositely charged ions, but rather aggregates of ions will form and extend indefinitely in all directions in space. Such aggregates are called ionic crystals. They are invariably very symmetrical arrays of ions alternating in charge, such that each positive ion can be as close as possible to as many negative ions as possible, consistent with being as far removed as possible from other positive ions. Similarly, the negative ions will tend to collect around themselves as many positive ions as possible, while avoiding other negative ions.

A good example of an ionic compound is sodium chloride, NaCl. Sodium atoms, with their outer shells containing but a single electron, can unite with chlorine atoms, whose outer shells contain seven electrons but only one vacancy, through formation of a single covalent bond, and this should complete the bonding for both. However, sodium is of very low electronegativity (0.85), and chlorine is of very high electronegativity (3.28). Consequently the electron pair that should form the covalent bond is very unevenly shared. In effect, the chlorine gains the electrons practically completely—its own as well as one from the sodium—and thus becomes a chloride ion, Cl^-. The sodium is left with no share in the electron from the chlorine and its own electron removed, and hence bears a positive charge, as the ion Na^+. In this particular combination of oppositely charged ions, the resulting solid structure is quite simple. Each sodium ion becomes surrounded by six chloride ions, and each chloride ion by six sodium ions, as shown in Figure 56. X-ray examination of such a crystal shows that all six distances are identical, and therefore no one ion can be described as belonging to any particular one of the six opposite ions surrounding it. Thus, in the solid state of the ionic crystal, no NaCl molecules have any independent existence. In ionic compounds, it is inaccurate to say that the basic units are molecules. However, if sodium chloride is evaporated, which requires a very high temperature because of the strength of the electrostatic attractions to be overcome, NaCl molecules occur as individual units of the vapor.

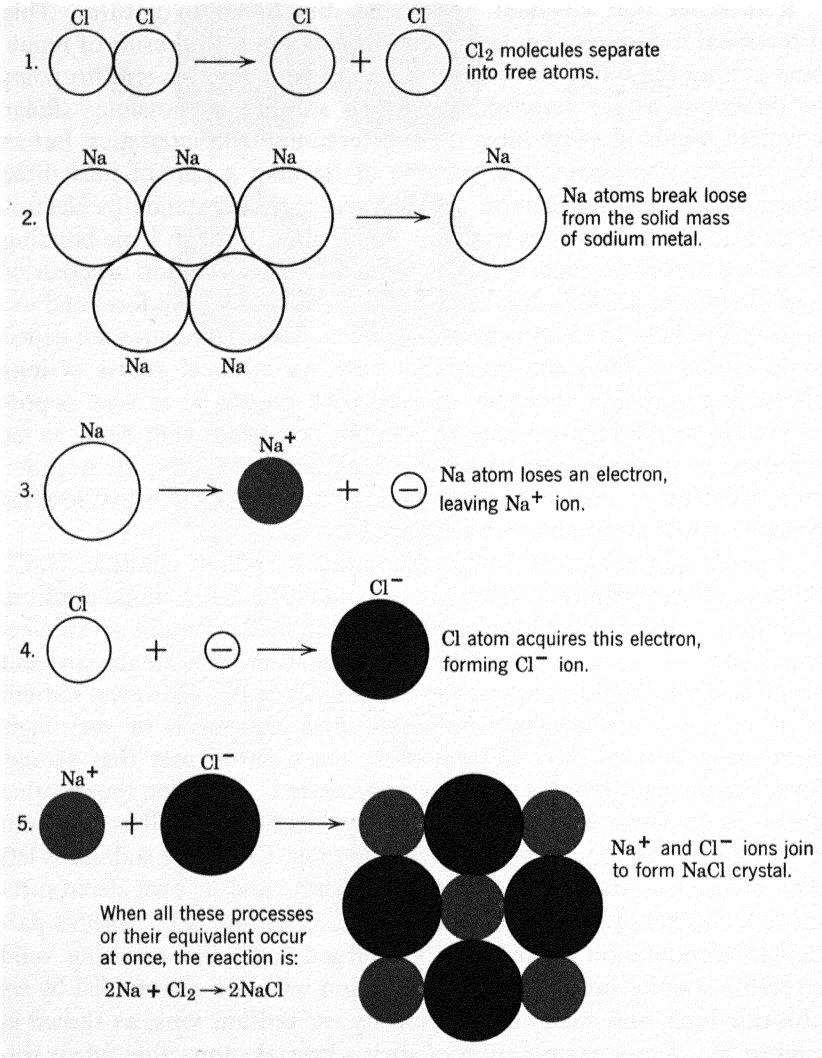


Figure 55. Formation of sodium chloride.

If one estimates the partial charge on sodium and chlorine in NaCl, one finds that they do not come out $+1$ and -1, but rather 0.67 for the sodium and -0.67 for the chlorine. At the present time, the question of whether individual sodium chloride molecules, such as occur in the vapor, are merely pairs of ions or truly polar molecules as indicated by charge remains controversial. This much seems to be well es-

tablished, however: When the bonds are about 50 per cent or more ionic, by the method of calculation described earlier, condensation of the molecules to ionic crystals occurs. Thus what one would calculate to be highly polar molecules turn out actually as ionic compounds. One might liken the positive ions in an ionic crystal to those in a metallic lattice, with this important difference. In each, the ion is surrounded by electrons, but whereas the electrons are relatively non-localized and mobile in metals, they are localized in pairs on the negative ions. Only those elements farthest apart in electronegativity form ionic crystals—especially the IA and IIA oxides and halides.

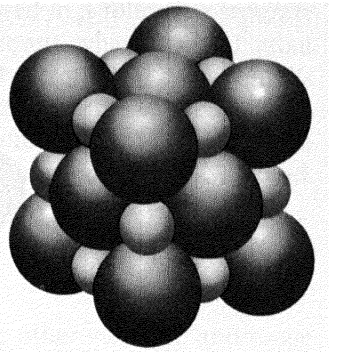


Figure 56. Sodium chloride—an ionic crystal.

COORDINATION

A variation of covalence can occur when, instead of each atom providing one electron and one vacancy to the bond, one atom supplies both electrons and the other atom an empty outer orbital. Such a bond is called a "**coordinate covalent**" bond. The atom supplying the pair of electrons is called the "**donor,**" or commonly the "**ligand.**" The terms "donor" and "ligand" apply also to molecules or complex ions containing the atom that supplies the pair of electrons. The atom having the available orbital is called the "**acceptor,**" or this term may be applied to a molecule containing such an atom. Coordinate covalent bonds form relatively rarely with atoms whose normal covalent capacity is not already used, but they are very common among compounds or ions whose normal covalence is filled. For example, boron, having only three outermost electrons per atom, can form only three covalent bonds, but having done so can still supply its fourth, empty orbital as an acceptor. Nitrogen, having five outermost electrons but only three vacancies, can form three single covalent bonds, and having done so has a pair of electrons that can be donated. Nitrogen in NH_3, for example, can donate an electron pair to boron in BCl_3, forming a coordination bond between the nitrogen and boron, the resulting molecule, $Cl_3B \cdot NH_3$, being called an "**addition compound.**"

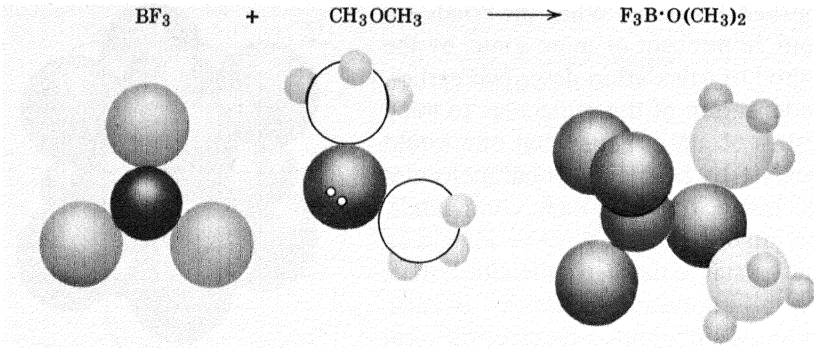


Figure 57. Formation of a molecular addition compound (coordinate covalent bond).

KINDS OF COMPOUNDS

Many kinds of compounds are possible, and many examples will be studied in later chapters. Here it may be helpful to consider some of the more important possibilities.

Molecular

When two or more nonmetallic elements unite, they form, through covalence, simple molecules in which all outer orbitals not involved in the bonding are filled with electrons. Intermolecular association is thus relatively slight, depending mainly on van der Waals interactions. The compounds are relatively nonpolar, low melting, and volatile. Such compounds can be formed between any two (or more) nonmetals. Some examples are: water, H_2O, a liquid; ammonia, NH_3, a gas; methane, CH_4, a gas; chloroform, $CHCl_3$, a liquid; carbon tetrachloride, CCl_4, a liquid; carbon dioxide, CO_2, a gas; phosphorus oxide, P_4O_{10}, a volatile solid. Included in this class might be the hydrocarbons and

their derivatives, which are, however, discussed in a following separate section. Molecular compounds also can result when a metal atom is combined with enough nonmetal atoms to surround it, preventing its contact with other atoms and thus permitting only van der Waals interactions between nonmetal exteriors. Some examples are $SnBr_4$, a liquid; $SbCl_5$, a volatile solid; OsO_4, a volatile solid; Mn_2O_7, a liquid.

Oxides

These are compounds of oxygen with one other element, and range in properties from volatile molecular oxides of nonmetals to relatively nonvolatile ionic crystalline oxides of metals. Oxides of all but the inert elements exist. Examples are Na_2O, MgO, Al_2O_3, SiO_2 (all nonvolatile solids); H_2O (liquid); N_2O_5 (volatile solid); CO_2 (gas); SO_3, Cl_2O_7 (volatile liquids).

Acids

These are usually molecular compounds, and are variously defined. The simplest definition, sufficient for present purposes, is any compound containing hydrogen and losing a proton to water in solution. A much more detailed explanation is deferred to Chapter 18, but we can observe here that water itself forms very small concentrations of ions:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

(Notice the use of opposed arrows to denote a reversible reaction.) The **hydronium ion,** H_3O^+, which consists of a proton attached to a water molecule, gives to a solution properties called "**acidic**": sour taste, ability to dissolve metal oxides and to neutralize bases, and corrosive action on some metals. The hydroxide ion, OH^-, gives to a solution properties called "**basic**": bitter taste, soapy feeling, ability to dissolve nonmetal oxides and to neutralize acids. Since these ions are formed from water in exactly equal and very small concentrations, water is neutral, having acid and base properties only to a relatively small extent.

An acid as defined above forms hydronium ion in water by losing a proton to water. The solution thus contains a surplus of H_3O^+ ions over OH^- ions and has acidic properties. Common acids are, hydrochloric acid (HCl gas dissolved in water); sulfuric acid, H_2SO_4; nitric acid,

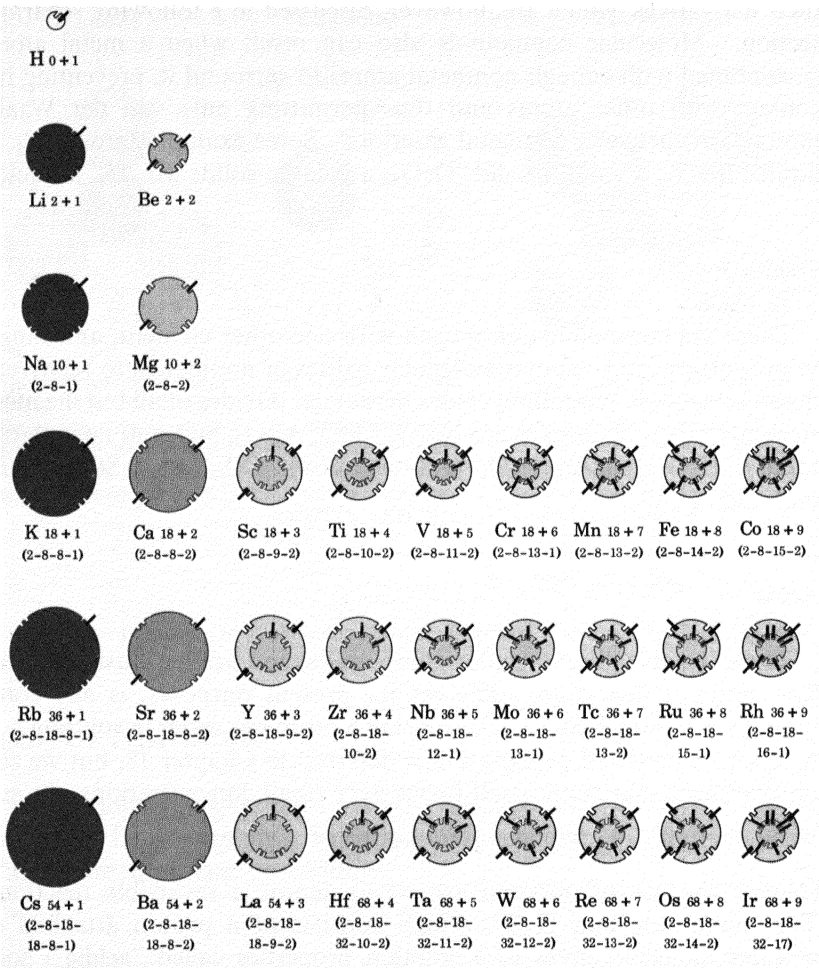
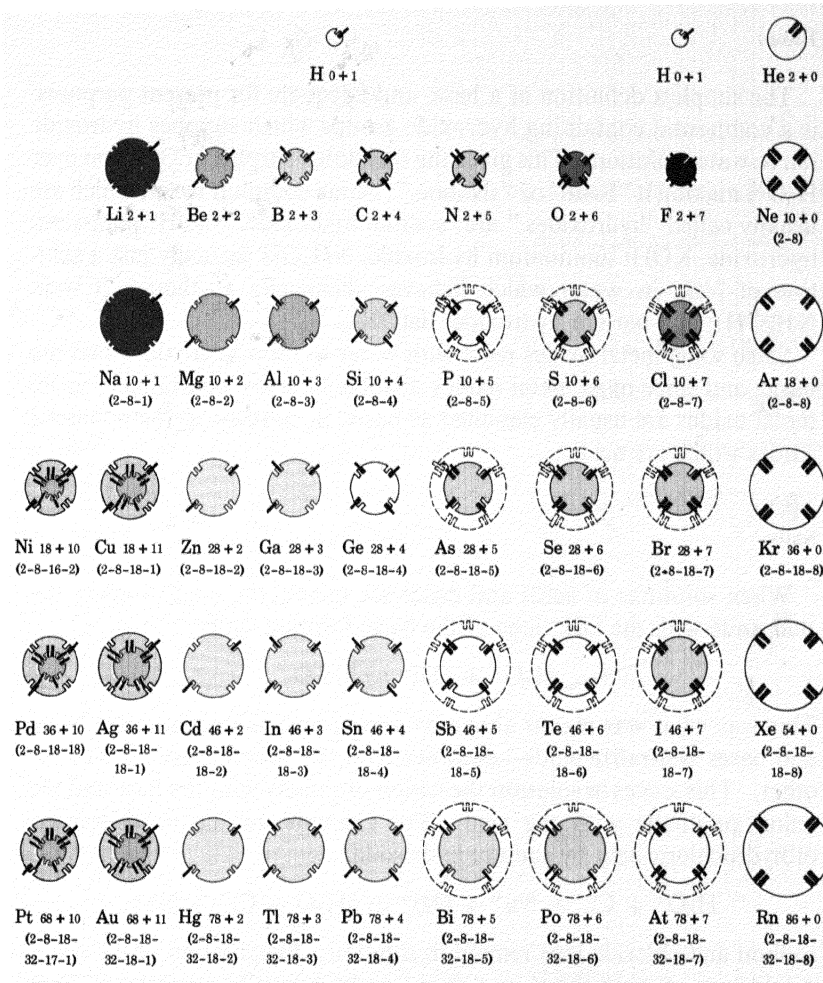


Figure 58. Valence structure of the elements. These atoms are like those on p. 66, but in addition show electronegativity

HNO_3; and phosphoric acid, H_3PO_4. All produce H_3O^+ in water by similar reactions:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^=$$
$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$



both by color and by depth of wells. Inner *d* orbitals are represented by inner circles and outer *d* orbitals by broken line circles.

Oxides of nonmetals tend to be acidic because they react with water to form acids:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3$$
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Bases

The simplest definition of a base, and adequate for present purposes, is a compound containing hydroxide groups which supplies hydroxide ion in water solution. This gives the solution a surplus of OH^- ion over H_3O^+, making it "**basic**" or "**alkaline.**" Some common bases, which are usually called "hydroxides," are: sodium hydroxide, NaOH; potassium hydroxide, KOH; ammonium hydroxide, NH_4OH (actually just a solution of NH_3 in water which behaves chemically as though it were NH_4OH); and barium hydroxide, $Ba(OH)_2$.

Since some metal oxides react with water to form hydroxides that are basic, and since most metal oxides dissolve in acids, neutralizing them, metal oxides are usually classified as basic, in contrast to the nonmetal oxides which are acidic.

Salts

When solutions of acids and bases are mixed, the H_3O^+ ions of the acid unite with the OH^- ions of the base, forming water:

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

This was what was meant above by saying that acids neutralize bases and bases neutralize acids—each destroys the characteristic ion of the other. This leaves in solution the cation originally with the base and the anion originally with the acid. For example, in the neutralization of hydrochloric acid by sodium hydroxide,

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightleftharpoons 2H_2O + Cl^- + Na^+$$

sodium and chloride ions remain in solution. Evaporation of the water would leave them behind, and they would naturally combine to form crystalline sodium chloride. This is commonly known as "salt." A salt in general may be defined as a combination of any cation other than hydronium ion with any anion other than hydroxide ion. Aqueous neutralization is said to form water and a salt—as you can see, the salt formation, in water, always happens but is incidental to the real reaction.

Since metals in general can form cations, and nonmetals in general can form anions, any binary compound (two elements) of metal with nonmetal may be termed a salt, except that oxides are conventionally classified separately. When the cation consists of only one element, and the anion of only one element, the combination is called a "simple" salt. Some examples are: NaCl, ZnS, CaI_2, Na_3As, BaSe. All such salts are solids.

When the cation or anion contains more than one element, it is called "**complex,**" and the salts derived from it are called complex salts. Two kinds of complex ion can occur, one in which the bonding is not coordinate covalent, and the other in which the central atom is acceptor to a number of donor ions or molecules. Examples of the first type are produced when oxides other than water combine. A basic oxide (metal oxide) can unite with an acidic oxide (nonmetal oxide) to form a complex salt:

basic oxide		acidic oxide		complex salt
Na_2O	+	CO_2	→	Na_2CO_3
CaO	+	SO_3	→	$CaSO_4$

Examples of the second type are: $[Co(NH_3)_6]Cl_3$; $[Al(H_2O)_6]Br_3$. Thousands of such compounds are known.

Organic Compounds

Organic compounds are compounds of carbon and hydrogen, called "**hydrocarbons,**" and compounds derived from them by substituting other atoms or groups of atoms in place of one or more hydrogen atoms. Most of these could be classed as molecular compounds, being low-melting solids or volatile liquids. Some examples are: ethane, C_2H_6; ethyl alcohol, C_2H_5OH; formaldehyde, HCHO; acetic acid, CH_3COOH.

Molecular Addition Compounds

As indicated earlier, these are the products of coordinate covalent bond formation between neutral molecules. Most commonly they form between IIIA compounds, in which the central atom has an empty orbital and can act as acceptor, and VA or VIA compounds, in which the central atom has one or two pairs of outer electrons available to donate. Typical acceptors, donors, and products are listed in Table 7.

Table 7 Typical Acceptors, Donors, and Addition Compounds

ACCEPTORS	DONORS	ADDITION COMPOUNDS (OR COMPLEX IONS)
BF_3	$(CH_3)_2O$	$BF_3 \cdot O(CH_3)_2$
BCl_3	$N(CH_3)_3$	$BCl_3 \cdot N(CH_3)_3$
$AlCl_3$	NH_3	$AlCl_3 \cdot NH_3$
Be^{++}	H_2O	$[Be(OH_2)_4]^{++}$
Ag^+	CN^-	$Ag(CN)_2^-$

Polymers

Many compounds, both organic and inorganic, exist in which chemical bonds either hold the entire mass of matter together, or the individual molecules are extremely large, containing many thousands of atoms. Such compounds are commonly known as "**high polymers.**" Examples are plastics, proteins, and complex minerals.

KINDS OF CHEMICAL REACTION

Direct Synthesis

Many compounds can be formed by direct combination of the component elements. This process is called "**direct synthesis.**" For example, hydrogen burns in chlorine:

$$H_2 + Cl_2 \rightarrow 2HCl$$

It also burns in air (oxygen):

$$2H_2 + O_2 \rightarrow 2H_2O$$

When zinc is heated with sulfur, the two unite:

$$Zn + S \rightarrow ZnS$$

Displacement

Often one element will displace another from its compound. For example, sodium displaces hydrogen from water:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

Or, aluminum displaces iron from its oxide:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

Double Displacement, or Double Decomposition, or "Metathesis"

Many reactions can be classified as "partner-swapping" reactions. For example:

$$3LiH + AlCl_3 \rightarrow AlH_3 + 3LiCl$$

Often such reactions occur when solutions of two salts are mixed and a new combination of ions would yield an insoluble salt, which then separates—"**precipitates**"—from solution:

$$\underset{\text{soluble}}{BaS} + \underset{\text{soluble}}{ZnCl_2} \rightarrow \underset{\text{insoluble}}{ZnS} + \underset{\text{soluble}}{BaCl_2}$$

Of course, aqueous acid-base neutralization could be included:

$$KOH + HI \rightarrow KI + H_2O$$

Such reactions are called "**metathetical,**" or more commonly "**double decomposition.**"

Addition

Sometimes a compound can simply add on more atoms. For example, carbon monoxide, CO, can add oxygen to become carbon dioxide, CO_2; zinc sulfide, ZnS, can add on oxygen to become zinc sulfate, $ZnSO_4$; copper sulfate, $CuSO_4$, can add water to become $CuSO_4 \cdot 5H_2O$.

Decomposition

Relatively complex compounds are usually broken down to simpler compounds, or even to the free elements, by heat. Even the simplest binary compounds may come apart the more easily the less stable their bonds, to liberate the component elements. Such reactions, often involving a single reactant, are called "**thermal decomposition,**" "**pyrolysis,**" or just plain "decomposition." Some examples are:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$2HgO \rightarrow 2Hg + O_2$$

Other Types

Many variations of the above exist. Indeed, many mechanisms of reaction appear possible, and some reactions that we classify alike, judging only by the net result, may in detail be quite dissimilar.

SPECIAL HELP

Test Your Memory

1. What is meant by "expanding the valence octet"?
2. Why does this produce two new bonds at once, instead of one at a time?
3. What is meant by "resonance hybrid"?
4. Define "electronegativity."
5. What is the "ionization potential"?
6. How does ionization potential change with atomic structure?
7. Define "electron affinity."
8. What is the relation of covalent radius to bond length?
9. Distinguish between covalent and van der Waals radius.
10. State the "principle of electronegativity equalization."
11. What is meant by "partial charge" of an atom?
12. What is a polar bond?
13. How does a coordinate covalent bond differ from an ordinary covalent bond?
14. Define: ligand, acceptor, donor.
15. Define: molecular compound, oxide, acid, hydronium ion, base, salt, organic compound, molecular addition compound.
16. What kind of chemical reaction is involved in each: direct synthesis, displacement, double displacement, metathesis, addition.

Test Your Math

1. How much sulfur would remain unchanged if 100 g reacts as far as possible with 40 g of cadmium?
2. Aluminum, 54 g, is heated with 50 liters of chlorine (at SC) until one or the other is completely combined. How much of what product is formed, and how much of which element remains?
3. By heating 20 g of barium sulfate with excess coke (consider it to be pure carbon), barium sulfide results. How much of it is formed, and what volume of CO is the other product?
4. A compound of phosphorus and iodine is treated with water to convert all the iodine to hydrogen iodide, which is then heated with zinc to form zinc iodide and hydrogen gas. What weight of water could be obtained by burning this gas if the initial weight of phosphorus was 340 g?

5. An oxide of iron of formula Fe_2O_3 is heated with carbon to liberate iron. The iron is treated with chlorine to form the (III) chloride, which is then heated with steam to convert all the chlorine to hydrogen chloride. Six moles of this compound results from how much iron oxide?

Test Your Understanding

1. Carbon atoms can form four single bonds, and hydrogen atoms only one single bond. How can a compound exist having the molecular formula, C_2H_2?
2. Known compounds of sulfur and fluorine have the formulas SF_2, SF_4, and SF_6, but SF_3 and SF_5 are unknown. Explain.
3. Why do neither ionization energy alone nor electron affinity alone suffice as a measure of electronegativity?
4. What does a shorter-than-expected bond length suggest about the nature of the bond?
5. What can be said about the bonding in any noncyclic triatomic molecule which is linear?
6. What does a pyramidal structure in a compound having three covalent bonds per molecule tell us about the presence or absence of outer unpaired electrons?
7. What kind of aggregation would you expect of a combination of Group IVA and VIA elements neither of which can form multiple bonds?
8. Predict a formula and structure for cadmium telluride.
9. What kind of atomic structure would be most likely in an element which can form long chains of like atoms, if no other elements are present?
10. In which compound, CH_4 or CHF_3, would you expect the more polar C-H bond, and why?
11. In which compound, CH_3Cl or CCl_4, would you expect a higher charge on chlorine, and why?
12. Write empirical formulas for each of the following compounds: (*a*) sodium bisulfite, (*b*) indium sulfate, (*c*) lithium carbonate, (*d*) ammonium phosphate, (*e*) zinc bisulfate, (*f*) magnesium bicarbonate, (*g*) aluminum nitrate.
13. Write empirical formulas for each of the following combinations of elements: (*a*) cadmium and sulfur, (*b*) magnesium and oxygen, (*c*) chromium and oxygen, (*d*) hafnium and fluorine, (*e*) rubidium and

phosphorus, (*f*) mercury and sulfur, (*g*) selenium and aluminum, (*h*) arsenic and lithium, (*i*) calcium and phosphorus, (*j*) barium and nitrogen, (*k*) bromine and titanium, (*l*) vanadium and oxygen.

14. Write electronic formulas for each of the following compounds, for which only the elements are given: (*a*) hydrogen and germanium, (*b*) phosphorus and bromine, (*c*) sodium and tellurium, (*d*) sulfur and chlorine, (*e*) cesium and chlorine, (*f*) gallium and fluorine, (*g*) zinc and iodine, (*h*) nitrogen and hydrogen, (*i*) a compound of boron and fluorine united with a compound of hydrogen and oxygen.

10

Oxidation and Reduction

MANY OF THE ELEMENTS form two or more compounds of different formulas with the same element. Some examples are $FeCl_2$, $FeCl_3$; N_2O, NO, N_2O_3, NO_2, N_2O_5; MnO, Mn_2O_3, MnO_2, Mn_2O_7. In recognition of this fact, a rather arbitrary method of distinguishing among such compounds has been devised.

OXIDATION NUMBERS

This method tries to indicate, simply, two aspects of valence: (1) How many of a given atom's electrons would be involved in its polar bonding if the polar bonds formed by the atom were all single covalent bonds or integral multiples thereof; and (2) as the result of initial electronegativity differences, is the combined atom more negative or more positive than in the uncombined element. These are indicated by (1) a number and (2) a plus or minus sign. The combination of sign and number is called the **"oxidation state"** or **"oxidation number"** of that atom in that compound. The assignment of oxidation number can best be understood from a few simple rules and applications.

1. A bond between two atoms of the same element in a molecule is considered to contribute nothing to the oxidation number. The oxidation state or oxidation number—the two terms are used practically interchangeably—of any element in its "free" state is therefore 0, no matter how many bonds may exist among the component atoms.

2. Except where a bond between two oxygen atoms is involved, or in compounds of oxygen with fluorine (the only element more electronegative than oxygen), the oxidation number of combined oxygen is always taken as -2, because oxygen forms two single covalent bonds or their equivalent and becomes negative.

3. In the great majority of its compounds hydrogen is assigned the oxidation number of $+1$. In its hydrides, compounds with less electronegative elements such as the metals, hydrogen has the oxidation number of -1.

4. Except in combination with oxygen or fluorine, the halogens normally are present in compounds in the oxidation state of -1. Combined fluorine is always -1.

5. Oxidation numbers of simple monatomic ions are always the same as their charges.

6. The formation of coordination bonds is not considered to influence the oxidation number of any of the elements involved.

7. The sum of the oxidation numbers in a compound must equal zero, and in a complex ion it must equal the charge on that ion.

The above rules are sufficient for assigning correct oxidation numbers to all the elements in most compounds wherein the assignment of oxidation numbers has much utility. Rule 7 states, in effect, that if we know the oxidation number of each element but one, in a given combi-

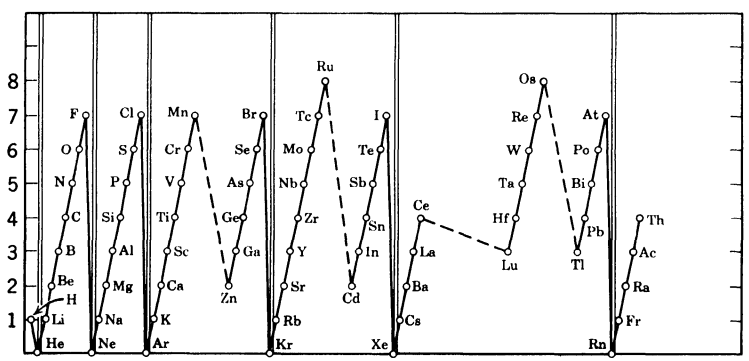


Figure 59. Maximum oxidation states of the elements: variation with atomic number.

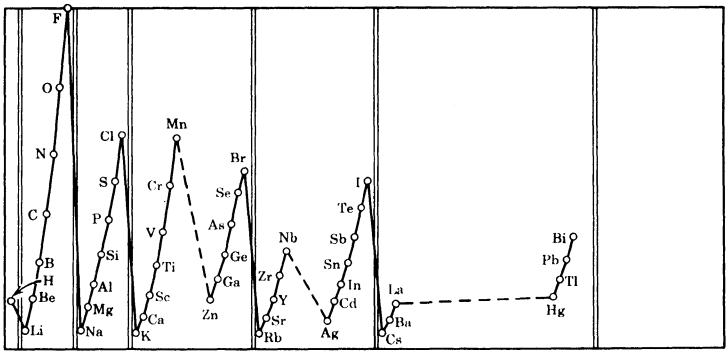


Figure 60. Average of ionization energies needed to produce maximum oxidation states of elements.

nation, we can easily calculate the value for that one. It will be the value needed to bring the total to zero for a compound, or to the charge on a complex ion.

Suppose, for example, we wish to know the oxidation state of phosphorus in the compound $Mg_2P_2O_7$. We know that oxygen must be $-2, \times 7 = -14$. We also know that magnesium is $+2, \times 2 = +4$. That leaves -10 to be balanced by the two phosphorus atoms, which therefore must be $+5$ each.

TERMINOLOGY AND NOMENCLATURE

The naming of chemical compounds has in many instances become unacceptably complex or confusing. Whereas sodium only forms one chloride, NaCl, which can therefore unambiguously be called "sodium chloride," copper and iron each form two chlorides, of empirical formulas CuCl and $CuCl_2$, $FeCl_2$ and $FeCl_3$. In general, the old practice is to call the lower of two positive states the "**-ous**" and the higher, the "**-ic**." Here the $+1$ state of copper is commonly called "cuprous," and the $+2$ state "cupric." Similarly, the $+2$ iron is "ferrous," and the $+3$ iron "ferric." But what about manganese, which can form $MnCl_2$, $MnCl_3$, and $MnCl_4$? If we call the first "manganous," then is the second or third the "manganic," and what is the other? Sometimes such a difficulty is surmounted by calling the compounds "manganese dichloride," manganese trichloride," and "manganese tetrachloride." Or, consider the oxides B_2O_3, Al_2O_3, N_2O_3, and As_2O_3. We are likely to find these called "boric oxide," "aluminum oxide," "nitrogen sesqui-

oxide," and "arsenic trioxide." (Sesqui- means one-and-one-half). To be consistent and also accurate, we should probably name these "diboron trioxide," "dialuminum trioxide," dinitrogen trioxide," and "diarsenic trioxide," but these names are unfamiliar to practicing chemists. A system which has been proposed and to a limited extent adopted is to use Roman numerals in parentheses immediately following the name or symbol of the element, to correspond to its positive oxidation state, assuming that the negative oxidation state of the other element in a binary compound is perfectly unambiguous and not necessary to mention. Thus the above chlorides of manganese would be called "manganese(II) chloride," "manganese(III) chloride," and "manganese(IV) chloride." Cuprous chloride would be called "copper(I) chloride," and cupric chloride, "copper(II) chloride." Instead of "ferrous" and "ferric," "iron(II)" and "iron(III)" would be used. This system is called the **"Stock system"** after the German chemist who first proposed it. It is not perfect, but seems better than most, and is used enough to justify our learning about it. Often in this book, however, as in most books, this system is not used because the "trivial" name or the ordinary chemical name leaves no doubt as to the identity of the compound. For example, we know that magnesium forms but one chloride, of formula $MgCl_2$. We might call this "monomagnesium dichloride," or "magnesium(II) chloride," but everyone concerned knows that just plain "magnesium chloride" is $MgCl_2$, and elaboration is not needed.

Consistent with this Roman numeral designation of oxidation states, we frequently have occasion to speak of compounds of a given element in a given oxidation state, and may use this system. For example, thousands of complexes of "cobalt(III)" are known, and many more of "cobalt(II)." These terms refer to coordination complexes consisting of ligands attached either to Co^{+++} or Co^{++} ions.

LIMITATIONS

Although oxidation numbers and oxidation states have a number of useful applications, we must bear in mind that their application does not always make good sense, and never do these numbers tell us any more than they are claimed to tell. For instance, phosphorus atoms in PF_3 doubtless have electrons withdrawn from them to a substantially greater degree than the phosphorus atoms in PCl_5. In the former the oxidation state of phosphorus is $+3$, in the latter $+5$. This means only that three single bonds or five single bonds are formed, and that the phosphorus becomes positive. It does not necessarily mean that the

positive charge on phosphorus in PF_3 must be smaller than in PCl_5, for it is actually the opposite. Atoms of the same element, compared in two different chemical compounds, may have formally the same oxidation number, but they may actually be in very different condition.

APPLICATIONS OF OXIDATION NUMBERS: OXIDATION-REDUCTION

The concept of bond polarity as arising from initial electronegativity differences has already been discussed. We have seen that in most combinations of the elements, the electrons become unevenly shared, imparting partial negative charge to the atoms acquiring more than a half share and partial positive charge to the atoms left with less than a half share. Oxygen is especially familiar and is especially noted for taking more than a half share of valence electrons. What oxygen does, in almost all instances, is called "**oxidation,**" and this word has become synonymous with "electron-withdrawal from." That is, any chemical reaction that removes electrons from an atom as oxygen would do is called "oxidation," even if oxygen is not involved at all. For example, chlorine, which likewise is high in electronegativity, and tends to take electrons from other atoms, is called an "**oxidizing agent**"; the process of chlorination is a form of "oxidation."

Clearly there can be no electron removal without electron donation as well as acquisition. Nothing can take away electrons unless something else can donate them. Oxidation, the taking away of electrons from something, is therefore only half the total process. The other half is the giving up of the electrons—they cannot be taken unless they are also given. Metals in compounds are always positive, which means they must have lost electrons, and the process of recovering metals from their compounds therefore is a process of giving the electrons back to the metals. This has been known industrially as the "reducing" of ores, and from this term, "**reducing**" and "**reduction**" have come to mean, in general, any process of giving electrons to something. The other half of the process of oxidation is therefore called the process of reduction, and we speak of the whole process as "**oxidation-reduction**" (often abbreviated, "**redox**").

Oxidation and reduction have been arbitrarily defined in terms of oxidation numbers. This practice has proven useful in many instances, but unfortunately, it is misleading in many instances also. Nevertheless, certain applications are quite useful to us, and since the concept is generally used in chemistry we ought to understand it.

Oxidation-reduction is a process in which oxidation numbers of

at least some of the elements change. The oxidation number of at least one element must be less negative or more positive in the products than it was in the reactants. The oxidation number of at least one other element, or of the same element in a different part of the products, must be less positive or more negative than in the reactants. Unless there is a change in at least some of the oxidation numbers, the reaction cannot, by this definition, be called "oxidation-reduction."

The oxidizing agent is the element (or the compound containing the element) whose oxidation number becomes more negative or less positive in the reaction. The reducing agent is the element (or the compound containing the element) whose oxidation number becomes less negative or more positive. Thus, the oxidizing agent is *reduced* and the reducing agent is *oxidized* in the reaction.

These definitions are helpful in balancing oxidation-reduction equations, because the total number of electrons lost must equal the number gained. To write a balanced equation, one first writes down the formulas of all the reactants and all the products. One then writes over these the oxidation number of each element in each compound. If these are unchanged in the reaction, of course, the reaction is not oxidation-reduction. Most commonly, only one element will become more positive and one more negative, or, sometimes, the same element will become both, in two different products. In either case, the electron "transfer" (even though it was probably *not* complete) is summarized below the equation. From this summary, one can see how many atoms of each are needed in order to maintain an electron balance in the reaction. For example, let us consider the simple oxidation of sodium by chlorine:

$$\overset{0}{\mathrm{Na}} + \overset{0}{\mathrm{Cl_2}} \rightarrow \overset{+1\ -1}{\mathrm{NaCl}}$$

$$\mathrm{Na} \rightarrow \mathrm{Na^+}, \text{ loss } 1e^-$$

$$\mathrm{Cl_2} \rightarrow 2\mathrm{Cl^-}, \text{ gain } 2e^-$$

We see that since chlorine occurs as Cl_2, the minimum gain of electrons must be 2, whereas each sodium atom can lose but one. Obviously, it will take two sodium atoms to reduce the two chlorine atoms, and the completed equation is

$$2\mathrm{Na} + \mathrm{Cl_2} \rightarrow 2\mathrm{NaCl}$$

Use of this method in so simple an application is clearly unnecessary, since we could easily have completed the equation from inspection. However, the method, of which numerous modifications are in use, can

be very helpful in more complicated equations. For example, the manufacture of nitric acid involves the action of nitrogen(IV) oxide on water, forming nitric acid and the (II) oxide:

$$\overset{4\ -2}{NO_2} + \overset{1\ -2}{H_2O} \rightarrow \overset{1\ 5\ -2}{HNO_3} + \overset{2\ -2}{NO}$$

$$N + 4 \rightarrow N + 5;\ \text{loss } 1e^-$$

$$N + 4 \rightarrow N + 2;\ \text{gain } 2e^-$$

This little summary tells us that for every nitrogen atom that is reduced from NO_2 to NO, two are oxidized to HNO_3. Therefore a minimum of 3 moles of NO_2 are needed, one to form NO and two to form $2HNO_3$. The completed equation is:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

As another example, consider the fact that although silver is unaffected by dilute sulfuric acid, it will dissolve in concentrated sulfuric acid —that is, in H_2SO_4 containing relatively little water. We cannot complete any chemical equation unless we know what the reactants and products are. In this particular reaction, we must know at the start that the products are silver sulfate, water, and sulfur dioxide.

$$\overset{0}{Ag} + \overset{1\ 6\ -2}{H_2SO_4} \rightarrow \overset{1\ 6\ -2}{Ag_2SO_4} + \overset{4\ -2}{SO_2} + \overset{1\ -2}{H_2O}$$

$$Ag\ 0 \rightarrow Ag\ 1;\ \text{loss } 1e^-$$

$$S\ 6 \rightarrow S\ 4;\ \text{gain } 2e^-$$

Notice that to have an electron balance, two silver atoms must each give up one electron before one sulfur can gain the necessary two. Therefore one molecule of sulfuric acid is sufficient to oxidize two atoms of silver. But notice here also—and this is especially important because it occurs so commonly in such reactions—that part of the sulfur did not act as oxidizing agent, but only to form silver sulfate, in which the sulfur has the same oxidation number as it did in the sulfuric acid. We need therefore to have present two molecules of sulfuric acid for each two silver atoms to be oxidized: one molecule to do the oxidizing, and the other just to form the sulfate. The completed equation must take this into account, as well as the requirements for a balanced electron transfer:

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

Whenever an oxyacid acts as an oxidizing agent, its hydrogen atoms are adequately accounted for in the amount of water that forms.

It might be helpful in understanding the significance of the two-fold function shown by sulfuric acid in the above reaction to imagine the reaction as occurring in two parts. The first part is the oxidation, forming silver oxide. The second part is the dissolving of the oxide in sulfuric acid, forming the silver salt and water:

$$2Ag + H_2SO_4 \rightarrow Ag_2O + SO_2 + H_2O$$
$$Ag_2O + H_2SO_4 \rightarrow Ag_2SO_4 + H_2O$$

The sum of these two equations, only the first of which is an oxidation-reduction, is the equation given above. Because the oxide reacts with the acid it would not form in the reaction in recognizable amounts even as an intermediate. Nevertheless, it is helpful to think of such reactions as involving (which in effect they do) (1) oxidation of the metal to the oxide with concurrent reduction of the acid, and (2) neutralization of the metal oxide (basic) by the acid, forming the metal salt of the acid plus water.

SPECIAL HELP

Test Your Memory

1. What does an oxidation number signify?
2. What is the common oxidation state of combined oxygen?
3. What is the "Stock system" name for PCl_5?
4. What is the relationship between oxidation-reduction and oxidation numbers?
5. What steps are desirable in completing an oxidation-reduction equation?

Test Your Math

1. What is the oxidation number of the central atom in each of the following ions? SO_4^{2-}, HCO_3^-, $CoCl_6^{3-}$, $P_2O_7^{4-}$, SeO_3^{2-}, $Ag(NH_3)_2^+$, ClO_4^-, PO_4^{3-}, NO_3^-?
2. What is the oxidation state of sulfur in each of the following compounds: H_2SO_3, Na_2SO_3, $MgSO_3$, ZnS, BaS_2O_7, SO_2, SO_3, $KHSO_4$?

Test Your Understanding

1. Since fluorine is much more electronegative than iodine, why is not the oxidation state of boron in BF_3 higher than in BI_3?
2. How could cobalt be in the same oxidation state in both $[Co(NH_3)_6]^{3+}$ and $[CoCl_6]^{3-}$?
3. Can a reaction occur in which only one element changes in oxidation number?
4. Complete equations for each of the following reactions:

(*a*) Hydrogen peroxide, H_2O_2, plus lead sulfide, PbS, form lead sulfate, $PbSO_4$, and water.

(*b*) Potassium permanganate, $KMnO_4$, sulfuric acid, and sodium chloride form chlorine, sodium bisulfate, $NaHSO_4$, potassium sulfate, K_2SO_4, manganese(II) sulfate, $MnSO_4$, and water.

(*c*) Sodium sulfite, Na_2SO_3 reacts with iodine, I_2, and water to form sodium sulfate Na_2SO_4 and hydrogen iodide.

(*d*) Nitrous acid HNO_2 and hydrogen iodide form nitrogen(II) oxide, iodine, and water.

(*e*) The same products are formed by action of nitric acid on hydrogen iodide.

(*f*) Iron(III) sulfate and potassium iodide form iron(II) sulfate, potassium sulfate, and iodine.

(*g*) Arsenous oxide, or arsenic(III) oxide, As_2O_3, reacts with iodine and water to form hydrogen iodide and arsenic(V) oxide, As_2O_5.

(*h*) Potassium dichromate $K_2Cr_2O_7$ with sulfuric acid and iron(II) sulfate form iron(III) sulfate, chromium(III) sulfate, potassium bisulfate $KHSO_4$ and water.

(*i*) Nitric acid and sulfur dioxide form sulfuric acid and nitrogen(IV) oxide.

(*j*) Potassium chlorate $KClO_3$ and hydrogen iodide and sulfuric acid react to form hydrogen chloride, $KHSO_4$, iodine, and water.

11

Structure and Physical Properties of Compounds

In CHAPTER 3, the general relationship between the structure of aggregates of atoms of the same element and the physical properties of that element was discussed in some detail. The same directional properties of covalence noted therein hold also for bonds and therefore structures of aggregates containing more than one element. The relationship between such structures and physical properties is similar. Just as in the free elements themselves, in compounds also the structures of the individual atoms determine the kinds of aggregates characteristic of the compound. The physical properties, however, depend *directly* on the nature of these aggregates, and only *indirectly* on the structures of the atoms. For example, striking differences in physical properties between graphite and diamond, or between red and white phosphorus, cannot be the result of differences in the atoms, which are all alike, but must be the result of differences in the structure, the way in which the atoms are connected.

In compounds, in addition to the effects arising from the geometric or spatial distribution of the atoms such as are significant in the free elements, the effects of differences in electronegativity among the com-

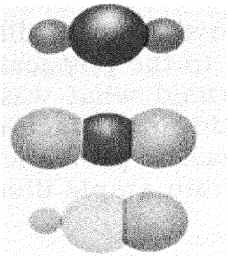
ponent elements are important. There are also significant differences in sizes of the different atoms which contribute to the physical properties of the compounds. We shall therefore extend what was said in Chapter 3 to include a discussion of these additional factors which become influential in compounds. Only the general principles will be discussed here; the following chapters will contain ample illustrations of their application.

BOND ANGLES

In compounds, as in the free elements, electron pairs on the surface of an atomic sphere tend to become separated as far from one another as possible. The effect on bond angles, when an atom forms more than one bond at the same time, is the same as that previously described. To review this briefly: When all the valence shell electrons of an atom are directly utilized in the formation of two bonds, whether single or multiple, the two bonds form an angle of 180°. When an atom forms only two bonds but electron pairs exist in its outer shell that are not involved in these bonds, then the effect on the bond angle is approximately that predictable by the same reasoning. If only one such unshared pair exists, the two bonds will form an angle of 120°, making a planar triangular configuration with the extra pair. If two such unshared pairs exist, the structure will be tetrahedral, the angle between the two bonds being close to 109°.

When all the valence shell electrons of an atom are directly utilized in the formation of three bonds, whether single or multiple, the bond angles are 120°, the structure being planar. But if a pair of electrons remains unshared, this will cause the bond angles to be more nearly tetrahedral, with resulting bond angles close to 109°.

When all the valence shell electrons of an atom are directly utilized in the formation of four bonds, the bond angles are normally near 109°, giving a tetrahedral distribution in space, that is, directed toward the corners of a regular tetrahedron. In addition, many compounds exist in which a central atom is surrounded by five or especially by six other atoms. The structure involving five bonds ordinarily is that of a trigonal bipyramid—three bonds directed toward the corners of an equilateral triangle in plane with the central atom, called the "equatorial" bonds, and one bond perpendicular to this plane upward and one downward, the "apical" bonds. With six bonds to the central atom, the farthest apart these can become located is at the corners of a regular octahedron around the central atom. Such a figure is formed by four bonds

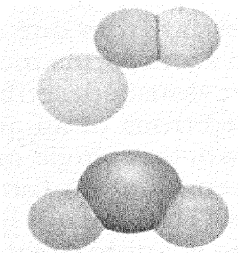


BeH_2 H:Be:H H—Be—H

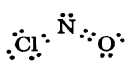
CO_2 :Ö::C::Ö: O=C=O

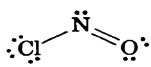
HCN H:C:::N: H—C≡N

When all outer electrons are used in only 2 bonds, a linear structure results (bond angle 180°). This is the farthest apart 2 electron groups can be.

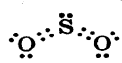


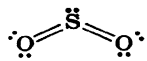
NOCl



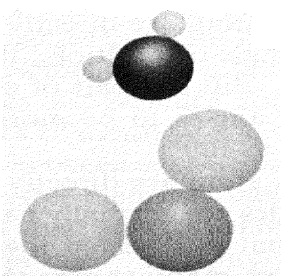


SO_2



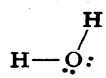


When only 2 bonds are formed, leaving an unshared electron pair, this pair causes the bonds to be bent at about 120°, itself filling the third corner of a triangle. Three groups of electrons can separate no farther than this on an atom.



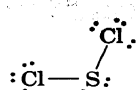
H_2O





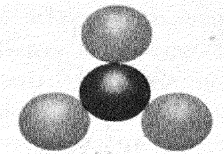
SCl_2





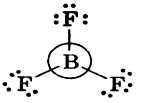
When only 2 bonds are formed, leaving 2 unshared electron pairs, these pairs occupy 2 corners of a regular tetrahedron, and the 2 bonds occupy the other 2 corners (bond angle 109°28′, but sometimes less, down to 90°).

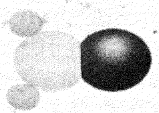
Figure 61. Directional nature of covalence.



BF_3

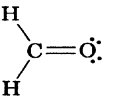




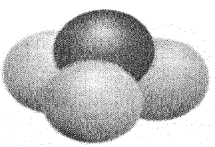


H_2CO

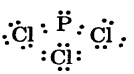


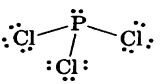


When all outer electrons are used in only 3 bonds, these are directed as far apart as possible, toward the corners of a triangle (bond angles 120°). The structure is planar.



PCl_3

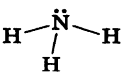




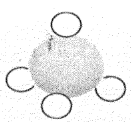


NH_3



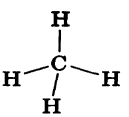


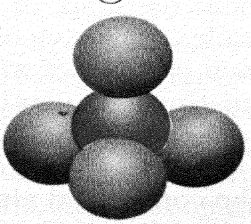
When formation of 3 bonds leaves an unshared pair of outer electrons, the total of 4 pairs separate as far as possible, toward the corners of a regular tetrahedron (bond angles 109°28′). The structure is pyramidal.



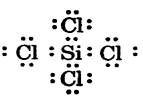
CH_4

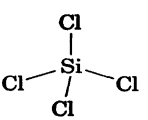




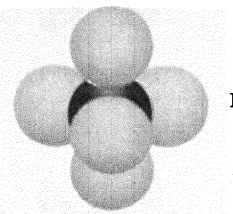


$SiCl_4$





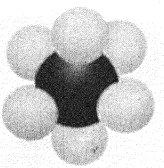
Four pairs of electrons separate to the corners of a regular tetrahedron, giving, for 4 bonds, bond angles of 109°28′.



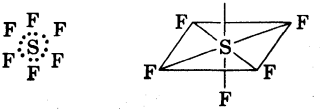
PCl_5



Promotion of one of an outer pair of electrons to an outer *d* orbital permits formation of 2 additional covalent bonds. Expansion from 3 to 5 bonds thus usually results in a trigonal bipyramid structure.



SF_6



Similar expansion to 6 bonds usually produces a regular octahedral structure (90° bond angles).

Figure 61 (*Cont.*)

from the central atom directed toward the corners of a square in plane with it, a fifth bond directed upward from that plane, and the sixth bond downward. Examples of various structural types are shown in Figure 61.

INTERMOLECULAR FORCES AND ASSOCIATION

In the free elements, as described in Chapter 3, the solid crystals were shown to be held together either through metallic bonding or by a network of covalent bonds extending throughout the solid, or by van der Waals forces among the individual molecules. The second, we might call a "giant molecule" structure, since each particle, of whatever size, is held together by covalent bonds. The situation is similar in compounds, but in addition, substantial electrostatic forces that supplement the van der Waals attractions can result from bond polarity produced by initial electronegativity differences among the component elements. Such electrostatic forces may come into effect when a partially charged atom of one molecule comes near to an oppositely partially charged atom of another molecule. Since these charges are an indication of electrical dissymmetry in the bonds, the bonds are polar and said to possess "dipoles." This kind of intermolecular attraction is called "dipole-dipole interaction." Similarly, if a partially charged atom of one molecule comes near to an oppositely charged ion, an attraction known as an "ion-

dipole" attraction occurs. The extreme of these forms of electrostatic attractions between molecules is, of course, that existing when the compound is ionic, with resulting "ion-ion" interaction.

When a molecule is geometrically unsymmetrical and also possesses polar bonds, it is likely that the positively charged parts of one molecule can come near enough to the negatively charged parts of another molecule to result in substantial attraction. However, many molecules exist in which the bond polarity is great but the geometrical symmetry prevents any such oppositely charged attractions between molecules. For example, fluorine is much more electronegative than carbon, and the bonds in CF_4 are therefore quite polar, with carbon positive and fluorine negative. The positive carbon, however, is completely shielded from outside approach by the tetrahedrally arranged fluorines. When two CF_4 molecules come together there can only be repulsion between negatively charged fluorines, despite the high bond polarity.

Protonic Bridging

A special form of association, through electrostatic attractions between oppositely charged atoms of different molecules, occurs when one of these atoms is positively charged hydrogen. Since hydrogen is the only element having, beneath its valence shell, no protective shield of electrons around the nucleus, the withdrawal of more than a half share of the bonding electrons leaves the hydrogen nucleus especially accessible to the influence of outside electrons. This is particularly true when the outside electrons are a pair on an atom that has both substantial negative charge and small size. The small size appears significant as a reason for the electron pair to be able to concentrate near the protonic hydrogen instead of spreading out over the atomic surface as in larger atoms. The requirement of negative charge arises because this makes the unshared pair more accessible to outside atoms. This combination of requirements practically limits the effectiveness of such attraction, between positive hydrogen and electron pair, to compounds of hydrogen with small and highly electronegative nitrogen, oxygen, and fluorine. The attraction among molecules of these is strong enough to produce a relatively weak but quite definite bond between molecules. The hydrogen, being positive, is called "**protonic,**" and serves to bridge two molecules, so the bond is named "**protonic bridge.**" An older term is "**hydrogen bond.**" In such a bridge, the hydrogen usually occupies an average position nearer to its own molecule than to the other.

Protonic bridges make important contributions to the forces of association in many OH, NH, and HF compounds.

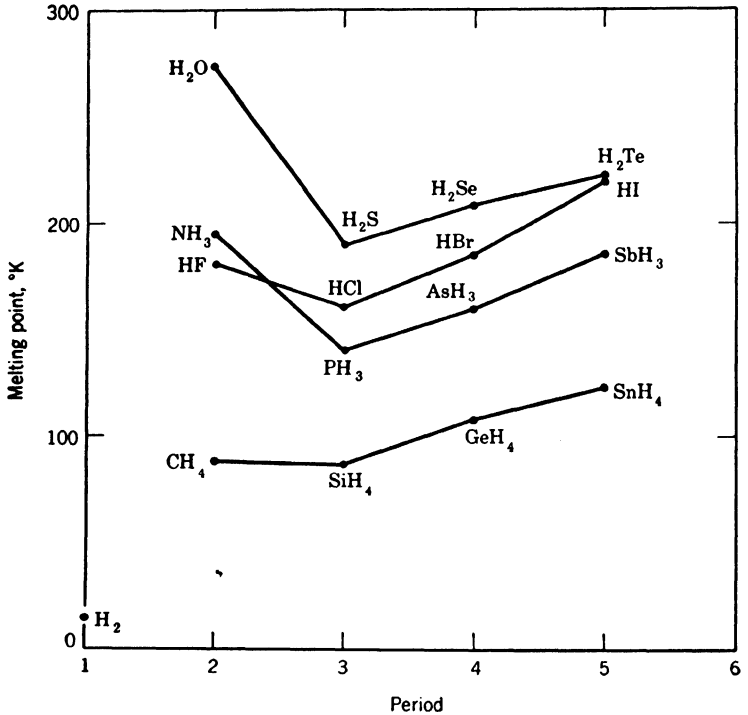


Figure 62. Melting points of some binary hydrogen compounds. Note that for H_2O, NH_3, and HF the high melting points show the effect of association through protonic bridging not possible in the other compounds.

PHYSICAL PROPERTIES

Just as in the free elements, the physical state of a substance depends on the relative effects of the kinetic energy of the component particles and the attractive forces between these particles. When the attractive forces are relatively high, the substance is solid; when they are relatively weak, the substance is more likely to be liquid or gaseous.

Molecular Crystals

When only van der Waals forces are in action, or when they are supplemented only to a very small extent by electrostatic effects such as previously described, the crystals formed by a compound are called "molecular crystals." Such crystals are commonly relatively soft, easily

crumbled, low melting, volatile, and, as will be discussed in detail later, soluble in nonpolar solvents. These properties are all a reflection of the easy separability of the molecules in the crystal.

Giant Molecules

When covalent bonds extend in all directions throughout a crystal, so that any given lump of crystal might be considered a giant molecule, the crystal is apt to be relatively hard, brittle, high melting, nonvolatile, and

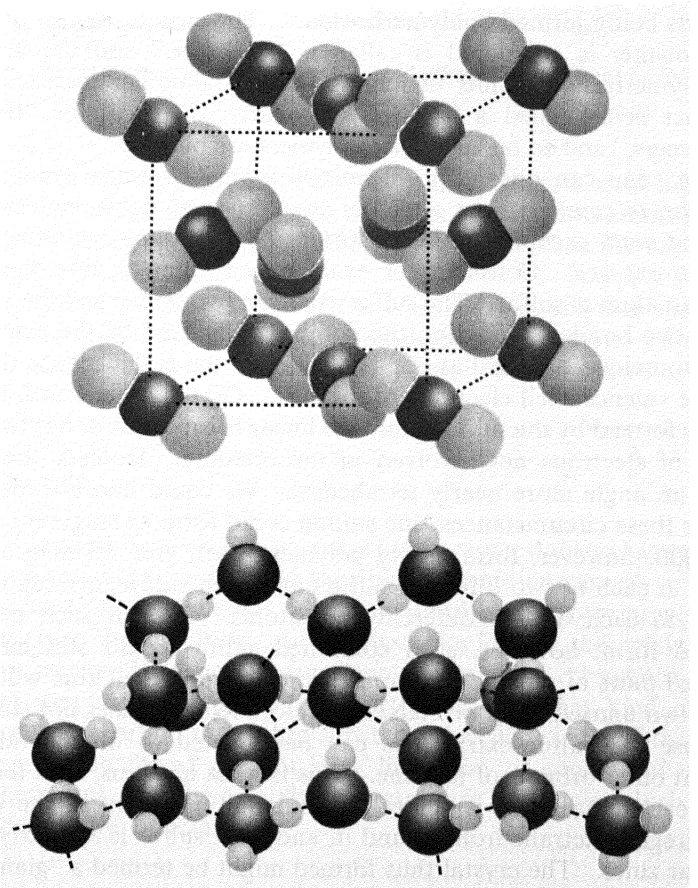


Figure 63. "Dry" and "wet" ice. Solid CO_2 is a molecular crystal. Solid H_2O is a good example of aggregation through protonic bridging. In both, remember that van der Waals radii are larger than the pictured covalent radii, and therefore the apparent open space is actually much smaller; **e.g. the CO_2 molecules are in contact** with their neighbors.

insoluble. These properties are to be expected wherever the separation of smaller particles making up a crystal would require the actual rupture of covalent bonds, for such bonds are usually much stronger than van der Waals forces and stronger also than ordinary dipole-dipole interactions.

Coordination Polymers

When relatively small molecules are able to join together chemically, forming larger molecules, the larger molecules are called "**polymers,**" the process being termed "**polymerization.**" The structural unit of which the polymer is composed is called a "**monomer,**" and the first step in polymerization results in joining of two monomer molecules, this product being called a "**dimer.**" Similarly, there can be "**trimers,**" "**tetramers,**" and so on, as higher polymers are built up.

Now, one can observe in chemistry a very common tendency for reaction *to continue* even after the simplest predictable molecules are formed *until,* except at the very surface of a solid, *no orbital vacancies remain exposed.* Consider, for example, an atom of zinc combining with an atom of sulfur. The sulfur can form two bonds and the zinc can form two bonds. However, the two bonds formed by the zinc would tend to extend outward at opposite sides of the zinc because they use all the valence shell electrons of the zinc. On the other hand, the two bonds formed by the sulfur cannot be linear because sulfur has two more pairs of electrons not involved in the bonding. Instead, they must form an angle more nearly tetrahedral. We could hardly expect that under these circumstances zinc sulfide could form as single molecules. It might, however, form zigzag polymers, each zinc forming a single bond to each of two different sulfurs and each sulfur forming a single bond to each of two different zinc atoms. Even if such polymers should form, however, each combined sulfur would still have two unused pairs of outside electrons, *and* each combined zinc would still have two unused outer orbitals. Therefore reaction does not stop here, because the sulfur extra pairs can be donated to fill the otherwise vacant outer orbitals of the zinc. This is what happens, with the result that each zinc atom is joined to four sulfur atoms at the corners of a regular tetrahedron around it, and each sulfur is similarly joined to four zincs. The crystal thus formed might be termed a "giant molecule," but in recognition of the fact that half of the bonds are coordination bonds rather than ordinary covalent bonds (although no difference is distinguishable in the compound), it is instead called a "**coordination polymer.**"

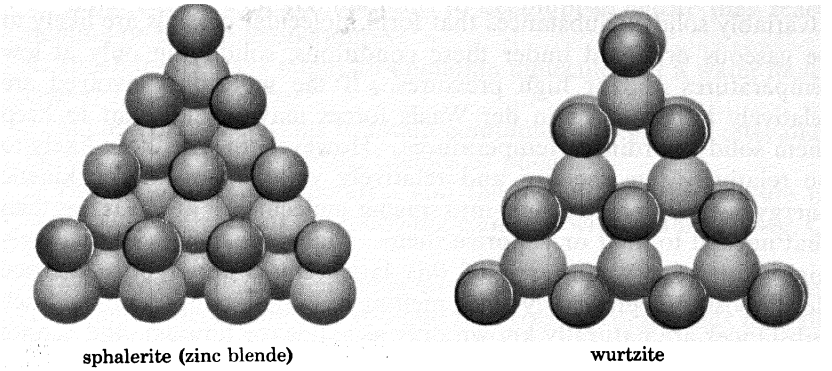


Figure 64. Forms of zinc sulfide crystal structures. Each zinc atom is joined tetrahedrally to 4 sulfur atoms and each sulfur atom to 4 zinc atoms.

It is important to note here that once a coordination bond has been formed it involves a sharing of two electrons between two atoms just as in ordinary covalence, and no difference is noted. Thus the bonds are exactly alike in zinc sulfide.

The physical properties of such a coordination polymer must, of course, resemble those of a giant molecule, since the crystal cannot be broken, melted, or vaporized without actually breaking these covalent bonds.

Ionic Crystals

Solids formed by electrostatic attractions among unlike charged ions are commonly very tightly held together. Exceptions are to be noted when at least one of the kinds of ions involved is relatively large. This must increase the repulsion among these like ions in the crystal, and therefore weaken it. Another exception occurs when at least one of the kinds of ions involved is easily distorted by the other kind of ion, so that decomposition into other substances occurs easily. Otherwise, the electrostatic forces prevent easy liberation or separation of the component ions, and the crystals as a result are brittle, very high melting, and very low in volatility.

SUMMARY

Under ordinary conditions of temperature and pressure, substances forming ionic crystals, coordination polymers, or giant molecules are

invariably solids. Substances that form molecular crystals are likely to be gaseous or liquid under these conditions, solidifying only at low temperatures and/or high pressures. If the molecules involved are relatively large, then van der Waals forces may be sufficient to keep them solid at ordinary temperatures. However, they still are likely to be relatively low melting and relatively volatile, unless the kinetic energy needed to break them into smaller molecules or atoms is less than that needed to melt or vaporize them. Many substances of relatively high molecular weight are of this latter class, undergoing thermal decomposition before they reach melting or boiling temperatures. Such substances are naturally known only as solids (or liquids), and cannot assume all three common states of matter as is possible for more stable compounds. However, all substances capable of existing as gases can also exist as liquid and solid, and all liquids can exist as solids.

SPECIAL HELP

Test Your Memory

1. Cite some evidence that physical properties do not directly reflect the atomic structure.
2. Boron has three valence electrons. Predict the formula and structure of boron bromide.
3. Compare the molecular structures of $ZnCl_2$, H_2S, and CaI_2 and explain.
4. List and describe the different kinds of intermolecular association in compounds.
5. Under what circumstances can a molecule have polar bonds yet be itself nonpolar?
6. Describe protonic bridging. What are the requirements for its occurrence, and why?
7. What is a molecular crystal? Giant molecule? Coordination polymer? Ionic crystal?

Test Your Understanding

1. Why do all portions of a pure crystalline substance melt at the same temperature?
2. Why is the melting point of an impure crystal always lower than that of the pure crystal?

3. What causes some compounds to decompose before they reach melting or boiling temperatures?
4. In what two ways might an ammonia molecule and a water molecule attract one another?
5. What can cause atoms to retain combining power even after they have formed as many covalent bonds as possible?
6. Predict formulas, structures, and the general physical nature of compounds of each of the following elements with sulfur: K, Mg, C, H, Cl, As.
7. When two immiscible liquids are heated together, each vaporizes as though it were alone. It is found that volatile compounds that are immiscible with water and unreactive with it may be distilled at lower temperatures with water than when alone. Why?
8. Suppose you should find, on distilling a liquid, that its boiling point slowly rises. How could this be explained?
9. Would $ZnCl_2$ be expected to be monomeric (single molecules of $ZnCl_2$) under ordinary conditions? Why or why not?
10. Why would "giant molecule" substances not be gaseous?
11. Without referring to a table of elements, predict what compound would result from combination of elements of atomic number 15 (A) and 53 (B). Explain the formula and describe and explain the structure. (Inert elements have atomic numbers 18 and 54.)
12. What could be predicted, and how, about the polarity of the bonds in the compound AB_3 of the preceding question?
13. What state of aggregation and what physical properties would you predict for the above compound?
14. When it forms an addition compound with ammonia, the compound BF_3 changes in structure. How and why?
15. Except for the hydrogen atoms, the molecule $(SiH_3)_3N$ has been found to be planar, the three silicon atoms forming a triangle with nitrogen at its center. What can be concluded about the bonding?

12

The Atomic Origin of Oxide Properties

PREPARATION OF OXYGEN

THE VERY NATURE of oxygen suggests that to recover it from its compounds one must take electrons from it. However, since oxygen is second only to fluorine in electronegativity, it would be difficult to find a chemical agent capable of taking electrons from combined oxygen. One alternative is to find some better way of removing electrons. As will be discussed in detail in Chapter 20, a positively charged electrode can do this, producing elementary oxygen from its compounds by use of electricity. This kind of decomposition of compounds is called "electrolysis." Electrolysis of water decomposes it to hydrogen and oxygen; this is a good source of pure oxygen.

Another possibility would be to find oxygen compounds that are unstable and give up oxygen when heated. Such compounds would need to be relatively low in polarity, since the more polar the bonds to oxygen the greater their strength is likely to be. We should look, then, for compounds of oxygen in which oxygen has not acquired high negative charge, or which are unstable because bonding tends to be weaker be-

tween atoms widely different in size. Compounds in which several oxygen atoms compete for the electrons of one atom would seem good possibilities, as would oxides of large atoms.

In the laboratory, HgO is of the latter type and $NaNO_3$, $KClO_3$, and $KMnO_4$ are of the former. All these, as well as a number of similar compounds, lose oxygen when heated:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$
$$2KClO_3 \xrightarrow{MnO_2\ cat.} 2KCl + 3O_2$$
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
$$2HgO \rightarrow 2Hg + O_2$$

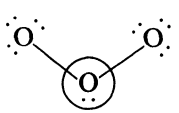
The best source of oxygen for large-scale uses is the atmosphere, of which about one-fifth of the volume is oxygen. By alternate compression, cooling, and expansion to produce further cooling, air can be liquefied. Impurities such as hydrocarbon traces are removed chemically. Then fractional distillation separates N_2 (b. $-196°$), leaving liquid oxygen (b. $-183°$).

Liquid oxygen is pale blue in color and a powerful oxidant. Its mixtures with combustible materials such as gasoline are violently explosive. Liquid oxygen cannot be maintained at ordinary temperatures because the critical temperature, above which liquid oxygen cannot exist, is $-119°$.

In both liquid and gas the molecules are O_2. The bond length is that expected for a double bond, but O_2 has magnetic properties suggesting the presence of two unpaired electrons. Since the molecules are very stable, gaseous oxygen does not begin to react as easily as it might, in reactions requiring the splitting into separate atoms. Once begun, its reactions are commonly self-sustaining and vigorous, and they evolve energy. Such reactions, with combustible materials used as fuels, are a major source of energy for the world's work.

Ozone

A much more reactive form of oxygen, called "ozone," is formed by passage of an electrical discharge through O_2 gas. The formula of ozone is O_3, the molecule having a bent structure with bond angle about 120°. The bonds, which appear to involve resonance as shown:



are much less stable than in O_2, giving the molecule its much higher reactivity. Atomic oxygen would be still more reactive. Ozone has an unpleasant odor and is toxic.

QUALITIES OF OXYGEN

With atomic number 8, oxygen has two electrons per atom in its first shell and 6 in the second shell where the capacity is 8. Thus there are two vacancies, or two half-filled orbitals, giving an oxygen atom the ability to form two covalent bonds. These may be two single bonds, each to a separate atom, or one double bond to one other atom. If single bonds, they are expected to be directed approximately toward the corners of a regular tetrahedron, with angle near to 109°. The reason for this is the presence of two unshared electron pairs also in the outer shell of the oxygen atom. These, when two single bonds are formed, make four electron pairs in all. As previously discussed, such electron pairs tend to become separated as far from one another as possible. However, two unshared pairs appear to have greater repulsive effect than two shared pairs. The unshared pairs are therefore presumably farther apart than the usual 109° angle, and this spacing would force the two bonds somewhat closer together than otherwise. The result is that the angle between two single bonds to an oxygen atom is always somewhat smaller than 109°, in the range from 100° to 105°.

You will recall that with increasing number of outer-shell electrons atoms tend to become increasingly compact, and correspondingly more electronegative. It should not be surprising, then, to realize that oxygen is very high in electronegativity—in fact, it is second only to fluorine among all the chemical elements. This means that it tends to acquire more than a half share of the electrons in combination with any element other than fluorine. For this reason, in practically all its compounds oxygen bears a partial negative charge.

You may also recall that the formation of a coordination, or coordinate covalent bond, requires one combined atom in a molecule to have a pair of outer unshared electrons which it can donate to an empty orbital of an atom of another molecule, or to a positive ion. In general, this donor ability increases in a given atom with increasing negative charge. Oxygen, with its two unshared pairs of electrons, can therefore act as donor in coordination, although normally only one of these electron pairs is used. The more negative the charge on this oxygen, the better its donor ability. Furthermore, when oxygen is united with an atom having relatively few outer electrons, such as a metal atom, then not only are

the bonds highly polar but also the metal atoms have vacant outer orbitals which might assist the attractive interaction between them and the combined oxygen with its extra electron pairs. It has previously been pointed out that such circumstances practically always result in highly condensed solids, ranging from ionic crystals to coordination polymers.

ACID-BASE PROPERTIES OF OXIDES

The subject of acids and bases will be discussed in some detail in Chapter 18, but since one can hardly consider the chemistry of oxides without mentioning their acid-base properties a brief discussion here should be helpful. In Chapter 9, an acid in water solution was described as furnishing an excess of hydrogen ions, H^+ (hydrated to hydronium ions, H_3O^+), and a base as furnishing an excess of hydroxide ions, OH^-. Although all oxides do not combine with water to form definite hydroxides, many do, and nearly all the rest behave as though they did. We may therefore consider the typical reaction of E oxide, E being any element:

$$E{-}O + H_2O \rightarrow E{-}O{-}H$$

Some actual examples are the following:

$$Na_2O + H_2O \rightarrow 2NaOH$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$N_2O_5 + H_2O \rightarrow 2O_2NOH \text{ (usually written } HNO_3)$$
$$SO_3 + H_2O \rightarrow O_2S(OH)_2 \text{ (usually written } H_2SO_4)$$

For simplicity, let us temporarily ignore other bonds to E and consider only the ionization of EOH. This may conceivably proceed in one of two ways:

$$(a)\ E{-}O{-}H \rightleftharpoons E{-}O^- + H^+$$
$$(b)\ E{-}O{-}H \rightleftharpoons E^+ + O{-}H^-$$

If it ionizes as indicated in (*a*), it is an acid. If it ionizes as indicated in (*b*), it is a base. Which will it be, and what factors determine this?

In general, it would seem reasonable to expect the extent of separation into ions to depend, at least in part, on how nearly ionic the bond was before separation. That is, if an atom already has nearly complete control of the electron pair bonding it to another, it may relatively easily separate as a negative ion. If the bond is not very polar, separation of a negative ion would seem to require a more drastic change. Similarly,

if the hydrogen is already quite positive, owing to extensive electron withdrawal from it by the oxygen, it would seem to be more readily available to separate as a proton. But if the bond between hydrogen and oxygen is not very polar, separation of the hydrogen as a proton would be expected to be more difficult and more unlikely. Since the oxygen and the hydrogen remain constant in their fundamental qualities, the decisive influence must be that of E. If E releases electrons to the oxygen easily, the oxygen's electronegativity, substantially reduced by its acquisition of negative charge, will be too low to withdraw electrons extensively from the hydrogen, and the hydrogen-oxygen bond will not be very polar, but the E—O bond will. We could predict ionization here as a base, liberating hydroxide ion, but not as an acid, liberating a proton. In other words, if E is low in electronegativity the hydroxide formed from its oxide will tend to be basic, and we can refer to the oxide itself as basic.

If E strongly resists the removal of electrons by the oxygen, the electronegativity of the oxygen cannot become so far reduced by the acquisition of partial negative charge, and it will therefore withdraw electrons from the bond to hydrogen more strongly, leaving the hydrogen more highly positive. Separation of hydroxide ion under these circumstances would not be predicted, but separation of a proton would be expected to occur relatively easily. In other words, if E is high in electronegativity the hydroxide formed from its oxide will tend to be acidic, and we can refer to the oxide itself as acidic.

The relationship between electronegativity of E and the nature of the E—O and O—H bonds can be understood from consideration of the electronegativity of the molecule, as determined by the principle of electronegativity equalization. The higher the electronegativity of E, the higher the electronegativity of the entire molecule. This corresponds to lower negative charge on oxygen and higher positive charge on hydrogen. Therefore as the polarity of the E—O bond diminishes the polarity of the O—H bond must increase, and vice versa. We have here an explanation of the fact that no compound can be both *strongly* acidic and *strongly* basic. We can recognize, however, that since the two bond polarities are inversely related, to get from one extreme to the other we must traverse an intermediate region. In this intermediate region, both the E—O and the O—H bonds are somewhat polar, but not highly so. We may therefore predict that slight ionization to liberate hydroxide ions could occur, and also slight ionization to liberate hydrogen ions. Such a hydroxide could neutralize either a strong acid or a strong base. This double behavior is called "amphoterism," and the hydroxide, as well as the oxide from which it is derived, are called **"amphoteric."**

An alternative viewpoint considers the partial charge on oxygen in the anion which is formed when a proton separates. As mentioned above, the electron-donating action of oxygen is closely related to its partial charge, increasing with higher partial negative charge. If an atom of combined oxygen bears a high negative charge, it will act strongly as a donor to a proton. This implies that an anion containing such oxygen will gain a proton strongly, which is another way of saying that the original hydroxy compound will give up the proton extremely reluctantly. In other words, the higher the negative charge on the anion oxygen, the less likely the separation of a proton, and therefore the less likely an acidic property of the hydroxide. Since acidic and basic properties are opposite in nature, we may conclude that the less acidic a hydroxide the more basic it is. If, on the other hand, an atom of combined oxygen bears only a slight negative charge, it will be a poor electron donor to a proton. An anion formed by the separation of a proton from a hydroxide will not be likely to attract the proton back again if its oxygen is only slightly negative. In other words, the lower the negative charge on the anion oxygen the more easily a proton can separate from the hydroxide compound, and the more acidic it is. Being more acidic, it is less basic. Since the partial charge on oxygen in E—O—H must vary with the electronegativity of E in an inverse manner, the lower the electronegativity of E, the more basic its oxide. The higher the electronegativity of E, the more acidic its oxide. When the electronegativity of E is intermediate, the oxide may be amphoteric. Thus the two viewpoints lead to the same predictions concerning the acid-base nature of oxides, predictions amply verified by experimental observations, as will be seen.

In the preceding discussion, E—O—H was considered without regard to other atoms that might also be attached to E. Since these are bound to affect E, and thus the whole molecule, we must recognize the direction of their influence. If in the hydroxide the other bonds to E should be essentially nonpolar, little effect on acid-base ionization would be expected. If, however, the other attached atoms are initially more electronegative than E, they will increase the electronegativity of the whole molecule and therefore its acidity. By withdrawing charge from E, they make it more difficult for the hydroxyl oxygen to withdraw charge from E, diminishing its chances for basic ionization and enhancing the chances for proton separation. But in the much less common circumstance of the other atoms being less electronegative than E, the reverse effect on the acid-base properties would be expected, with resulting greater basicity and reduced acidity.

It must be emphasized that these are not the only factors influencing acid-base strength behavior of oxides, which is actually a very complex

phenomenon. They do serve, however, to permit roughly accurate predictions, and to give an approximate understanding of the differences and relationships of metal and nonmetal oxides.

PROPERTIES OF OXIDES: PREDICTION AND FACT

Knowing all this about the nature of oxygen, it should be possible for us to achieve a reasonably good understanding of its compounds with other elements if similar information concerning the qualities of the other elements is also available. Indeed, merely to memorize the descriptive chemistry of oxygen would be much less useful than to arrive at a fundamental understanding from a consideration of the qualities of the atoms involved. Let us therefore examine some atoms of other elements and see how well we can predict the properties of their compounds with oxygen.

Oxygen and Hydrogen

Water. Hydrogen is the element of atomic number 1, which means that its atom has but a single electron, and therefore one vacancy, since the first principal quantum level can hold only two electrons. We can predict, therefore, that a hydrogen atom can form but one single covalent bond. Since an oxygen atom can form two such bonds, a logical prediction would be that two hydrogen atoms could unite with one oxygen atom. The formula of this compound would be H_2O. Furthermore, from the spatial distribution of orbitals on the oxygen, we can predict that these two hydrogen-to-oxygen bonds will form an angle somewhere near tetrahedral, but probably smaller, because of the greater repulsive forces exerted by the unshared electron pairs. In addition, if we compare the relative electronegativities of the two elements, we find that the value for oxygen, 3.46, is much higher than for hydrogen, 2.31. A polarity is therefore predictable for each bond, with the oxygen becoming partially negative at the expense of the hydrogen atoms, which are left partially positive. The electrical dissymmetry of the molecule caused by the combination of bond polarity and geometric dissymmetry would be predicted to have the effect of causing the molecule to become oriented in an electrical field, the positive hydrogen end of the molecule approaching the negative pole and the negative oxygen end of the molecule approaching the positive pole. This tendency to become oriented in an electrical field is measured as the **"dipole moment,"** the product of the charge times the distance of separation.

From the prediction of a partial negative charge (calculated −0.25) on the oxygen, we can predict also that with its two unshared electron pairs it can act as an electron donor. Therefore H_2O should be able to enter into coordination compounds. We can further recognize that a partially positive hydrogen (calculated 0.12) might, by leaving the molecule as a free proton, act as an electron pair acceptor. In addition, from a knowledge of protonic bridging (page 215) we could recognize in this molecule the requisites for extensive protonic bridging, and might predict that such molecules would become highly associated through such bridging. The effect of such bridging, since it contributes significantly to the forces of intermolecular attraction, should be to make it more difficult to melt or volatilize this compound, and we can therefore predict that its melting and boiling points may be much higher than otherwise expected.

We can also note that although oxygen in this compound does bear a partial negative charge, this is not as high a charge as the oxygen might acquire in some other combination. A very important general tendency in chemistry is for a highly electronegative element to leave a given compound in order to form a new compound in which it can bear higher negative charge. From this tendency we can predict that water can act, under appropriate circumstances, as an oxidizing agent. Similarly, in contact with more electronegative compounds water might act as a reducing agent. But neither in oxidizing nor reducing action would water be expected to be highly active, for the charge on oxygen is moderate but not extremely high or extremely low.

After all this prophecy, based on a few simple rules and on the qualities of atoms that are inherent in their electronic structure, what are the facts? Doubtless you are already familiar with most of them. Hydrogen does indeed combine with oxygen, two atoms to one, forming molecules of water, H_2O. The molecules are indeed angular instead of linear (Figure 53), with measured bond angle of 104.5°. The bonds are indeed polar, with the hydrogen partially positive and the oxygen partially negative. And although the dipole moment is the resultant of a number of factors of which bond polarity is only one, water does indeed have a high dipole moment (1.83 D), as would be expected from the combination of geometric and electrical dissymmetry. We predicted that the compound could form coordination compounds; hundreds of such compounds are well known, in which water coordinates as an electron donor through its oxygen. The physical properties of water are quite consistent with predictions based on the assumption of protonic bridging as a means of intermolecular association. Water melts (0°) and boils (100°) much higher than would otherwise be expected (Figure 62). Furthermore, the structure of ice is that which would be expected if

each unshared pair of electrons on oxygen could attract a hydrogen of another water molecule. The result is an open structure in which each water molecule is surrounded at the corners of a regular tetrahedron by four more water molecules, through four protonic bridges (Figure 63). Water can indeed act as an oxidizing agent, as is spectacularly shown, for example, by its vigorous reaction with sodium, which loses its valence electron to the water:

$$2Na + 2H_2O \rightarrow H_2 + 2Na^+ + 2OH^-$$

Its action as reducing agent is also known. It reduces fluorine, for instance, forming hydrogen fluoride and liberating oxygen:

$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$

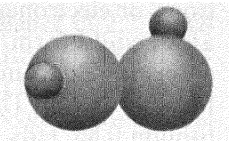
Water is one of the most important of chemicals, and will be discussed in further detail in later parts of this book. For the present, let us summarize the discussion thus far by emphasizing, if emphasis be needed, how completely dependent are the properties of any compound on the qualities of the individual atoms of which it is composed. We do not need to memorize the properties of the compound as though they were independent facts. We need only to understand the fundamental qualities of the atoms, and from these we know how to predict the nature of the compound. This does not mean that a preparation and study of the compound is unnecessary. Many interesting facts remain to be learned by such experiments. But it does mean that we will find it very useful and helpful to be confident that chemistry makes sense, and that the sense is not necessarily too difficult even for beginning students to begin to understand.

Hydrogen Peroxide

Water is not the only possible combination of hydrogen with oxygen. For, suppose only one hydrogen atom should become attached to an oxygen atom—could not two such oxygens then use their second half-filled orbitals to join by a single covalent bond? If this were to happen, the compound would have the composition, H—O—O—H. What would it be like?

We could predict at once, from the angular orientation of the oxygen orbitals, that this molecule would not be linear. We could also predict that the hydrogen atoms would have higher positive charge, and the oxygen lower negative charge, by observing that here only one hydrogen, instead of two, contributes electrons to the oxygen. As we did for water, we could recognize the requisites for protonic bridging and pre-

dict that such bridging should contribute very significantly to the intermolecular attraction, giving this compound higher melting and boiling points than would otherwise be expected.



H_2O_2

Figure 65. Hydrogen peroxide model.

Such a compound, H_2O_2, indeed exists. It is called "hydrogen peroxide." In keeping with the oxidation number convention that a bond between two like atoms has no effect on oxidation number, the oxidation number of oxygen in this compound is -1 rather than the -2 found in practically all other oxygen compounds except peroxides. The hydrogen peroxide molecule is indeed nonlinear, and gives evidence, through relatively high melting ($-0.9°$) and boiling points ($151.4°$), of considerable intermolecular association through protonic bridging. Chemically, the compound is acidic and an oxidizing agent, both consistent with the higher positive charge on the hydrogen and the lower negative charge on oxygen than are found in water.

Hydrogen peroxide can be prepared by treatment of sodium peroxide, Na_2O_2, or barium peroxide, BaO_2, with a dilute acid, such as sulfuric acid, H_2SO_4:

$$Na_2O_2 + H_2SO_4 \rightarrow H_2O_2 + Na_2SO_4$$

$$BaO_2 + H_2SO_4 \rightarrow H_2O_2 + BaSO_4$$

It can also be made by passing an electric current through a cold, concentrated sulfuric acid solution, which forms "peroxydisulfuric acid," $H_2S_2O_8$. This can be isolated as the potassium salt, which decomposes when acidified:

$$K_2S_2O_8 + 2H_3O^+ \rightarrow 2H_2SO_4 + H_2O_2 + 2K^+$$

Hydrogen peroxide is an oxidizing and bleaching agent, even in dilute solution. Unless carefully purified, it is quite unstable in the highly concentrated form. In this form it has been used as an oxidizing agent in rocket motors.

OTHER BINARY OXIDES

Lithium Oxide

Lithium atoms are relatively large, considering their low atomic number of 3, with but one electron in the outermost shell. The large size suggests that the attraction between nucleus and outer electron is relatively small. This is confirmed by the fact that lithium has a very low ionization potential (5.4 volts) and very little attraction for outside elec-

trons, or electronegativity (0.86). We could easily predict that a lithium atom could form but one single covalent bond, and that two lithium atoms would combine with one oxygen atom giving a compound of formula Li_2O. The large electronegativity difference, oxygen 3.46 and lithium 0.86, tells us that such bonds would be highly polar, indeed so much so as to be termed "ionic," with the oxygen highly negative and the lithium highly positive. We would therefore expect a high degree of association, forming an ionic crystal.

A factor aiding in the strength of this association would be the vacant orbitals on the lithium that would otherwise remain unoccupied in the bonding, for we have previously observed that a strong tendency exists for reaction to continue until all such vacancies are either utilized or shielded from outside contact. Relatively high melting and boiling points would be predicted to result from the strong ionic bonding in the crystal. We also observed earlier that in general an electron donor atom becomes more effective as a donor the higher its negative charge. We would therefore expect the oxygen in lithium oxide to be very effective as an electron donor. We would not expect oxygen here to be an effective oxidizing agent, however, because the oxygen already bears high negative charge, and has thereby lost most if not all of its original electronegativity.

What does happen when lithium and oxygen atoms come together? An ionic crystalline substance of formula Li_2O is formed, just as predicted. This is a white solid melting at 1727°. It reacts very readily with water, its oxygen serving as donor to a proton from the water:

$$Li_2O + H_2O \rightarrow 2LiOH$$

The compound LiOH, lithium hydroxide, is a strong base, as will be explained further in Chapter 18, which means that it is completely in the form of ions in water solution. These are lithium ions, Li^+, and hydroxide ions, OH^-. In the latter, the oxygen is again very negative, thus acting readily as an electron donor.

Lithium oxide not only reacts with water, as shown, but also with other oxides to which its negative oxygen can contribute electrons. For example, with carbon dioxide, CO_2, it reacts to form carbonate ion:

$$Li_2O + CO_2 \rightarrow Li_2CO_3$$

Beryllium Oxide

Beryllium atoms, atomic number 4, have 2 electrons in the first shell, which fill it, and 2 more electrons in the second shell. The latter are

available for bond formation, and give beryllium a valence of 2. Beryllium atoms are considerably smaller than those of lithium, and beryllium is correspondingly higher in electronegativity (1.37). We might predict, from these facts and our knowledge of oxygen atoms, that beryllium and oxygen should unite one to one, forming beryllium oxide, BeO. This should have highly polar bonds, although less so than with lithium. A Be=O double bond could hardly be expected, because the two bonding orbitals of beryllium extend in opposite directions. The oxygen, with its two otherwise unshared electron pairs, and the beryllium, with its two otherwise vacant orbitals, should continue to condense, and form a highly polar if not ionic solid. The oxygen here is drawing negative charge from only one beryllium atom instead of two lithium atoms, and beryllium holds its electrons more securely than does lithium. We would predict that the charge on oxygen in beryllium oxide, although substantially negative (calculated -0.43), could not be nearly as negative as in lithium oxide (-0.80). This means that the oxygen could not behave so effectively as an electron donor.

In fact, beryllium does react with oxygen to form the oxide, BeO, which is a white solid melting at 2547°, not ionic but a coordination polymer having quite polar bonds. This is not as good an electron donor as is lithium oxide, but it will react with water in a similar way:

$$BeO + H_2O \rightarrow Be(OH)_2$$

However, beryllium hydroxide does not liberate hydroxide ions readily, as does lithium hydroxide. In fact, it forms them only weakly, and also forms hydrogen ions and accepts hydroxide ions. We call this activity, both of acid and of base, "amphoteric." An oxide that is amphoteric can act as acid or base but only weakly either way. The oxygen of beryllium oxide can also supply electrons for other oxides in which oxygen is not nearly as negative, and although carbon dioxide does not attract them strongly enough, sulfur trioxide does:

$$BeO + SO_3 \rightarrow BeSO_4$$

Boron Oxide

Boron, atomic number 5, has a filled first shell and 3 electrons in the second, which can hold 8. Its atoms can therefore form three single covalent bonds, which should be toward the corners of an equilateral triangle around the boron, or the equivalent of these in partially multiple bonds. When such bonds have been formed, boron still has one outer orbital available for further bond formation. If there are other-

wise unshared electron pairs on the other atom, these may make use of this boron orbital, or another molecule which has an electron donor atom may add on to the boron compound, forming a coordinate covalent bond and thus an "addition compound." Boron is higher in electronegativity than beryllium (1.37), and yet not very high (1.88).

We can predict with confidence that boron will react with oxygen to form an oxide of formula, B_2O_3. We can also predict that the bonds will be polar, with oxygen partially negative (-0.24) and the boron partially positive (0.36), but not as polar as in beryllium oxide. This should suggest that the oxide should be less basic than that of beryllium. But since beryllium oxide is amphoteric, being weakly acidic and weakly basic at the same time, we would predict boron oxide to be more acidic and less basic because of the lower charge on oxygen. As for the structure, other than to predict the bond angles if only single bonds are formed we can hardly be more specific when the relative numbers of atoms are two to three.

In fact, boron does unite with oxygen to form an oxide, B_2O_3. This is a white solid of complex structure, evidently highly polymeric, which melts at 450°. It has essentially no basic properties but is as predicted, very weakly acidic. With water it forms boric acid, $B(OH)_3$. It reacts with more basic oxides to form mixed oxides of usually indefinite composition, called "borates." A few of these have definite composition, for example, sodium metaborate, $NaBO_2$, and sodium tetraborate, $Na_2B_4O_7$, the hydrate of which is the familiar mineral "borax." Boron oxide and silicon oxide melted together form the major ingredients of Pyrex glass.

Carbon Oxides

Carbon atoms have 4 outermost electrons and 4 outermost vacancies, and therefore the capacity to utilize the outer shell completely through the formation of 4 single covalent bonds, or their equivalent. Carbon atoms are more compact than those of boron, and correspondingly more electronegative (2.47). From these properties and those of oxygen atoms, we can predict that carbon should unite with oxygen in a 1 to 2 ratio, forming an oxide of formula CO_2. This might be molecular, with oxygen double-bonded to the carbon, or it might be polymeric, with each carbon joined tetrahedrally to 4 oxygen atoms by single covalent bonds and each oxygen joined to 2 carbon atoms. We have as yet no certain basis for predicting which of these possibilities is more

likely. From the increased electronegativity of carbon over boron, and the increased number of oxygen atoms competing for electrons, we can predict that the bonds will be less polar, the oxygen bearing lower partial negative charge (calculated -0.11). Carbon dioxide should therefore be acidic, somewhat more so than boron oxide.

In fact, carbon burns in abundant air or oxygen to form the compound carbon dioxide, CO_2. The fact that this is gaseous rather than solid suggests that it must be molecular rather than polymeric, and indeed it is. Now, if all the carbon electrons are used in only two bonds to oxygen, as must be the case here, we would predict these two bonds to form at an angle of 180°. The carbon dioxide molecule is indeed observed to be linear, the two oxygens at opposite sides of the carbon atom. Carbon dioxide gas dissolves in water to an extent depending on the pressure, and in solution it reacts with water to a small degree forming the extremely unstable carbonic acid, H_2CO_3. Although the acid itself cannot be isolated, its salts are well known. Na_2CO_3 is sodium carbonate; hydrated it is "washing soda." $NaHCO_3$ is "sodium bicarbonate;" it is called "baking soda." Calcium carbonate, $CaCO_3$, is limestone and also marble.

When carbon or carbon-containing substances are burned in insufficient oxygen, or when carbon dioxide is subjected to very high temperatures, carbon monoxide, CO, is formed. This is a gaseous substance boiling at $-190°$. There is no good basis for predicting the formation of this compound, for it certainly seems to violate our notions of valence. However, once we know that it exists, rationalizing it is not too difficult. The atomic number of carbon is 6; that of oxygen is 8. In between is nitrogen, atomic number 7. Remember that one of the stablest of all chemical bonds is the triple bond readily formed between two nitrogen atoms. If by some means oxygen could lose one electron to carbon, both atoms would have 7 electrons, like nitrogen. Then both might form a very stable triple bond, just as two nitrogen atoms do. From the original electronegativity difference, one would expect the oxygen to withdraw negative charge from the carbon. By a transfer of an electron from oxygen to carbon, this effect would certainly be cancelled. In fact, measurement of the dipole moment of carbon monoxide shows it to be very small, a fact that is at least consistent with our hypothesis that the molecule closely resembles the N_2 molecule. The bond has the length predicted for a triple bond, and a strength even greater than that in the N_2 molecule.

Carbon monoxide is notoriously deadly as a poison, and many a person, unbelievably ignorant considering how widespread the warnings,

lies dead of exhaust fumes of an automobile engine, which contain this gas. Since it can acquire more oxygen, it will burn in air, and is a component of certain fuel gases. Most noteworthy of these is "water gas," produced by passing steam over hot coke:

$$H_2O + C \rightarrow CO + H_2$$

Carbon monoxide is consequently a reducing agent, and it enters into the production of metals from their oxides. Its carbon atom has an unshared electron pair and can act as donor in the formation of numerous coordination complexes. Its complexing with the iron in the hemoglobin of the blood inhibits the complexing of oxygen by taking its place, causing death by asphyxiation. Carbon monoxide appears to function as neither acid nor base, being unreactive with water.

Nitrogen Oxides

Nitrogen, although not as electronegative as oxygen, is still quite high in electronegativity (2.93). With its five outermost electrons per atom, one of the four orbitals is filled and therefore unavailable for ordinary covalent bond formation. There are only three vacancies, and therefore only three covalent bonds can be formed. When these have formed, however, the nitrogen can act further as electron donor, forming a total of four bonds, three covalent and one coordinate covalent. As observed in general for oxygen and other atoms, this electron donor property is expected to be greater as the nitrogen acquires higher partial negative charge.

Judging from the capacity of a nitrogen atom to form three covalent bonds and an oxygen atom to form two, we might predict the most likely compound of these two elements to have the formula N_2O_3. The bonds would be only slightly polar, so that the compound should show very little intermolecular attraction and be either gaseous or volatile liquid. One could predict that such an oxide should be acidic. In addition, since the oxygen cannot acquire very much negative charge from nitrogen, it should rather easily leave the nitrogen to join some other combination in which it can be more highly negative. This departure could be aided by the high stability of the nitrogen molecule which would form when the nitrogen atoms are liberated. We would therefore predict an oxide of nitrogen to be a fairly strong oxidizing agent. It should also be acidic.

In fact, N_2O_3 is only one, and one of the least stable, of the known compounds of nitrogen and oxygen. Also known are nitrous oxide,

N_2O, nitric oxide, NO, nitrogen dioxide NO_2 and its dimer N_2O_4 (dinitrogen tetraoxide), and N_2O_5. To what can this unexpected group of compounds be ascribed?

Before considering these compounds individually, we should know that at least our general predictions are correct. All the nitrogen oxides are relatively nonpolar, very volatile compounds, and potentially good oxidizing agents. The predicted compound, N_2O_3, reacts with water to form the weak acid HNO_2, nitrous acid, and the compound N_2O_5 reacts with water to form the strong nitric acid, HNO_3. The other oxides are not converted to corresponding acids by water, but have also an acidic nature.

Now, why such compositions? We do not know, but it may be instructive to consider the question. When we survey the chemical elements for examples of multiple bonding, which includes any bonding involving more than two electrons per bond, or more than one vacancy per atom, we find that by far the most frequent occurrence of such bonding is with three elements, carbon, nitrogen, and oxygen. It appears that once a single covalent bond is formed between two of these atoms, alike or unlike, other orbitals are brought into such position that they tend to overlap, thus easily becoming themselves involved in the bonding. This is evidently why carbon forms two double bonds to oxygen, for example. All of the oxides of nitrogen are held together through multiple bonding. Although we could not necessarily have been expected to predict the formulas of the nitrogen oxides, nevertheless we can to some extent excuse our failure by pointing out the complications arising from the tendency toward multiple bonding. It may be especially significant that this bonding appears to be principally of a nonintegral type, involving what has previously been described as "resonance" (page 168). The structures of the nitrogen oxides are represented in Figure 66.

Nitrous oxide, N_2O, would systematically be named "nitrogen(I) oxide," the oxidation state here being clearly an arbitrary assignment based on -2 for oxygen. Nitrous oxide is a gas, melting at $-90.8°$ and boiling at $-88.46°$. It induces mild hysteria when applied as an anaesthetic, and therefore is called "laughing gas." It is formed by thermal decomposition of ammonium nitrate—cautiously to avoid violent explosion:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

It does not react with water. It gives up its oxygen so readily that it supports combustion, a glowing wood splint bursting into flame in N_2O almost as easily as in pure oxygen.

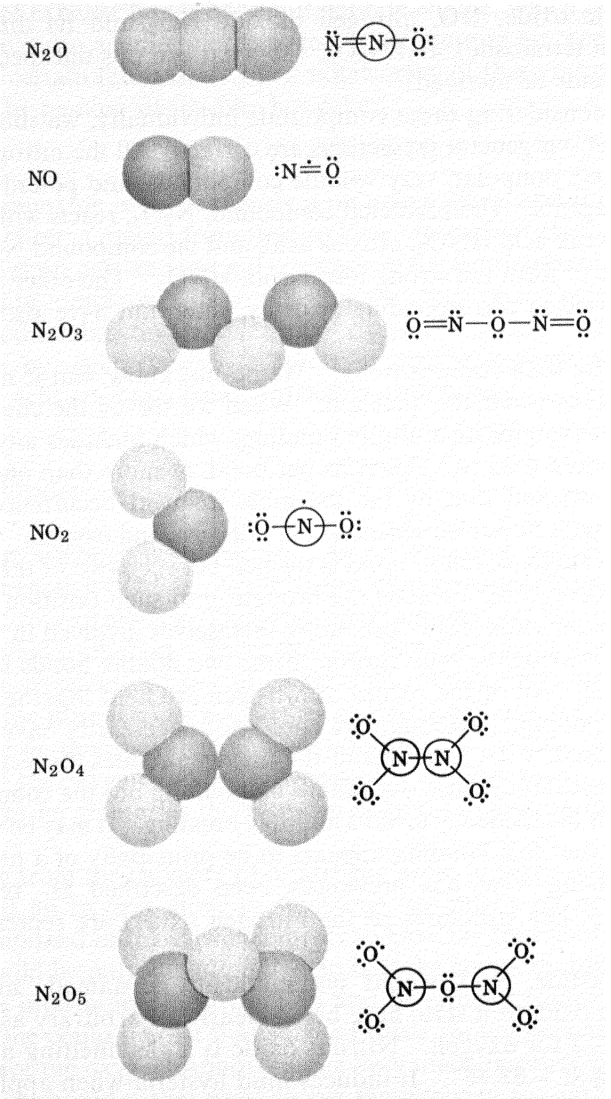


Figure 66. Oxides of nitrogen.

Nitric oxide (or nitrogen(II) oxide), NO, is also a gas, melting at $-163.7°$ and boiling at $-151.8°$. It very easily unites with oxygen, forming NO_2. Both NO and NO_2 are dangerous lung irritants, having sometimes no noticeable immediate effect but some time after exposure causing "pleural edema"—filling of the lungs with fluid and consequent

drowning. Nitric oxide is usually formed by catalytic oxidation of ammonia:

$$4NH_3 + 5O_2 \xrightarrow[\text{Pt cat.}]{} 4NO + 6H_2O$$

NO_2 which might be expected is not formed because it is unstable at the high temperature of the reaction. Nitric oxide also results as a reduction product when moderately concentrated nitric acid acts as an oxidizing agent. Hence reactions with concentrated nitric acid should always be carried out under a fume hood so that gaseous products cannot be inhaled.

Nitrogen(III) oxide, N_2O_3, is very unstable, decomposing at ordinary temperatures to an equimolar mixture of NO and NO_2. This mixture acts chemically, however, as though it were N_2O_3, which is the "anhydride" of nitrous acid, HNO_2:

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

Nitrogen(IV) oxide, or dioxide, NO_2, is a brown gas that is in equilibrium (see Chapter 15) at ordinary temperatures with its colorless dimer, N_2O_4. At 60° and one atmosphere pressure, the mixture is half dimer, half monomer. The proportion of dimer increases as the temperature is diminished. The mixture is strongly oxidizing, and reacts with water, forming nitric acid:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Thermal decomposition of certain nitrates forms NO_2; it also results when concentrated nitric acid acts as an oxidizing agent. Concentrated nitric acid itself is not very stable, the pure solutions being water-white, but turning brownish-yellow on standing as the result of slow decomposition with the formation of the colored NO_2 as one of the products.

Nitrogen(V) oxide, N_2O_5, appears, in white crystalline form, to be arranged as though it were "nitronium nitrate," $NO_2^+NO_3^-$. However, the crystal is low melting (30°) and boils at 45–50°. It is a strong oxidizing agent, and the anhydride of nitric acid:

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

It decomposes slowly, forming NO_2 with the release of oxygen.

Oxygen and Fluorine

An atom of fluorine has seven outermost electrons, one less than a full shell, and with this one vacancy may be expected to form but one

single covalent bond. Fluorine is the most electronegative of all the elements, having a value of 3.92 compared to that of oxygen, 3.46. We may therefore predict that two fluorine atoms will unite with one oxygen atom, and that the covalent bonds so formed, making an angle near to 109°, will be only slightly polar, but in the opposite direction to that usual for oxygen. The fluorine atoms will become partially negative (calculated −0.04), leaving the oxygen, for once, partially positive (+0.07). Such a compound could not properly be termed an oxide, but rather a fluoride. Since its bonds could not be very polar, the compound would be predicted to have very low intermolecular attractions and hence high volatility, probably existing under ordinary conditions as a gas. Since neither of the two highly electronegative elements has accomplished much toward satisfying its electronegativity in this combination, we would predict that the compound should be, potentially at least, a powerful oxidizing agent.

A compound, oxygen fluoride, of formula OF_2, is indeed known. It is a gas, not very stable, probably owing to repulsions between unshared pairs of electrons on oxygen and fluorine, and a strong oxidizing agent. The observed bond angle is 100°.

Trend Thus Far

We have observed in this series of compounds certain trends which can usefully be summarized now. As we cross the periodic table from left to right, we observe a consistent change in the character of the element, associated with the number of outermost electrons. When this number is low, the element is actively metallic and very low in electronegativity. As the number increases, the element changes from metallic to nonmetallic, becoming more electronegative. These trends determine the nature of the compounds which these elements form with oxygen, in a predictable way. The left-hand elements form highly polar bonds with oxygen, in which the oxygen, having relatively high negative charge, becomes highly basic, a strong donor of electrons, and loses its oxidizing power almost completely. The oxides being polar and also having otherwise vacant orbitals on the metal atoms, as well as unshared pairs of electrons on the oxygen atoms, continue to condense, forming ionic solids. With the trend toward less metallic properties and higher electronegativity in the elements from left to right, the oxides show a trend toward less ionic, more volatile substances in which the oxygen does not have so high a partial negative charge. With diminishing negative charge on oxygen, the trend in the oxides is toward lower

basicity, weaker donor properties, greater acidity, and greater oxidizing power.

It should now be of interest to consider similarly some of the oxides of elements of higher atomic number.

Sodium and Oxygen

Sodium atoms are larger than lithium atoms, but resemble them in having but one outermost electron available for bonding, in being relatively low in compactness, and in being very low in electronegativity (0.85). The ionization energy for sodium (119 kcal/mole) is even lower than for lithium (124 kcal/mole), showing that its electron is even easier to remove. On this basis, we should have little trouble in predicting that sodium should react readily with oxygen, two atoms to one, forming a compound of formula Na_2O. The bonds should be highly polar, and therefore the substance should be a stable, nonvolatile solid. We should expect highly basic properties in this oxide, owing to the high negative charge on oxygen (calculated -0.81), and correspondingly no appreciable oxidizing power.

The actual reaction between sodium and oxygen is surprising. Instead of the predicted Na_2O, the chief product is Na_2O_2, called "sodium peroxide." This is a white solid that reacts with water to liberate oxygen and form sodium hydroxide, a strong base:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

Where did our prediction fall short? What we did not know was that oxygen molecules are capable, under favorable conditions, of acquiring electrons from other atoms without first breaking apart into atoms. But actually, if oxygen molecules could react as a unit, they could react much more readily, because the multiple bond that holds them together is a very strong one and must otherwise be broken before reaction can occur. Evidently, sodium atoms lose their valence electrons readily enough that oxygen can form "peroxide" ions, $O_2^=$, by direct reaction with sodium. Remember that a peculiarity of the oxygen molecule, O_2, is that although it possesses an even number of electrons, magnetic properties show that two of them are unpaired. The acquisition of two more electrons, one from each of two sodium atoms, suggests that in this process the two unpaired electrons are becoming paired. This kind of reaction appears to occur, however, only with those elements from which electrons can be removed most easily.

By other reactions, a normal sodium oxide, Na_2O, can be formed. This compound has indeed the properties we have already predicted for it.

Magnesium and Oxygen

Magnesium atoms resemble those of beryllium, but are larger, less compact, and therefore lower in electronegativity (1.21). We may predict these atoms, with their two valence electrons, to unite with oxygen one to one, forming an oxide, MgO, in which the bonds should be very polar. An ionic crystal would therefore be expected, with high melting and boiling points and very low volatility. The oxygen should be more negative (-0.50) than in BeO but less negative than in Na_2O. We might therefore predict MgO to be less basic than the sodium oxide but more so than the beryllium oxide, which, you recall, is amphoteric. This suggests that the MgO would not have acidic properties like BeO, being fairly basic but not amphoteric. Certainly oxygen combined with magnesium should have acquired sufficiently high negative charge (-0.50) to remove practically all its tendency to act as an oxidizing agent.

In fact, magnesium does burn, with a brilliant white flame that found much early use in flash photography, forming MgO, an ionic solid of very high melting (2800°) and boiling points and low volatility. It is not acidic, but only moderately or weakly basic, forming the quite insoluble hydroxide, $Mg(OH)_2$, in water. Under ordinary conditions it would not be classified as oxidizing.

Aluminum and Oxygen

Aluminum, with three outermost electrons per atom, resembles boron in its ability to form three covalent bonds and have one orbital left which may participate in further bonding. The atoms are larger and less compact than those of boron, and correspondingly less electronegative (1.39). We could predict from these facts that aluminum should combine with oxygen to form an oxide, Al_2O_3, with highly polar bonds and therefore presumably high melting and boiling temperatures and very low volatility. With a higher partial charge on oxygen (-0.36) than in the oxide of boron, this oxide should be more basic than boron, yet less basic than MgO.

Actually, Al_2O_3 is the oxide formed when aluminum combines with

oxygen. It is a very stable solid, highly associated and therefore with low volatility and high melting (2027°) and boiling points. It is insoluble in water, but since it is soluble in both aqueous acids and bases, we know that it is amphoteric. In certain crystalline forms (e.g. "corundum"), alumina, as the oxide is frequently called, is very hard and abrasive and useful in grinding and polishing.

Silicon and Oxygen

Silicon atoms, like those of carbon, have four outermost electrons and thus the capacity to form four covalent bonds. Three significant differences between carbon and silicon need to be pointed out here, however. First, silicon atoms are larger, have their valence electrons in their third principal quantum level, and thus, unlike carbon, can on occasion make use of outer *d* orbitals which are not available in carbon. The "valence octet" can therefore be expanded, which means that more than four single covalent bonds or their equivalent can sometimes be formed. Second, silicon atoms are considerably less compact than those of carbon, and appreciably less electronegative (1.74). Third, so far as ordinary double bonding using *s* and *p* orbitals is concerned, atoms having shells of 8 electrons underlying the valence shell (e.g. silicon) appear unable to permit the closeness of approach needed for stable double bonding, whereas atoms having shells of only two electrons underlying the valence shell (e.g. carbon) can form double bonds readily.

We can predict easily that silicon should react with oxygen in a one-to-two ratio, forming an oxide of formula SiO_2. With carbon, we encountered the question of whether the bonds would be single or double, but with silicon the same question is more easily answered because silicon atoms appear relatively unable to form ordinary double bonds. In addition, silicon-to-oxygen bonds should be much more polar than carbon-to-oxygen bonds, which might also contribute to polymerization as opposed to the formation of simple molecules. We might therefore predict here that SiO_2 would be polymeric, rather than molecular. Each silicon should then be surrounded by four oxygens, joined to them by single bonds, and with bond angles close to 109°. Each oxygen should be joined to two silicon atoms, the bond angle being near to 109°. This would result in a giant molecule structure, very high melting and boiling and low in volatility. The partial negative charge on oxygen being larger here than in carbon dioxide (calculated -0.23 compared to -0.11), we might predict that silicon dioxide should be less acidic, at least, and possibly slightly basic.

What are the facts? Silicon does indeed join oxygen to form a polymeric oxide, SiO_2. No analog of the gaseous CO_2 is known. In the polymer, or giant molecule structure, each silicon atom is surrounded by four oxygen atoms, joined to them at bond angles of 109°. Each oxygen atom is joined to two silicon atoms—but the bond angle here is about 140° instead of 109°. How is this large angle to be explained? We do not yet know the answer, but a tentative explanation is derived from the facts that (1) each oxygen has two pairs of electrons in the outer shell not used in single bonding, and (2) silicon atoms, especially when made more electronegative through oxidation, can use their outer *d* orbitals. It is possible that a form of double bonding of oxygen to silicon could occur to some extent. To this same extent, the outer electrons of the oxygen would be fully occupied with two bonds, tending to make the bond angle 180°. The partial nature of this form of double bonding might then result in the actual bond angle of 140°.

Silicon dioxide, or "silica" as it is commonly called, appears to have no basic properties, but it is weakly acidic. Most of the earth's crust consists of silica combined with various more basic oxides, forming salts called silicates. Uncombined silica is also very abundant as sand or quartz.

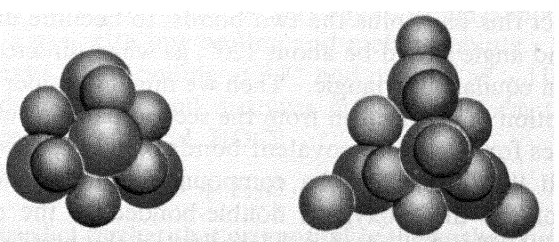
Phosphorus and Oxygen

Phosphorus atoms have the same outer electronic configuration as those of nitrogen, but differ from nitrogen atoms in much the same respects in which silicon atoms differ from those of carbon. That is, phosphorus has less tendency toward ordinary double bond formation, but can use outer *d* orbitals on occasion to expand its normal bonding capacity. Its atoms are larger, less compact, and much less electronegative than those of nitrogen (2.16 compared to 2.93). We could predict from these facts that phosphorus should unite with oxygen to form more polar bonds and hence stabler bonds than are formed by nitrogen. If the three single covalent bonds of which phosphorus atoms are most easily capable are formed, the oxide should have the formula P_2O_3. If, in addition, the unshared pair of electrons on the phosphorus could be split by promoting one of them to an outer *d* orbital, then two more covalent bonds could form, and the expected formula would be P_2O_5. It would be difficult to predict whether these substances would be polymeric or molecular. We could observe, however, that they are less likely to be polymeric than silica, because of the lower polarity in the bonds. Furthermore, we could predict them to be more acidic than

silica, consistent with the lower partial negative charge on oxygen (calculated -0.18 in P_2O_3, -0.13 in P_2O_5). However, they should be expected to be less acidic than the corresponding nitrogen oxides.

In fact, the most important oxides of phosphorus do have the empirical formulas we predicted. They are molecular, although tending to be polymeric, and they are acidic, although not strongly so. The molecular formulas, however, are not those predicted. The phosphorus(III) oxide is not P_2O_3 but P_4O_6. The phosphorus(V) oxide, familiarly known as "pentoxide" or "P-2-O-5," actually has the molecular formula P_4O_{10}. Once more we find our predictions not exactly verified, but once more, knowing the facts, we can see that they are at least reasonable. The structure of P_4O_6 shows how it might have been derived from the tetrahedral P_4 molecule, by adding one oxygen atom along each of the six edges of the tetrahedron to bridge the two phosphorus atoms. This would result in an expansion of the tetrahedron, so that the phosphorus atoms would no longer be in direct contact, but their relative positions would still outline a regular tetrahedron in space. The OPO bond angles are 99°, showing some distortion from a regular tetrahedron if the unshared electron pair on the phosphorus is considered to form the fourth corner. The POP bond angles are not about 109° or less, as we would predict for two single bonds, but about 128°. The explanation for this may possibly be similar to that for the wider angles in silica—partial use of outer *d* orbitals of the phosphorus for a kind of partial double bonding with the oxygen, using the otherwise unshared pairs of the oxygen to occupy these *d* orbitals.

The (V) oxide, P_4O_{10}, is easily derived from P_4O_6 by merely adding an oxygen atom to each phosphorus, filling the fourth position. This oxygen is found to be joined to the phosphorus by a very short bond, suggesting multiplicity and almost certainly implying promotion of one of the electron pair on phosphorus to an outer *d* orbital.



P_4O_6 P_4O_{10}

Figure 67. Phosphorus(III) and (V) oxides.

P_4O_6 reacts with water forming phosphorous acid, H_3PO_3. This is found to have only two replaceable hydrogens, suggesting that the third hydrogen is attached to phosphorus rather than to oxygen. P_4O_{10}, which has such a strong affinity for water that it dehydrates air down to an extremely low humidity and is therefore very useful as a drying agent, unites with water to form orthophosphoric acid, H_2PO_4. Both phosphorous and phosphoric acid are somewhat weaker acids than are usually classified as strong, but they are not extremely weak. The (III) acid and its salts are reducing agents, being easily oxidized to phosphoric acid and phosphates. Phosphorus in the (V) state thus contrasts strongly with nitrogen in the (V) state, which is a strong oxidizing agent.

Sulfur and Oxygen

Sulfur atoms have electronic configurations closely resembling those of oxygen atoms. The chief difference is that sulfur atoms have the underlying shell of 8 but oxygen only of 2, thus making it easier for oxygen atoms to form double bonds. But sulfur atoms are larger, less compact, much less electronegative (2.66), and can utilize outer *d* orbitals unavailable in oxygen. We could predict a variety of possibilities for reaction between oxygen and sulfur. First, we might predict a molecule, SO, analogous to O_2, since each sulfur atom can form two covalent bonds, and so can each oxygen. The bonds would be somewhat polar, but not highly so, because sulfur itself is fairly high in electronegativity. Then, we could observe that sulfur, like phosphorus, might expand its valence capacity by promotion of one of an unshared electron pair to an outer *d* orbital. This would create, as such a promotion always does, the capacity for two more bonds at once. Then sulfur could form four single bonds or the equivalent, and might unite with oxygen to form a compound of formula, SO_2, with each oxygen double-bonded to the sulfur. Since there would still be an unshared electron pair on the sulfur, we would expect this pair, plus the two bonds, to become distributed so that the bond angle would be about 120°, as when directed toward the corners of an equilateral triangle. Then we might consider the possibility of promotion of an electron from the second pair on sulfur, creating the requisites for two more covalent bonds or their equivalent. This could permit the formation of a compound having the formula SO_3, with each of the three oxygens double-bonded to the sulfur. This molecule, with all sulfur electrons involved in the bonding, would be triangular and planar, the bond angles 120°. These compounds would be oxidizing and acidic.

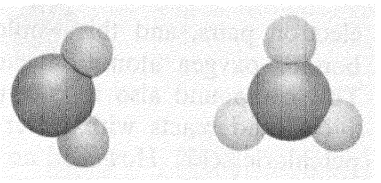


Figure 68. Models of sulfur dioxide and sulfur trioxide.

In fact, what are the important oxides of sulfur? Although SO has been reported, more recent work seems to establish it as S_2O instead, in which case SO is unknown. But when sulfur is burned in air, the major product is sulfur dioxide, SO_2, which is capable of taking on another oxygen under favorable conditions to form sulfur trioxide, SO_3. Sulfur dioxide in water forms a very unstable, weak acid, but is a reducing rather than oxidizing agent, being readily oxidized to sulfuric acid. Sulfur trioxide is a good oxidizing agent, and unites with water to form sulfuric acid:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Structurally, both SO_2 and SO_3 are exactly as predicted (Figure 68).

Chlorine and Oxygen

Chlorine atoms contain seven outer electrons in a shell that could hold 8 very stably, and hence has but one vacancy for ordinary covalent bond formation under usual conditions. However, the shell is number 3, and outer *d* orbitals can sometimes be employed—especially in combining with a more electronegative element. Chlorine is third highest in electronegativity among the elements, having the value 3.28 compared to 3.46 for oxygen.

From these facts, we may predict that the simplest compound of chlorine with oxygen would be of formula Cl_2O. The bonds in this could only be very slightly polar, with oxygen slightly negative, and therefore the compound should be acidic and a strong oxidizing agent. Intermolecular attraction would be very slight, so the compound should probably be a gas, with low boiling and melting points. Such a substance does exist, a gas boiling at 3.8° and melting at −116°, which is a strong oxidizing agent and dissolves in water to form the unstable weak acid hypochlorous acid, HOCl:

$$Cl_2O + H_2O \rightarrow 2HOCl$$

We might predict further that promotion of the unshared pairs of electrons on the chlorine in Cl_2O could permit addition of extra oxygen atoms to each chlorine atom by double bonds. There are three such

electron pairs, and this would permit a maximum of three double-bonded oxygen atoms on each chlorine, giving the formula Cl_2O_7. This compound also is known. It is unstable, a powerful oxidizing agent, and reacts with water to form the very strong acid $HClO_4$, perchloric acid. However, no such oxides of intermediate oxygen content are known. Instead, there are the highly unstable and explosive ClO_2 and ClO_3. The whole series of acids is known: HOCl, HOClO, $HOClO_2$, and $HOClO_3$. These go from weak to very strong in the order mentioned, and are named hypochlorous, chlorous, chloric, and perchloric acids.

THE PERIODICITY OF OXIDES

We might proceed as above throughout the entire periodic table, but enough details have now been discussed to enable you to see the general trends. You can see what is meant by "chemical periodicity" as you examine the range of properties shown by the compounds of the various elements with oxygen. You can see that the period from lithium to fluorine is roughly paralleled by that from sodium to chlorine, that in general, across the periodic table from left to right, the oxides change from ionic, stable, high melting, nonvolatile, nonoxidizing, basic compounds, gradually to molecular, unstable, low melting, volatile, oxidizing, acidic compounds. The oxygen remains constant but its condition varies with the nature of the other atoms to which it is attached. We can therefore achieve a fair understanding of the chemistry of oxygen in terms of its partial charge, used as an index of its combined condition. We can say that when the partial negative charge on oxygen is high, the compound is likely to be solid, high melting, high boiling, ionic, nonvolatile, nonoxidizing, and basic. If the partial negative charge on the combined oxygen is low, the compound is likely to be relatively unstable, volatile, molecular, oxidizing, and acidic. The rough distinction between metal oxides and nonmetal oxides is thus explained, for it is in metal oxides that the oxygen is most likely to be of highest negative charge, and in nonmetal oxides of lowest charge.

Transition Metal Oxides

Oxides of all the transition metals are known, and although partial charges on oxygen have not been calculated for lack of reliable electronegativity values for these elements, the properties are not unexpected.

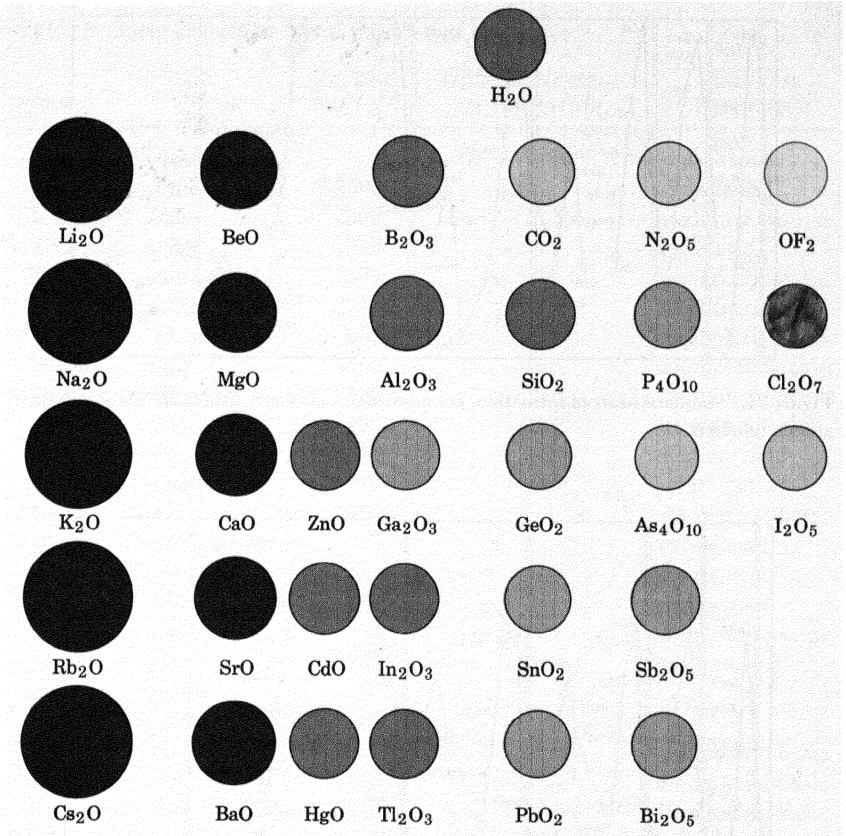


Figure 69. Chart showing radius and charge of oxygen in binary compounds.

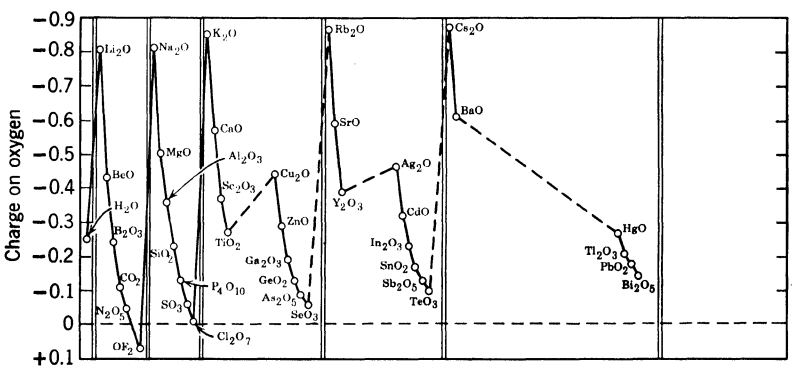


Figure 70. Charge on oxygen in binary oxides, with increasing atomic number.

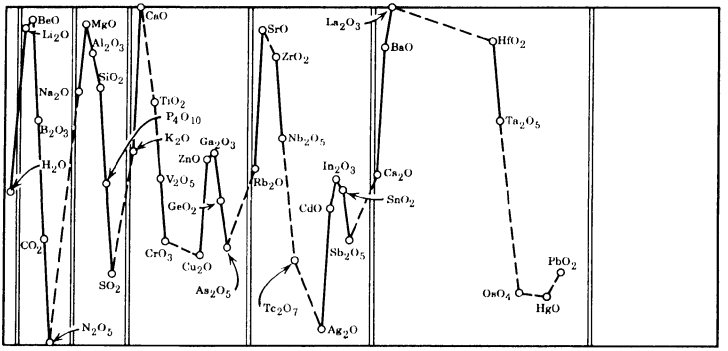


Figure 71. Standard heats of formation, per equivalent, of binary oxides, in relation to their atomic numbers.

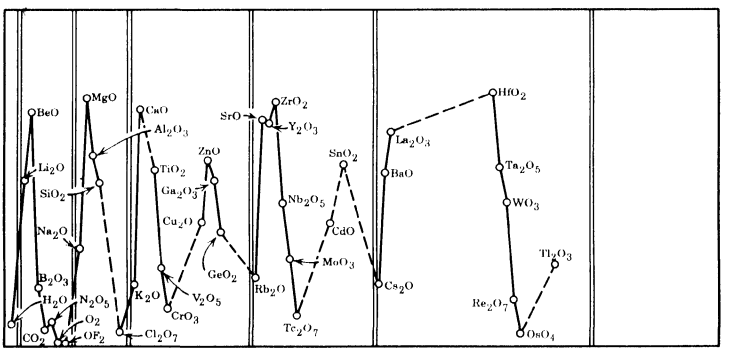


Figure 72. Melting points of oxides in relation to atomic number of element.

When the same oxidation state is compared across a transition series, a slow trend toward lower basicity is observed, which would correspond to a trend of slowly increasing electronegativity of the metal. When different oxidation states of the same element are compared, the lowest is always most basic and basicity decreases, with acidity increasing, as the metal becomes more positive. In general, the oxides are nonvolatile solids, but with reduced charge on oxygen and greater symmetry, in the higher oxides they tend to become more molecular, melting and boiling at low temperatures.

Formulas and properties of some transition metal oxides are summarized in Table 8; a more detailed account will be found in Chapter 26.

Table 8 Some Transition Metal Oxides and Properties

FORMULA	COLOR	MELTING POINT, °C	EQUIVALENT HEAT OF FORMATION	ACID-BASE REACTIVITY
Sc_2O_3	white			weak base
Y_2O_3	white	2690		weak base
La_2O_3	white	2590	−76.3	moderate base
TiO_2	white	1800	−54.5	weak acid
ZrO_2	white	2677	−64.6	amphoteric-basic
HfO_2	white	2774	−67.9	amphoteric-basic
V_2O_5	red orange	685	−37.3	amphoteric-acidic
Nb_2O_5	white	1460	−46.3	amphoteric-acidic
Ta_2O_5	white	1880	−50.0	amphoteric-acidic
CrO_3	dark red	190	−23.1	strong acid
MoO_3	white	795		medium acid
WO_3	lemon	1473	−33.5	acid
Cr_2O_3	green	2450		amphoteric-basic
Mn_2O_7	green-brown	20		strong acid
Tc_2O_7	lt yellow	119.5		strong acid
Re_2O_7	yellow	296		strong acid
MnO_2	grey black	d	−31.1	amphoteric-acidic
MnO	green	1785	−46.0	weak base
RuO_4	yellow	25		
OsO_4	pale yellow	40	−11.5	
Fe_2O_3	red brown		−32.1	amphoteric-basic
FeO	black	d 1370	−31.9	amphoteric-basic
CoO	olive	1810	−28.6	amphoteric-basic
NiO	green	1960	−29.2	base
Fe_3O_4	black	1600	−33.4	

ACIDIC AND BASIC ANHYDRIDES: COMPLEX OXIDES

We have been discussing acid-base properties of oxides in a general way, and have observed that basic oxides react with water to give solutions containing an excess of OH^- ions. For example, lithium oxide forms LiOH, which gives OH^- ions in water. Acidic oxides, on the other hand, react with water, giving solutions having excess H_3O^+ ions. For example, N_2O_5 forms HNO_3, whose aqueous solutions are rich in hydronium ions.

An oxide that unites with water to form a basic hydroxide is the "anhydride" of that base. Lithium oxide, for example, is the anhydride of lithium hydroxide, LiOH:

$$Li_2O + H_2O \rightarrow 2LiOH$$

Similarly, an oxide that unites with water to form an acidic hydroxide (or acid) is the "anhydride" of that acid. Thus N_2O_5 is the anhydride of nitric acid:

$$N_2O_5 + 2H_2O \rightarrow 2HNO_3$$

As briefly explained in Chapter 9, and to be detailed in Chapter 18, an acid in aqueous solution reacts with a base to form water and a salt:

$$LiOH + HNO_3 \rightarrow H_2O + LiNO_3$$

As also noted in Chapter 9, the anhydrides may react similarly, without forming water:

$$Li_2O + N_2O_5 \rightarrow 2LiNO_3$$

In other words, a complex oxide results through combination of a basic oxide with an acidic oxide. The basic oxide is almost invariably an oxide of a metal, and the acidic oxide is most commonly an oxide of a nonmetal. The product is a salt in which metal cations are associated with complex oxyanions containing the nonmetal at the center.

Reasonably, the same salt could also be formed from only one anhydride:

either $$2LiOH + N_2O_5 \rightarrow 2LiNO_3 + H_2O$$

or $$Li_2O + 2HNO_3 \rightarrow 2LiNO_3 + H_2O$$

The most common compounds of this type are sulfates, carbonates, nitrates, phosphates, and silicates. Many others are also known. Of the metals, the most stable such salts are formed by the most active metals—those of lowest electronegativity. The factors influencing stability are numerous and complex, but certain general trends are observable which help to explain it. A salt of a complex oxyanion appears to be more stable, the more completely the anion can control the electrons. The anion appears to be made less stable by a cation capable of deforming it, pulling it out of its normal symmetrical shape. A cation can deform (polarize) an anion by exerting a strong pull on its electron cloud. This pull naturally tends to be stronger the higher the positive charge on the cation, and also the closer this charge can come to the anion, that is, the smaller the cation. Thermal decomposition of such a salt, which usually involves release of volatile nonmetal oxides with nonvolatile metal oxide remaining, therefore tends to occur at higher temperatures for alkali metal salts, next for alkaline earth metal salts. Stable oxyanion salts of tripositive cations are much less common (for example, aluminum carbonate is unknown), and of tetra-

positive cations, which would be smaller yet as well as more highly charged, quite rare indeed. Within a periodic group, the salts tend to be more stable with increasing cation size down the group.

A nonvolatile acidic oxide can displace volatile acid oxides from their salts. Sand is slightly acidic, but being of "giant molecule" structure it has very low volatility. Heated with salts of oxyanions, it reacts forming silicates, for example:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \rightarrow Na_2SiO_3 + SO_3$$

When different metal silicates, especially of sodium and calcium, are melted together, they form a colorless liquid which does not easily crystallize but cools to a transparent, hard, very durable substance called "glass." Hundreds of different glasses are known, and since all are mixtures the composition has almost infinite variability. Melted sand (fused quartz) also solidifies without crystallizing. Fused quartz, and glasses in general, are of course extremely useful materials.

The classification of oxides as acidic or basic is extremely useful, but cannot always be decided from behavior in water because some oxides are insoluble. However, an oxide will usually dissolve in an acidic or basic solution, even if insoluble in pure water, by forming a complex oxide salt. An oxide is classified as basic if it dissolves in acid, acidic if it dissolves in base. If the oxide refuses to dissolve in an aqueous solution of any kind, it can still be classified as basic if it can be fused with an anhydrous acid (such as SiO_2), or acidic if it can be fused with an anhydrous base (such as CaO).

The more negative its oxygen the more basic an oxide is, and the less negative the more acidic. Oxides whose oxygen is intermediate in charge are "amphoteric": they can join more basic oxides by acting acidic, or more acidic oxides by acting basic. Water itself is a good example. Another is ZnO:

$$ZnO + Na_2O \rightarrow Na_2ZnO_2$$
$$ZnO + SO_3 \rightarrow ZnSO_4$$

SPECIAL HELP

Test Your Memory

1. What qualities of an oxygen atom contribute to its bonding ability, and how?

2. How is oxygen prepared in the laboratory? Industrially?
3. What properties of water can be predicted from the structure of hydrogen and oxygen atoms, and how?
4. How is hydrogen peroxide different from water?
5. What differences between lithium atoms and beryllium atoms make beryllium hydroxide a weaker base than lithium hydroxide?
6. Compare carbon dioxide with carbon monoxide in all respects possible.
7. How would oxides of nitrogen be expected to behave as oxidizing agents, and why?
8. Should a compound of fluorine and oxygen be called an oxide or a fluoride, and why?
9. Trace the trends in physical and chemical properties of oxides across the periodic table. What is their relation to the partial charge on oxygen?
10. What factors should cause similarities, and what factors differences, among oxides of beryllium and magnesium and calcium?
11. Similarly, compare oxides of boron and aluminum.
12. What is the molecular formula of the phosphorus(V) oxide, and how might it be derived from white phosphorus?

Test Your Math

1. How much potassium chlorate is needed to produce one liter of oxygen (SC)?
2. How many liters of oxygen (SC) could be prepared from 5 moles of $KMnO_4$?
3. Lithium oxide (4 moles) reacts with how many moles of water to form lithium hydroxide?
4. How many liters of oxygen beyond the amount expected for the normal oxide would be taken up by 460 g Na in forming the peroxide?
5. How much sodium hydroxide could be formed from 460 g of sodium?
6. What volume of hydrogen would be liberated in (5)?
7. Sodium hydroxide is used to absorb SO_3 gas forming sodium sulfate. What weight of NaOH would be required to remove all the SO_3 from 20 liters of air (SC) containing 1 per cent SO_3 by volume?
8. From 11.2 liters (SC) of oxygen, how many grams of each of the following nitrogen oxides could be formed? (*a*) N_2O_5, (*b*) NO, (*c*) NO_2, (*d*) N_2O, (*e*) N_2O_3.

Test Your Understanding

1. Electronically, what must be done to a combined oxygen atom to liberate it as the free element?
2. Would it be easier to liberate oxygen from its compound with an active metal or from its compound with an active nonmetal, and why?
3. In the industrial production of oxygen, why is air not liquified merely by increased pressure?
4. If reducing ability increases with increasing negative charge on an atom, why is not negative oxygen a good reducing agent?
5. Which of the oxides, Tl_2O or Tl_2O_3, would you expect to be more basic, and why?
6. Predict the formula and general physical nature of oxides of each of the following elements: tin, zinc, indium, selenium, titanium, tungsten.
7. Why would you expect hydrogen peroxide, H_2O_2, to be a stronger oxidizing agent than water?
8. Compare the highest possible oxide of a major group element, in general, with that of its right hand neighbor in the periodic table.
9. Certain elements (1) and (2) both burn in air. The oxide of (1) is much more volatile than the oxide of (2). If these elements are in the same period, which has smaller atoms and how do you know?
10. What would you predict, and on what basis, concerning the reactivity of the oxide of a relatively volatile element with sodium hydroxide?
11. Would a volatile element be expected to form a volatile or nonvolatile oxide, and why?
12. A certain element that has a high melting point forms an oxide of relatively low melting point. Explain.

13

Fundamental Interpretations of Hydrogen Compounds

PREPARATION AND PROPERTIES OF HYDROGEN

HYDROGEN OCCURS free on earth only in traces. For any practical use, it must be prepared from its compounds. It is released simultaneously with oxygen when electricity is passed through water (Chapter 20), and simultaneously with chlorine when the water contains chloride ion. It can be prepared by the action of acids on certain, but not all, metals. As will be explained in Chapter 20, any metal that can liberate hydrogen from an acid solution could in principle react similarly with water. The type reaction would be:

$$M + H_2O \rightarrow M{-}OH + \tfrac{1}{2}H_2$$

Whether this reaction could continue depends on whether the hydroxide thus formed coats and protects the metal. If the hydroxide is soluble in water, no protection is given to the metal and it continues to displace hydrogen from the water. An insoluble hydroxide coating stops the hydrogen displacement almost immediately. For these reasons lithium,

sodium, and calcium, which form soluble hydroxides, readily displace hydrogen from water alone. In fact, sodium reacts with dangerous vigor. But magnesium, aluminum, zinc, and iron, whose hydroxides are insoluble, only react superficially with water and then stop.

If something is added to the water to dissolve away the hydroxide coating as fast as it forms, evolution of hydrogen can continue. This is the purpose of the acid, which dissolves the metal hydroxide as an acid-base neutralization:

$$M{-}OH + HA \rightarrow H_2O + M^+ + A^-$$

The hydroxides of zinc and aluminum are amphoteric, which means that base will dissolve them as well as acid. Therefore these metals will continue to displace hydrogen from a basic solution also:

$$Zn + 2H_2O + 2NaOH \rightarrow Zn(OH)_4^= + 2Na^+ + H_2$$

$$2Al + 6H_2O + 2NaOH \rightarrow 2Al(OH)_4^- + 2Na^+ + 3H_2$$

$$(\text{or } [Al(OH)_4(H_2O)_2]^-)$$

In the laboratory, hydrogen is generated most commonly by action of dilute hydrochloric or dilute sulfuric acid on zinc or aluminum.

It can also be produced, as will be described below, by reaction of a compound of positive hydrogen, usually water, with a compound of negative hydrogen.

On a large scale, hydrogen is produced as a major component of "water gas," formed when steam is passed through red-hot coke (carbon):

$$C + H_2O \rightarrow CO + H_2$$

This may be followed by a further reaction:

$$H_2O + CO \rightarrow CO_2 + H_2$$

The carbon dioxide can then be separated from the hydrogen by dissolving the CO_2 in water under pressure. Thermal decomposition of "hydrocarbons," compounds containing only carbon and hydrogen, also provides hydrogen gas on an industrial scale. Much of this is used in the synthesis of ammonia.

The Nature of Hydrogen Atoms

Hydrogen is the only element that uses all its electrons for bonding. The hydrogen atom has, of course, only one electron. This, in an orbital that can hold two electrons, means the existence also of a vacancy capable of accommodating an outside electron. A hydrogen atom thus

possesses the requisites for the formation of one single covalent bond. Having formed such a bond, it has neither a vacant orbital for acceptor action nor an unshared pair for donor action. Yet, as we shall see, in a manner of speaking it seems to have both. But very important in the nature of hydrogen chemistry is the fact that unlike all the other elements, there is no electron cloud beneath the valence shell. The interaction of other atoms is restricted by the repulsions between their underlying clouds, but not so hydrogen.

Hydrogen also is especially interesting because of its intermediate electronegativity, 2.31. By combining with other elements, hydrogen can become partially negative if the other elements are below it in electronegativity and partially positive if the other elements are above it in electronegativity. Combined hydrogen thus is found in a wide range of conditions that are consistent with a wide range in the physical and chemical properties of the compounds. From a knowledge of this quality of hydrogen and of the qualities of atoms of the other elements, we can predict, explain, and understand hydrogen chemistry in much the same way as was demonstrated in the preceding chapter for oxygen chemistry.

BINARY COMPOUNDS

Lithium and Hydrogen

Lithium, as we have seen, has relatively large atoms considering its small atomic number of 3, and these therefore cannot be very compact. Lithium has therefore a very low electronegativity (0.86), and loses its outer and valence electron rather easily. From this knowledge, and knowing the general nature of hydrogen atoms, it is easy to predict that lithium and hydrogen should combine to form a compound of formula LiH, in which the bonds must be highly polar since hydrogen is so much higher than lithium in electronegativity. Ionic crystals would be expected, through condensation of the highly polar single molecules that might first form. These would be relatively high melting and low in volatility.

Chemically, what should we expect of negative hydrogen? Remember that hydrogen itself can give up part of its electron to elements more electronegative and thus act as a reducing agent. Certainly we should expect any atom capable of reducing action to become more capable as it acquires higher negative charge. The better its supply of electrons, the more freely it can donate them. So if elementary hydrogen is a re-

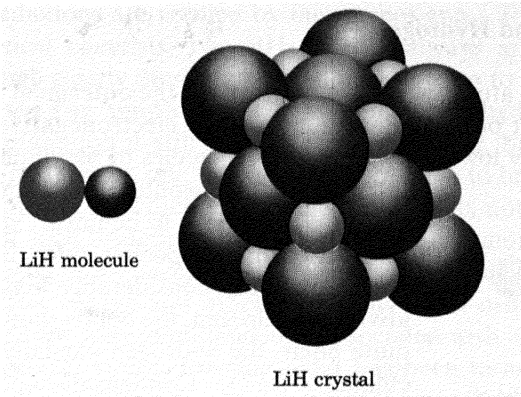


Figure 73. Lithium hydride: single molecule and crystal. The relatively great expansion of hydrogen in the hydride ion, H^-, is probably associated with the doubling of its electronic cloud and the highly polarizing environment produced by six surrounding Li^+ ions.

ducing agent, negatively charged hydrogen should be a much better reducing agent. At the same time, of course, it should have lost any oxidizing ability it may have had before the reaction in which it became negative. Negative hydrogen should be able to act as electron donor in the formation of coordination compounds.

In fact, lithium metal, when heated in hydrogen gas, becomes oxidized by the hydrogen to a salt-like solid having the formula LiH. That this is highly polar is shown by the fact that when the salt is melted and an electric current passed through it, hydrogen is liberated at the positive electrode and lithium at the negative electrode. Lithium hydride is a good reducing agent. The negative hydrogen is oxidized by a variety of oxidizing agents, even including compounds of positive hydrogen, such as water, which react and liberate hydrogen gas:

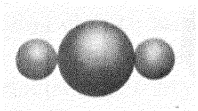
$$LiH + H_2O \rightarrow H_2 + Li^+ + OH^-$$

The hydrogen is also, as predicted, able to act as electron donor. It can form a number of complex hydrides, of which one of the best known is the very useful reducing agent called "lithium aluminum hydride," $LiAlH_4$, which consists of a positive Li^+ ion and a negative complex ion, AlH_4^-:

$$Li^+ H:^- + AlH_3 \rightarrow Li^+ \left[\begin{array}{c} H \\ \cdot\cdot \\ H:Al:H \\ \cdot\cdot \\ H \end{array} \right]^-$$

Beryllium and Hydrogen

Beryllium atoms, with two electrons in the outermost shell, can form two covalent bonds. Beryllium is more electronegative than lithium, but still fairly low (1.37). If single molecules of beryllium hydride were to be formed, we would predict them to have the formula, BeH_2, and to be linear, with a hydrogen atom at each of opposites sides of the beryllium atom. With the considerably higher electronegativity of hydrogen, the bonds should, however, be quite polar, the hydrogen partially negative (calculated -0.17). Condensation of the molecules to form a solid polymeric type of solid would therefore be expected. Something of the nature of this polymerization will be discussed under the next section, on boron. Chemically, we would predict this hydride to be reducing in action, to be easily hydrolyzed with water, liberating hydrogen, and to form complex hydrides under appropriate conditions.



BeH_2

Figure 74. Model of single molecule of beryllium hydride.

In fact, beryllium does not appear to react directly with hydrogen, but by indirect methods a compound having the formula BeH_2 can be prepared. This appears to be a polymeric solid. It is a reducing agent, is hydrolyzed readily by water, liberating hydrogen, and can form certain complexes. In short, the two elements have a chemistry that is in general predictable from a knowledge of the atoms.

Boron and Hydrogen

Boron atoms, although more electronegative than those of beryllium, are still appreciably less electronegative (1.88) than those of hydrogen (2.31). We might easily predict that boron-hydrogen bonds should be polar, with hydrogen negative (-0.05). With three outermost electrons, one would predict that boron should form three single covalent bonds directed toward the corners of an equilateral triangle. The formula of a boron-hydrogen compound should therefore be BH_3. Its molecules should be triangular and planar. They should react with oxidizing agents easily, and with positive hydrogen compounds such as water, with liberation of molecular hydrogen. There being an unused orbital left on the boron atom, BH_3 should be able to act as electron acceptor in the formation of coordination compounds—molecular addition compounds—with electron donors.

All these predictions are verified by fact except one. To the frustration of theoretical chemists, two BH_3 groups always are associated together, although clearly there are not enough electrons to form normal covalent bonds. The simplest molecule of a boron hydride is then B_2H_6. The explanation is still somewhat controversial, but it appears that two of the hydrogens, one from each boron, serve to bridge the two borons. The means by which this bridging occurs is not thoroughly understood, but such bridging appears to be most commonly observed when the hydrogen bears partial negative charge and the bridged atoms have both positive charge and otherwise empty outer orbital. It is as though two electrons were simultaneously associated with one hydrogen atom and two boron atoms, forming what has been termed a "**three-center**" bond. We may call this, to designate the negative character of

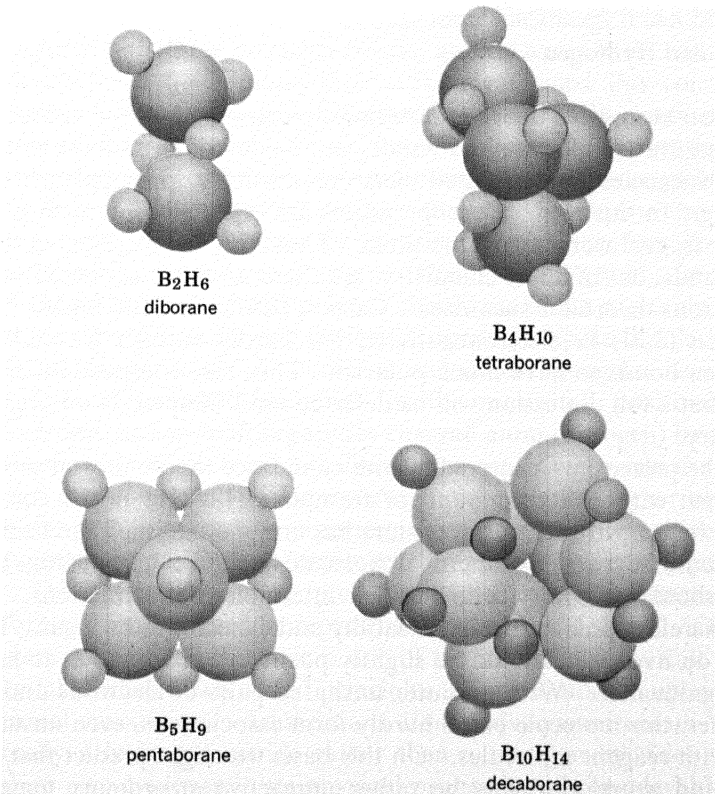


Figure 75. Some hydrides of boron. None of these can be explained satisfactorily in terms of conventional covalent bond structures, and their existence exposes an important limitation to the simple theory of electron pair sharing.

the hydrogen bridge, "**hydridic bridging,**" and postulate that similar bridging permits polymerization in such solid hydrides as those of beryllium and aluminum.

Several other boron-hydrogen compounds are known, all presenting similar problems in valence, and presumably explainable in part in terms of hydridic bridging, but in part also by the special character of boron, which is intermediate between metal and nonmetal. Some of the better-known compounds have formulas B_4H_{10}, B_5H_9, and $B_{10}H_{14}$. All are volatile and easily oxidized. They have attracted special attention as potential rocket fuels, because their heat of combustion per pound is considerably higher than that of hydrocarbons. The higher heat is not surprising, in view of the greater polarity of boron-oxygen compared to carbon-oxygen bonds.

Carbon and Hydrogen

Carbon atoms, having four outermost electrons and four vacancies, can form four single covalent bonds, and having done so have neither orbital vacancies nor unshared electrons available for supplementary bonding. In this respect, carbon atoms are especially interesting, for only hydrogen atoms resemble them. Thus only in hydrogen-carbon compounds, out of all of chemistry, are there no outer unshared pairs of electrons or orbital vacancies. Carbon (2.47) is a little higher than hydrogen (2.31) in electronegativity, but hardly enough for carbon-hydrogen bonds to have much polarity. This, too, is especially interesting, but a full discussion will be deferred until Chapter 24 on organic chemistry.

For the present, we can predict with confidence that hydrogen should form with carbon a compound of formula CH_4. We might equally well, or better, write H_4C, but custom has firmly established the former. This should be a very symmetrical molecule, a regular tetrahedron, and thus it should offer very little basis for intermolecular attractions. We could therefore predict its high volatility and expect it to be a gas. The charge on hydrogen should be slightly positive, but so low as to have little significance. With no outer unshared pairs of electrons and no vacancies, this molecule could hardly form associations, even unstable ones, with reagent molecules. On this basis we might predict that the compound would probably be rather unreactive at ordinary temperatures. However, it should burn readily when ignited in air, since both carbon and hydrogen alone burn readily.

Our predictions are verified by fact. Methane, CH_4, is a well-known compound. It is a gas of very low melting ($-182.5°$) and boiling ($-161.5°$) points. It is relatively unreactive under ordinary conditions, except that it burns easily, forming carbon dioxide and water as the sole products:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

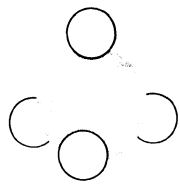
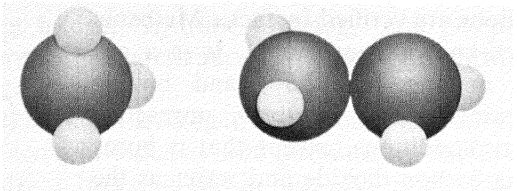


Figure 76. Model of methane.

Nitrogen and Hydrogen

Nitrogen, with electronegativity 2.93 compared to 2.31 for hydrogen, should remove electrons from hydrogen rather than vice versa. With its five outermost electrons but only three vacancies, it can be predicted to form only three covalent bonds, and its compound with hydrogen should have the formula H_3N. Having formed this compound the nitrogen, with its acquired negative charge and its extra pair of unshared outer electrons, should be able to act as electron donor in the formation of coordinate covalent bonds. The structure of H_3N should be that of a low pyramid, because the three bonds *and* the extra electron pair should tend to be directed toward the four corners of a tetrahedron, around the nitrogen. This dissymmetry of spatial arrangement added to the bond polarity should make the molecule polar, and some association among molecules through dipole-dipole interaction should be expected. In addition, one should recognize here the possibilities of protonic bridging, for the requisites, positively charged hydrogen and a small negatively charged atom (nitrogen) having an unshared pair of electrons, are clearly present. One would therefore predict this compound to be somewhat less volatile, higher melting and boiling, than otherwise expected. The presence of positive hydrogen suggests the possibility of acidic reactions under favorable circumstances.

The fact that verifies our predictions is the compound ammonia, whose formula could indeed be represented as H_3N, and should, if our system were consistent. But here is one of the inconsistencies that appear inevitable when newly found principles are superimposed upon old, traditional empiricism. Ammonia is almost always written as NH_3. It is really a hydrogen nitride rather than a nitrogen hydride. Ammonia does give evidence in its physical properties of considerable protonic bridging. Although under ordinary conditions it is a gas (boiling at $-33.4°$), it is easily liquefied, a pressure of 10 atmospheres at 25° being



NH_3 N_2H_4

Figure 77. Models of ammonia and hydrazine.

enough. In the liquid state, it has interesting properties as a solvent, resembling water in several respects. It does have some acidic properties, as predicted, such as action on active metals to liberate hydrogen:

$$2Na + 2NH_3 \rightarrow H_2 + 2Na^+ + 2NH_2^-$$

The NH_2^- ion is called "amide." It is more basic than hydroxide ion. Ammonia also acts as electron donor very readily, hundreds of coordination complexes of ammonia, called "ammines," being known, as well as the familiar ammonium salts, in which ammonia coordinates a proton:

$$H^+ + :NH_3 \rightarrow NH_4^+$$

The NH_2 group in NH_3 is closely analogous to the OH group in H_2O. Analogous to hydrogen peroxide, HO—OH, is "hydrazine," $H_2N—NH_2$. This is an unstable liquid (boiling at 113.5°) that has some use as rocket fuel.

Oxygen and Hydrogen

The combination of these two elements follows predictions very closely, as already discussed in some detail in the preceding chapter, page 228.

Fluorine and Hydrogen

Fluorine atoms have seven outermost electrons, with only one vacancy. They can therefore form but one single covalent bond. The high electronegativity of fluorine (3.92) compared to 2.31 for hydrogen, plus the valence, enable us to predict that hydrogen should unite with fluorine to form HF, with a quite polar bond, the hydrogen positive (0.25) and

the fluorine negative (−0.25). We can recognize here again the requisites for protonic bridging, and predict on this basis a relatively high degree of association in hydrogen fluoride, leading to higher than expected melting and boiling points. The positive hydrogen should be acidic, and substantially more so than it is in water.

Hydrogen fluoride is indeed an extremely stable compound, having the formula HF. So strongly does it tend to become associated through protonic bridging that it is much less volatile than might be expected, boiling at about 19° and even associated in the vapor below 100°. It dissolves in water to form the weak acid hydrofluoric acid. The weakness of its acidity is discussed in Chapter 18. The salts of this acid, the fluorides, are as a class among the stablest of compounds. So readily do hydrogen and fluorine unite to form hydrogen fluoride that under almost all conditions they combine spontaneously and with violence. Metallic salts can be made by heating the metal or its oxide in a stream of hydrogen fluoride gas.

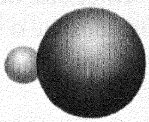


Figure 78. Model of hydrogen fluoride.

Hydrogen fluoride attracts special interest because of its action on the normally quite inert SiO_2 and metal silicates. It readily displaces the oxygen from the silicon, forming SiF_4, a stable gas:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Glass, which is a mixture of silicates, is therefore unsuitable for containing hydrofluoric acid, which must be stored in certain plastic or wax containers.

Hydrogen fluoride causes exceedingly painful and slow-healing burns when even a little of the gas comes in contact with the skin, the pain developing later even when no sensation was observed on contact. Despite this dangerous quality, hydrogen fluoride is used industrially on a large scale as a catalyst for making gasoline, with practically no injury to personnel because adequate safety precautions are taken.

Trend Thus Far

As stated earlier, the intermediate electronegativity of hydrogen allows us to observe a very wide trend in properties of hydrogen compounds across the periodic table. In physical properties, they change from ionic crystals, through hydridic bridged polymers, to unassociated gases, to molecular compounds associated through protonic bridging.

In chemical properties, they change from active reducing agents, basic compounds, easily oxidized and easily hydrolyzed and able to act as electron donors, through relatively unreactive substances to acidic, oxidizing agents able to act as electron acceptors through liberation of protons. Associated with these changes so closely that it may be used as an index of the condition of combined hydrogen, and therefore to predict these properties, is the partial charge on hydrogen. It changes from high negative to moderately high positive across the table.

To check on whether this is a typical trend, it will be interesting to consider in a similar manner the next period of elements, beginning with sodium.

Sodium and Hydrogen

The close outer resemblance of sodium to lithium suggests that its compound with hydrogen might be similar. From the monovalence of sodium, we can predict the formula of the sodium compound with hydrogen to be NaH. From the very low electronegativity of sodium (0.85), even lower than that of lithium although only slightly so, we can predict that the hydrogen should become quite highly negative (calculated -0.50), leaving the sodium positive (0.50), and thus the compound should be ionic. Its negative hydrogen should be strongly reducing, a good electron donor, reactive with positive hydrogen compounds such as water to liberate molecular hydrogen and form a strongly basic solution (in water).

How are these predictions? Accurate. Sodium metal when heated

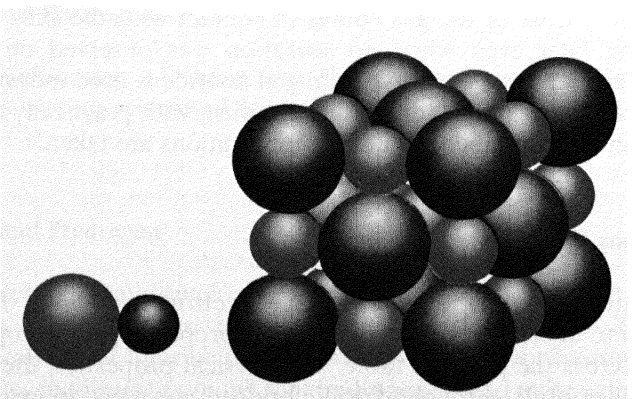


Figure 79. Models of sodium hydride: molecules and crystal. (Notice the great expansion of hydrogen in hydride ion in the crystal, as in LiH.)

in hydrogen gas unites with it to form the salt NaH, which has all the properties just predicted. Sodium hydride is applied industrially to the removal of traces of oxide from the surface of iron. First, the hydride is dissolved in fused NaOH. The iron is plunged into this solution, then lifted out and plunged into cold water. In keeping with its strong reducing properties, sodium hydride presents an interesting problem in fire control, for it easily catches fire and burns in air. The common extinguishing agents are water, carbon tetrachloride, and carbon dioxide. All three of these "add fuel to the flame" when directed on burning sodium hydride, by reacting vigorously with it. The fire must be smothered with a relatively inert substance such as sand.

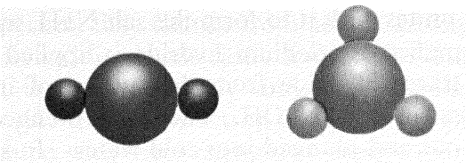
Magnesium and Hydrogen

Magnesium atoms have two outermost electrons and can therefore form two covalent bonds. The bonds are expected to be linear in direction if single molecules are formed. Magnesium is appreciably less electronegative than beryllium, 1.21 compared to 1.37, and would form correspondingly more polar bonds with hydrogen. We can therefore predict a magnesium hydride of formula MgH_2, having quite polar bonds and probably polymerizing, perhaps through hydridic bridging. It should have the chemical properties we can now recognize as characteristic of negative hydrogen: reducing power, electron donor ability, reactivity with compounds of positive hydrogen such as water, liberating molecular hydrogen.

Actually, magnesium hydride is a polymeric white solid of formula MgH_2, having properties just as predictable for it.

Aluminum and Hydrogen

From the similarity of aluminum atoms to those of boron, we might be tempted to predict the same kind of chemistry with hydrogen. Just as in the chemistry of oxygen with these two elements, however, we must recognize certain important differences. One is that aluminum is considerably less electronegative than boron, 1.39 instead of 1.88, and therefore should form much more polar bonds with hydrogen. The other is that aluminum now has its valence electrons in principal quantum shell number 3, which means that outer *d* orbitals are present that are not available in boron, permitting aluminum to form more than four bonds at once. We might on this basis predict a higher degree of association in aluminum hydride than the dimerization observed in



MgH_2 AlH_3

Figure 80. Model of single molecules of magnesium and aluminum hydrides. (With two vacant orbitals on Mg and one on Al, and high negative charges on H, these molecules condense readily to highly polymeric solids.)

diborane, B_2H_6. But in a sense this is speculation after the fact. Actually we can only predict that aluminum-to-hydrogen bonds should be more polar than boron-to-hydrogen bonds. The expected formula is, of course, AlH_3, and the chemistry is that expected for negatively charged hydrogen (−0.15).

Aluminum hydride of the expected formula does exist. It is not dimeric like the boron compound, but much more highly polymeric. This association presumably occurs through hydridic bridging, perhaps using the outer *d* orbitals to some extent. The compound is spontaneously inflammable, and generally strongly reducing, and reacts with water to liberate molecular hydrogen:

$$AlH_3 + 3H_2O \rightarrow 3H_2 + Al(OH)_3$$

It is also capable of acting as electron acceptor, which suggests that the hydridic bridging, as in diborane, can readily be broken if a better electron donor comes in view. As mentioned under lithium, the hydride ion of LiH donates an electron pair to AlH_3 in forming $LiAlH_4$.

Silicon and Hydrogen

Silicon atoms, as discussed in the chapter on oxides, differ from carbon atoms in two important respects—the same, in fact, as just discussed between aluminum and boron. Although we would predict a silicon-hydrogen compound analogous to methane in formula, SiH_4, we would predict different properties for it because the hydrogen here, instead of being nearly neutral, is distinctly negative (−0.05). The physical properties should be little affected by this difference, since the molecule should be highly symmetrical and present an outward view only of hydrogen atoms. We might predict then that SiH_4 should be very volatile, lacking intermolecular attractions of any substantial

nature, and probably gaseous. Chemically, however, we should be inclined to predict that this compound should be easily oxidized, a much more effective reducing agent than methane, and hydrolyzed by water liberating hydrogen gas, in contrast to methane which water does not affect.

The facts bear out these predictions. The simplest compound of silicon and hydrogen is indeed a gas having the formula SiH_4. This gas is spontaneously inflammable in air and generally a good reducing agent. With water its behavior is curious, in that no reaction appears to occur in the complete absence of alkali, but a mere trace is enough to promote rapid hydrolysis to silica and molecular hydrogen:

$$SiH_4 + 4H_2O \rightarrow SiO_2 \cdot 2H_2O + 4H_2$$

Phosphorus and Hydrogen

Phosphorus is still less electronegative than hydrogen, but only by a very small amount (2.16 compared to 2.31). We would therefore predict phosphorus-to-hydrogen bonds to be nearly nonpolar, with small partial positive charge on phosphorus (0.04) and negative charge (−0.01) on hydrogen. The electronic configuration of phosphorus outwardly resembles that of nitrogen, and the predictable formula of the hydrogen compound is therefore PH_3. This should resemble ammonia structurally, having a low pyramidal shape corresponding to a tetrahedron with one corner occupied by an unshared pair of electrons. It would be difficult to predict whether the very low negative charge on hydrogen would be sufficient to give the compound chemical properties characteristic of negative hydrogen. From the known ready oxidizability of phosphorus, at least, one would predict the compound to be easily

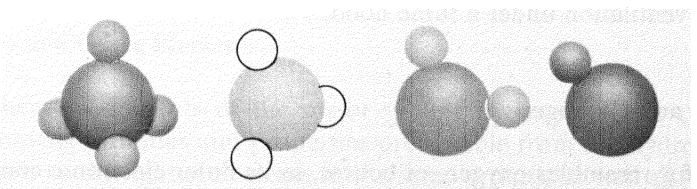


Figure 81. Models of molecules of hydrogen compounds of silicon, phosphorus, sulfur, and chlorine.

oxidized—in other words, a good reducing agent. No appreciable hydrolysis would be expected if the proton of water were to become attached to the unshared pair of electrons on phosphorus instead of uniting with a hydrogen attached to phosphorus, although it would actually be difficult to predict whether a reaction with water would occur. We could, at least, predict that the pair of electrons on the slightly positive phosphorus atom would be considerably less available to electron acceptors than the pair of electrons on the nitrogen in the ammonia molecule. In other words, the phosphorus compound would be predicted to much less basic, or weaker as electron donor. Also, it would not be expected to be acidic. It should not associate through protonic bridging, and therefore should be more volatile than ammonia.

In fact, a compound of phosphorus with hydrogen has the formula PH_3, and is called "phosphine." It is gaseous, boiling at $-87.7°$, showing no tendency toward intermolecular association through protonic bridging, and only weakly able to donate an electron pair. It is not spontaneously inflammable when pure, although as commonly prepared it contains traces of P_2H_4, which make it spontaneously inflammable. It is generally a good reducing agent. In water, it does not hydrolyze, but takes on a proton only to a very slight extent, forming traces of "phosphonium" ion, PH_4^+, and hydroxide ion. The phosphonium salts analogous to ammonium salts are much less stable, only the iodide being somewhat stable at ordinary temperature and pressure.

In the laboratory, phosphine is frequently made by hydrolysis of calcium phosphide, Ca_3P_2:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

The gas is evolved under water, and the bubbles rise to the surface where they ignite spontaneously, giving a flash of light and puff of smoke. Phosphine is extremely toxic, as are many other compounds of phosphorus, and this experiment must not be carried out without adequate ventilation under a fume hood.

Sulfur and Hydrogen

Sulfur resembles oxygen, of course, in its outer electronic configuration, but possesses outer *d* orbitals permitting an expansion of its valence shell. These *d* orbitals should have little significance in the reaction of sulfur with hydrogen. We may predict a compound analogous to water. We must observe, however, that sulfur atoms are larger and much less electronegative (2.66) than oxygen atoms, so that the com-

pound which we predict as H_2S should not have the requisites for protonic bridging so important in water. With little likelihood of appreciable intermolecular attractions except relatively weak dipole-dipole interactions, we might well predict the compound to be gaseous. The hydrogen should be slightly positive, however, and therefore impart some acidity to the compound.

In fact, hydrogen and sulfur form the gaseous hydrogen sulfide, H_2S. This shows no tendency toward appreciable intermolecular association except at very low temperatures (boiling point $-60.3°$). It dissolves to some extent in water, forming a weakly acidic solution, and is absorbed by alkaline solutions with the formation of sulfides. This compound will be discussed in more detail later in the book.

Chlorine and Hydrogen

The outer electronic configuration of chlorine atoms resembles closely that of fluorine atoms, and we may expect a similar reaction with hydrogen. However, we can predict that HCl, once formed, will lack one requisite for protonic bridging, namely the *small* negatively charged atom, and will therefore not be as highly associated as HF. In water, as we know, it should be acidic, consistent with the positive charge on hydrogen (0.16), and, as we shall see later, aided by the relative weakness of the chloride ion as a donor to the proton.

Hydrogen does of course combine with chlorine forming hydrogen chloride, HCl. This is a gas (boiling point $-85.0°$), thus obviously much less associated than HF (boiling point 19°). Also, it dissolves in water wherein it is a strong acid, not weak like HF. Like all acidic substances, it can show oxidizing power through the electron attracting ability of its positive hydrogen.

Hydrogen and Other Elements

With heavier elements of the major groups hydrogen forms compounds having formulas and properties predictable from the hydrogen compounds of the lighter elements in the same groups, as well as from the fundamental properties of the atoms. One important trend must be noted, however: in general, less stable bonds are formed between atoms widely different in size, and bonds between hydrogen and larger atoms are noticeably weaker. As a result, the binary compounds of hydrogen with major group elements from Period 4 on down the chart

are relatively unstable, even HI not being very stable, and the hydrides of Hg, Tl, Pb, and Bi are too unstable to have been studied in detail.

As for the transition metals, the distinctive characteristics of inner *d* orbital bonding show up very obviously in their hydrogen chemistry. They do not form typical metal hydrides, either stoichiometrically or chemically typical. Definite compositions corresponding to predicted formulas are in a few instances approached, but never reached. In general, hydrogen appears to be absorbed in the metal lattice in varying amounts according to the metal and the conditions. The products may keep or lose metallic appearance, and may be reactive or amazingly inert, but they cannot be properly classified with the conventional hydrogen compounds of major group elements. Instead, they are usually termed "**interstitial**" or "**alloy-type**" hydrides.

PERIODICITY OF HYDROGEN CHEMISTRY

The above brief survey of the predictability of properties of hydrogen compounds should, it is hoped, add to your confidence that a knowledge of the fundamentals of atoms is a highly worthwhile preparation for a study of chemical reactions and properties. We have found a consistent relationship between the electronic configuration of an atom and the partial charge on hydrogen in the binary compound of that atom with hydrogen. As the number of outermost electrons changes across the periodic table, from one to seven, the atoms grow smaller and more electronegative. The compounds with hydrogen change from ionic solids in which the hydrogen, highly negative, is electron donating, reducing, and reactive with positive hydrogen liberating hydrogen

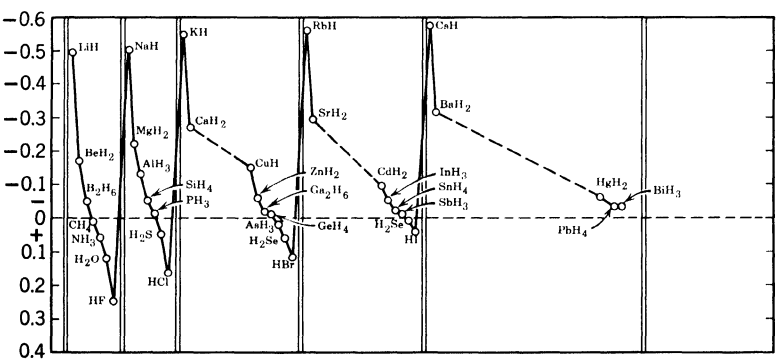


Figure 82. Partial charge on combined hydrogen.

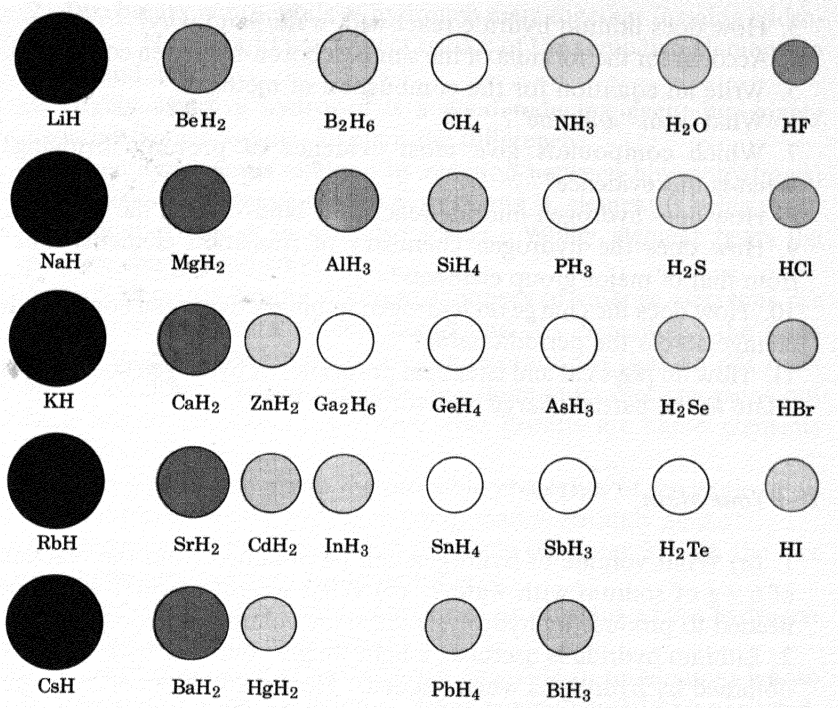


Figure 83. Chart showing partial charge on hydrogen in binary compounds.

gas; through polymeric hydrides in which the molecules are held together through hydridic bridging, whose chemical properties remain those characteristic of negative hydrogen; through volatile compounds of neutral hydrogen having essentially no basic properties; to volatile compounds of positive hydrogen which tend to be associated through protonic bridging if the other atom is small, which are acidic and oxidizing.

SPECIAL HELP

Test Your Memory

1. In what ways (other than atomic number) do hydrogen atoms differ from those of all other elements?
2. What qualities of lithium atoms make lithium hydride a salt-like solid?

3. How does lithium hydride react with water, and why?
4. Account for the formula of the simplest boron-hydrogen compound.
5. Write an equation for the combustion of methane.
6. What is an "ammine"?
7. Which compounds give most evidence of protonic bridging? What is this evidence?
8. How does hydrogen fluoride react with sand? Write the equation.
9. How does the hydrogen chemistry of transition elements differ from that of major group elements?
10. How does the charge on hydrogen in binary hydrogen compounds change across the periodic table?
11. How do physical and chemical properties of hydrogen compounds relate to the partial charge on hydrogen? Why?

Test Your Math

1. (*a*) What volume of hydrogen can be obtained from the reaction of 6.9 g of sodium with water? (*b*) What weight of NaH would be needed to produce by hydrolysis the same volume of hydrogen?
2. Lithium hydride is useful as a light weight source of hydrogen gas, obtained by hydrolysis when needed. How many liters of hydrogen at SC could be liberated from one pound of LiH?
3. What weight in grams of lithium hydride would be contained, in effect, in one pound of $LiAlH_4$?
4. What volume of hydrogen at SC could be obtained by hydrolysis of one pound of $LiAlH_4$?
5. (*a*) What weight of methane must be burned to produce one ton of CO_2? (*b*) What weight of water would be produced at the same time?
6. One liter of nitrogen is converted to ammonia, which then combines with hydrogen chloride forming ammonium chloride. What weight of this salt results?
7. What volume of HBr is needed to convert 6 moles of potassium hydride to potassium bromide, and what volume of hydrogen is obtained?

Test Your Understanding

1. A hydrogen compound of a major group element reacts with water forming a strongly basic solution. To which major groups could this element belong, and why?

2. Two binary compounds of hydrogen react together forming hydrogen gas. How would you expect oxides of the same two elements to react, and why?
3. Highly negative hydrogen is a good reducing agent but highly negative oxygen is not. Explain the difference.
4. When hydrogen is released by reaction between binary hydrogen compounds of hypothetical elements A and B, element B being much less volatile than A, a salt also forms. Which element bears the positive charge, and why?
5. Two elements having different numbers of valence electrons per atom unite to form a volatile compound X. Separately, the same two elements form binary hydrogen compounds that do not react with each other. Neither element has three outer electron pairs, but each has at least one. Of what two groups are these elements members?
6. What can be said about the probable properties of the oxide of an element whose binary hydrogen compound is strongly acidic?
7. Reconcile the Pauli exclusion principle (Chapter 3) with the fact that hydrogen can form protonic bridges.
8. Would an acid react with an oxide of an element whose hydrogen compound is readily hydrolyzed? Why?
9. A nonmetal oxide is heated with an oxide of an element whose hydrogen compound is acidic. What reaction would be expected, and why?
10. Would you predict that a water solution could be prepared of the hydrogen compound of an element whose atoms are close packed in its natural state of aggregation when "free"? Why?
11. The hydrogen in H_2S bears essentially the same partial charge as that in NH_3. Why is H_2S much more volatile?
12. A certain compound of hydrogen with one other element is volatile and unreactive with water, electron acceptors, or electron donors. In what group of the periodic table would you expect to find this element, and why? Which element(s) might it be?

14

Some Chemistry of the Halogens

CHLORINE IS THE MOST COMMON and well known of the family of elements known as the "halogens," which means "salt-forming." The halogens, fluorine, chlorine, bromine, iodine, and the little known astatine, are most similar to one another when they react as oxidizing agents, for all acquire the oxidation state of -1. We should, of course, predict this tendency from the atomic structure, for the atoms are all alike in having seven outermost electrons and therefore but one vacancy. They can thus form but a single covalent bond when they act as oxidizing agents. The outer *d* orbitals, which are present in all but fluorine, are not ordinarily available until the atom has been oxidized, not reduced, which means that they seem inoperative in compounds of halogen in the -1 state.

The halogens as a family are high in electronegativity, fluorine being highest of the elements (3.92), chlorine third highest (3.28), bromine tieing for fourth place with nitrogen (2.96, 2.93), and iodine only a very little more electronegative (2.50) than carbon (2.47). But there is enough similarity that we can find in a study of chlorine compounds a

fairly accurate picture of the chemistry of the other halogens in the -1 state. Instead of emphasizing the individual elements in this study, we can here consider the elements by groups of the periodic table, basing our discussion on the chemical intuition developed in the preceding two chapters.

THE PREPARATION AND PROPERTIES OF THE HALOGENS

Details of the occurrence and preparation of the halogens are deferred until Chapter 25. In brief, these elements occur in nature principally as metal halides, salts in which the halogen is present as a negative ion, F^-, Cl^-, Br^-, and I^-. The production of free halogen therefore depends on accomplishing the removal of an electron from each halide ion. This may best be done electrically, as described in Chapter 20; a high positive charge is used to pull electrons from the negative ions. Since fluorine is most electronegative of all the elements, no chemical agent can oxidize a fluoride ion, and here the electrical method (electrolysis) is the only one available. Chlorine is also high in electronegativity and, although strong oxidants can remove electrons from chloride ions, electrolysis is most convenient for chlorine production, too. Bromide and iodide ions are easier to oxidize, and numerous oxidants can accomplish the production of free bromine and iodine. One of the cheapest and best is chlorine itself, for in the activity series, F—Cl—Br—I, each halogen can displace any others to its right from their compounds with less electronegative elements.

All the halogens, since their electronic configurations are one electron short of an inert element structure, have seven outermost electrons and one vacancy. This gives them the capacity to form but one covalent bond per atom (without expansion of the "valence octet"). Lacking another element to attack, they join one another, forming diatomic molecules held together by single covalent bonds. This fully utilizes their ordinary bonding capacity, leaving to van der Waals forces the only possibility of further association. The effect on these forces of increasing the number of



Figure 84. Valence structure representations of the halogens.

Table 9 Some Properties of the Halogens

	F	Cl	Br	I
atomic number	9	17	35	53
electronic structure	2-7	2-8-7	2-8-18-7	2-8-18-18-7
or, one electron less than:	Ne	Ar	Kr	Xe
atomic weight	19.00	35.45	79.91	126.90
formula	F_2	Cl_2	Br_2	I_2
color	yellow	greenish yellow	brown red	violet brown
covalent radius, Å	0.72	0.99	1.14	1.33
ionic radius, X^-, Å	1.36	1.81	1.95	2.16
electronegativity	3.92	3.28	2.96	2.50
density, g/ml	1.11 (liq. at b.p.)	1.57 (liq. at b.p.)	3.14	4.94
melting point, °C	−219.6	−102.4	−7.2	113.6
heat of fusion, kcal/mole	0.061	0.77	1.26	1.87
boiling point, °C	−187.9	−34.0	58.2	184.5
heat of vaporization, kcal/mole	0.78	2.44	3.59	4.99
electrode potential, volts	−2.87	−1.360	−1.065	−0.5355
heat of atomization, 25°, kcal/g-atom	19	28.61	26.71	25.48
ionization energy, first, kcal/g-atom	402	300	273	241

electrons is well represented in the halogens. With 18 electrons, F_2 is a very low-melting (−219.6°), low-boiling (−187.9°) yellow gas. Chlorine, with 34 electrons per molecule, is still a greenish gas, but melts at −102.4° and boils at −34.0°. Bromine, however, with 70 electrons per molecule, is a deep red liquid, melting at −7.2° and boiling at 58.2°. And with 106 electrons per molecule, iodine is a dark violet solid, melting at 113.6° and boiling at 184.5°.

GROUP IA

In our study of oxides and hydrides we saw that lithium and sodium atoms are relatively large, very low in electronegativity, and have but one outer electron, permitting the formation of but one single covalent bond. These elements are but the first two of a family called the "alkali

metals," whose electronic configuration is that of a single outer-shell electron over a structure like that of an inert element. Thus, lithium is one element beyond helium, sodium one beyond neon, and then going down the group potassium is one beyond argon, rubidium is one beyond krypton, and cesium one beyond xenon. The little-known francium is one beyond radon. As a family, or major group of the periodic table, these elements all have relatively large atoms of very low electronegativity. Some of their atomic properties are listed in Table 28, p. 498.

Although we can never afford to lose sight completely of the inherent chemical *individuality* of the elements, we can predict with confidence that as a group they will show marked similarities in their behavior toward any one reagent. We have already noted that lithium and sodium oxides, of formula M_2O, are closely similar in properties, as are lithium and sodium hydrides. We could have extended these observations to include oxides and hydrides of the heavier members of this group, for all form highly basic oxides and ionic hydrides. So with chlorine we must expect all these metals to react in a similar manner, forming products of similar nature in which the condition of chlorine will be very nearly the same. To the extent that the properties of chlorides can be interpreted in terms of the condition of the combined chlorine, the alkali metal chlorides can be predicted to be very nearly alike. All should have the formula MCl, all should have highly polar bonds and hence exist as ionic crystals. What should be the chemistry of negative chlorine?

We have seen that any electronegative element loses electronegativity to the extent that it is successful in acquiring partial negative charge. In the chemistry of oxygen, the ionic oxides illustrate the practically complete absence of oxidizing power in oxygen so negative. Even in the chemistry of hydrogen, we observed that in the hydrides, wherein hydrogen is very negative, no residual oxidizing power of hydrogen exists. The same observation can be made in the compounds of chlorine. In combination with the alkali metals chlorine becomes highly negative, and hence we would predict that these chlorides will certainly not be oxidizing agents.

In the preceding chapters we observed also that reducing power tends to increase with the acquisition of partial negative charge. This is logical, in that any atom should be better able to supply electrons when it has more than its normal supply. But the ionic oxides are not reducing agents, although the ionic hydrides are. What is the difference? The difference here lies in the difference in electronegativity between oxygen and hydrogen. Oxygen was initially much higher than hydrogen in electronegativity. What we are talking about when we speak of

reducing action or reducing ability is the relative weakness of the hold that the atom has on electrons. It is reasonable that an atom which initially attracts outside electrons strongly will, when it acquires them, hold them tightly and hence be a weak reducing agent. A weak reducing agent is one from which electrons can be removed only by a strong oxidizing agent. But when an atom initially attracts outside electrons less strongly, it will, when it acquires them, hold them less tightly and hence be a strong reducing agent. A strong reducing agent is one from which electrons can be removed so easily that even a weak oxidizing agent can accomplish this. It follows that oxygen, which initially attracts outside electrons so strongly, will give them up most reluctantly when it has gained them. The ionic oxides therefore do not function easily as reducing agents, even though the oxygen carries high partial negative charge. Hydrogen, however, is enough lower in electronegativity that when it has acquired high negative charge, as it can do best from the alkali metals, it does not hold the electron strongly but can give it up even to relatively weak oxidizing agents. This is why hydrides, especially the ionic hydrides, are good reducing agents.

Carrying this reasoning to chlorine, we can see that since chlorine is initially so highly electronegative (much more nearly resembling oxygen than hydrogen), then once it has come close to acquiring an electron it will hold on to it. The alkali metal chlorides can therefore be predicted to be poor reducing agents, requiring powerful oxidizing agents before they can be oxidized.

We also noted that the acquisition of negative charge increases the ability of an atom to act as electron donor, if it has in its outer shell at least one pair of unshared electrons. Just as oxide oxygen and hydride hydrogen can act as electron donors, negative chlorine also should exhibit this ability.

Table 10 Some Properties of IA Chlorides

FORMULA	LiCl	NaCl	KCl	RbCl	CsCl
heat of formation, kcal/mole	−97.7	−98.2	−104.2	−102.9	−103.5
charge on chlorine	−0.66	−0.67	−0.71	−0.72	−0.73
melting point, °C	610	808	772	717	645
heat of fusion, kcal/mole	3.2	6.8	6.1	4.4	3.6
boiling point, °C	1382	1465	1407	1381	1300
heat of vaporization, kcal/mole	36.0	40.8	38.8	36.9	35.7
lattice energy, kcal/mole	192.1	179.2	163.2	157.7	147.7

In fact, our predictions are verified by the actual qualities of alkali metal chlorides. They are all white ionic solids, of high melting point and low volatility. Individual differences among their physical properties must be expected, mainly as the result of differences in the size of the metal atom. Some of their properties are listed in Table 10.

Chemically, the alkali metal chlorides are relatively inert. They are nonoxidizing and nonreducing, as predicted. Negative chlorine, especially the chloride ion, does have some ability as electron donor, forming numerous complex chlorides. In these, the chlorine becomes part of a complex anion, the metal atom remaining unchanged as the cation of the crystal.

GROUP IIA

These elements consist of atoms having two electrons in the outermost shell beyond the inert element structure. Beryllium has the helium structure plus an outer shell of two electrons; magnesium the neon structure plus two; calcium the argon structure plus two; strontium the krypton structure plus two; barium the xenon structure plus two; and radium the radon structure plus two. We have already considered the bonding capacity of beryllium and magnesium. The remaining elements of this group are like these first two, except that they have larger atoms, which are less compact and have lower electronegativity. If individual molecules were to result from the action of chlorine on these metals, we would predict them to be linear, since the formulas would be MCl_2, and the chlorines would be at opposite sides of the metal atom. But in a single molecule, two orbitals would remain vacant on M, and three pairs of electrons would be unused on each chlorine. Furthermore, the bonds with chlorine should be highly polar, although not so much as in the alkali metal chlorides. Therefore we can predict that condensation to ionic crystals should occur.

Table 11 Some Properties of IIA Chlorides

FORMULA	EQUIVALENT HEAT OF FORMATION	CHARGE ON Cl	MELTING POINT, °C	HEAT OF FUSION/MOLE	LATTICE ENERGY/MOLE
$BeCl_2$	−61.2	−0.29	405		713
$MgCl_2$	−76.7	−0.34	714	10.3	595
$CaCl_2$	−95.0	−0.40	782(P)	6.78	537
$SrCl_2$	−99.0	−0.42	875	4.1	506
$BaCl_2$	−102.8	−0.44	962	5.4	488

What was said above about the chemical properties of alkali metal chlorides should apply here, with the difference in degree caused by lower negative charge on the chlorine. Some physical properties of these salts are listed in Table 11.

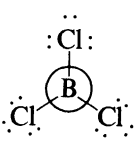
GROUP IIIA

Boron trichloride, BCl_3, is a volatile compound, a colorless liquid below its boiling point (12.4°) which is extremely susceptible to hydrolysis. (Hydrolysis is reaction with water, in which the water is decomposed.) Boric acid, as we call the trihydroxide, is only very weakly acidic but shows no basic properties. Reaction of the chloride with water therefore goes quantitatively:

$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$$

The hydrolysis of halides in general occurs readily and completely if the hydroxy-product does not ionize as a base, because the hydroxide group, once attached to the other element, has no way of separating again as a hydroxide ion. In other words, the reaction cannot be reversible. As will be illustrated amply in the following sections, when the hydroxide is able to ionize as a base, furnishing hydroxide ions, the hydrolysis of the halide can be reversible.

The above compound is just as we could have predicted from a knowledge of the qualities of boron and chlorine atoms. Three bonds to boron must be directed at 120° angles, since all the boron electrons are involved in the bonding. The molecule should therefore be planar, and it is. But an extra orbital, the fourth, on the boron atom remains unoccupied in this structure, except if otherwise unshared electron pairs on the chlorine atoms can in some measure occupy this orbital, strengthening the overall bonding. The molecule might then be represented as involving resonance:



One wonders whether the negative charge on chlorine, −0.14, is sufficient to give it some donor property, and, if it is, why one chlorine on one BCl_3 could not act as donor to a boron of another BCl_3 molecule. This would amount to polymerization through coordination. In fact, however, boron trichloride shows no evidence of such association, at

least not in the vapor at low temperatures. For further examination of this point, we need information on the fluoride and also on the behavior of aluminum.

Boron trifluoride, BF_3, is a much more important compound than the chloride, for it has excellent catalytic properties used in industrial chemistry as well as in the research laboratory. Like the chloride, the fluoride shows no indication of association, being a gas down to the boiling point of $-99°$. The structure of BF_3 is like that of BCl_3, but the B—F bonds are enough shorter than expected for single bonds to suggest that it must have a resonance structure like that written for the chloride. This does not prevent the fourth boron orbital from being employed in coordination bond formation, however. A fourth fluorine atom can be accommodated if it bears a high enough negative charge to be a good donor. Such is the nature of the fluoride ion, which forms with BF_3 the complex "fluoroborate" ion, BF_4^-. For years, boron trichloride was thought incapable of coordinating a chloride ion in a similar manner, but recently the ion BCl_4^- has been shown to exist in certain solid structures. Possibly the difference has been mainly that the fluoroborate ion is stable in aqueous solution, boron trifluoride itself being only slowly hydrolyzed, whereas boron trichloride cannot exist in aqueous solution to form complexes.

Aluminum differs from boron in two important ways. (1) It is less electronegative (1.91 instead of 2.84). (2) It can employ outer *d* orbitals in bonding. The first of these differences is most important in the chlorides, the second in the fluorides. The compound aluminum fluoride, AlF_3, is highly polymeric, being a nonvolatile crystalline substance with six fluorines around each aluminum. The chloride is quite different. Aluminum unites with three chlorine atoms as we would predict. If the molecule were $AlCl_3$, it would doubtless be planar and triangular, as we would also predict. We should also calculate that the

Table 12 Some Properties of IIIA Chlorides

FORMULA	EQUIVALENT HEAT OF FORMATION	CHARGE ON Cl	MELTING POINT, °C	BOILING POINT, °C
BCl_3	−31.5	−0.14	−107	12.4
$AlCl_3$	−55.4	−0.22	192(P)	180.1(s)
$GaCl_3$	−41.8	−0.11	77.5	200
$InCl_3$	−42.8	−0.14	586(P)	
$TlCl_3$	−28.0	−0.12	25	(d 40)
TlCl	−49.0	−0.23	429	806

Al—Cl bonds should be much more polar than the B—Cl bonds, giving the chlorine a higher negative charge (−0.22 as compared to −0.14 in BCl_3) and thus making it a better electron donor. At the same time, the aluminum should be more positive (0.67) and therefore a stronger acceptor than the boron (0.41). Here these differences do lead to coordination polymerization. In the solid, the structure is complex. However, aluminum chloride is low melting (192° under pressure) and sublimes easily (180.1°), and in both liquid and vapor phases its structure is that of a simple dimer, Al_2Cl_6. As shown in Figure 85, two of the chlorine atoms, one from each aluminum, appear to act as a bridge to the other aluminum, a pair of electrons of one chlorine being donated to the fourth orbital of the other aluminum. With now four electron pairs about each aluminum atom instead of three, the directional character of the covalence is shifted from planar to tetrahedral.

This dimerization of aluminum chloride persists to moderately high temperatures in the vapor, showing the bonding to be fairly stable, yet it is not so stable as to prevent activity of the $AlCl_3$ groups as acceptors toward other donors. This presumably is responsible for the fact that

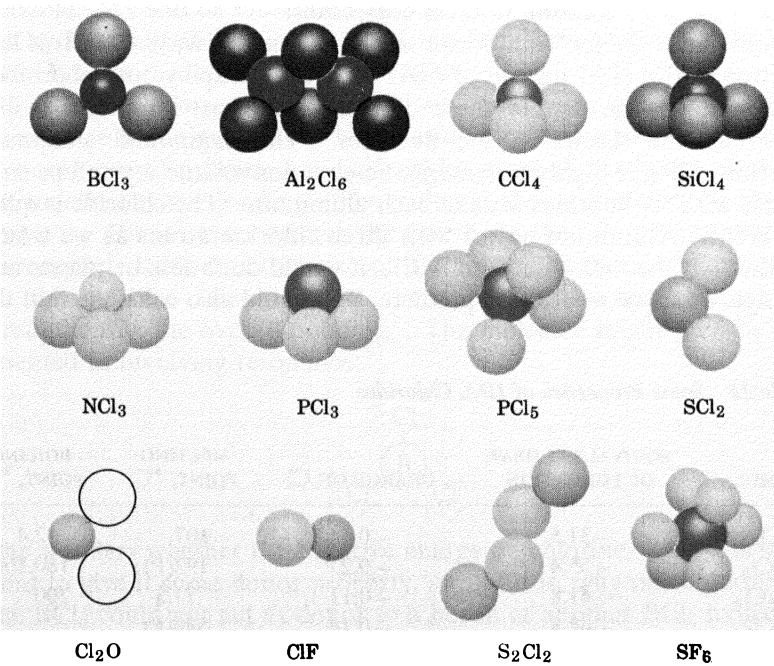


Figure 85. Models of some volatile halogen compounds.

aluminum chloride is one of the most valuable of catalysts, having a host of useful applications in preparative and industrial chemistry.

On a large scale, aluminum chloride is made by heating the oxide with coke and chlorine:

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow Al_2Cl_6 + 3CO$$

When aluminum chloride comes in contact with relatively small amounts of water, it is completely hydrolyzed to the hydroxide, liberating hydrogen chloride. When aluminum hydroxide is dissolved in hydrochloric acid, the solution of aluminum chloride formed is actually a solution of hydrated aluminum ion $[Al(H_2O)_6]^{+++}$ and chloride ion. Attempts to prepare the anhydrous chloride from this solution by evaporation of the water lead to the crystalline hexahydrate, or to hydrolysis products. Anhydrous aluminum chloride cannot be prepared from aqueous solution.

Gallium, indium, and thallium all form solid trichlorides of similar nature, but with thallium comes greater stability of the I state than of the III. This is a phenomenon observed in numerous instances, ascribed to increasing inertness of the *s* electrons the higher the principal quantum level. The effect is called the "inert pair effect." It contributes to relatively low stability of compounds of mercury(II), thallium(III), lead(IV), and bismuth(V), with a tendency toward oxidation states two lower than expected from the number of outer-shell electrons. Thus, thallium trichloride, $TlCl_3$, easily loses chlorine to become thallium(I) chloride, TlCl. With only one chlorine atom here to attract an electron from the thallium atom, the chlorine can become much more negative. The compound is therefore much more saltlike, and indeed in some respects resembles the alkali metal chlorides.

GROUP IVA

All the atoms in this group have four outer-shell electrons, and can therefore form four bonds to chlorine atoms. The configuration must be tetrahedral, which means that four chlorine atoms are symmetrically placed around the central atom. No matter what the bond polarity, this practically insures that the resulting molecules will display an exterior essentially only of chlorine atoms, with no net polarity in the molecule because the four individual bond dipoles cancel one another. Consequently, the only intermolecular attraction must be of a van der Waals type, leading to weak association and thus liquids rather than solids. All the tetrachlorides of these elements are volatile liquids, as

Table 13 Some Properties of IVA Chlorides

FORMULA	EQUIVALENT HEAT OF FORMATION	CHARGE ON Cl	MELTING POINT, °C	BOILING POINT, °C
CCl_4	−8.3	−0.06	−22.9	76.7
$SiCl_4$	−38.3	−0.13	−68	57.0
$GeCl_4$	−32.5	−0.07	−49.5	83.1
$SnCl_4$	−32.6	−0.10	−33.3	113
$PbCl_4$		−0.10	−15	(d)
$SnCl_2$	−41.8	−0.15	247	633
$PbCl_2$	−42.9	−0.16	498	954

expected, having the predicted tetrahedral structures. Together with some of their properties, they are listed in Table 13. The higher volatility of $SiCl_4$ may perhaps be ascribed to greater repulsion among the molecules, resulting from the higher negative charge on chlorine, the consequence of the fact that silicon has lowest electronegativity in the group.

Carbon tetrachloride is the most familiar of these compounds. It has wide application as a solvent, and is used some in household cleaning. For this purpose, unfortunately, it is very dangerous, because its vapors are damaging to the body, especially the liver, and the equally dangerous liquid can be absorbed through the skin. Use for cleaning clothing under poor ventilation has resulted in permanent disability and sometimes death, after relatively short exposure. Carbon tetrachloride, representing carbon already quite thoroughly oxidized by the chlorine, cannot burn, and having heavy vapors which do not conduct an electric current it has application as a fire extinguisher fluid. Here again the hazard of breathing the vapors must be kept in mind. An even worse complication results when the carbon tetrachloride is sprayed, as often in an electrical fire (where a spray of water might result in electrocution of the fireman), on hot metal. This aids the replacement of two of the chlorine atoms by oxygen, forming the exceedingly deadly "phosgene," or carbonyl chloride, $COCl_2$, a gas that may be fatal even in traces. It is far better to use the more modern carbon dioxide extinguishers.

Carbon tetrachloride is very resistant to hydrolysis, forming merely an immiscible layer with water, but this is probably the result of the absence of an available mechanism by which the hydrolysis can occur. The carbon and its bonds are too completely protected by the chlorines. Otherwise, since the hydrolysis product, carbonic acid, H_2CO_3 [or $(HO)_2CO$], gives no hydroxide ion in solution, complete and irreversible hydrolysis of carbon tetrachloride would be expected. Carbon tetra-

chloride is a very valuable solvent for fats and other organic compounds. With a charge of only -0.06 on chlorine, CCl_4 is potentially a good chlorinating agent. This potential is realized at elevated temperatures.

Silicon tetrachloride, on the other hand, hydrolyzes immediately and practically explosively:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$

The difference is not in the nature of the hydroxide, for the "silicon hydroxide" (actually hydrated silica) gives no hydroxide ions in solution. It evidently arises from the larger size of the silicon and the availability of outer *d* orbitals to which attacking water molecules can become temporarily attached, such orbitals not being available in carbon.

Germanium and tin tetrachlorides are reversibly hydrolyzed. This would be expected from the fact that their oxides are amphoteric, and in water can supply either hydronium or hydroxide ions. In high concentrations of hydrochloric acid, then, the hydrolysis is at a minimum, but there is a tendency here for the outer *d* orbitals to be used in forming coordination complexes by acting as acceptors for electron pairs of chloride ions. The resulting complexes have the formulas $GeCl_6^=$ and $SnCl_6^=$.

The tetrachloride of lead is very unstable, in keeping with the "inert pair" tendency, and loses chlorine easily to become $PbCl_2$. In the presence of a high concentration of chloride ion, however, it is stabilized by forming the $PbCl_6^=$ complex. In $PbCl_2$, there being only two chlorine atoms instead of four to compete for the electrons of the lead, each acquires a higher negative charge (-0.16 instead of -0.10), with the result that $PbCl_2$ is a solid salt instead of a volatile liquid.

GROUP VA

In the atoms of these elements, promotion of one electron from the pair in the outermost shell to a position in an outer *d* orbital, creates at once two additional bonding possibilities. Where such promotion can occur, we may expect chlorides with three atoms of chlorine per atom of other element, or five atoms of chlorine per atom.

Nitrogen has no outer *d* orbitals that can be used for bonding. Four bonds, three ordinary covalent and one coordinate covalent, are the most a nitrogen atom can form at one time. Therefore only NCl_3 is possible. This compound is an oily liquid, notoriously and violently ex-

plosive. Its instability arises in part from the high energy to be gained by formation of a nitrogen molecule, N_2, and in part from the fact that the N—Cl bonds are not strengthened much by polarity since both elements are high in electronegativity. Furthermore, bonds between atoms unlike in size are less stable, and nitrogen atoms are much smaller than chlorine atoms.

Nitrogen trifluoride, NF_3, is a gas and quite stable in contrast to NCl_3. Presumably the higher polarity of the bonds and the similarity in atomic size contribute to this higher stability. The tribromide, however, is too unstable to exist except at very low temperatures, and nitrogen triiodide has only been made as a complex with ammonia, $NI_3 \cdot NH_3$, of uncertain structure and very touchy disposition. It is a brown-red solid that is likely to detonate with great violence at the slightest nudge.

Phosphorus forms both the (III) and the (V) chlorides. The first, as we could predict, has a pyramidal structure owing to the unshared electron pair on the phosphorus, which fills the fourth tetrahedral corner (Figure 85). The second has three chlorine atoms in a triangle about the phosphorus, one above and one below—also as we might predict. Both can be formed by direct chlorination of phosphorus. Both can be hydrolyzed completely and irreversibly. The PCl_5 can be hydrolyzed by steps, first forming the liquid "phosphorus oxychloride," $POCl_3$, boiling at 108.7°. Both PCl_3 and PCl_5 can act as chlorinating agents because in neither is the charge on chlorine very negative: -0.10 in PCl_3 and -0.07 in PCl_5. The latter, however, is much more reactive as a chlorinating agent.

Complete hydrolysis of the (III) chloride leads to phosphorous acid, H_3PO_3, which should probably be written $OPH(OH)_2$, since it has only two of its three hydrogens attached to oxygen and therefore acidic. Hydrolysis of the (V) chloride leads to phosphoric acid, H_3PO_4. In both, hydrogen chloride is the other product. Hydrolysis of phos-

Table 14 Some Properties of VA Chlorides

FORMULA	EQUIVALENT HEAT OF FORMATION	CHARGE ON Cl	MELTING POINT, °C	BOILING POINT, °C
NCl_3	18.2	−0.03		71
PCl_3	−27.0	−0.10	−92	76
$AsCl_3$	−26.7	−0.06	−16	130
$SbCl_3$	−30.4	−0.10	73.2	221
$BiCl_3$	−30.2	−0.11	232	441
PCl_5	−22.1	−0.07	160(P)	(159)
$SbCl_5$	−21	−0.07		(d 140)

phorus halides in general is a good way of preparing the corresponding hydrogen halide. For example,

$$PI_3 + 3H_2O \rightarrow OPH(OH)_2 + 3HI$$

Arsenic forms only $AsCl_3$ and bismuth only $BiCl_3$, but antimony forms also an unstable $SbCl_5$. In general, the halides of these elements are of low bond polarity, and hence of low intermolecular attraction. They tend to be low melting and volatile, as well as active halogenating agents by virtue of the low negative charge on halogen.

GROUP VIA

Compounds of oxygen with the halogens have been discussed briefly in Chapter 12. Except for fluorine, the halogens are all less electronegative than oxygen, and form compounds with it in which the oxidation state of the halogen is positive. Sulfur, on the other hand, is less electronegative than any of the halogens except iodine. Sulfur forms no stable compounds with iodine. The combinations of sulfur with fluorine and with chlorine are best known. From the outer electronic configuration of sulfur atoms, one would predict their ability to form two covalent bonds. This they do, in the most common compound with chlorine, but one of the bonds is to sulfur. The compound "sulfur monochloride" or "sulfur(I) chloride" has the formula S_2Cl_2, and the arrangement Cl—S—S—Cl. The bond angles, as predicted from the presence of two pairs of unshared electrons on each sulfur, are near to tetrahedral (109°). This is a rather unstable liquid which has only slightly polar bonds, and which, consistent with the smallness of the negative charge that chlorine is able to attract away from sulfur, is an active chlorinating agent.

With fluorine, the outer *d* orbitals of sulfur appear easily involved. If one electron is promoted to such an orbital, the sulfur can form four covalent bonds. This it does in SF_4, a highly reactive gas—highly reactive largely because no one of the four fluorine atoms is able to acquire much negative charge from the single, also quite electronegative sulfur. In keeping with the important general principle regarding highly electronegative elements, such compounds are reactive as oxidizing agents, because the highly electronegative element tends to leave a combination from which it cannot acquire negative charge, and to join in some new combination which will give it higher negative charge. SF_4 is therefore an active fluorinating agent. One might then expect that if promotion of an electron from the final pair on sulfur could per-

Table 15 Properties of Some VIA Chlorides

FORMULA	COLOR	EQUIVALENT HEAT OF FORMATION	CHARGE ON Cl	MELTING POINT, °C
S_2Cl_2	orange brown	−7.2	−0.09	−76.5
Se_2Cl_2	brown yellow	−10.0	−0.09	<25
SCl_2	red	−6.0	−0.06	
$TeCl_2$	black green		−0.11	208
SCl_4	pale yellow	−3.4		−30(d)
$SeCl_4$	white	−11.3		305(P)
$TeCl_4$	white	−19.3		224.1

mit joining to two more fluorine atoms, the compound would be even more active as a fluorinating agent. Sulfur does acquire six fluorine atoms, forming the gaseous compound SF_6. Surprisingly, at least at first, this is not an active compound at all. In fact, it is extraordinarily inert, for surely fluorine having only −0.05 charge should be highly reactive. The reason for inertness is merely that the particular geometric structure formed here presents, to outside influences, an exterior that is quite impervious to attack—nothing but the rear sides of fluorine atoms. The structure (Figure 85) is that of a regular octahedron, with six fluorine atoms symmetrically disposed about the sulfur atom so that neither the sulfur atom nor the sulfur-fluorine bonds are exposed. The properties of the compound present an excellent example of the fact that chemical reactions depend not just on the relative stabilities of reactants and products, or on how much energy is released in the reaction, but also on whether possible mechanisms exist by which the necessary atomic interchanges can occur. We have already seen this fact illustrated by the properties of carbon tetrachloride.

Selenium and tellurium also form a number of halides.

GROUP VIIA

Compounds in which the component atoms are all halogens are called "interhalogen compounds." A number of them exist. Their formulas represent combinations in which one, three, five, or in one instance seven more reactive halogen atoms surround a single less reactive halogen atom—never the reverse. Fluorine is thus never a central atom in such a compound. The interhalogens react chemically much as though they were mixtures of the component halogens, with the

added factor that their bonds may tend toward greater strength as the result of polarity and toward lesser strength as the result of disparity in atomic sizes. Some interhalogens and their boiling points are listed in Table 16.

TRANSITION METAL HALIDES

A large number of chlorides and other halides of transition metals are known; some of these are listed in Table 17, which also gives some of their properties. As we observed for oxides, the physical properties, which reflect the strength of association, vary with increasing oxidation state of the metal from nonvolatile, ionic crystal toward molecular, volatile substances. Chemically, the halogen is usually quite negative in the halides of lower oxidation state of the metal, and therefore not active as a halogenating agent. As the metal oxidation state becomes more positive, the competition for electrons among the halogen atoms increases and no one halogen becomes very negative. The potential halogenating ability is thus increased.

SUMMARY: PERIODICITY OF HALIDES

In a general way, fluorine forms the most stable halides and iodine the least. Related to this and also to the smaller size of fluorine is the fact that fluorine usually forms fluorides representing higher oxidation

Table 16 Properties of Some Interhalogen Compounds

FORMULA	COLOR	MELTING POINT, °C	BOILING POINT, °C
ClF	gas—none liq.—yellow	−155.6	−100.3
ClF_3	gas—none liq.—pale green	−82.6	12.1
BrF	gas—pale brown liq.—dark red	(−33)	20
BrF_3	liq.—pale yellow green	8.8	127
BrF_5	liq.—none	−60.5	40.5
IF_5	liq.—none	8.5	97
IF_7	solid—white	4.5	5.5
ICl	red	27.3	
ICl_3	yellow		

Table 17 Some Transition Metal Halides and Properties

FORMULA	COLOR	EQUIVALENT HEAT OF FORMATION	MELTING POINT	BOILING POINT
ScF_3	white			
$ScCl_3$	white	−73.6	960	>1000(s)
$ScBr_3$		−59.8	960	
ScI_3			945	
TiF_4	white	−93	solid	284
$TiCl_4$	none	−44.8	−23	135.8
$TiBr_4$	amber	−39	40	230
TiI_4	red brown	−25.5	150	365
CrF_2	green	−90.5	1100	≫1300
$CrCl_2$	white	−47.3	815	
$CrBr_2$	white			
CrI_2	dark red	−27.1	795	
MnF_2	rose	−95	856	
$MnCl_2$	pink	−57.7	650	1190
$MnBr_2$	pink	−45.4		
MnI_2	pink	−29.7	(d 80)	
FeF_2	white	−88.9	(1000)	>1100
$FeCl_2$	white	−40.8	672	1030
$FeBr_2$	yellow or brown	−30.0		
FeI_2	dark red	−15.0	177	
CuF	ruby		908	
CuCl	white	−32.2	430	1367
CuBr	greenish yellow	−25.1	490	1345
CuI	white	−16.2		
TaF_5	white		96.8	229
$TaCl_5$	yellow		211	232.9
$TaBr_5$	pale yellow			
TaI_5	brown black		365	

states of the elements than can be reached with chlorine. Chemically, the ease with which oxygen can replace the halogen in halides increases from fluoride to iodide, some anhydrous iodides even burning readily in air when heated.

The observation can be made about all the halides that across the periodic table the trend is from ionic, nonvolatile solids toward less ionic, more volatile solids, liquids, or gases; from electron-donor prop-

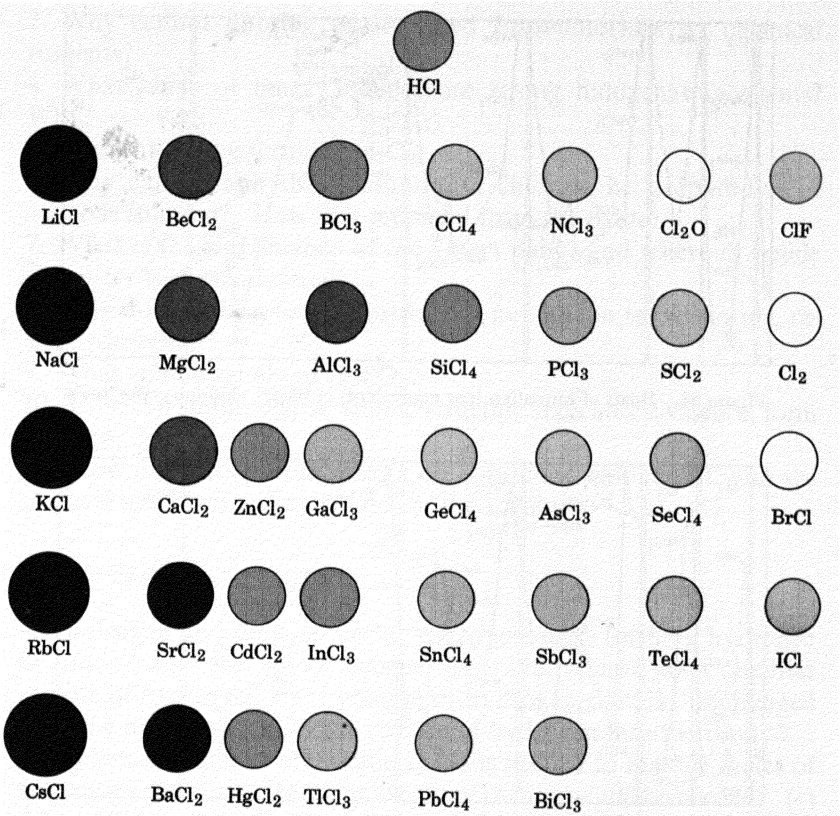


Figure 86. Chart showing partial charge and relative radius of chlorine in binary compounds.

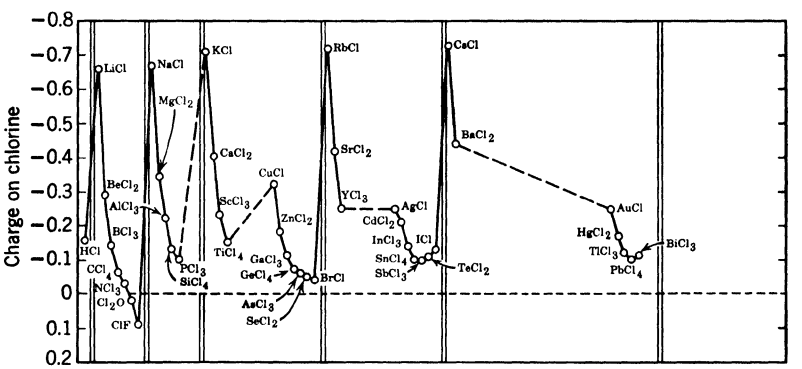


Figure 87. Partial charge on chlorine in binary compounds.

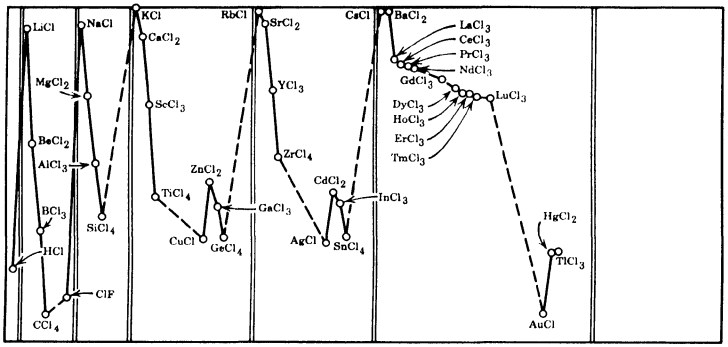


Figure 88. Heats of formation (per equivalent) of binary chlorine compounds.

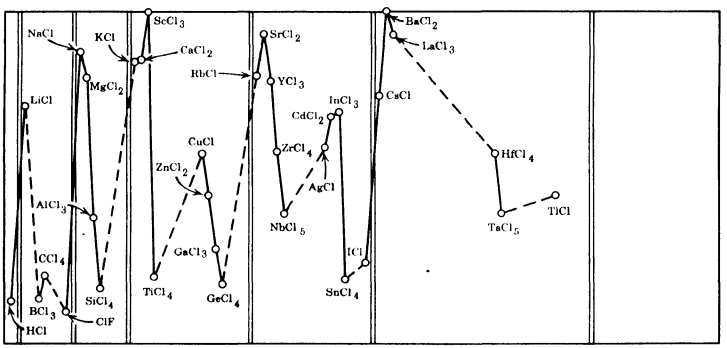


Figure 89. Melting points of binary chlorides.

erties to highly oxidizing properties; from halides stable toward hydrolysis toward halides completely and irreversibly hydrolyzed. Within a group, halides are quite similar, though varying as the size and electronegativity of the other elements vary. In general, the physical and the chemical properties of all the halides are closely consistent with the extent to which the halogen atom has succeeded in its quest to acquire a negative charge.

SPECIAL HELP

Test Your Memory

1. What do IA halides have in common?
2. How do the different halides compare in reducing power?

3. Why cannot fluorine be liberated from fluorides by chemical reagents?
4. What kinds of binary halides are strong halogenating agents? Why?
5. Account for the formula Al_2Cl_6.
6. Why cannot anhydrous aluminum chloride be prepared from aqueous solution? How is it prepared from the oxide?
7. What is the significance of the "inert pair," and where in halide chemistry is it encountered?
8. Why does carbon tetrachloride, but not silicon tetrachloride, resist hydrolysis?
9. What is unusual about H_3PO_3?
10. How can sulfur, whose atomic structure indicates divalence, form SF_4 and SF_6?
11. How does the partial charge on combined halogen fit with the physical and chemical properties of the halides?

Test Your Math

1. Hydrogen and fluorine unite very vigorously, forming hydrogen fluoride. (*a*) If 200 ml of fluorine gas is introduced to a one-liter sample of hydrogen, what volume of hydrogen remains unchanged after the reaction? (*b*) What volume of hydrogen fluoride results?
2. (*a*) What weight of aluminum oxide is needed to make 6 moles of anhydrous chloride? (*b*) What weight of carbon would be needed? (*c*) What volume of carbon monoxide at SC would be formed?
3. How much more, or less, chlorine would be needed to make 200 g of $SiCl_4$ than would be needed for 150 g of CCl_4?
4. The commercial synthesis of $SiCl_4$ resembles that of anhydrous aluminum chloride. What weight of $SiCl_4$ could be made from 500 g of sand?
5. Titanium tetrachloride can also be formed by chlorination while the oxide is heated with coke. (*a*) Assuming the coke to be pure carbon, how much would be needed to convert one ton of the oxide? (*b*) What weight of the chloride could be obtained?

Test Your Understanding

1. Predict, with reason, the polarity of a bond of chlorine joined to an atom of an element which in the free state has more than 6 closest neighbors.
2. How would you expect the heats of formation of the different halides of an element to compare, and why?

Table 18 Comparisons of Some Halides

COMPOUND	STANDARD HEAT OF FORMATION/EQUIV.	CHARGE ON HALOGEN	MELTING POINT	BOILING POINT
NaF	−136.0	−0.75	995	1704
NaCl	−98.2	−0.67	808	1465
NaBr	−86.0	−0.62	755	1390
NaI	−68.8	−0.54	661	1300
AlF_3	−104	−0.27	1290	1257(s)
$AlCl_3$	−55.4	−0.22	192	180.1(s)
$AlBr_3$	−41.9	−0.20	97.5	265
AlI_3	−25.1	−0.15	191	382
PF_3	−73	−0.15	−151.5	−101.2
PCl_3	−27.0	−0.10	−92	76
PBr_3	−15.8	−0.08	−41.5	176
PI_3	−3.6	−0.03	61	—
HF	−64.2	−0.25	−83.1	19.9
HCl	−22.1	−0.16	−114.2	−85.0
HBr	−8.7	−0.12	−86.9	−66.7
HI	6.2	−0.04	−50.8	−35.4

Notes: (1) In halides of the same element, the fluoride is always most stable and the iodide least, as shown by the heats of formation from the elements. The bond polarity always decreases from fluoride to iodide, similarly.

(2) In the ionic halides, the melting points and boiling points go down with increasing size of the anion and correspondingly diminished crystal energy or electrostatic attractions in the melt. In the less polar halides, van der Waals forces increase with increasing atomic number, making iodides tend toward higher melting and boiling points. HF properties show protonic bridging effects.

3. Predict the state of a chloride of an element whose oxide is acidic.
4. How would you predict the volatility of a hexafluoride?
5. The bromide of a certain element is a white crystalline solid of very low volatility and high melting point. Would the hydrogen compound of this same element react with hydrogen chloride?
6. A certain element forms a difluoride and also a trichloride. Which would probably be more volatile, and why?
7. The chloride of a certain element is volatile. Would it chlorinate an element having fewer outer electrons than vacancies? Why?
8. Chlorine liberates from a certain halide its halogen, which melts either lower or higher than chlorine. How do you decide?
9. What can you say about the number of outer electrons per atom of an element whose bromide does not react with water?

15

Causes, Mechanisms, and Rates of Reactions: Chemical Equilibrium

A CHEMICAL EQUATION tells us that certain specified substances react with one another to produce certain other specified products. It tells us also what relative quantities of reactants and products are involved. What it does not tell us, unfortunately, or even hint at, is why the reaction occurs, or by what mechanism, or how fast. Furthermore, if the reaction happens to be one of the many that is reversible, the degree of completeness of the reaction is not even suggested by the mere chemical equation. In this chapter, certain fundamental principles and concepts will be introduced to help shed some light on what really goes on in a chemical reaction, and why. Lacking the ability to observe intermolecular actions directly, we must rely on what observations of matter in bulk can tell us, and on our ability to deduce from these observations more fundamental facts.

WHY REACTIONS OCCUR

In general, reactions occur because atoms attract electrons of other atoms. But since in the active elements the atoms have already reacted

as much as they can, this fails to explain why different elements then react with one another. And in compounds all atoms have usually done their best at combining. Then what makes atoms change partners when different compounds come together?

Thermochemistry: Heat Content and Heat of Reaction

All different substances have different energy content at any given temperature. No change in composition, therefore, is possible without a corresponding change in energy content. Since every chemical change involves a change in the chemical composition of substances, it must also involve a change in energy content. Energy, usually in the form of heat, must therefore either be absorbed or released in every chemical reaction. Heat content is called "**enthalpy.**" The change in enthalpy that is part of every chemical change is called the "heat of reaction."

A "**calorimeter**" is a device for measuring enthalpy changes. Usually it consists of a well-insulated vessel in which the chemical reaction under study can be carried out and the heat effect measured as a temperature change in materials of known heat capacity. By the exercise of great experimental care, heats of reaction can be measured quite accurately in a calorimeter.

A chemical reaction that produces heat is very likely to proceed to completion once some means of starting it has been employed. A reaction that absorbs heat can sometimes be forced to occur, but only by continuous application of drastic means. In other words, if the total heat content of the products is less than that of the reactants the reaction tends to proceed, giving out enough heat to account for the difference. Otherwise it does not proceed.

The heat of reaction of elements to form a compound must always be measured experimentally. This heat is called the "**heat of formation**" of the compound. A "standard heat of formation of a compound at 25°," symbolized as $\Delta Hf°$, is defined as the heat evolved (or absorbed) when the compound in its usual physical state at 25° is formed from its elements, each in their "**standard state**"—their usual state at 25°, and, for a gas, at one atmosphere pressure. The heat content of each element in its standard state is arbitrarily taken as zero. For example, the heat of reaction of hydrogen and oxygen to form water is measured as −68.3 kcal/mole. In the equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

the heat of formation of water is the measured heat of reaction (per mole) minus the heats of formation of $2H_2$ and O_2, both taken as zero.

For a reaction among compounds, however, if we know the heat of formation of each compound, we can easily calculate the heat of reaction without measuring it experimentally. For the enthalpy difference between reactants and products depends only on their individual nature, and is completely independent of the way in which the reaction might occur. Suppose, for example, we wish to know the heat of reaction of methane with oxygen—in other words, the heat of combustion. The reaction is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The heat of formation of O_2 is taken as zero since this is an element in its standard state. The heats of formation of the compounds are: CH_4, -17.9; CO_2, -94.0; and H_2O, -68.3 kcal/mole. The sum for the products, $-94.0 + 2 \times -68.3 = -230.6$, minus the sum for the reactants, $-17.9 + 0 = -17.9$, is -212.5 kcal, which is the heat of combustion of methane. Experimentally, this has been determined to be very close to -213 kcal/mole, by burning the methane in a calorimeter and measuring the heat evolved. Conventionally, evolved heat (**exothermic** change) is minus; absorbed heat (**endothermic** change), plus.

Entropy and Free Energy

Heats of reaction are actually only an approximate and partial measure of the tendency for a reaction to occur. A spontaneous change is favored not only by an increase in the strength of the bonding (decrease in enthalpy) but also by an increase in the *probability* of the state of matter in products as compared to reactants. The more random, and therefore the more disordered, the arrangement of atoms in the products, the more likely it is that spontaneous change can occur. This probability, or tendency, toward randomness is called "**entropy.**" The concept of entropy is difficult to explain in terms of chemical change, but some relatively simple physical examples may be helpful:

(1) Two unreactive gases, for instance helium and argon, are far more likely to become thoroughly mixed, as the result of their kinetic energy, than they are to become separated. If a barrier separating a sample of helium from a sample of argon is removed, the two gases will proceed spontaneously to become thoroughly mixed. But the probability that such a mixture would ever separate spontaneously, into argon gas on one side of the container and helium on the other, is so extremely small that for practical purposes it may be taken as zero. The *mixture* of gases is described therefore as being much more probable—having greater entropy.

(2) Imagine a system consisting of two isolated bars of iron, one at a

temperature of 400°, the other at 200°. If these bars are brought into contact, we know that heat will flow spontaneously from the first to the second until both reach the same intermediate temperature. The total energy has not changed, but it is now no longer as available for use as it was initially. The entropy of the system has increased. The final state is the more probable one, for what chance would there be that bringing two bars of equal temperature together would result in a spontaneous heat flow from one to the other, ending with one hot, the other cold? Essentially, no chance at all.

(3) Compare the three states of matter. Surely the atoms and molecules are arranged in more orderly array in a crystalline solid than they are when the lattice breaks down to a liquid. And surely there is more disorder in a gas than in a liquid, where the molecules are certainly not unconstrained. These differences are described by saying that a gas has higher entropy than a liquid, which in turn has higher entropy than a crystalline solid. The physical processes of melting and vaporization are therefore processes that produce an increase in entropy.

A more reliable criterion of spontaneous reactivity is therefore the "**free energy,**" which takes into account both the enthalpy and the entropy:

$$\Delta G = \Delta H - T\,\Delta S$$

ΔG, the free energy, is the "useful" or available energy of a reaction, obtained by subtracting the energy that becomes unavailable, $T\,\Delta S$, from the total energy change, ΔH. T is the absolute temperature and ΔS the entropy change. The true criterion for the possibility of a spontaneous reaction is that the free energy content must decrease—that is, ΔG must be negative. From the above expression, it can be seen that ΔG can be negative under the following conditions:

(1) if ΔH is negative and ΔS is positive (that is, the bonding is stronger in the products and the state is more random).

(2) if ΔH is negative and ΔS is negative but $T\,\Delta S$ is smaller than ΔH (that is, the bonding is enough stronger in the products to compensate for the creation of a less random state).

(3) if ΔH is positive but ΔS is positive and $T\,\Delta S$ exceeds ΔH (that is, the bonding is weaker but the greater randomness of the products predominates).

A fuller account of entropy and free energy comes more appropriately under an advanced treatment of energy changes called "**thermodynamics.**" For our present purposes, it is sufficient to understand that *at ordinary temperatures* the entropy term $T\,\Delta S$ is usually appreciably (or much) smaller than the ΔH term. This means that the dominant factor

is the total bonding strength, and most chemical change may safely be predicted to tend to occur spontaneously in the direction of more stable products (higher bond strength, negative ΔH). This is especially true if ΔH is more than a few kilocalories. It becomes less reliable when ΔH is small. At temperatures high enough, if ΔS is positive, $T\,\Delta S$ will become high enough to permit any reaction to occur spontaneously even when ΔH is positive. In other words, all compound substances will tend to break into smaller particles (decompose) as the temperature is increased, thus increasing the disorder (the entropy). But under more commonplace circumstances in which ΔH is negative, we may expect ΔG to be negative also, and usually not very different in magnitude. This is fortunate, for ΔH values of a chemical reaction are frequently much easier to obtain experimentally, and therefore more readily available, than values of ΔG.

Bond Strengths

The heat of formation of a compound is really a measure of the relative strength of bonding in the compound compared to the strength of bonding in the elements which compose it. When heat is evolved in the formation of a compound we know that, *on the average, the bonds are stronger in the compound than they were in the free elements.* In partial answer to the question of why chemical change occurs, we can then point out that it occurs because stronger bonds can form, and therefore greater stability results. Assuming that some physical means exists whereby combined atoms can interchange, we can expect this interchange to favor the strongest union, since an atom will be less likely to move from positions where it is more tightly held. For example, in order for iron to rust (combine with oxygen) the iron atoms must be able to break loose from the other iron atoms, and the oxygen atoms must be able to break loose from their association in O_2 molecules. The iron atoms then unite with the oxygen atoms. If these iron-oxygen bonds were not more stable than the original iron-iron and oxygen-oxygen bonds, the latter would form in preference. But obviously the iron-oxygen bonds are stronger, for iron rusts readily.

Accepting the rough picture of chemical reaction as occurring because stronger bonds are formed, we can now attempt to expand this picture by considering what determines bond strength. What makes a bond strong? What kinds of bonds are strongest?

We can perhaps best consider the various factors that contribute to the strengths of bonds by listing them one at a time.

(1) *Size of atoms.* Covalent bonds tend to be stronger between smaller atoms and between atoms more nearly similar in size.

(2) *Multiplicity.* Among atoms that can form multiple bonds, such bonds are stronger than single covalent bonds between the same atoms.

(3) *Resonance.* Structures wherein electrons and/or orbitals may be used partially in several bonds at once, rather than in one particular bond exclusively, are more stable than if these extra electrons or orbitals were confined to one particular bond.

(4) *Polarity.* Bond strength appears to be greater with higher polarity. One of the most important guides to chemical reaction, especially displacement and metathetical or double displacement reactions, is that the *tendency is toward formation of the most polar bond possible.* This means that a highly electronegative atom that has not been able to acquire a very high negative charge in a given compound will tend to leave that compound to join a new combination from which it can acquire a higher negative charge. This is well illustrated by the high oxidizing power of compounds in which oxygen or halogen have not acquired very high negative charge, and by the fact that almost any element will displace another element to its right in the periodic table from combination with oxygen or halogen. It is probably a significant if not dominant factor contributing to the driving force in almost all metathetical or displacement reactions which do not depend on solubility differences.

(5) *Crystal Energy.* The tendency just discussed seems to prevail in about 90% of reactions wherein all reactants and products are gaseous, but its reliability falls to about 65% where crystalline solids are involved. Commonly, substances having more polar bonds tend to condense to stronger aggregates, but not always. Sometimes greater crystal energy may dictate reaction toward less polar bonds.

(6) *Ions.* Ionic compounds tend to be more stable when the ions are smaller and simpler, permitting closer interaction of the electrostatic charges. They also tend to be more stable the higher the charge on the ions, except that such compounds tend to be less ionic, especially where the charge would exceed ± 2.

(7) *Coordination.* Coordinate covalent bonds usually tend to be stronger, the more readily the donor atom can supply electrons and the more easily the acceptor atom can take on electrons. Other factors being equal, an acceptor atom is more effective the higher its partial positive charge. A donor atom is a better donor the higher its partial negative charge.

The above generalizations oversimplify the subject of bond strength, which indeed presents a challenge to our best theoretical minds, but

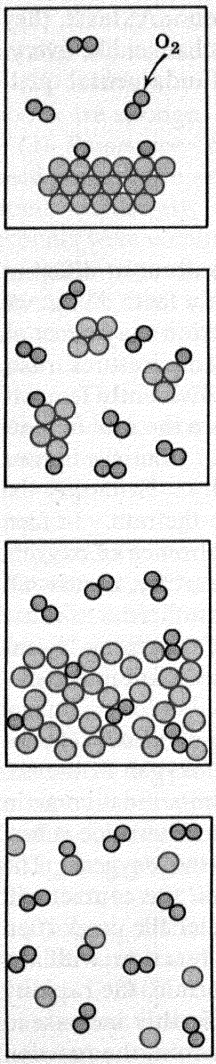
they may serve as a rough guide to chemical reaction. At least, they serve to show that the course and nature of chemical change, like everything else in chemistry, are logically related to the fundamental qualities of the individual atoms.

RATES: QUALITATIVE

We know already that different chemical reactions occur at different rates, some being exceedingly slow, others explosively fast. What we may not recognize immediately is that the *same* reaction may occur at different rates. For example, iron at ordinary temperatures rusts slowly. If the iron is heated, it rusts more rapidly. Evidently temperature has some effect on the rate. Now, if we compare the rate of rusting of a massive piece of iron with that of "steel wool," iron in a fibrous form, we find that the latter rusts much more rapidly. Evidently the state of division of the iron has something to do with the rate. In fact, if iron is prepared in a finely powdered form in the absence of oxygen, and then suddenly exposed to air at ordinary temperature, it rusts almost instantaneously, the heat of the reaction being sufficient to cause light to be emitted. Such iron is called "pyrophoric," meaning "burning spontaneously." The significant quality that causes this rapid burning is the iron's state of being finely divided.

What is the importance of the reactant being finely divided? The reaction of rusting is the combination of iron with the oxygen of the air. Before iron can combine with oxygen the two elements must come in contact. The more finely divided the iron is, the more surface it has, and the more surface, the better is its exposure to the oxygen. The better the exposure to the oxygen, the more likely that the contact will produce a chemical combination. Therefore the greater the proportion of surface atoms in the iron, the more rapid the reaction with the oxygen. In this particular reaction, which is exothermic, the rapidity of reaction permits heat to accumulate, causing still further increase in speed as the temperature goes up. In the pyrophoric iron, the reaction is so fast that before the evolved heat can be dissipated into the surrounding air it raises the temperature of the solids to such a high value that they become incandescent—emit light.

Another way of increasing the rate of rusting exists. Every encounter between oxygen and iron does not result in reaction, for if it did rusting would occur practically instantaneously. Only a certain proportion of the encounters results in combination. The reason for this can best be explained a little later. But the probability that combina-



Oxidation at a solid surface occurs much more slowly when the solid is not finely divided. Grinding the solid increases the surface and therefore the rate of oxidation.

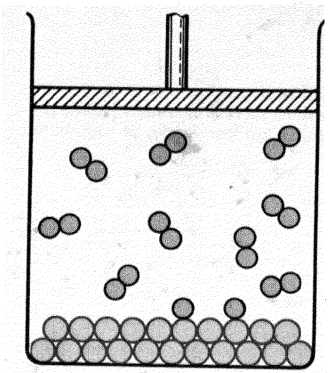
When the solid is finely divided, the oxygen molecules can get at the solid much more rapidly. If the solid is suspended in the air as dust, the rate of oxidation, once begun, may be explosively fast.

Oxidation of a liquid can occur fairly rapidly because (1) the surface molecules of the liquid are continually replaced and (2) oxygen may dissolve in the liquid and thus come in contact with molecules at the interior as well as the surface.

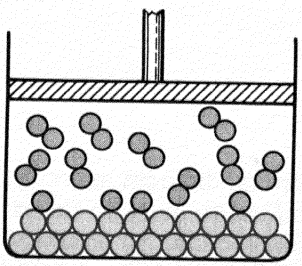
Oxidation of a gas can be most rapid of all because the oxygen molecules can diffuse completely through the gas.

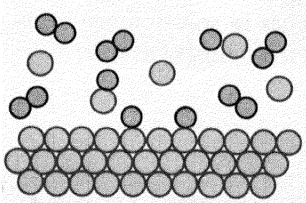
Figure 90. Factors affecting reaction rates.

tion will occur must increase if the rate of encounters increases. Keeping the surface of the iron unchanged, we can consider the effects of changing the concentration of the oxygen. Suppose, for example, pure oxygen were to be substituted for the air. This would mean increasing the partial pressure of the oxygen, and therefore the concentration, by a factor of approximately five, since the concentration of oxygen in air



Compressing the oxygen by diminishing the volume increases the rate at which oxygen molecules strike the solid surface, and therefore increases the rate of oxidation. At high pressure, oxygen may react explosively fast.

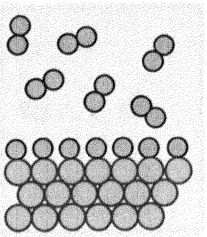




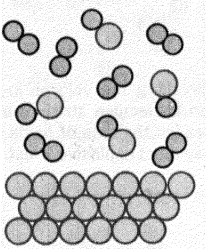
At higher temperatures, the rate of reaction with oxygen is increased not only because the rate of collision is higher and the concentration of activated molecules increases, but also because the vapor pressure of the solid increases and in the vapor state oxygen can make perfect contact.

is only about 20 per cent. Experimentally, it would be found that the iron would rust much more rapidly in the pure oxygen than in air.

What has just been said about the rusting of iron might almost equally well be said about any other chemical reaction. All chemical reactions depend on contact among reagents—with the one exception of reactions in which a single molecule without outside contact breaks



If the product of oxidation of a solid is also solid, it may form a protective coating which hinders or prevents further oxidation. Such protection is afforded by aluminum oxide, but iron oxide, or rust, is too porous to be very effective.



If the product of oxidation of a solid is volatile, no protective coating can form and a fresh surface is continuously exposed to the action of the oxygen. Carbon burns readily for this reason.

Figure 90 (*Cont.*)

up or rearranges into a different molecule or several different molecules or atoms. Anything that can be done, therefore, to increase the extent of contact will increase the possibility that reaction will occur. A solid will react most rapidly when it is most finely divided. A liquid will react most rapidly when it is in the form of a spray or mist. A gas will react most rapidly of all, other factors being equal, because in it the maximum exposure of reactant molecules exists. Similarly, as will be discussed in the following chapters, substances in solution are likely to be especially susceptible, through exposure, to chemical attack.

Catalysts

We know also that the same reaction may occur at different rates depending on the presence or absence of additional substances called "catalysts." To gain some understanding of catalysts, we must first think about the well-known fact that contact between reactants alone does not necessarily produce reaction. For example, the power-producing action in your automobile is the action of liquid gasoline with oxygen of the air to form gaseous water and carbon dioxide, simultaneously liberating much heat which by speeding up these gas molecules

increases even more their pressure on the pistons in the cylinders. That same gasoline, when your gas tank is only partly full, shakes around thoroughly with the air above it for hours at a time, yet refrains from appreciable interaction until it reaches the engine. Why does it react in one place and not in the other? Collisions between reactants are occurring in both places, but within the gas tank, fortunately, these collisions are ineffective. They do not occur with sufficient force. Remember that force is needed, for the reactants have a certain stability of their own that prevents them from easily undergoing change. Oxygen molecules, O_2, obviously cannot form H_2O molecules, in each of which is only a single atom of oxygen, or CO_2 molecules, in each of which the two oxygen atoms are separated by carbon, without coming apart. Hydrocarbon molecules, which constitute gasoline, consist of hydrogen atoms and carbon atoms strongly attached to one another, and these cannot easily be pulled apart, either. Before a chemical reaction between oxygen and gasoline can occur, energy must be supplied in sufficient quantity to initiate the reaction, by at least forcing the reactant molecules out of their most stable configurations. Once initiated, the reaction can proceed under its own power, for the reason that carbon dioxide and water are more stable than hydrocarbons and oxygen.

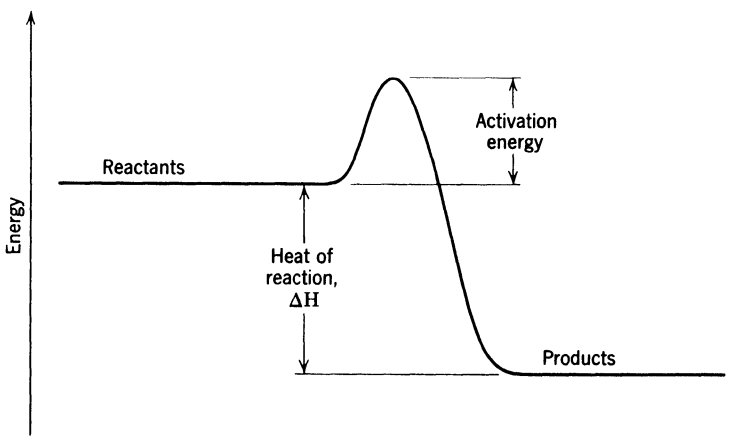


Figure 91. Representation of energy relationships for an exothermic reaction. The difference in the enthalpy (heat content) between products and reactants is the heat evolved in the reaction. The activation energy may represent the energy difference between the reactants and an "activated complex" containing them, which must form in an intermediate step before the products can result. A catalyst functions to lower the activation energy requirement. Without it, so much thermal energy might be required that the reverse reaction would be favored (since it would absorb heat).

Energy liberated in the initial reaction is adequate to perpetuate it. But that essential initial energy is simply not present in the gas tank, even though the reactants are there.

Activation Energy. This minimum energy required to initiate a chemical reaction is called the "**activation energy.**" For gasoline and air, it is supplied by the spark in the cylinder; the careless motorist who tries to see into the dark interior of the gasoline tank with the light of a flaming match also supplies the activation energy—much to his sorrow and distress. For initiation of the reaction is all that is necessary. Once it starts, the high amount of energy released is sufficient to activate other molecules, and the reaction sweeps rapidly through the mixture without further aid from outside.

A good illustration of the action of a catalyst is given by the ingenious device used to locate tiny leaks of gasoline vapors or similar gaseous hydrocarbons from pipelines. These hydrocarbons, mixed with air at ordinary temperatures, will not burn. However, at an active metal surface, they may react very readily. Platinum metal, for example, is noted for its catalytic activity. The leak detector has a small coil of platinum wire which offers a certain small resistance to a constant electric current passed through it. Ordinary air is passed over this coil, with no effect on the resistance. But if hydrocarbons are present, even in quite small traces in the air, they are oxidized by the oxygen at the surface of the platinum. This reaction produces heat, which raises the temperature of the wire and therefore raises its electrical resistance. The increase in resistance is easily noted, and serves to indicate the presence of combustible materials in the air, which might be exceedingly difficult to detect in any other practical way.

Industrial chemistry, as we shall see in Part Four of this book, makes much use of catalysts, which make feasible certain valuable chemical reactions that otherwise would be unsuccessful because of their slow rate. For example, nitrogen ordinarily will not unite with hydrogen even when heated, but in the presence of a catalyst the reaction goes readily and the exceedingly important compound, ammonia, NH_3, is formed. Sulfur dioxide will not combine with oxygen to form sulfur trioxide unless a catalyst is present, and this reaction is essential to the production of sulfuric acid. Many catalytic processes lie at the heart of the petroleum refining industry. Indeed, catalysts are marvelous and indispensable aids to practical chemistry.

The function of a catalyst, in terms of activation energy, is to reduce the requirement of activation energy so that the reaction can proceed more easily. Two general kinds of catalysis are common: homogeneous

and heterogeneous. A homogeneous catalyst is a substance that is mixed in the same phase with the reactants. A heterogeneous catalyst is a substance that occupies a separate phase from the reactants, and presumably is effective only at the interface between the phases. The exact mechanism by which the activation energy requirement is reduced by a catalyst is not well understood, and probably varies for each individual reaction and catalyst. The catalyst may react chemically with one of the reactants, forming an unstable intermediate which then reacts further and more easily, giving the desired products. This kind of functioning is probably more typical of homogeneous catalysts. On the other hand, the catalyst may merely hold one or more of the reactants to its surface in such a way as to render it more vulnerable to chemical attack by the other reactant. In either type, the result is ordinarily an increase in the rate. Sometimes, however, the desired result is a decrease in the rate. For example, processes of corrosion are usually harmful, and should be slowed as much as possible if they cannot be prevented altogether. Catalysts used for such purpose are called "negative catalysts," or more commonly, "inhibitors." They probably function by interfering with and terminating processes which would otherwise proceed indefinitely, at a much faster rate. Thus a single molecule of inhibitor may sometimes prevent the conversion of hundreds of molecules of desired substance to undesirable products.

The effect of temperature on reaction rates is also related to the activation energy. Remember that the temperature is only a measure of the *average* vigor of motion of trillions of molecules. Individually, the energies of these molecules vary over a wide range. At any one instant most of the molecules at a given temperature have approximately the same kinetic energy, but some have less and a few much less. Similarly, some have more and a few much more. A very slow reaction may be one in which only those few molecules having much higher than average energy have the required activation energy for reaction. Thus only a small fraction of the collisions can result in chemical change. An increase in temperature shifts the whole molecular energy distribution curve, with the result that a higher proportion of the molecules have enough energy to react. A greater fraction of collisions can thus result in reaction. Furthermore, there are more collisions because of the increased average speed of the molecules at the higher temperature. Both these factors result in increased reaction rate as an effect of increased temperature. A rough rule of thumb is that the rate doubles with a 10° rise in temperature. The pressure cooker, which permits water to be heated above 100° without evaporating away, is one of

the most familiar examples of practical applications of this principle, for food cooks much faster when the temperature is raised relatively little higher.

RATES—QUANTITATIVE, AND MECHANISMS

The rates at which chemical reactions proceed depend not only on the various factors discussed above, but also on the mechanisms by which the reactants interact. Unfortunately, we can seldom know exactly what does take place on the atomic level. Often, however, helpful clues may be obtained from a study of the effects of changing the concentrations of reactants in a systematic way, measuring the concentrations of products after successive time intervals. Such studies have established definite mechanisms in some reactions, and it will be profitable for us to consider one of those reactions here.

The Hydrogen-Iodine Reaction

Two reactions have been observed to occur in the gas phase at appropriate temperatures. One is a combination of hydrogen and iodine to form the compound hydrogen iodide, HI:

$$H_2 + I_2 \rightarrow 2HI$$

The other is the decomposition of hydrogen iodide, forming hydrogen and iodine:

$$2HI \rightarrow H_2 + I_2$$

As you can see, one is exactly the reverse of the other.

Detailed studies of these reactions have shown that they occur in a straightforward manner. In the first, a molecule of hydrogen collides with a molecule of iodine, forming an intermediate unstable complex which then may split in either of two ways. It may break apart as the original molecules, one of hydrogen, H_2, one of iodine, I_2. Or it may break apart as two new molecules, each of hydrogen iodide, HI. In the second reaction, a molecule of hydrogen iodide collides with a second molecule of hydrogen iodide, forming an intermediate unstable complex which then may split in either of two ways. It may break apart as the original molecules, each one hydrogen iodide, or it may break apart as hydrogen and iodine molecules. For both reactions, the unstable intermediate is the same, and its two possible paths of disruption are the

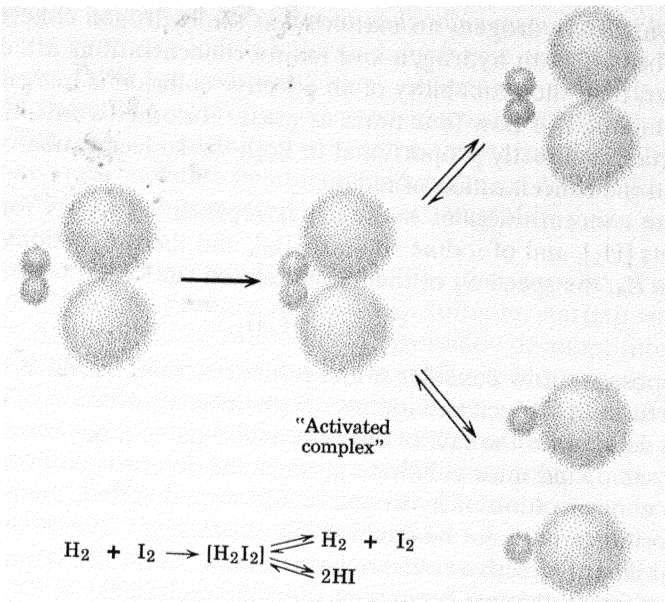


Figure 92. Reaction involving hydrogen, iodine, and hydrogen iodides.

same. Naturally, the identical breakdown of intermediate which produces products in the first reaction produces only reactants in the second reaction.

The unstable intermediate may be considered to form only when the molecules collide hard enough to overcome the initial repulsion, which ordinarily causes elastic bouncing apart without reaction. Consequently, at a given temperature only that proportion of collisions wherein this activation energy is attained can be expected to be effective. This proportion will be the same, however, whatever the concentration of molecules. The higher the concentration, the more frequent the collisions, and the greater the probability that the collisions will be effective.

It is found that in the reaction between hydrogen and iodine the rate of reaction initially depends on the initial concentrations of both hydrogen and iodine. If the concentration of hydrogen in one instance is double that of hydrogen in another instance, we must expect twice the likelihood of an effective collision with iodine, no matter what might be the concentration of iodine molecules, as long as it is the same in both instances. If the hydrogen concentration is kept constant, on the other hand, doubling the iodine concentration will double the probability of a

collision with hydrogen, no matter what the hydrogen concentration might be. If both hydrogen and iodine concentrations are doubled, however, then the probability of an effective collision is increased even more: in fact, it is now four times as great. In other words, the speed of reaction is directly proportional to both the concentration of hydrogen and the concentration of iodine.

If the concentration of hydrogen is represented by its formula in brackets $[H_2]$, and of iodine similarly $[I_2]$, and the proportionality constant is K_A, the speed S_A of their combination can be expressed as:

$$S_A = K_A[H_2][I_2]$$

Suppose we now consider the opposite reaction, in which hydrogen iodide forms hydrogen and iodine. Here the concentration of hydrogen iodide determines the rate of effective collisions, too, but two molecules of the same kind must collide to produce the observed products. If the initial concentration of hydrogen iodide were doubled, the rate of decomposition would not be doubled but *quadrupled.* This is because the probability of effective collision between like molecules is quadrupled. Let us assume that we begin with four like molecules, A, B, C, and D. The possibilities for collision are: A-B, A-C, A-D, B-C, B-D, C-D—six in number. Now double the number of like molecules, giving eight: A, B, C, D, E, F, G, H. The possibilities for collision are now these: A-B, A-C, A-D, A-E, A-F, A-G, A-H, B-C, B-D, B-E, B-F, B-G, B-H, C-D, C-E, C-F, C-G, C-H, D-E, D-F, D-G, D-H, E-F, E-G, E-H, F-G, F-H, G-H. Count them—there are 28. Now double the number once more, and the number of possibilities for collisions increases to $15 + 14 + 13 + 12 + 11 + 10 + 9 + 8 + 7 + 6 + 5 + 4 + 3 + 2 + 1$, or 120. Whereas 28 is 4, or 25%, more than $4 \times 6 = 24$, 120 is only 8, or 7%, more than $4 \times 28 = 112$. When the number of molecules is very large, as in any ordinary sample of gas, then doubling the concentration comes so close to quadrupling the possibilities for collision that there is no significant difference.

In both reactions, collision between two molecules is required. The only difference is that in the second reaction, the two molecules happen to be of the same kind. We could therefore write an expression for the rate of the second reaction:

$$S_B = K_B[HI][HI] = K_B[HI]^2$$

If the concentration of HI is x, then doubling it will make it $2x$. The square of $2x$ is $4x^2$. The rate in the first instance is Kx^2; in the second it is $4Kx^2$, or four times as fast.

Recognizing that both these reactions can occur, let us consider what

must actually happen when hydrogen and iodine react to form hydrogen iodide. As hydrogen iodide is formed, hydrogen and iodine are consumed. As these are consumed, their concentrations go down. As their concentrations go down, the rate at which they react must go down. The reaction, beginning with given concentrations of hydrogen and iodine, must therefore be at its maximum speed when it first starts, while these concentrations are highest, and must slow down as the reaction proceeds.

But we have observed that hydrogen iodide too is capable of reaction, with itself, to form hydrogen and iodine. Initially, starting with pure hydrogen and iodine, the rate of hydrogen iodide decomposition must be zero, because there is no hydrogen iodide to decompose. However, as it is formed, its concentration builds up. As its concentration builds up, the possibility of intermolecular collisions reforming hydrogen and iodine increases. Thus, hydrogen and iodine begin to be formed. As the rate of combination of hydrogen and iodine to form hydrogen iodide decreases, the rate of decomposition of hydrogen iodide to hydrogen and iodine must simultaneously be increasing. Soon a steady state must be reached, in which the rate of formation of hydrogen iodide from hydrogen and iodine must exactly equal the rate of formation of hydrogen and iodine from hydrogen iodide. No alternative exists. These equal and opposite reactions must then proceed at exactly the same speed, and no further change in the concentrations of the components of the system, hydrogen, iodine, and hydrogen iodide, can occur.

Since the speeds are equal, we can equate them:

$$S_A = K_A[H_2][I_2] = S_B = K_B[HI]^2$$

Then,

$$\frac{K_A}{K_B} = \frac{[HI]^2}{[H_2][I_2]} = K$$

Any system in which exactly opposite chemical reactions are simultaneously occurring at equal rates is said to be at "**chemical equilibrium.**" The ratio of the two rate constants, which therefore must also be a constant, is called the "**equilibrium constant,**" and is denoted by K.

Other Mechanisms

Not all reactions—in fact, relatively few—take place by as simple a mechanism as that described above for hydrogen, iodine, and hydrogen iodide. Even reactions whose equations look quite analogous to the

hydrogen iodide equation may not necessarily proceed as the result of simple bimolecular collisions. Many occur, for example, as "chain reactions," involving active species not normally stable, called "free radicals." A "free radical" is an atom or group of atoms having one (usually, sometimes more) outer electron-plus-vacancy combination still available for bonding. Normally, such radicals have only a very brief existence, for their chemical reactivity is so high that they almost immediately combine with one another or react with some other species. For example, hydrogen atoms, and chlorine atoms, uncombined in diatomic molecules, may be considered as "free radicals." They are much more reactive than the molecular species because they are immediately ready for reaction, whereas the molecular species must first be disrupted, or at least deformed. When sunlight enters a mixture of hydrogen and chlorine molecules, some of the chlorine-chlorine bonds absorb enough energy to split apart, forming "atomic chlorine":

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

Then the atomic chlorine, or free chlorine radical, can attack a hydrogen molecule, forming a molecule of HCl and liberating a free hydrogen atom:

$$Cl + H_2 \rightarrow HCl + H$$

This in turn can strike a chlorine molecule forming another molecule of HCl and liberating another free chlorine atom:

$$H + Cl_2 \rightarrow HCl + Cl$$

By such a mechanism, the absorption of a single quantum of light energy by a single molecule of chlorine can set off a whole chain of reactions that can continue indefinitely. In the gas phase, such chain reactions can occur explosively fast if appropriate concentrations of the reactants are present. One might think that chance collision of two atoms of hydrogen, or two atoms of chlorine, would terminate chains by the formation of the molecular species. However, before such molecules can be stable they must rid themselves of the energy released by their combination. In other words, a third body must be present to absorb this energy, or else the molecule retains enough energy to break apart again. Other materials, present in the gas phase or at the surface of the container, may accordingly serve to terminate the chains, either by permitting combination into diatomic molecules or by reacting with the free radical to form some more stable species.

Relatively few reactions can be written as though only two molecules were involved, however. Many require three or more, often many more. What mechanism can be involved here? Actually, the probability that

three different particles will collide simultaneously in exactly the right way for the formation even of an intermediate complex is very small, compared to the probability of two-body collision. The probability that four or more particles will come together at the same time is even more remote. We cannot expect, therefore, that chemical reactions involving more than two particles can occur at reasonable rates by such improbable means. Instead, they ordinarily involve a series of reactions. Often the intermediate products of such reactions are so unstable that they cannot be isolated, and all we can observe are the initial reactants and the final products. But the reactions occur in steps, nevertheless. One of the most important aspects of this is that the rates of these individual intermediate steps may differ widely from one another. Suppose a reaction occurs by five successive steps, all at different rates, one of which is much slower than any of the others. This one is then called the "rate-controlling" step; it is the bottleneck in the production of final products. Nothing we might do to speed up any of the other steps is therefore likely to have much effect on the rate of the overall reaction.

The science of "**kinetics,**" which deals with the rates of chemical reactions, is much concerned with reaction mechanisms. Measurement of the rates can only suggest the probable nature of the rate-controlling step, without identifying that step. Chemists must then speculate concerning various possible intermediate reactions that would produce the observed rate results. In some reactions, they can arrive at amazingly shrewd deductions concerning various mechanisms involved in the overall reaction. The possibility must always be recognized, and guarded against, however, that some intermediate step mechanism as yet unimagined might produce the same observations, and be, indeed, the correct mechanism for the reaction.

The Law of Mass Action

Nearly 100 years ago, two Norwegian chemists, Guldberg and Waage, recognized the relationship between "active mass" (concentration) of reactants and the rate of reaction. They enunciated the "Law of Mass Action," according to which the rate of a reaction is proportional to the product of the concentrations of each reactant, each raised to a power equal to the number of molecules or units involved in the chemical equation. In a generalized expression, the rate of reaction between m moles of A and n moles of B would be proportional to $[A]^m[B]^n$.

If the products C and D are formed in the proportions p moles of C and q moles of D and the reaction is reversible, the rate of the reverse

reaction is proportional to $[C]^p[D]^q$. At equilibrium, then, the ratio of the proportionality constants, which is the equilibrium constant K for the reaction,

$$mA + nB \rightleftharpoons pC + qD$$

is given by the expression:

$$K = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

This expression for the equilibrium constant is valid even though the mechanism of the reaction may consist of a series of consecutive intermediate steps. We were able to derive this same expression for the simple case of hydrogen and iodine reaction, and we could have derived it similarly for reactions among ions and molecules in dilute solution. Experimentally, it can always be determined if the concentrations of all components in a chemical reaction system at equilibrium can be measured. In general, equilibrium constants can be determined by methods involving thermodynamics, a topic requiring treatment at a higher level than is appropriate for this book.

The great practical significance of equilibrium constants is that they tell us whether a given reaction is capable of producing products in good yield or not. A relatively large constant, one or higher, means that reasonably good or better yields of products are present in the equilibrium mixture. A relatively small constant, 10^{-1} or smaller, means that relatively little of the products are present at equilibrium. Numerous practical applications of equilibrium constants will be described and discussed in the chapters to follow.

Le Chatelier's Principle in Chemical Equilibria

Equilibrium expressions also suggest ways of influencing chemical equilibria in a desired manner. The behavior of a system at chemical equilibrium is analogous to that of a system at physical equilibrium when stress is applied. The Principle of Le Chatelier, discussed on page 99, deals equally successfully with predictions regarding reversible chemical reactions.

Only three ways are apparent of applying stress to a chemical system at equilibrium in the gas phase:

(1) The partial pressure of one component may be changed. Pressure and concentration are proportional for a gas. Changing the partial pressure is therefore changing the concentration. If the concentration is increased, the rate of formation of products of this component must increase. A new equilibrium is reached at which the proportion of

these products is higher than before. If the concentration of the same component is decreased the rate of formation of its products decreases, and a new equilibrium is reached at which the proportion of these products is lower than before. Le Chatelier's Principle would predict these changes by stating that anything done to change a concentration will result in an adjustment to compensate for that change. The concentration appears to be trying to remain the same. If molecules are removed, more are formed by the appropriate reaction. If you add molecules, the excess tends to disappear by reacting. These changes are necessary because the equilibrium *constant* is maintained. You cannot change the numerator without changing the denominator, and vice versa.

Obviously, even when a desired product is present only in very small concentration at equilibrium, continuous removal of that product prevents attainment of equilibrium, and the equilibrium poor yield becomes a quantitative practical conversion. When the desired product cannot be removed continuously, but must be extracted in batches, better concentrations in the equilibrium batch can be formed by increasing the concentration of one or more of the reactants.

(2) The pressure on the entire system may be changed. For example, an increase will increase the rates in both directions. If the reaction itself involves no change in the total number of molecules, no shift in equilibrium will occur. But if the reactants have not the same number of molecules as the products, pressure change will affect the system, as is predictable by the principle of Le Chatelier. An attempt to squeeze molecules closer together, according to this principle, should be met by a net reduction of the total number of molecules, to keep the pressure unchanged. This can be achieved by favoring that reaction which forms fewer molecules. An illustration of this is given by the synthesis of ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

A total of four molecules of reactants forms two molecules of products. Yields of ammonia are favored by high pressures.

(3) The temperature may be changed. An equilibrium constant is constant only when the temperature is fixed; it changes with temperature. The change in equilibrium constant that accompanies a rise in temperature favors the endothermic reaction. In the example above, nitrogen combines exothermically with hydrogen. The endothermic reaction, which is the decomposition of ammonia, is favored by a rise in temperature. Therefore, better yields at equilibrium are obtained at a lower temperature. A practical difficulty which prevents taking full advantage of this fact is that all reactions go more slowly at lower tem-

peratures, and the rate of reaching equilibrium may be immeasurably slow. For example, nitrogen and hydrogen simply do not react at temperatures where the best yields of ammonia would theoretically be attained.

Le Chatelier's principle would predict the temperature effect, for the addition of heat would tend to raise the temperature. The system reacts to absorb the heat without raising the temperature—by speeding the endothermic reaction to a greater extent than the exothermic reaction.

It is important to recognize that in heterogeneous systems—systems of more than one phase, such as solid plus gas—only the gas concentration is variable. *The concentration of a solid or liquid phase cannot be changed.* Consider, for example, the thermal decomposition of limestone:

$$CaCO_3 \rightarrow CaO + CO_2$$

At equilibrium, one might write for the system a constant:

$$K = \frac{[CaO][CO_2]}{[CaCO_3]}$$

Both $CaCO_3$ and CaO, however, are solids. The amounts can be changed, but not the concentration, which is really equivalent to the density rather than the mass. Hence the only variable is the concentration of CO_2, which is equivalent to its pressure. The correct equilibrium constant for this reaction is therefore simply

$$K = p_{CO_2}$$

Le Chatelier's principle would allow us to predict that raising the temperature would favor the endothermic reaction, thus increasing the equilibrium pressure of CO_2. This is amply verified experimentally. Also, increasing the pressure would favor the reverse reaction, by which pressure is reduced.

SPECIAL HELP

Test Your Memory

1. What is meant by "pyrophoric"?
2. What factors influence the rate of a chemical reaction? How, and in what way, do they operate?
3. What is a catalyst and how does it function?

4. What is "activation energy"?
5. Write the equilibrium constant expression for the H_2—I_2 reaction.
6. What is meant by a "chain reaction"?
7. What is the meaning of "kinetics"?
8. What is meant by "rate-controlling step"?
9. How does a temperature change affect an equilibrium constant?
10. Under what conditions does a change in pressure affect a system under equilibrium?

Test Your Math

1. The standard heats of formation are: $CaCO_3$, -288.5; CaO, -151.9; and CO_2, -94.1 kcal per mole. What is the heat of reaction of CaO with CO_2?
2. The heat of reaction when nitrogen combines with hydrogen is -22.1 kcal. What is the heat of formation of ammonia?
3. For a system of gases A, B, C, and D at equilibrium,

$$A + 2B \rightleftharpoons C + 3D$$

the partial pressures are found to be: A, 0.20; B, 0.10; C, 0.30; and D, 0.50 atm. What is the numerical value of the equilibrium constant?

Test Your Understanding

1. Heating sodium nitrate liberates oxygen and leaves sodium nitrite. (*a*) Write the equilibrium expression. Then tell what effect on the equilibrium would be shown by (*b*) increasing temperature, (*c*) adding sodium nitrite, (*d*) increasing pressure, and (*e*) removing some of the nitrate.
2. Inside a flash bulb are the necessary ingredients for a vigorous chemical reaction producing a brilliant light, but the reaction does not proceed unless something is added. Why?
3. Under what conditions, and how, can a very small concentration of a negative catalyst, or inhibitor, protect a large amount of a compound from, for example, oxidation by the air?
4. (*a*) Write the equilibrium expression for a decomposition of carbon dioxide to the monoxide plus oxygen. This is an endothermic reaction. (*b*) Predict the effect of increasing pressure on the system. (*c*) Predict the effect of decreasing the temperature. (*d*) What would happen if some CO_2 were removed?

PART THREE

Solutions

16

The Nature of Solutions

EVERYONE IS FAMILIAR with the fact that when a limited quantity of sugar or salt is added to water and the mixture is stirred, the solid disappears without any visible change to the water. The most rational explanation for this observation seems to be that the sugar or salt must become mixed with the water in particles too small to be seen with the naked eye. Possibly, then, the solid particles would be detectable under a microscope. But it is found that even under the highest power of magnification possible, they are not. Furthermore, if a beam of light is directed into a liquid containing extremely small suspended particles that are not visible to the eye, some of the light is reflected by the particles so that the path of the beam becomes visible. But when such a beam is directed into the sugar or salt mixture with water, the path of the beam cannot be seen. What can this mean?

Experimental evidence to be discussed later has been interpreted to mean that the mixture of water with salt or sugar is as intimate a mixture as possible, one in which the individual molecules of water and the individual molecules of sugar, or the individual ions of salt (since salt is

not molecular), are thoroughly mixed together. Such a mixture is called a "solution." The term is general, not limited merely to mixtures of solid and liquid; any mixture of two or more substances, on a molecular basis or its equivalent, is called a solution.

KINDS OF SOLUTION

By the above general definition, a molecular mixture of gases—and no other kind than molecular is possible—is a solution. Air, for example, is a solution of gases. When you loosen the cap of a bottle of soda pop and the liquid starts to fizz, the fizzing is due to hundreds of tiny gas bubbles forming and rising to the surface. Where did they come from, but inside the liquid? Here is a good example of a solution of a gas in a liquid: carbon dioxide in an aqueous solution of sugar, dye, and flavoring. Fish can breathe under water, but where do they get their oxygen? By decomposing water? No, indeed; water in contact with the atmosphere always dissolves some of it, and it is the dissolved oxygen, not the combined oxygen, which supplies the fish. If something occurs to deplete this supply, the fish die. You pour alcohol or ethylene glycol, both liquid compounds, into the water of your automobile radiator to help prevent freezing—do two liquid layers form? No, they mix and appear as a single liquid—they dissolve. These are examples of solutions of liquid in liquid. When rocks are heated, small amounts of gases are evolved. Are these formed by decomposition of the rock? Sometimes, but also they were dissolved in the solid rock. This is an example of a solution of gas in solid. Finally, when two or more different metallic elements are melted together, they sometimes form a homogeneous liquid, which means a solution, and often when the solution is cooled and solidifies the solution persists. Here we have a solid solution, or a solution of solid in solid. Examples of solutions of solid in liquid have already been mentioned: this is the most common and most abundant kind of solution to be encountered in the elementary study of chemistry.

SOLVENT AND SOLUTE

When one of the substances that form a solution is solid and the other liquid, then the former is said to dissolve in the latter. The process of dissolving is called "**dissolution.**" The solid is called the "**solute,**" and the liquid is called the "**solvent.**" The solute dissolves in the solvent.

But when two liquids form a solution, the assignment of the terms, solute and solvent, becomes somewhat arbitrary. For instance, alcohol and water will dissolve in one another in all proportions. If the solution is 5 per cent alcohol and 95 per cent water, one would expect to refer to this as a solution of alcohol in water, more specifically, as a 5 per cent alcohol solution. If the solution is 95 per cent alcohol and 5 per cent water, it should be called, to be consistent, a solution of 5 per cent water in alcohol. But it is not. It is called a 95 per cent alcohol solution. The percentage always refers to the solute, and the implication here is that alcohol is the solute even though it is present in far higher concentration than that of the solvent. Such terminology is somewhat exceptional, however. Ordinarily, the liquid present in higher concentration is thought of as the solvent, the other the solute.

THE SPECIFICITY OF SOLUBILITY

Just as everyone is familiar with the fact that a limited amount of sugar or salt will dissolve in water, so everyone knows also that one cannot dissolve an unlimited amount of sugar or salt in water. Presently a "saturation point" is reached, beyond which, if the amount of solvent is kept constant, no further dissolution seems to occur. Furthermore, this point is not the same for different solutes. For instance, if one studied the solubility of salt compared to sugar, one would find it to be considerably less. Alcohol, on the other hand, has unlimited solubility in water, for these liquids can form solutions in all possible proportions. (Such pairs of liquids are said to be "completely miscible"). Yet one might stir a tiny amount of sand with a large amount of water for days and days without observing any appreciable

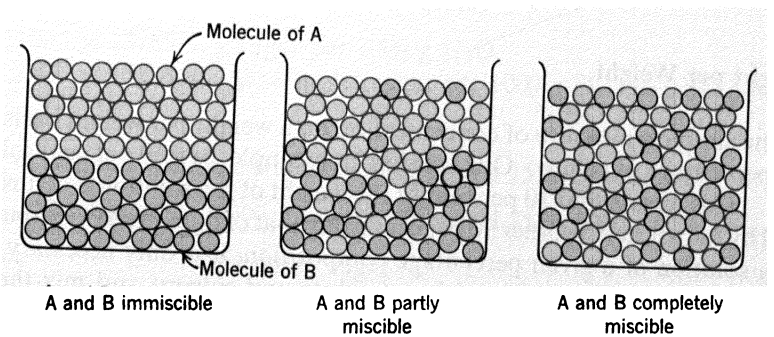


Figure 93. Miscibility of liquids.

decrease in the quantity of sand. Clearly, different substances do not dissolve in water to the same extent.

Furthermore, other solvents do not necessarily resemble water. Gasoline, a mixture of compounds containing carbon and hydrogen, has no observable solvent action on salt, yet it will dissolve alcohol readily. Carbon tetrachloride, CCl_4, is an excellent solvent for fats and grease and for other organic substances, but not for salt, nor will it dissolve much water.

Indeed, when a quantitative study of solutions is made, it is found that no two solutes are alike in their ability to dissolve in a given solvent, and no two solvents are alike in their ability to dissolve a given solute. There is obviously something highly specific about solubility.

A solution which contains as much solute as it can stably hold is called a "**saturated**" solution. The concentration of such a solution is called the "**solubility**" of that solute in that solvent. Several ways of expressing solubilities quantitatively, and thus of expressing concentrations of "unsaturated" solutions as well, are in use.

QUANTITATIVE DESCRIPTION OF THE CONCENTRATION OF A SOLUTION

Solutions are mixtures, and mixtures are characterized as being adjustable over a wide range, in contrast to the definite proportions of elements in a pure compound. All possible concentrations of a given solute in a given solvent under fixed conditions of temperature and pressure are possible, from zero to the maximum of a saturated solution. Some means of specifying the amount of solute per given quantity of solvent is necessary in order to deal quantitatively with solutions.

Weight per Weight

The simplest measure of concentration on a weight per weight basis is the percentage of solute. One speaks, for example, of a 10 per cent solution. This means that 10 per cent of the weight of the solution is contributed by the solute, the other 90 per cent being that of the solvent. To make up a solution of a given percentage composition, it is only necessary to weigh the appropriate quantities of solute and solvent and mix them together until dissolution occurs. To measure out that quantity of solution which contains a given amount of solute, the correct amount of solution must be weighed.

Another system for expressing the concentration of a solution is that of "molality." This is defined as "the number of moles of solute per 1000 grams of solvent." The special advantages and uses of this expression of concentration will become apparent a little later.

Still another system is devised to tell how many molecules of solute there are, per molecule of solvent. Under this system, the "mole fraction" of the solute is defined as the number of moles of solute per total number of moles of solute plus solvent. The mole fraction of the solvent is similarly the number of moles of solvent per total number of moles of solute plus solvent. Obviously, the sum of the mole fractions of solute and solvent must equal 1.000. A mole fraction of 0.200 means that for every molecule of solute, there must be five molecules of solute plus solvent, or, four molecules of solvent.

EXAMPLES. 1. How much sodium sulfate is in 50 g of a 10% solution? The solution is 10% Na_2SO_4 and 90% H_2O. 10% of 50 g = 5 g Na_2SO_4 ANS.

2. To supply 100 g of salt (NaCl) by evaporation, how much 2% solution would be needed? How much water would be separated?

100 g is 2%. Then 100% is 100/2 = 50 times as much
50×100 g = 5,000 g of solution ANS.
5,000 − 100 = 4,900 g of water to be evaporated ANS.

3. What is the molality of a 15% solution of sugar ($C_{12}H_{22}O_{11}$)? 15% means 15 g sugar to 85 g H_2O.

Molality is moles per 1000 g H_2O. One mole of sugar = 342 g (by adding the atomic weights in the formula)

$1000 \times 15/85$ = g sugar per 1000 g H_2O
$1000 \times 15/85 \div 342$ = moles sugar per 1000 g H_2O = 0.52 molal ANS.

4. What is the mole fraction of sugar in a 15% solution?

0.52 mole sugar; 1000/18 = 55.5 moles H_2O in 1000 g

$$\begin{array}{r} 0.52 \text{ moles sugar} \\ \underline{55.5 \text{ moles } H_2O} \\ 56.02 = \text{total moles (sugar plus } H_2O) \end{array}$$

Mole fraction of sugar is 0.52/56.02 = 0.009 ANS.

5. How many molecules of water per molecule of sugar in the 15% solution?

56.02/0.52 = approximately 112 H_2O molecules to one sugar molecule
ANS.

Weight per Volume

Under each of the systems described above, the process of weighing must be carried out not only in the preparation of the solutions but also in making any quantitative use of them. Weighing a solution, and especially weighing an exactly specified amount, may be a laborious process. It is certainly much simpler to measure a volume of liquid accurately than to weigh it. Furthermore, by means of "burettes" (long vertical tubes calibrated in units of volume, open at the top and having a stopcock at the bottom) it is very simple to measure out exactly a prespecified volume. Therefore, a number of systems of expressing concentration in weight per volume have been devised.

One system is to weigh out the solute, and dissolve it in enough solvent to produce a certain volume of solution. The volume of a solvent is changed in an unpredictable manner by the addition of solute, which is why the volume of the *solution* must be measured. For example, one might weigh out 100 grams of solute and dissolve it in enough solvent to make one liter of solution. One could then measure out any part of that solution by volume, and easily compute how much solute it contains, from the fact that each milliliter contains 0.1 gram.

But more often, especially in the chemical laboratory, one wishes to measure moles of solute. The system used here is to express concentration as "molarity," defined as the number of moles of solute *per liter of solution.* Be very careful not to confuse this with "molality," which is the number of moles of solute *per 1000 g of solvent.* The letter "*M*" is used to abbreviate molarity. For example, a 6*M* solution of sulfuric acid is one that contains 6 moles of H_2SO_4 per liter of solution.

Closely related to this system of molarity is that of "normality." This is defined as the number of *equivalent weights* of solute per liter of solution. This expression of concentration is particularly useful in carrying out reactions between reagents in solution, for it is easy to calculate the exact volume of one solution needed for complete reaction with any specified volume of the other solution. The letter "*N*" is used to abbreviate normality. For example, a 3*N* solution of sodium hydroxide, NaOH, is one that contains three equivalent weights of sodium hy-

droxide per liter of solution. We know that an equivalent weight of NaOH is the same as the weight of one mole, so in this case normality and molarity are the same. We could describe this solution as $3N$ or $3M$. However, suppose we were describing a sulfuric acid solution. Here each molecule of H_2SO_4 produces two active hydrogens, and one mole would furnish *two* grams of hydrogen. An equivalent weight is the amount that would produce one gram of active hydrogen, so an equivalent weight of sulfuric acid is only half a mole. Consequently, a $3M$ solution of sulfuric acid would be the same as a $6N$, not a $3N$, solution.

EXAMPLES. 1. A sample of 1.00 g of sugar is dissolved in enough water to make exactly 1 liter of solution. How much sugar is present in a 5-ml portion of this solution?

1 g sugar in 1 liter or 1000 ml = 0.001 g/ml
5 ml × 0.001 g/ml = 0.005 g sugar. ANS.

2. What is the molarity of a solution containing 0.001 g of NaCl per ml?

0.001 g/ml = 1 g/liter.
1 mole NaCl = 58.5 g (23 + 35.5)
1 g = 1/58.5 = 0.017 mole. Solution is $0.017M$. ANS.

3. What is the molarity of chloride ion in a solution containing 9.5 g $MgCl_2$ per liter?

The formula weight of $MgCl_2$ is $24 + 2 \times 35.5 = 95$.
9.5 g/95 g/mole = 0.1 mole $MgCl_2$. Hence the solution is $0.1M$ $MgCl_2$.

But be aware that the ions of salts are separated in solution. One mole of $MgCl_2$ would give 2 moles of Cl^-. Therefore the solution is $0.2M$ Cl^-. ANS.

4. A 2-ml solution of $6M$ HCl is diluted to one liter. What is the final molarity?

Remember the rule that the total quantity of solute is always equal to the product of the concentration times the volume, and the total amount of solute cannot be changed by changing only the amount of solvent. Then, for a given amount of solute, *any concentration times the corresponding volume equals any other volume times the corresponding concentration.*

Here, volume $\times$ molarity = volume $\times$ molarity.

$$Vm = V'm'$$

We know $V = 2$ ml, $m = 6$, and $V' = 1$ liter, and we can therefore solve for m'. The units *must* be alike, however. Either V must be changed from 2 ml to 0.002 liter, or V' must be changed from 1 liter to 1000 ml.

$$2 \times 6 = 1000m'$$

or

$$0.002 \times 6 = 1m'$$

Either way, $m' = 0.012$. The solution is $0.012M$ HCl. ANS.

Problems in normality can be handled the same way.

5. What volume of $0.4N$ H_2SO_4 is required to neutralize 35 ml of $2N$ NaOH?

We know that *equivalent* quantities of these compounds will react. This problem is therefore very similar to asking what volume of $0.4N$ H_2SO_4 would contain the same amount of H_2SO_4 as 35 ml of $2N$ H_2SO_4, because, by definition of normality, 35 ml of $2N$ H_2SO_4 is exactly the right quantity to react completely with 35 ml of $2N$ NaOH.

$VN = V'N'$

$V \times 0.4 = 35 \times 2 = 70$

$V = 70/0.4 = 175$ ml ANS.

It is easy to check whether such answers are of the right order of magnitude by remembering that if a solution is more dilute it will take more of it to do a job, but if it is more concentrated, less will be needed. In the above example, we start with 35 ml of $2N$ and wish to know what volume of $0.4N$ would correspond to it. Since $0.4N$ is obviously much more dilute than $2N$, a much larger volume of it should be necessary. In fact, $2N$ is exactly 5 times more concentrated than $0.4N$, and therefore 5 times as great a volume of $0.4N$ should be required. 5×35 is 175 ml.

FUNDAMENTALS OF DISSOLUTION

If we keep clearly in mind what a solution is, a mixture of substances on a molecular basis or its equivalent, we can begin to examine the fundamental nature of the dissolution process that produces it. First, let us consider the physical nature of the solute and the solvent separately,

before they are mixed. The solute, unless it happens to be a gas, is held together in either liquid or solid state by relatively strong attractive forces. These may be covalent bonds, electrostatic attractions between oppositely charged ions or ends of dipoles, protonic or hydridic bridges, or van der Waals forces. The molecules of the solvent are attracted to one another by similar forces. We know from the fact that energy must be expended in order to expand, melt, or vaporize these substances, that these attractive forces are significantly large.

Now, what about the nature of a solution? Here, where solvent molecules were once held together closely by appreciable attractive forces, are now intervening solute particles, keeping the solvent molecules on the average farther apart than they were in the pure solvent. Here also are the solute particles, although originally they held one another tightly together, now all separated from one another by solvent molecules. How did they get that way? Clearly energy has been expended on both solute and solvent. Where did this energy come from?

If you have prepared many solutions, for instance of salts in water, you have probably observed that during some dissolutions the solution grows warm, even fairly hot, and in others, less commonly, the solution grows cold. Such observations show that energy changes occur in the formation of solutions. But the quantity of heat absorbed, even when dissolution is endothermic, is ordinarily much less than would be expected to be necessary in order to separate the component particles of solute and of solvent to the extent that they are separated in solution. Furthermore, many dissolutions are exothermic. How can a process that requires energy expenditure occur spontaneously and give out energy besides?

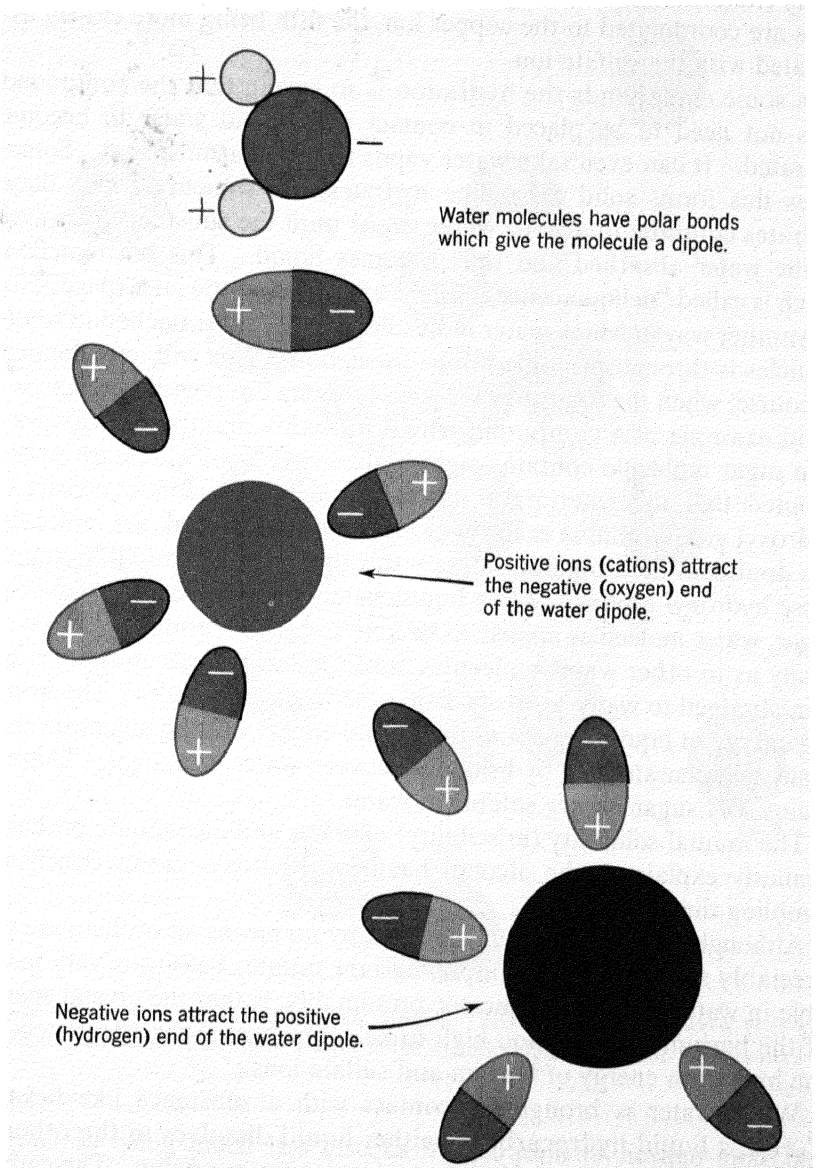
The answer must lie, of course, in that aspect of dissolution not yet mentioned: the coming together of solute particles and solvent molecules. The forces of attraction between solute and solvent must be the origin of the energy needed to separate solute particles and to separate solvent molecules. In other words, the process of dissolution must be simultaneously (1) an endothermic separation of solute particles, (2) an endothermic separation of solvent particles, and (3) an exothermic joining together of solute with solvent. Inherent in this picture is the essential modification or destruction of certain labile structures that may have existed within the pure solvent (such as the protonic bridging in water).

Here we have an excellent clue to the specificity of solvent action. If a given solute will dissolve spontaneously in a given solvent, it seems to prove that the interattractions between solute and solvent particles are adequate to compensate for the disruption of interattractions within

the solute and within the solvent. If the "solute" will not dissolve, it seems reasonable to infer that the interattractions between solute and solvent particles are not sufficient. We can therefore look to the nature of the molecules or other component particles of solute and solvent to decide whether or not the solute is likely to attract the solvent enough to cause dissolution.

In general, a polar liquid is required to dissolve a polar solid or liquid. Water is exceptionally well suited as a solvent for polar solids—ionic compounds—on this account. For example, consider the dissolution of sodium chloride. The sodium ions and chloride ions in the crystal are held strongly together by the electrostatic attractions between opposite charges. They cannot possibly be caused to separate without substituting some attraction to compensate for the overcoming of the original attractions. Furthermore, the water molecules themselves are interconnected through a labile network of protonic bridges, which help to prevent their separation. But when liquid water comes in contact with solid sodium chloride, the electrical charges on the surface ions attract the water molecules through their dipoles. Chloride ions attract the positive, hydrogen end of the water molecules. This attachment of water molecules to the ions is called "**hydration.**" The general term applied to attachment of solvent molecules to solute particles is called "**solvation.**" Hydration appears to compensate for interionic attraction, or lattice energy, in the crystal, and the hydrated ions separately drift off into the liquid phase.

All degrees of hydration may occur, depending on the conditions and the substance being hydrated, ranging from a relatively weak dipole-ion interaction to (in cations only) coordination of water molecules through donation of an electron pair from each water oxygen to an outer vacant orbital of the cation. Such coordination may result in strong bonds between cation and water. Differences in degree of hydration may be recognized when solvent is evaporated from the solution, leaving the solute in undissolved form. If the hydration is relatively weak, as in solutions of sodium chloride, the ions will reform the original crystal lattice with no water of hydration left attached to them. If the hydration is strong, as when coordination bonds are formed, the solute may crystallize with water still attached, especially to the cation, in a new crystalline hydrate form. For example, aluminum chloride, when crystallized from solution in water, retains six water molecules around each aluminum (although here it is not certain whether the attraction should be described as coordinate covalence or merely strong dipole-ion interaction). The formula of the crystal is $[Al(H_2O)_6]Cl_3$. Similarly, copper sulfate crystallizes as the pentahydrate $CuSO_4 \cdot 5H_2O$.



The ions may be loosely hydrated as shown, or they may be firmly hydrated with definite numbers of H_2O molecules (e.g. 4 or 6) stably held in regular geometric configuration (tetrahedral or octahedral).

Figure 94. Hydration of ions as an aid to dissolution.

X-ray examination of the crystal discloses that four of the water molecules are coordinated to the copper ion, the fifth being more closely associated with the sulfate ion.

In some compounds the hydration is so strong that the compound does not need to be placed in contact with liquid water to become hydrated. It can even take water vapor from the atmosphere. Sometimes this forms solid crystalline hydrates, but sometimes also these hydrates continue to absorb water vapor until the substance dissolves in the water absorbed and thus becomes liquid. This phenomenon, which is called **"deliquescence,"** will be explained a little later (page 350).

Another way in which water molecules can become attached to solute particles is through protonic bridge formation. This will only happen, of course, when the requisites for such bridging are present. Sugar is a good example of a compound which probably dissolves in this way. The sugar molecule contains eight hydroxyl groups, which are so distributed that the exterior of the molecule must seem to consist of hydroxyl groups almost exclusively. In the sugar crystal, the molecules are doubtless held together largely through protonic bridging among these hydroxyl groups. When liquid water comes in contact with solid sugar, water molecules appear to be able to become bridged to sugar as easily as to other water molecules, and similarly, sugar molecules become bridged to water as easily as to other sugar molecules. The bridging energy in liquid water and the crystal energy in solid sugar are thus easily compensated for by bridging between water and sugar. This explains why sugar is very soluble in water.

The mutual solubility (miscibility) of water and alcohol are probably similarly explained, the alcohol having a hydroxyl group closely resembling that in water.

Although water dissolves many salts, by no means all of them are appreciably soluble. For example, barium sulfate, $BaSO_4$, is very insoluble in water. What this means, presumably, is that the crystal energy of the barium sulfate is too high to be compensated for adequately by the hydration energy of barium and sulfate ions.

When water is brought in contact with a substance like hexane, C_6H_{14}, a liquid hydrocarbon, neither liquid dissolves in the other to any appreciable extent. Hexane molecules are nonpolar. The carbon and hydrogen of which they are composed are so nearly alike in electronegativity that no substantial separations of charge occur. Hexane molecules therefore attract one another only by van der Waals forces, which are relatively weak. The result is that hexane is relatively low in density, meaning that the molecules are relatively far apart on the average, and relatively volatile, boiling much lower than water (68.7°),

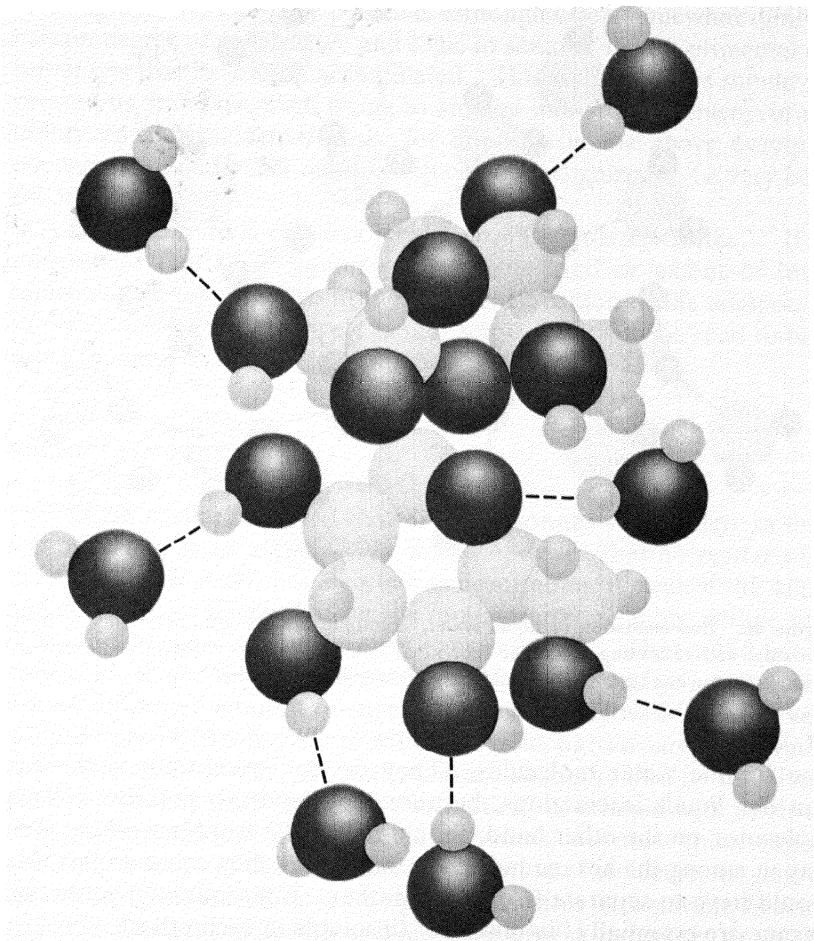


Figure 95. Sugar molecule in aqueous solution. Protonic bridges between H_2O and $C_{12}H_{22}O_{11}$ substitute for similar bridges in the sucrose crystal and in the liquid water.

as well as being much less viscous. Separation of hexane molecules from one another should obviously be relatively easy, and from this viewpoint hexane should be very soluble in many solvents. Indeed it is. Dissolution in water, however, is not just a matter of separating hexane molecules. In order for hexane molecules to work their way in among water molecules, they must push water molecules apart, thus overcoming to some extent the protonic bridging which holds water together. This they could only do if they themselves had some attrac-

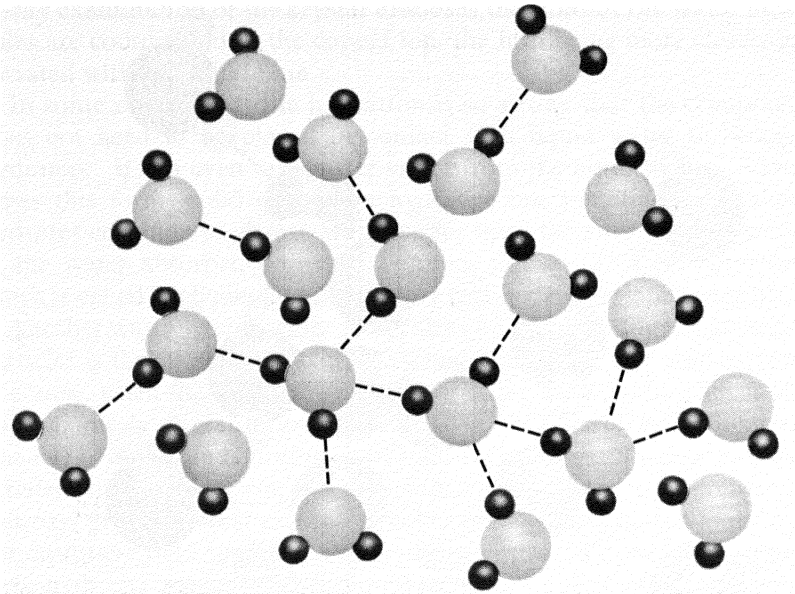


Figure 96. Representation of liquid water. Protonic bridges are continually forming, breaking, and reforming while the individual molecules move constantly through the liquid. At any one instant, the liquid has considerable "structure."

tion for the water molecules. They do not, except for very weak van der Waals interactions, because they have no polarity. Water molecules, on the other hand, should have little trouble working their way in among the hexane molecules, but before they could do this they would have to separate from one another. Consequently, water and hexane are essentially "immiscible" (insoluble in each other).

For very similar reasons, water and carbon tetrachloride are immiscible. But carbon tetrachloride and hexane, although chemically quite different, resemble one another in lack of polarity and in weakness of intermolecular attractions. Consequently, these molecules should mix relatively easily, and they do. They are miscible in all proportions.

From the above discussion, one might acquire the impression that the property of solubility is always logically and simply explainable in terms of the fundamental nature of the solute and solvent. Unfortunately, we do not yet understand enough about the nature of forces in the crystal, the structure of liquids, or the processes of dissolution and the structure of the solution to be able to understand solubility

thoroughly. We can only perceive, although often somewhat dimly, a certain degree of consistency and logic in some of the experimental observations that have been accumulated. This state of affairs should not prevent us, however, from trying to analyze individual problems of solubility on a fundamental basis, for often, as in the above examples, enough cause-and-effect relationship can be recognized to be very helpful and useful.

A rough empirical rule has long been, "Like dissolves like." If we understand that "like" refers more to the kind or extent of intermolecular attractions than to the exact composition of the compounds under consideration, this rule makes sense, for it can be seen to have some fundamental basis.

SOLUBILITY EQUILIBRIA

We have earlier observed that different solutes vary widely in their solubility in a given solvent. We know, however, that no matter what the solute, after it reaches a certain concentration, typical of the solute and solvent and dependent on the temperature, no more will go into solution however long the contact is maintained. What could be the reason for this? Why, if some sugar will dissolve easily in water, will not an unlimited amount of sugar do likewise? How is it that a very minute trace of barium sulfate will dissolve in a given sample of water, and not a speck more? Does the solvent suddenly lose its dissolving ability? What is really meant by "saturation" of a liquid with a solute?

To understand and answer these questions, we must think closely about the nature of the process of dissolution. Molecules or ions of the solute, when the solute is brought into contact with solvent, become attached to solvent molecules and leave the crystal, to become separated by solvent molecules. This is action. Is there any reason why such action should stop? Of course, one can see that such action would be forced to stop when all the solvent was used up, but in most instances solubility reaches a limit long before there is any likelihood of depletion of the solvent. As long as there is plenty of solvent, why should not a solute continue to dissolve?

We can think of one way, and only one, in which a solute *can* continue to dissolve in a fixed amount of solvent without increasing its concentration in the solution. This can happen if, at the same time and at the same rate, the reverse process is occurring—if the solute comes out of solution as fast as it goes in. Experimentally, this is actually found to happen. If a radioactive isotope of an element is made into

a compound, the compound is thus radioactive and can be detected by very sensitive instruments. Now, if a solution is made to contain all of the nonradioactive form of the compound that it can hold, so that it is thoroughly saturated with it, no additional amount of that compound can be observed to dissolve no matter how long the contact. But if some of the radioactive form of that compound is placed in contact with the saturated solution of the nonradioactive compound, the *solution* very soon becomes radioactive. This means that although the total concentration of solute in the solution has remained unchanged, some of the radioactive material has exchanged places with the nonradioactive material that was in solution. This proves what was suggested above, that the process of dissolving does not cease when saturation of the solution is reached, while more undissolved solute is still present. Instead, it keeps occurring, but the reverse process also occurs, and at the same rate.

One would hardly expect that this reverse process would be initially absent and then suddenly occur when saturation is reached. Rather, it must be occurring all the time that the solute and solvent are in contact. We are here concerned, then, with relative rates of two processes, one the reverse of the other. What determines rates?

The probability that a particle of the surface of a crystal (we are considering the dissolution of a solid in a liquid) will leave the surface to enter the solution must depend primarily on the amount of surface, or surface area. The probability that a dissolved particle will strike that surface and stick to it must depend, per unit surface, chiefly on the concentration of such particles in solution. We may expect, therefore, that when a fresh sample of soluble material is placed in contact with pure solvent the rate of dissolution will reach its maximum at once and remain there, so long as the soluble substance is present in excess of its solubility. The rate of recrystallization will be zero at first, because the concentration of dissolved solute is initially zero, but as the concentration of the solution increases the rate of recrystallization must also increase. Finally, the rate of recrystallization becomes equal to the rate of dissolution, and then the two processes *do not stop,* but continue indefinitely at equal rates. The concentration of the solution at which this *dynamic equilibrium* occurs is called the "**solubility**" of the solute. A "saturated solution" is defined as one in which the concentration is the same as the equilibrium concentration. This does not mean that these equal and opposite processes must actually be occurring in the saturated solution, for we may have saturated solution in the absence of undissolved solute. For example, the undissolved solute can be removed by filtration. As long as any undissolved solute remains in con-

tact with the solution, however, the saturated solution is one in which these processes are actively in progress.

Supersaturation

More often than not, solubility of a given solute increases with temperature. A solution that is saturated at a certain temperature thus may contain a higher concentration of solute than would be contained in a saturated solution at a lower temperature. Ordinarily, and especially if solid solute is present in equilibrium with the solution, cooling will merely slow the dissolution process, without affecting to the same extent the rate of recrystallization. Solute therefore precipitates faster than it dissolves, until a new equilibrium, a new, less concentrated saturated solution, is reached at the lower temperature.

But crystals cannot easily form "out of nowhere." They must have some base on which to build—a tiny crystal, a speck of dust, a microscopic roughness on the inner surface of the container. If a solution saturated at high temperature is first separated from undissolved solute, and then carefully cooled, crystallization may be slow to develop. The solution as it exists at the lower temperature is "supersaturated"—contains more than the maximum equilibrium solubility would permit. Such a solution is "**metastable,**" which means "only apparently stable." When crystallization is induced, by agitation, by scratching the inside of the container, or by "seeding"—adding crystals of the solute material to serve as nuclei for crystallization—it usually continues rapidly, all the excess solute precipitating out until the true equilibrium of the saturated solution is reached.

Solubility Product

Molecular substances must be expected to go into solution as molecules. Nonmolecular substances, such as ionic crystals, cannot dissolve as molecules, for molecules do not exist as such in the crystal. This means that they give in solution two or more species (exclusive of different degrees of solvation) instead of one. This must affect the rate of recrystallization, which now, instead of being proportional to a single concentration of dissolved molecules, depends on the concentration of each of the components in solution. For example, in a solution of sodium chloride in equilibrium with undissolved crystal the concentrations of both sodium ion and chloride ion determine the rate of re-

crystallization. This is very important, for here there are two species whose concentration might be varied *separately*. For instance, to a saturated solution of sodium chloride you could add a concentrated solution of the much more soluble sodium hydroxide, thus increasing the concentration of sodium ion. Or, you could add a concentrated solution of the much more soluble hydrochloric acid or, better yet, pass in hydrogen chloride, thereby increasing the concentration of chloride ion. Either way, can you guess what would happen? Sodium chloride would be precipitated out of the solution. Why?

We can express the rate of recrystallization of any solute that is molecular in solution as proportional to the concentration of dissolved solute, using the proportionality constant, k_m:

$$S = k_m[M]$$

where S is the rate and M is the solute. But if the rate depends equally on two species, then the rate must be proportional to the concentration of each. For NaCl,

$$S = k[\mathrm{Na^+}][\mathrm{Cl^-}]$$

Since at equilibrium this recrystallization speed must equal the speed of dissolution, which is fixed, we can incorporate S and the proportionality constant k into a new constant:

$$K = [\mathrm{Na^+}][\mathrm{Cl^-}]$$

This constant is called the "**solubility product,**" and usually designated K_{sp}. If this product must remain constant, we cannot *in*crease the concentration of one ion without *de*creasing the concentration of the other, or vice versa. The increase in concentration of either ion speeds up the rate of recrystallization of the compound. It was already occurring at the same rate as dissolution, so any increase makes it faster than dissolution. If crystals are forming faster than they are dissolving, obviously they must be appearing out of the solution—in other words, precipitating. They must continue to appear until the concentrations of ions in the solution are reduced to the point where their rate of recrystallization again equals the fixed rate of dissolution. A new equilibrium is thus reached, and no further net change in the relative amounts of dissolved and undissolved solute will occur.

The addition of concentrated sodium hydroxide would have the effect of increasing the recrystallization rate by increasing the sodium ion concentration. The addition of hydrogen chloride would produce the same effect by increasing the chloride ion concentration. We could describe the new equilibria reached following these additions by saying

Table 19 Solubility Products

CaF_2	3.4×10^{-11}	$CaCO_3$	4.8×10^{-9}
AgCl	1.6×10^{-10}	$BaCO_3$	5×10^{-9}
Hg_2Cl_2	1×10^{-18}	$FeCO_3$	2×10^{-11}
$PbCl_2$	1.7×10^{-5}	$PbCO_3$	1×10^{-13}
AgBr	5×10^{-13}	Ag_2CrO_4	1×10^{-12}
AgI	1×10^{-16}	$PbCrO_4$	2×10^{-14}
CuI	1×10^{-12}	Ag_2SO_4	1.2×10^{-5}
PbI_2	9×10^{-9}	$PbSO_4$	2×10^{-8}
$Al(OH)_3$	1×10^{-33}	$BaSO_4$	1×10^{-10}
$Ca(OH)_2$	8×10^{-6}	FeS	10^{-22}
$Fe(OH)_3$	1×10^{-38}	ZnS	10^{-24}
$Mg(OH)_2$	6×10^{-12}	CdS	10^{-28}
$Zn(OH)_2$	1×10^{-15}	PbS	10^{-28}
		CuS	10^{-40}
		HgS	10^{-54}

that sodium chloride is less soluble in sodium hydroxide solution or in hydrochloric acid solution than it is in pure water. The amount of sodium chloride dissolved in the sodium hydroxide solution corresponds to the amount of chloride ion, and the amount of sodium chloride dissolved in the hydrochloric acid solution corresponds to the amount of sodium ion.

The "Common Ion Effect." The above described result, of decreasing the solubility of a salt in water by adding some other source of one of the ions characteristic of that salt, is called the **"common ion effect."** This effect has considerable practical importance, but in practice is subject to certain significant limitations, which will be discussed in Chapter 19.

The solubility product when more than two ions per mole unit are formed in solution assumes a more complicated form, similar to that discussed in Chapter 15. For example, if silver sulfide, Ag_2S, is the salt, $K_{sp} = [Ag^+]^2[S^=]$.

Relation of Solubility Product to Solubility. If the solubility of a compound is known, the numerical value of the solubility product can readily be calculated. For example, if the compound dissolves to form one positive ion to each negative ion, the concentration of each ion is the same as the solubility of the compound. The solubility product is simply the product of these concentrations, and is thus equal to the square of the solubility. If the compound dissolves to form more of one kind of ion than of the other, the calculation is only a little more complicated. For example, if two negative ions are formed for every

positive ion, the concentration of positive ion is the same as the solubility of the compound, but the concentration of negative ions is twice that amount, since every mole of solute which dissolves gives two moles of anions. The solubility product is then the product of the concentration of cations times the concentration of anions squared. But remember that in equilibrium involving only the pure salt and its water solution, the concentration of anions is twice the solubility. The solubility product is therefore four times the solubility cubed (solubility times twice the solubility squared).

EXAMPLES. 1. The solubility product of AgBr is 5×10^{-13}. What is its solubility?

$K_{sp} = [Ag^+][Br^-] = 5 \times 10^{-13}$. Since $[Ag^+] = [Br^-]$ when AgBr is their sole source, then let $[Ag^+] = x$, and $x^2 = 5 \times 10^{-13} = 50 \times 10^{-14}$.

$x = \sqrt{50 \times 10^{-14}} = 7 \times 10^{-7}$ mole/liter ANS.

2. Lead chloride, $PbCl_2$, has a solubility product of 1.7×10^{-5}. What is its solubility?

$$K_{sp} = [Pb^{++}][Cl^-]^2$$

If x moles of $PbCl_2$ dissolves, it will form $2x$ moles of Cl^- ion and x moles of Pb^{++}. Therefore, $1.7 \times 10^{-5} = x\ 2x^2 = 4x^3$

$$x = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = \sqrt[3]{\frac{17 \times 10^{-6}}{4}} = \sqrt[3]{4.3} \times 10^{-2} = 1.6 \times 10^{-2}$$

mole/liter ANS.

In reverse, if the solubility product is known, the solubility can be calculated from it. In the simple case of a compound giving one cation to one anion, the solubility is merely the square root of K_{sp}. But when the number of cations does not equal the number of anions, the calculation is somewhat more complicated.+

EXAMPLES. 1. The solubility of $BaSO_4$ at 25° is 10^{-5} mole per liter. What is its solubility product?

All the $BaSO_4$ in solution is considered to be in the form of Ba^{2+} ions and SO_4^{2-} ions, since in such a dilute solution, all of a salt would

be ionized. Hence, $[Ba^{++}] = [SO_4^{=}] = 10^{-5}$. $K_{sp} = [Ba^{++}][SO_4^{=}] = 10^{-5} \times 10^{-5} = 10^{-10}$. ANS.

2. The solubility of Ag_2CrO_4 is 6.3×10^{-5} mole/liter. What is its solubility product?

Here each mole of Ag_2CrO_4 that dissolves forms 2 moles of Ag^+ and one mole of $CrO_4^{=}$. Therefore the $[Ag^+] = 12.6 \times 10^{-5}$, and $[CrO_4^{=}] = 6.3 \times 10^{-5}$.

$$K_{sp} = [Ag^+]^2[CrO_4^{=}] = 12.6 \times 12.6 \times 10^{-10} \times 6.3 \times 10^{-5} = 1000 \times 10^{-15} = 10^{-12} \quad \text{ANS.}$$

3. Aluminum hydroxide, $Al(OH)_3$, has a solubility product of only 10^{-33}. What is its solubility?

$$K_{sp} = 10^{-33} = [Al^{+++}][OH^-]^3$$

Consider every mole in solution to be in the form of a mole of Al^{3+} and three moles of OH^-. If the solubility is x, $K_{sp} = 10^{-33} = [x][3x]^3 = 27x^4$.

$$x = \sqrt[4]{10^{-33}/27} = \sqrt[4]{(1000 \times 10^{-36})/27} = \sqrt[4]{40 \times 10^{-36}} = \sqrt[4]{40} \times 10^{-9}$$
$$= \sqrt{6.3} \times 10^{-9} = 2.5 \times 10^{-9} \text{ mole/liter} \quad \text{ANS.}$$

Although a more complete explanation must be deferred until Chapter 18, it should be pointed out here that certain ions react to some extent with water to form other ionic species, their original concentration thus being diminished. Unless conditions preventing such reaction with water (hydrolysis) are established, solubility products cannot be used so simply to calculate the solubilities of salts of those ions. For example, the solubility product of $CaCO_3$ would lead to a calculated solubility in water of 7×10^{-5} mole per liter. Because some of the carbonate ion reacts with water, thus being transformed into other species and reducing its concentration, the actual solubility of $CaCO_3$ in water is about 1.26×10^{-4} mole per liter, or nearly twice as great as simply calculated. A more detailed explanation is given later (page 381).

The calculation of solubility in solutions containing a common ion is of great practical importance. The following examples are illustrative.

EXAMPLES. 1. The solubility of $BaSO_4$ is 10^{-5} mole per liter in pure water. What is it in $2M$ Na_2SO_4 solution?

It must be assumed that the common ion does not unite with the solute ions but only influences solubility through increasing the rate of recrystallization.

$$K_{sp} = 10^{-10} = [Ba^{++}][2M]$$

$$[Ba^{++}] = \frac{10^{-10}}{2} = 5 \times 10^{-11}.$$

The solubility of $BaSO_4$ is therefore 5×10^{-11} mole per liter. ANS.

2. $PbCl_2$ is precipitated by making a solution $0.3N$ with HCl. The solubility product of $PbCl_2$ is 1.7×10^{-5}. What concentration of Pb^{2+} remains in solution?

$$K_{sp} = [Pb^{++}][Cl^-]^2 = 1.7 \times 10^{-5}$$

$$[Cl^-] = 0.3$$

$$1.7 \times 10^{-5} = [Pb^{++}][0.09]$$

$$[Pb^{++}] = \frac{1.7 \times 10^{-5}}{0.9 \times 10^{-1}} = 2 \times 10^{-4} \text{ mole/liter}$$ ANS.

3. We have already calculated that silver bromide, with a solubility product of 5×10^{-13}, has a solubility in pure water of 7×10^{-7} mole per liter. What would be its solubility in $0.1M$ NaBr solution?

Here the solubility must be determined as equal to the silver ion concentration, since the bromide ion concentration is very much greater. Let the solubility be equal to the silver ion concentration, $[Ag^+] = x$.

$$K_{sp} = 5 \times 10^{-13} = [Ag^+][Br^-] = x \times 0.1 \text{ or } 0.1\,x$$

$$x = 10 \times K_{sp} = 5 \times 10^{-12} \text{ mole/liter}$$ ANS.

Note that this is only about 10^{-5} as great as the solubility of AgBr in pure water.

It must be kept in mind that, especially for compounds of very low solubility, neither solubilities nor solubility products can be determined with reproducible accuracy without extraordinary experimental precautions, if at all. The values available are therefore useful in providing rough approximations to the truth, applicable in qualitative analysis, but are not rigorously valid under ordinary laboratory conditions.

Solubility of Gases

When gases are in contact with liquids with which they form no chemical combinations they dissolve slightly. Examples are O_2 and N_2

over water. The mole fraction of dissolved gas is found to vary directly with the pressure of that gas over the solution: $P_A = kX_A$. This is called "Henry's law." However, gases which react with the solvent are much more soluble and do not obey Henry's law. Common examples are aqueous solutions of ammonia, hydrogen chloride, and carbon dioxide. The amount of these in solution is, however, proportional to the pressure of gas over the solution also, although the relationship is not so simple.

SPECIAL HELP

Test Your Memory

1. What is a solution?
2. Define "solute" and "solvent."
3. Distinguish between a saturated and a supersaturated solution.
4. Define "molarity" and "molality."
5. Why is normality sometimes the same as, and sometimes different from, molarity?
6. Distinguish between "hydration" and "solvation."
7. Why should it be more difficult for polar molecules to mix with nonpolar molecules than with each other?
8. What is meant by "solubility product"?
9. What is the K_{sp} expression for MgI_2?
10. What kind of gases obey Henry's law?

Test Your Math

1. What weight of ethyl alcohol (C_2H_5OH) is needed to make 500 g of a 20% solution?
2. Evaporation of a 2% solution of NaCl to dryness left 25 g NaCl. How much solution was there before evaporation?
3. In a 1-molal solution in chloroform ($CHCl_3$), how many molecules of solvent are there per molecule of solute?
4. What is the molality of a 25% solution of CCl_4 in heptane (C_7H_{16})?
5. What is the mole fraction of sodium sulfate in an aqueous solution that is 0.4 molal?
6. What weight per cent solution is a 1-molal aqueous sugar ($C_{12}H_{22}O_{11}$) solution?
7. How much chloride ion is in 10 ml of a $6M$ $CaCl_2$ solution?

8. What volume of $3M$ solution could be made from 100 g of H_2SO_4?
9. How many grams of NaOH would be contained in 2 liters of $6M$ solution?
10. How many ml of $0.001M$ solution can be made from 10 ml of $0.1M$ solution?
11. What volume of $0.36N$ H_2SO_4 is needed to neutralize 46 ml of $0.58N$ KOH?
12. If the solubility product of a certain hypothetical compound is 10^{-16}, what is the solubility of the compound if the formula is (*a*) AB, (*b*) AB_2?
13. What is the solubility of AgI in $0.1M$ KI solution if the K_{sp} is 10^{-16}?
14. If the solubility of hypothetical salt AB is 10^{-7} g per liter and the formula weight is 100, what is the solubility product?
15. The solubility product of Ag_2CrO_4 is 10^{-12}; what is its solubility?

Test Your Understanding

1. Why does mole fraction give a better fundamental idea of the composition of a solution than any other expression of concentration?
2. What does the fact that "oil and water do not mix" tell about the attraction between oil molecules and water molecules?
3. Most alkali metal salts are soluble in water, even when other salts of the same acids are insoluble, and even though most metal ions are more strongly hydrated than alkali metal ions. Explain.
4. Practically all nitrates are easily and extremely soluble in water. What does this fact suggest about the nature of a nitrate ion?
5. Explain the most common effect of temperature on solubility.
6. How might one account for diminished solubility with increasing temperature?
7. Practically all compounds containing only carbon and hydrogen tend to be miscible in all proportions. Why?
8. Would you expect liquid ammonia to dissolve sodium chloride? Why?
9. Would you expect C_5H_{12} to dissolve in water? Why?
10. In what two ways might a water molecule become attached to a cation, and why?

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The Physical Properties of Solutions

THE PHYSICAL PROPERTIES of solutions, especially dilute solutions, are in general those of the solvent, modified by the presence of dissolved solute. The effects of solute on the properties of the solvent are commonly of great interest, and deserve careful examination here.

Perhaps the most important fundamental effect of a solute is on the concentration of the solvent. Remember that a solvent and a solute dilute *each other.* In a solution, not only the molecules of solute are farther apart than in the pure solute, but also the molecules of solvent are farther apart than in the pure solvent. But they are not farther apart because there is more empty space, on the average, between them. They are farther apart because foreign particles (solute) are between them. Thus, the rate at which they can encounter any given area of surface in contact with the solvent is reduced. We can think of several phenomena in which the contact between a surface and a liquid is important.

FREEZING POINT

One such phenomenon is that of freezing, or melting. At the melting point, a dynamic equilibrium between solid and liquid phases of a substance exists. Molecules of solid are leaving the solid surface and entering the liquid phase. Simultaneously, molecules of liquid are striking the solid surface and remaining there as part of the crystal. At the melting point, these two processes are occurring at exactly the same rate of speed. Now, suppose something happens to the liquid to reduce its concentration. In other words, compare, at the same temperature, the system of pure liquid in equilibrium with its solid phase with a system of solution in contact with solid *solvent.* In the first system, the rate of crystallization at a given temperature must be greater than it could be at the same temperature in the solution, because the probability of a molecule of liquid striking the crystal surface and remaining there is less in the lower concentration of liquid molecules. The rate at which the solid phase would melt, however, must depend only on the temperature, assuming both these systems to be "adiabatic"—which means perfectly insulated from the environment so heat can neither enter nor leave. If both systems are considered to be at the same temperature, the rate of melting must be the same in each.

In the first system, where the rate of melting equals the rate of crystallization, equilibrium exists at that temperature. In the second system, where the rate of melting exceeds the rate of crystallization, obviously there is not equilibrium. The only way in which equilibrium can be attained in the second system is to lower the temperature until the rate of melting equals the rate of crystallization. In other words, since these equilibria are by definition the melting points, the melting point of the solution must be lower than that of the pure solvent.

Most solids that are soluble in liquid water are insoluble in ice. This is why, when an aqueous solution is sufficiently cooled, the first crystals formed are those of pure ice rather than solid solution. If the solute happens to be near its limit of solubility, however, and reduction of temperature makes it less soluble, cooling the solution may produce crystals of pure solute (or its hydrate) before the melting point of the solvent in the solution is reached. In this discussion, we are considering mainly dilute solutions of quite soluble substances, in which crystals of solvent may correctly be expected to appear first.

Now consider the effect of dissolving a solute in the liquid phase of a pure solvent in equilibrium with its solid phase. For example, picture a thermos bottle (to maintain adiabatic conditions) in which crushed ice and water are at equilibrium at 0°. We shall add some

sugar and stir it around. Let us assume that the dissolution of the sugar gives no appreciable heat effects, and that the sugar is initially at 0° also. The sugar dissolves. So doing, it dilutes the liquid water. This slows the rate at which liquid water joins the ice crystals. But nothing has happened yet to change the rate at which the ice was melting. Therefore, the ice now melts faster than it reforms. Remember that this was not merely phase equilibrium, it was also thermal equilibrium. The endothermic process of melting was equalled exactly by the exothermic process of freezing. But now, with the endothermic process occurring more rapidly than the exothermic process, heat is being absorbed faster than it is being replaced, and in an adiabatic system the temperature must therefore go down. As the temperature goes down, however, the rate of melting must decrease. A new equilibrium point is reached when the rate of melting again equals the rate of freezing. But since this is a lower temperature than 0°, a larger proportion of the total water originally present both as ice and liquid must now be in the liquid phase, the molecules retaining as potential energy what was previously present as kinetic energy of both solid and liquid phases. If the amount of ice were initially insufficient to accommodate this change, it might all disappear by melting before the new melting temperature could be reached—before equilibrium could be regained.

We are all familiar with the use of ice-salt mixtures as freezing mixtures for homemade ice cream, and with the melting of ice on the roads by the addition of salt. These are practical examples of the effect on freezing point of reducing the concentration of a liquid.

VAPOR TENSION

Another phenomenon in which the contact between a surface and a liquid is important is vaporization. Here, the surface is that of the liquid itself. We know that when a pure liquid is placed in a container that encloses it but leaves space above the liquid surface, this space is quickly filled with the vapor of the liquid, to a pressure that is characteristic of that liquid at that particular temperature. The system of vapor and liquid reaches equilibrium, in which the rate at which vapor rejoins the liquid phase exactly equals the rate at which the liquid vaporizes. Compare this system with one at the same temperature, which contains solution instead of pure liquid, that same liquid acting as solvent. In this system, the liquid is at a lower concentration than when it is pure. As a result, it will vaporize more slowly. The vapor will therefore not build up to as high a value when its rate of condensa-

tion equals this slower rate of vaporization. Equilibrium will be reached, but at the same temperature it will be at a lower vapor tension than that of the pure liquid. The vapor tension of a solvent is lowered by the presence of a dissolved solute.

Since the boiling point is defined as the temperature at which the vapor tension of a liquid equals the pressure of the atmosphere above the liquid, the solute effect of lowering the vapor tension must be to elevate the boiling point. It will take a higher temperature to bring the vapor tension of a solution up to that of the pure solvent. A solution boils higher than the solvent.

Deliquescence

Substances such as NaOH, which are extremely soluble in water, form concentrated solutions in which the vapor tension of the water is greatly reduced. If the substance is exposed to air containing water vapor at a pressure exceeding the vapor tension of a saturated solution of that substance, the initially dry substance may take up water until it actually dissolves in it. This process of becoming liquid by absorbing solvent from the atmosphere is called "deliquescence." It can continue until the concentration of the solution formed is sufficiently low that its vapor tension at equilibrium equals the partial pressure of water vapor in the air.

Concentrated solutions of very soluble salts have some application in air conditioning, for controlling humidity. For example, a LiCl solution in contact with an air stream will supply the air with moisture to a partial pressure equal to the vapor tension of the solution. If the incoming air contains a higher concentration of water vapor, the solution will extract some of it, thereby itself becoming somewhat more dilute but keeping the humidity nearly constant.

Efflorescence

Crystalline hydrates such as washing soda, $Na_2CO_3 \cdot 10H_2O$, are sufficiently unstable to exert an appreciable pressure of water vapor at ordinary temperatures. If the humidity of the atmosphere does not reach this equilibrium decomposition pressure, the crystal slowly loses water to the air, slowly forming lower hydrates or the anhydrous salt. This phenomenon is called "efflorescence," and is, in a sense, opposite to deliquescence, although of course not exactly opposite.

OSMOTIC PRESSURE

In living tissue are many membranes so thin that they permit the passage of water through them in both directions but prevent free passage of dissolved particles. Similar membranes have been made by man. They are called, for obvious reasons, "semipermeable membranes." The process of flowing through such a membrane, or similar tissues, is called "osmosis." When pure water is on both sides of the membrane, it passes through at equal velocities in both directions. The rate is proportional to the temperature and to the surface of the membrane. Similarly, if solutions of equal strength, in which the concentrations of solvent are equal, are on opposite sides of a membrane, the rate of passage of solvent through the membrane is the same in both directions. But when the concentration of solvent is not the same on both sides of the membrane, the rate of flow of solvent through the membrane is greater at a higher concentration of *solvent*—in other words, in a more dilute solution. A net transport of solvent occurs, then, from the more dilute to the more concentrated solution.

Consider a vertical tube, open at both ends and held with one end under the surface of a container of water. The air inside the tube being at the same pressure as the air outside the tube, water will rise in the tube until it is at the same level inside as outside. Now suppose that instead of the lower end of the tube being open, it is closed by a semipermeable membrane, and contains a sugar solution, with the upper level even with the surface of the water on the outside. Water can pass freely through this membrane, but sugar cannot. Water inside the tube, in the sugar solution, is at a lower concentration than the pure water outside the tube. It will therefore flow out through the membrane, but not as rapidly as the water flows through from the pure water side. The result must be that the level of the inside solution, as it becomes diluted, rises in the tube, creating a hydrostatic head of pressure in the tube. The inside level will continue to rise, until this extra pressure, indicated by the height of the column of solution inside the tube, causes the rate of flow of water down through the membrane to equal the rate from the pure water into the solution. The pressure needed to produce this result is called the "**osmotic pressure.**" It represents the tendency for a liquid to flow through a membrane. The more concentrated the *solute* in the solution, the more dilute is the solvent and the lower its pressure, or the higher the osmotic pressure of the solution.

If the more concentrated solution were confined behind the membrane, the influx of solvent might create enough pressure to burst it. This is what happens when the blood is diluted with water. Blood con-

tains a certain concentration of dissolved salts, the same concentration inside the red corpuscles as in the fluid outside them. Addition of water to the blood would dilute the solution outside without changing the concentration inside the corpuscles. These are enclosed in a skin which is a semipermeable membrane. When water passes through this skin faster from outside to inside than from inside to outside, they swell up and burst. This is why all intravenous injections must have the same concentration of salts as is present in the blood and other body fluids.

The above discussion should also make clear why you cannot quench your thirst with sea water. The concentration of salts in it is the same as in fish and other sea life, but higher than in your body. Instead of your being able to absorb water out of the salt solution, it absorbs water from you, and you are worse off after drinking sea water than before.

Osmosis is extremely important in many biological processes, for example, enabling water to travel into the roots of plants and trees. It bears a close analogous relationship to vaporization, as we shall see in the following sections.

ELECTRICAL PROPERTIES OF SOLUTIONS

Very pure water alone will not conduct an electric current. Water is such a good solvent, however, that it easily becomes conducting, even when impurities are present in low concentrations. A fireman playing a hose of ordinary hydrant water onto an open electrical source may discover this, to his sorrow. But even so, water under ordinary circumstances is relatively resistant to the flow of electric current, enough so that the effect of solutes has been startling and of great interest. It was early discovered that certain solutes, when dissolved in water, had a striking effect on its conductivity, making it change to an easily conducting substance. Other solutes, when dissolved in water, had no effect whatever on conductivity. Still others were intermediate in nature, making of water a weakly conducting or moderately conducting substance.

The theory of ionization was originally postulated by Arrhenius, a young Swedish scientist, who sought to explain these electrical effects of solutes on solvent properties. He considered that solutes which did not impart conductivity dissolved as molecules, electrically neutral, but that solutes giving conducting solutions did so by virtue of forming ions in solution. We will consider in some detail in Chapter 20 the conduc-

tion of an electric current through a fused salt, or a solution, in which the electrons are transported in effect through only the liquid. Actually, electrons are able to leave the liquid at the anode (positive electrode) only by their separating from anions (negative ions), which are thus discharged to neutral atoms there. Electrons enter the liquid at the cathode (negative electrode) only by becoming part of the cations (positive ions), discharging them likewise to neutral atoms. This kind of conductance is called electrolytic conduction. The conducting liquid is called an "**electrolyte.**" Aqueous solutions are very similar to fused salts, with differences due to the presence of solvent, which will be explained presently. Most acids, bases, and salts that dissolve in water give solutions containing ions, hence conducting electricity, and hence called electrolytic solutions.

On the other hand, substances like sugar or alcohol give aqueous solutions that do not conduct the electric current, and thus are shown to have no ions. These are called "**nonelectrolytes,**" and give "nonelectrolytic" solutions. There is some lack of preciseness in the usage of these terms. Sometimes electrolyte is used to denote any substance which when added to water will give a conducting solution, and sometimes the term is used instead to denote the actual conducting solution only. Both uses seem common enough to be accepted.

Intermediate types of solutes are those which contribute relatively slightly but nevertheless appreciably to the conductivity of water. These are considered to remain chiefly in the molecular form in solution, but to ionize incompletely, giving some degree of ionization. Such substances, or their solutions, are called "weak electrolytes." Examples are acetic acid, CH_3COOH, and ammonia.

CORRELATION OF ELECTRICAL WITH PHYSICAL PROPERTIES OF SOLUTIONS

When the effect of these same substances on other physical properties of solvents or solutions was studied quantitatively, it was found that in dilute solutions of nonelectrolytes, the effects were independent of the identity of the solute and dependent only on the concentration. When equal molal concentrations of different nonelectrolytes were studied, they were found to give exactly the same reduction of the melting point, elevation of the boiling point, and effect on the osmotic pressure.

When the concentration of a solution of a nonelectrolyte is expressed

Table 20 Molal Freezing, and Boiling Point Constants

SOLVENT	FREEZING POINT	LOWERING	BOILING POINT	ELEVATION
benzene	5.50	5.12	80.1	2.53
acetic acid	16.7	3.9	118.5	3.07
phenol	42	7.3	181.2	3.56
camphor	180	40	208.3	6.0
carbon tetrachloride	−22.9	30	76.5	5.02
naphthalene	80.2	6.9	218	5.65
cyclohexane	6.5	20	80.9	2.79
water	0.0	1.86	100.0	0.52

in molality, which you will recall is the number of moles of solute per 1000 grams of solvent, important numerical physical properties can be evaluated. The most common are called the "**molal freezing point depression**" and the "**molal boiling point elevation.**"

The molal freezing point depression is the number of degrees by which the melting point of a one-molal solution of a nonelectrolyte differs from the melting point of the pure solvent. The actual freezing point depression is thus directly proportional to the molality of the solution. The depression is three times as great, for example, when the concentration is three times as great.

The molal boiling point elevation is the number of degrees by which the boiling point of a one-molal solution of nonelectrolyte differs from the boiling point of the pure solvent. The actual boiling point elevation is thus directly proportional also to the molality of the solution. These molal values are important physical properties of liquid compounds. Some common compounds and their molal freezing point depressions and boiling point elevations are listed in Table 20.

Molecular Weight Determination

You will recall that a useful way of measuring the molecular weight of a volatile compound is by determining its vapor density. When the compound is not volatile, only one easy way of determining its molecular weight is available. This is, to determine it from the effect of this compound on the physical properties of an appropriate solvent. One needs only to weigh the sample of the compound and weigh the amount of solvent. The solution is then formed and its melting or boiling point

carefully determined. Knowing the molal values for that solvent, we can determine the molality of the solution, and from this, to calculate the molecular weight is simple.

EXAMPLES. 1. A sample of an unknown compound, 0.20 g, was dissolved in exactly 10 g of benzene. The melting point of the solution was found to be 4.99°C. What was the molecular weight?

First, the amount of solute per 1000 g of solvent must be calculated: 1000/10 = 100; 100(0.2 g in 10 g) = 20 g in 1000 g

Next, the molal freezing point lowering and the melting point of benzene must be found, from Table 20. These are, 5.12° and 5.50°.

The actual lowering was 5.50 − 4.99 = 0.51°. This is 0.51/5.12 of one mole of solute, or 0.1 mole. If 0.1 mole is 20 g, 1 mole = 200 g; from this, the molecular weight of the solute is known to be 200. ANS.

2. What is the weight per cent composition of an aqueous sugar solution that boils at 100.13°?

The molal boiling point elevation of water is 0.52°. The observed elevation for the sugar solution is 100.13 − 100.00 = 0.13°.

The molality of the solution is thus 0.13/0.52 = 0.25. Therefore 1000 g of water must contain 0.25 mole of sugar. Sugar is $C_{12}H_{22}O_{11}$, with molecular weight 342.

$$0.25 \text{ mole} \times 342 \text{ g/mole} = 85.5 \text{ g solute}$$

$$\frac{1000.0 \text{ g } H_2O}{1085.5 \text{ g solution}}$$

Weight per cent of sugar = 85.5 × 100/1085.5 = 7.9% sugar. ANS.

Electrolytes

When the solute is an electrolyte, its effects on the physical properties of the solvent are found to be greater than expected on the basis of molality. But this should not be too surprising in view of our previous observation that the effects in nonelectrolytes are independent of the identity of the compound but dependent directly on the concentration of particles. We should expect that any substance that dissociates in solution, forming more than one particle per molecule or molecular

formula, should thus give a higher concentration of particles than its molality would indicate. In fact, we find that dilute solutions of sodium chloride give twice the effect that was calculated on a molality basis. This is exactly what should be expected, considering that one mole of sodium chloride gives two moles of ions (one of Na^+ and one of Cl^-) in solution. What would you expect of a dilute solution of calcium chloride, $CaCl_2$? Each mole of this gives three moles of ions in solution.

Concentrated Solutions and Activities

The preceding discussion deals only with dilute solutions from a quantitative viewpoint, ranging up to perhaps one molar at most. At higher and higher concentrations, the simple quantitative expressions become increasingly approximate. This is true of all solutes, but especially of electrolytes. In dilute solutions, the number of solvent molecules far exceeds the number of dissolved particles. For example, in a one-molar solution of even a three-ion compound like $CaCl_2$, which is therefore three molar with respect to particles, the number of moles of water per liter is approximately 55. This means an average of 18 water molecules for every ion. In more dilute solutions, the surplus of water is of course far greater. The individual solute particles are then sufficiently far apart, on the average, that they have little or no effect upon one another. In these circumstances, it makes little difference what the particles are—it is only the concentration of particles that has significance.

But as the solution becomes more concentrated the solute particles come, on the average, closer together, close enough so that their spheres of hydration can interfere with one another, close enough especially so that if the particles bear electrical charge, as do ions, they can exert electrostatic interactions on one another. Thus they seem to become a drag on one another, to get in each other's way, and in general to prevent the almost complete independence of action they would have in more dilute solutions. Quantitative treatment of concentrated solutions therefore requires extremely complicated mathematics. However, there are relatively simple ways of determining numbers called "**activity coefficients,**" which measure approximately the extent to which the activity of a solute particle is hampered in the more concentrated solutions, compared to a very dilute solution. These must be multiplied by the measured concentration to give the "effective concentration," which is termed the "**activity.**" For example, suppose the activity coef-

ficient of a certain ion in a certain solution is 0.6. This means that the effect on the physical properties of the solution is as if the particle were only 60 per cent efficient, or as if the concentration were only 60 per cent as high as it really is. Strictly, we should use activities in place of concentrations in all such equilibrium expressions as that described earlier as the solubility product. If the solutions are dilute, however, activity coefficients approach unity, and we can use concentrations as though they were identical with activities, without appreciable error.

THE CHEMICAL IMPORTANCE OF SOLUTIONS

The rate at which any chemical reaction between separate particles can occur is, of course, vitally dependent on the rate at which encounters between interacting particles can take place. If there is no encounter, there is no reaction. Therefore, any reaction can be speeded by increasing the rate of encounter. The reactivity of any ion or molecule thus depends on its being accessible to the attacking reagent. In solids, and to a lesser extent in liquids, the reactivity is limited to the surface particles, for if a particle is on the interior its potential for reaction is completely nullified by the fact that nothing can reach it. Its reaction must wait either until some reagent can slowly diffuse through the mass to reach it, or until all the particles between it and the surface have reacted and the reaction products have left it vulnerable.

A much more rapid contact between reagents is possible, the more finely divided they are, because the more finely divided the more surface for reaction. The most finely divided form of matter possible is the gaseous state, for here each molecule is exposed on all sides to encounter and reaction. But a solid or liquid cannot always easily be converted to gas. The next most effective mixing is in solution, for here the solute resembles a gas, and only solvent molecules can interfere with contact between reagents. That this interference is not ordinarily great is shown by the fact that reactions between different solutes often occur extremely rapidly. Solutions are therefore of extremely great chemical importance, for the solvent as a reaction medium makes reactants much more thoroughly accessible to one another than in any but the gas phase—which itself is a solution when two or more substances are present.

SPECIAL HELP

Test Your Memory

1. What is the solid phase formed first when a dilute solution of a very soluble substance is cooled?
2. How does addition of salt to ice cause melting?
3. Why does a solution of a nonvolatile solute always boil at a higher temperature than does the pure solvent?
4. What is a semi-permeable membrane?
5. What causes osmotic pressure?
6. Distinguish among "weak," "strong," and "non-" electrolytes.
7. Why is the molal freezing point lowering of a solvent the same for all nonelectrolytes?
8. What is an "activity coefficient"?

Test Your Math

1. What is the freezing point of a 10% solution of $C_{10}H_8$ (naphthalene) in benzene?
2. What is the molecular weight of a compound whose 5% solution in camphor melts at 175°?
3. What is the molality of an aqueous solution of nonelectrolyte that melts at −0.46°?
4. How many grams of $CaCl_2$ would be equivalent to 10 g of sugar in its effect in melting ice? (Sugar is $C_{12}H_{22}O_{11}$)
5. The boiling point of CCl_4 containing 6% solute is 77.0°. What is the molecular weight of the solute?
6. What is the boiling point of acetic acid containing 0.3 mole fraction of phenol?

Test Your Understanding

1. If the molecular weight of a solute as determined by the boiling-point ("ebullioscopic") method is less than the empirical formula weight, what does this tell us about the compound?
2. If the molecular weight of a solute computed from the freezing point of the solution is an integral multiple of the empirical formula weight, what does this tell about the compound?

3. The conductance of solutions of different solutes, even when equimolal with respect to ions and the charges on the ions are similar, is different. Can you guess why?
4. In what respect is a solute in equilibrium with its solution analogous to a solid or liquid in equilibrium with its vapor?
5. A certain hydrate was found to become anhydrous on standing in the open air for several hours, but a few days later it was found to be hydrated again. Explain.
6. How could you account for an effect of a solute on the melting point of the solvent only one-third as great as was calculated for the solute compound?
7. How would you separate a solute from a solvent if the solute were unstable at the solvent boiling point?

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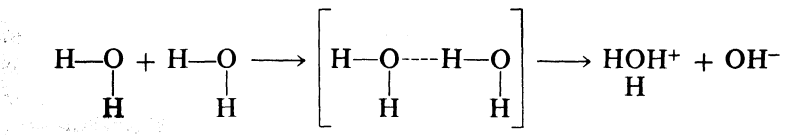
Acids and Bases

WATER IS BY FAR the most important solvent. We should learn as much about it as we can. Already we have learned that the water molecule is quite predictable from the nature of the atoms of hydrogen and oxygen, that it is an angular molecule having polar bonds and a net dipole moment, that its oxygen with negative charge and unshared electron pairs can act as an electron donor, and that water molecules associate through protonic bridging. It will be useful here to consider some of the chemical consequences of protonic bridging.

IONIZATION OF WATER

For simplicity, let us think of only two water molecules, joined through a protonic bridge. The hydrogen involved in the bridge is on the average much closer to the oxygen of its own water molecule than it is to the oxygen of the other molecule; this is characteristic of protonic bridging. The atoms in a molecule do not, however, maintain fixed positions with respect to one another, as seems to be implied when we speak of a definite molecular structure. They are constantly vibrating, twisting, stretching—perpetually in motion around their average position. It is the average position that is indicated in any description

of structure. Unfortunately, we cannot determine exactly what is happening in any one molecule. We can, largely from measuring the interactions of molecules with various types of energy waves (spectroscopy), get a fair idea of what is happening to billions of molecules on the average. But it does not seem unreasonable to speculate, concerning our pair of water molecules, that every now and then, certainly only very infrequently, the bridging proton may find itself momentarily more closely associated with the oxygen of the other water molecule. If some molecular collision should now occur at exactly the right moment to break the bridge, the proton would be left stranded on the wrong molecule. Thus would be formed, simultaneously, two different ions, one of formula H_3O^+, the other of formula OH^-. The first is called a "hydronium" ion, the second, of course, the hydroxide ion.



The hydronium ion is a water molecule to which an extra proton is coordinated. It is sometimes thought of as a hydrated proton. But once the proton is attached to the water molecule, it has just as much attraction for the electrons as do the two protons initially on the molecule. Therefore it will pull electrons toward its own control at the expense of the oxygen, which will in turn pull electrons from the other hydrogens. The end product is an ion in which all three hydrogens are indistinguishable. All are now much more positive than they are in water. The oxygen is much less negative than it is in water. This makes hydronium ion an oxidizing agent, a strong proton donor, and a much weaker electron donor.

Unquestionably, in water solution, hydronium ions are associated with water molecules much as water molecules are associated with one another. Very likely, the qualities of hydronium ions as just described are modified to some extent by this additional association. Recent evidence suggests that a proton in water may perhaps be better described

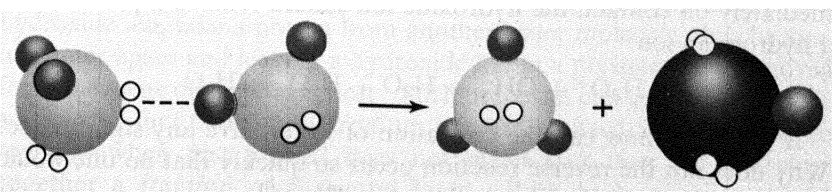


Figure 97. Ionization of water.

as a tetrahydrate. One could easily picture such a tetrahydrate as resulting from the attachment of three water molecules to the hydronium ion, through the three very positive hydrogens of the latter, serving as protonic bridges. But at any given instant the proton must be attached primarily to one pair of electrons and therefore to but one water molecule, the attachment of three more water molecules being more in the nature of a secondary attachment. Even a "tetrahydrate" of a proton would be joined also to other water molecules, through additional protonic bridging. Therefore there is no apparent advantage to regarding the proton as any more than a monohydrate, the hydronium ion.

A hydroxide ion is a water molecule from which one proton is missing. As such, it contains the electron that once belonged to the proton as a hydrogen atom. This electron, left to the full control of the remaining oxygen and hydrogen, makes the oxygen less electronegative than in water, so that one calculates that the hydrogen has more than a half share of the electrons it shares with the oxygen. The oxygen has a high partial negative charge (-0.66), and even the hydrogen has a high negative charge (-0.34). The oxygen here, having much higher negative charge, must be a much better electron donor than water. It must have lost all the oxidizing power it had in water.

Again, in water solution the hydroxide ion is undoubtedly attached to other water molecules through protonic bridging, water hydrogen to hydroxide oxygen. Through such attachment its properties may well be somewhat modified.

If a hydronium ion and a hydroxide ion were to come into contact, a chemical reaction would certainly be expected. We can think of the meeting as a competition between a hydroxide ion oxygen and a water molecule oxygen for a free proton. For the hydronium ion is actually a water molecule that has acquired a free proton; the fact that this has already happened does not change the competition when a hydroxide ion approaches. It is not a competition between hydronium ion and hydroxide ion; it is a competition between water molecule and hydroxide ion. Clearly, the much more negative oxygen in the hydroxide ion (-0.66) should be better able to donate an electron pair to a proton than is the oxygen (-0.25) of a water molecule. The result is that, immediately on contact, the hydroxide ion should remove a proton from a hydronium ion:

$$H_3O^+ + OH^- \rightarrow H_2O + H_2O = 2H_2O$$

If this is so, how can the ionization of water have any significance? Why does not the reverse reaction occur so quickly that no one would ever find out that ionization had ever happened?

The answer seems to be that, in the instant before recombination of these ions could occur, something causes them to become separated from one another. They cannot recombine until they meet. There are several ways by which one could imagine that this separation would happen. One would be by direct collision of a third water molecule with one of the ions at the moment of its formation, knocking it out of the zone of influence of the other ion. Even more easily, however, the ions could each migrate *in effect* from the scene of formation.

Consider first the water molecule that gains the proton and becomes a hydronium ion. We were considering mainly a pair of molecules, but of course in the bulk liquid this pair must be surrounded on all sides by others. Some of these will constantly be making and breaking and remaking protonic bridges with the first water molecule. When it becomes a hydronium ion, all its hydrogens become changed. In a protonic bridge between a hydronium ion and a water molecule, a competition actually exists between two water molecules for the extra proton. That is, the energy involved is exactly the same whether the proton sits on one water molecule or on any other water molecule. Consequently, migration of a proton from one water oxygen to another can occur very readily. If, as soon as a hydronium ion is formed, one of its other protons departs, becoming attached to a third water molecule, only a water molecule is left behind. The hydronium ion has not literally migrated, but in effect it has, through migration of a different proton. The hydronium ion, before it can give back its extra proton to the original owner, is converted to a water molecule, leaving the original owner unable to find its proton.

In a similar manner the hydroxide ion, once formed, can *in effect* migrate from the scene of formation. When a hydroxide ion comes in contact with a molecule of water—and the chances are excellent that it is already in contact with other water molecules at the moment of its formation—a competition exists, in effect, between two hydroxide ions for a proton. One hydroxide ion (the water molecule) has, of course, already gained the proton, but this is no reason why another hydroxide ion cannot take the proton away from it. The proton is exactly as stable in one place as in the other. Thus, almost at the same time that a water molecule loses a proton to become a hydroxide ion, it may, as a hydroxide ion, take a proton from another water molecule, thus becoming water again and leaving a hydroxide ion in a position once removed from the scene of original action. Such processes can go on indefinitely, so that the fact that the hydronium ion and hydroxide ion were close together when first formed does not mean that they are still close together a fraction of a second later. Both hydronium ions and

hydroxide ions can, in effect, wander rather freely throughout the mass of water, by the mechanism of proton transfer.

The result of this immediate separation of such opposite ions is that an appreciable concentration of each can accumulate within the water, despite their reactivity with one another. We must expect that, whenever a hydronium ion encounters a hydroxide ion, interaction to form two water molecules will occur. Therefore, the rate of recombination will depend on the probability that, wandering around in the liquid, these ions will meet. This probability will naturally depend on the concentration of the ions, for the more highly concentrated, the more likely a meeting. In pure water at 25°, the concentration of each ion can build up to 10^{-7} mole per liter. At these concentrations, the rate of recombination exactly equals the rate at which the ions happen to form and equilibrium exists. This is probably the most important equilibrium in solution chemistry. We could write for it the usual equilibrium expression from the ionization equation. However, these concentrations are so small, representing only one pair of ions to more than 550,000,000 water molecules, that the concentration of undissociated water molecules is not appreciably affected by the ionization. In other words, the concentration of water molecules may be considered constant. The equilibrium constant can then be consolidated, omitting the constant concentration of undissociated water, which gives us an "ion product" constant, K_W:

$$K_W = [H_3O^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

Often simply H^+ is written instead of H_3O^+, it being understood that H^+ cannot exist in water unattached to it. The two as used in equations have exactly the same meaning.

The importance of this constant rests in its meaning that the concentrations of hydronium ion and hydroxide ion are interdependent, that one cannot be increased without decreasing the other. The *product* must remain constant. If the concentration of either ion is increased, the probability of an encounter with an oppositely charged ion is likewise increased and the rate of recombination is increased, the equilibrium being momentarily upset. But as the recombination occurs momentarily faster than the formation of the ions, ions of the species not increased are used up faster than they are formed, until they reach a new and lower concentration at which the probability of encounter with an opposite is the same as it was originally, but with the concentration of one ion higher than originally, the other lower than originally.

AQUEOUS ACIDS AND BASES

Many solutes affect the hydronium ion (and therefore hydroxide ion) concentration in water. As described earlier, in Chapter 9, solutions in which the hydronium ion concentration (commonly referred to merely as the "hydrogen ion concentration") is higher than in pure water, have certain properties that are characteristic of hydronium ion. The taste is sour, the solution dissolves metal oxides that are insoluble in water, and it destroys hydroxide ions. Such solutions are called "acidic." Acidic solutions may now be defined as aqueous solutions in which the hydrogen ion (hydronium ion) concentration is larger than 10^{-7} mole per liter. If this concentration is only a few times larger, the solution is described as very weakly acidic. If the concentration is thousands of times as large, the solution is strongly acidic.

Acids

Although various types of solutes can increase the hydronium or hydrogen ion concentration, those most commonly known to do this are the class called "acids." The simplest definition of an acid, as given in Chapter 9, is one that will be useful for most of our purposes here: *Any substance that contains hydrogen and, dissolving in water, produces a surplus of hydrogen ions.* This implies a reaction between the acid and the water:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For such a reaction, an equilibrium expression can be written as usual for a chemical reaction:

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since in dilute solutions the concentration of the solvent remains essentially constant, this can be omitted in K, giving

$$K = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad \frac{[H^+][A^-]}{[HA]}$$

K is called the "ionization constant" of the acid. The differences among strong, intermediate, and weak acids may now be expressed quantitatively by comparing their ionization constants. Any acid having a K value about 100 or greater is a strong acid; values from about 1 to 100

Table 21 Acid Ionization Constants

	(first, second, third)
H_3BO_3	5.8×10^{-10}
H_2CO_3	2×10^{-4}
HCN	4×10^{-10}
CH_3COOH	1.8×10^{-5}
H_4SiO_4	1×10^{-10}
HNO_2	4.5×10^{-4}
H_3PO_4	7.5×10^{-3}, 6.2×10^{-8}, 10^{-12}
H_2O_2	2.4×10^{-12}
H_2S	1.1×10^{-7}, 1.0×10^{-14}
H_2SO_3	1.2×10^{-2}, 1×10^{-7}
H_2Se	1.7×10^{-4}, 1×10^{-11}
H_2Te	2.3×10^{-3}, 1×10^{-11}
HClO	3.2×10^{-8}
$HClO_2$	10^{-2}

represent intermediate acid strength; values below 1 represent from fairly weak to extremely weak acids. Table 21 lists some common acids and their ionization constants.

Sometimes it is convenient to express such constants as "***pK* values,"** pK (analogous to pH) being defined as the negative logarithm of the ionization constant. Thus if $K = 10^{-9}$, $pK = 9$. The larger the pK value, the smaller the K and the weaker the acid.

Causes of Acid Strength Differences. In aqueous solutions, all acid ionizations must be regarded as involving competition between the anion from the acid and the water molecule, both acting as electron donor toward protons. The acid strength, or degree of ionic dissociation of the acid, thus depends on the various factors which determine the strength of coordinate bond formation between proton and acid anion. Water remains constant in its ability to coordinate a proton. If this ability exceeds or even equals that of the acid anion, since the water is ordinarily largely in excess, the acid ionizes completely, or nearly so, and is characterized as strong. If the acid anion has greater ability than water to coordinate a proton the acid ionizes only incompletely, and the less completely it ionizes, the greater the coordination power of the anion. The strength of acids in water solution thus varies inversely with the ability of the acid anion to coordinate protons.

The factors that determine the ability of an acid anion to donate a pair of electrons to a proton are doubtless numerous and complex. Acquisition of a proton involves a major rearrangement in the anion,

usually in the direction of diminished symmetry. In other words, the anion is likely to represent greater stability than the acid. In fact, we recognize many examples of this, in the often far greater stability of ionic salts of acids than of the free acids, some of which, like carbonic and sulfurous, cannot even be isolated. We may therefore expect the energy changes that must accompany anion rearrangement to contribute to the extent of acid ionization. Another factor must be the relative energies of hydration of the acid, its anion, and the proton, since water is ever present. Perhaps the most influential factor of all is the condition of the donating atom in the anion. We have already seen that partial charge on an atom has an important effect on its donating ability. In general, the higher its partial negative charge the better this ability. But partial charge is only one part of the condition of a combined atom. Geometrical structure is also significant, changing the condition of a given atom according to what other atoms may be near to it, and how near—whether partially protecting it from outside attack, or not. In addition, the nature of the other atoms is important, for an atom donating a pair of its electrons to some outside acceptor can probably do this more effectively if the other atoms to which the donor is already attached can replenish at least part of any lost charge from their own supply of electrons. In other words, given two oxygen atoms, both alike in partial negative charge, but one attached to a poor electron reservoir and the other to a good reservoir, one would expect the latter oxygen to be the more effective donor. In short, interpretation of various acid strengths is not easy, and perhaps not always possible, in our present state of knowledge.

Nevertheless, despite the complexity of the phenomena and the limitations to our knowledge, we can reach some degree of useful understanding of acid strengths in many instances.

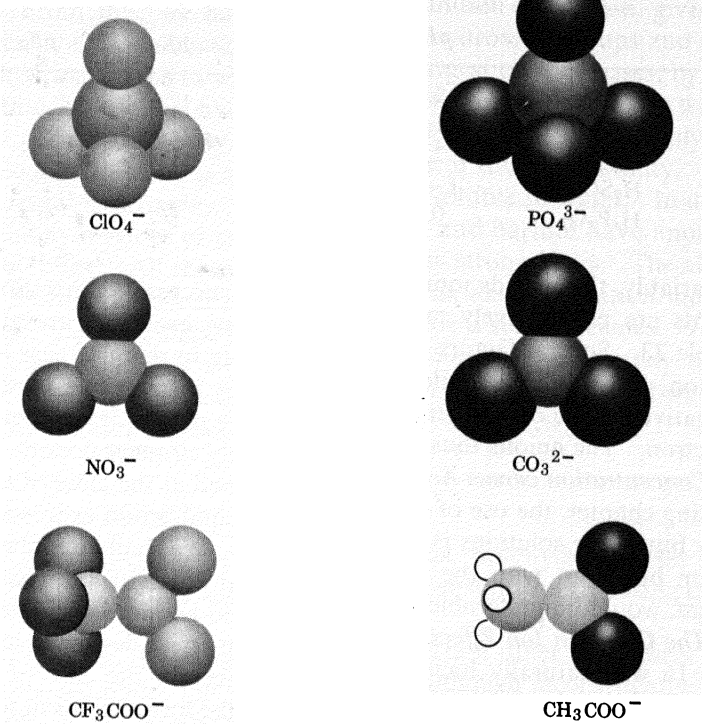
Probably the least complex acids are the binary hydrogen compounds in which hydrogen bears partial positive charge. Most important of these, as acids, are the hydrogen halides, HF, HCl, HBr, and HI. The first is only a weak acid, whereas the other three are very strong, their strength increasing in the order listed. We know from consideration of protonic bridging that fluorine atoms bearing partial negative charge are capable of attracting positive hydrogen of other molecules much more strongly than can chlorine atoms, for example. We may interpret this difference, admittedly somewhat speculatively, as indicating a greater concentration of an electron pair on the fluorine than on the larger chlorine. Whatever the correct interpretation, the fact of negative fluorine being so much more effective in attracting positive hydrogen seems consistent with a superior ability of fluoride ion to act

as electron donor to a proton. This in turn is consistent with the fact that hydrofluoric acid is weak and the other hydrohalic acids strong.

Among the most important and common of acids are many having complex oxyanions. It is especially interesting to consider the relationship of the partial charge on oxygen in these anions, and the strengths of the acids. Even when ignoring the contributions of other factors such as those mentioned above, we find, as stated in Chapter 12, a remarkably consistent trend of increasing acid strength with decreasing partial negative charge on the oxygen in the anion. This trend is of course not perfectly smooth, as shown in Table 22. It does emphasize the importance of differences in the condition of combined oxygen, to the extent that these differences can be evaluated in terms of partial charge. Since partial charge is a consequence of initial electronegativity differences, hydroxy compounds of elements relatively high in electronegativity must have relatively low negative charge on oxygen in their anions, whereas hydroxy compounds of elements relatively low in electronegativity must have relatively high negative charge on oxygen in their anions. This, then, affords a more fundamental explanation of the familiar distinction between oxides or hydroxides of metals and those of nonmetals. The former are basic or very weakly acidic, the latter strongly acidic.

Table 22 Relation of pK of Oxyacids to Charge on Oxygen in Anion

ACID	*pK*	ANION	CHARGE ON O
H_2O	15.97	OH^-	−0.66
$HPO_4^=$	12.44	$PO_4^{\equiv}$	−0.66
$HSiO_3^-$	12	$SiO_3^=$	−0.63
HCO_3^-	10.22	$CO_3^=$	−0.56
HBO_2	9.14	BO_2^-	−0.50
HOCl	7.43	OCl^-	−0.52
$H_2PO_4^-$	7.23	$HPO_4^=$	−0.45
HSO_3^-	7.0	$SO_3^=$	−0.55
HNO_2	3.35	NO_2^-	−0.38
H_2CO_3	3.3	HCO_3^-	−0.33
H_3PO_4	2.12	$H_2PO_4^-$	−0.31
HSO_4^-	1.89	$SO_4^=$	−0.44
H_2SO_3	1.77	HSO_3^-	−0.32
HNO_3	−1.4	NO_3^-	−0.29
H_3O^+	−1.74	H_2O	−0.25
H_2SO_4	−3	HSO_4^-	−0.27
$HClO_4$	−10	ClO_4^-	−0.21



These anions, having donor oxygen of not very high negative charge, are not good electron donors to a proton. Thus their acids are very strong, and the anion parts of their salts do not hydrolyze.

These anions, having donor oxygen of high negative charges, are good donors to protons, forming acids which are therefore only weakly dissociated. In solutions of their salts these anions remove some protons from water, creating, by this hydrolysis, an excess of hydroxide ions.

Figure 98. Oxyanions of strong and weak acids.

We are also given a clue to differences in the acidity of different oxidation states. For example, nitrous acid is weaker than nitric acid, and sulfurous acid weaker than sulfuric acid. Addition of oxygen atoms around the central atom must reduce the partial negative charge on each of the competing oxygens in the anion, with the result that the corresponding acid is stronger.

Successive Ionizations of Acids. Numerous acids exist, especially those having more than one hydroxy group, which can ionize to give more than one proton. Such acids, of which sulfuric acid, H_2SO_4, is a common example, are called "polyprotic" or "polybasic" acids. Almost

Table 23 pK Values for Successive Ionizations of Polyprotic Acids

	pK_1	pK_2	pK_3	pK_4
H_3PO_4	2.1	7.2	12.0	
H_3PO_3	1.8	6.2		
H_3AsO_4	2.3	7.0	13.0	
H_2SO_4	(−3)	1.9		
$H_4P_2O_7$	0.9	2.0	6.7	9.4

invariably, these acids ionize by steps. The successive ionization constants are progressively much smaller. Some examples are given in Table 23. Several factors no doubt contribute to this decrease in ionization, but evidently quite important among them is the increase in negative charge on oxygen as each successive proton leaves behind its electron. The anions thus become successively stronger donors.

Concentration versus Activity. As mentioned at the close of the preceding chapter, the use of concentrations in equilibrium expressions for any but dilute solutions is only approximate. We shall continue to use them here, but with the understanding that "activities," if we knew them, would be preferable because they would be more accurate.

The Common Ion Effect. The common ion effect described in Chapter 16 will naturally have an analogous effect in the case of solutes which, although completely dissolved, are in the form of ions in solution. When to a solution of an acid is added some other source of hydrogen ions, such as a strong acid, if the first acid is weak its ionization will be suppressed. For example, acetic acid is only weakly ionized in dilute solution, but if a strong acid like hydrochloric acid were added to this solution the acetic acid would scarcely be ionized at all. Addition of hydrogen ion would increase the hydrogen ion concentration, and therefore increase the rate of combination of hydrogen and acetate ions, shifting the equilibrium to a point where nearly all or essentially all the acetic acid is present as undissociated molecules. If instead acetate ions were added, as by means of a sodium acetate solution, this too would suppress the acetic acid ionization. By increasing the acetate ion concentration, it would accelerate the recombination of the ions, ending with an equilibrium where the acetic acid is practically un-ionized.

Bases

Likewise, many substances when dissolved in water increase the hydroxide ion concentration. This can be accomplished in several

ways, but perhaps the most common is by ionizing to supply hydroxide ions. From this, we have the simple definition of a base, given in Chapter 9, as any substance that contains hydroxide groups and supplies hydroxide ions to water. By far the largest class of bases, by this definition, is the metal hydroxides. Most of these are insoluble in water, except perhaps to a very limited extent. Their capacity to supply hydroxide ions to water is thus poor by virtue of their insolubility. The alkali metal hydroxides, however, are very soluble in water. In addition, the hydroxides of calcium, strontium, and barium have appreciable solubility. All these are strong or fairly strong bases. The alkali metal hydroxides are ionic in the solid form, and dissolution merely separates the ions, dispersing them among the water molecules. Their equilibrium constants would therefore be practically infinitely high. But for weaker bases, some reversibility is of course noted, and we can write equilibrium expressions such as:

$$K = \frac{[M^+][OH^-]}{[MOH]}$$

Just as we observed for polyprotic acids, polyhydroxybases can ionize by steps, with a separate ionization constant representing each step.

In addition to the metallic hydroxides, certain other substances are usually classed under this simple definition, although inconsistently, because they do not necessarily contain hydroxide groups in an isolatable form. The most common example is ammonia, whose solutions in water are called "ammonium hydroxide" although no NH_4OH can be isolated. The reaction may be written:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

For this reaction, again considering the concentration of water to be constant, the equilibrium constant can be written:

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Ammonium hydroxide is a weak base, as can be seen from the small value of the constant.

Neutralization

The mutual destruction of acidic and basic characteristics that occurs when an acid and a base encounter one another is called "neutraliza-

tion." An acid is said to neutralize a base, and a base neutralizes an acid. In aqueous solutions, the reaction is solely between the ionic species that characterize these kinds of compounds, between the hydronium ion of the acid and the hydroxide ion of the base. Neutralization is thus the exact opposite of the ionization of water:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

The other ions, the anion of the acid and the cation of the base, ordinarily do not enter the reaction, and are sometimes, for this reason, termed "spectator" ions. They remain in the solution after the ion product for the water has been brought down to the equilibrium value of 10^{-14} by the neutralization process. If later the water is evaporated, the concentration of these ions increases, and eventually reaches the level at which the solubility product of a compound formed by their combination would be exceeded. Here the compound begins to precipitate from the solution, and complete evaporation of the water leaves the compound isolated. This compound is called a "salt." A salt is defined as any combination of a cation other than hydrogen with an anion other than hydroxide, to form a neutral compound.

Since mixing of aqueous solutions of acid with base always leaves the essential ingredients of a salt after the hydronium ions have reacted with the hydroxide ions to form water, neutralization is commonly thought of as a *reaction between acid and base to form water and a salt.*

Although in water solutions the dominant factor in neutralization is the reaction between hydronium ion and hydroxide ion, very similar reactions can occur in the absence of water. An oxide is basic if it reacts with water, furnishing hydroxide ions. Such an oxide may be termed a "basic anhydride." An oxide is acidic if it reacts with water, furnishing hydronium ions. Such an oxide may be termed an "acidic anhydride" or an "acid anhydride." A basic anhydride can neutralize an acidic anhydride by combining with it to form a salt, and water is not involved except perhaps in minute quantities which exert a catalytic effect on the reaction. The relationship between neutralization in aqueous solution, with formation of water and bringing together of the ingredients of a salt, and neutralization in the absence of water, forming a salt, can be appreciated by the study of the following chemical equations, each of which represents a reaction that occurs readily:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$
$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$
$$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O$$
$$CaO + SO_3 \rightarrow CaSO_4$$

Amphoteric Substances

Numerous substances exist which are capable of reacting either as acid or as base. The simplest of these, perhaps, is water itself. We have already seen that water can form both hydronium ions and hydroxide ions. As an oxide of an element of intermediate electronegativity, it can also combine with a basic oxide in much the same way an acidic oxide would, but instead of forming what is conventionally called a "salt" it forms the "hydrogen salt" or a hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Likewise, it can combine with an acidic oxide in much the same way a basic oxide would:

$$H_2O + SO_3 \rightarrow H_2SO_4$$

Here, of course, the conventional definition of salt is not met, because this "hydrogen salt" is called an acid. But notice that in the first reaction the hydrogen becomes part of the anion, and in the second part of the cation—in fact, the cation itself.

Oxides having a partial negative charge similar to that in water behave in similar manner. Zinc oxide is one, and aluminum oxide is another. Both of these can react, as does water, in either way, as acid or as base. When they react with a basic oxide, the metal becomes part of the anion, just as hydrogen did. When they react with an acidic oxide, the metal becomes the cation, just as hydrogen did. For example:

$$ZnO + Na_2O \rightarrow Na_2ZnO_2$$
$$Al_2O_3 + Na_2O \rightarrow 2NaAlO_2$$
$$ZnO + SO_3 \rightarrow ZnSO_4$$
$$Al_2O_3 + 3SO_3 \rightarrow Al_2(SO_4)_3$$

Both ZnO and Al_2O_3 are insoluble in water, but show their amphoteric nature by dissolving readily in both acid and base. The solubility in acid is doubtless a straightforward removal of hydroxide ions by combination with hydronium ions of the acid, which permits the process of dissolution to proceed as it does at equilibrium but prevents the reverse process. The dissolution in base is probably not so simple as a removal of hydronium ion furnished by the metal hydroxide, but involves coordination of additional hydroxide ions to the metal, forming soluble complexes. These can be better understood later.

In general, substances that are amphoteric can be only weakly acidic and weakly basic. The same factors that permit them to be basic at all

Table 24 Some Conjugate Acids and Bases

ACID	BASE
HCl	Cl^-
H_2SO_4	HSO_4^-
HSO_4^-	$SO_4^=$
HNO_3	NO_3^-
H_2CO_3	HCO_3^-
HCO_3^-	$CO_3^=$
H_3O^+	H_2O
H_2O	OH^-
NH_4^+	NH_3
NH_3	NH_2^-
H_3PO_4	$H_2PO_4^-$
$H_2PO_4^-$	$HPO_4^=$
$HPO_4^=$	$PO_4^{\equiv}$

prevent strong acidity, and those that permit them to be acidic prevent strong basicity.

The Brönsted-Lowry Concept

A scheme for classification of acids and bases somewhat differently from the simple one of Arrhenius was proposed by Brönsted and by Lowry, and has come to receive wide acceptance as a useful scheme. According to this, an acid is defined as a proton donor and a base as a proton acceptor. The special value of this scheme is that it helps us to recognize the relationship between an acid and its anion, which is a very significant one. The anion of an acid is able to accept a proton, thereby becoming the acid. The anion is therefore, by this definition, a base. It is called the "conjugate base of the acid." Similarly, the acid is called the "conjugate acid of the base." Some examples are given in Table 24.

The Lewis Concept

G. N. Lewis, an American chemist, proposed that since all acid-base reactions are essentially electron donor-acceptor reactions, all such donor-acceptor reactions (all formation of coordinate covalent bonds) should be called "neutralization." An acid should be defined as any electron acceptor, and a base as any electron donor. The relationship pointed

out by this broad concept explains what you may have observed in our earlier consideration of the chemistry of oxides and hydrides: The tendency for compounds that are electron donors to be basic and for those that are acceptors to be acidic. We might add here that substances able to accept electrons are likely to be, although not necessarily, highly electronegative. Substances able to donate electrons are likely to be relatively low in electronegativity. We can thus recognize a certain parallel between oxidizing agents and acids and electron acceptors, and likewise between reducing agents and bases and electron donors. In fact, the broadest concepts of acids and bases include oxidation-reduction as one of the types of acid-base reactivity. Such concepts, however, tend to lose their value by trying to include too much within a single classification.

The pH Method of Evaluating Acid-Base Properties

For many purposes, it is much more important to know the hydrogen ion concentration of a given solution than to know what produced the hydrogen ions. A scale devised to represent this concentration uses the symbol "pH," which is defined as the negative logarithm of the hydro-

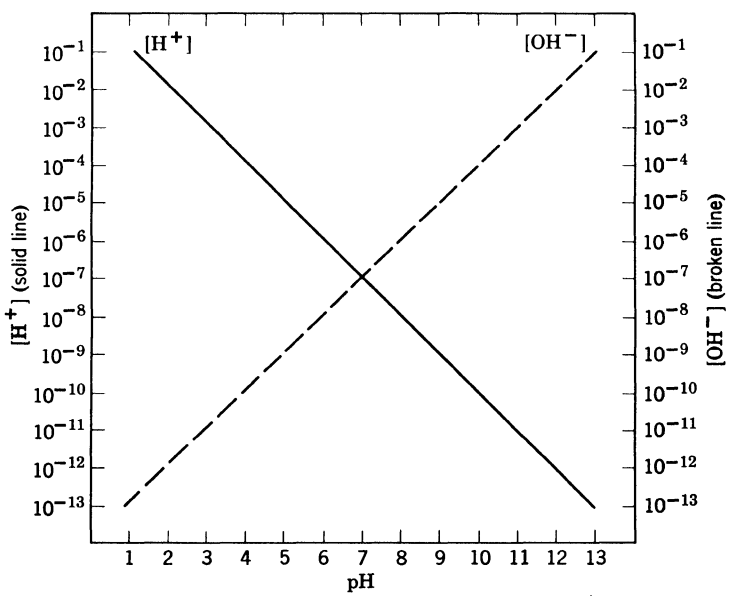


Figure 99. Representation of radiation of pH to $[H^+]$ and $[OH^-]$.

gen ion concentration (strictly, of the hydrogen ion *activity*) in moles per liter. The negative logarithm is the logarithm of the reciprocal. In other words, pH could be defined as "the logarithm of one over the hydrogen ion concentration." The logarithm of any number, to the base 10, is the power to which 10 must be raised to equal that number. For example, the logarithm of 100 is the power to which 10 must be raised to equal 100; $10^2 = 100$, so 2 is the logarithm of 100. Similarly, the logarithm of 10^{-7} is -7. If the pH is the negative logarithm, and the hydrogen ion concentration is 10^{-7} as it is in pure water, then the negative logarithm of 10^{-7} is minus -7 or 7. The pH of pure water, or of any solution having an equal hydrogen ion concentration, is 7.

If the concentration of hydrogen ion in a solution is 10^{-6} mole per liter, the pH is 6. If the concentration of hydrogen ion is 10^{-8} mole per liter, the pH is 8. Note that 10^{-6} is not smaller than 10^{-7}, but ten times as large. Similarly, 10^{-8} is not larger than 10^{-7} but only one-tenth as large. Therefore the pH values go in the opposite direction from the hydrogen ion concentration, which is quite confusing until one becomes accustomed to it. Remember that pH values *larger* than 7 all represent *basic* or alkaline solutions; pH values *smaller* than 7 represent *acidic* solutions.

EXAMPLES. 1. What is the pH of a solution that is 0.5*M* in HCl?

$$[H^+] \text{ is } 0.5 = 5 \times 10^{-1}$$
$$\log 5 \times 10^{-1} = \log 5 + \log 10^{-1}$$
$$\log 5 = \quad 0.70$$
$$\log 10^{-1} = \underline{-1}$$
$$-0.30 \qquad \text{pH} = -\log [H^+] = 0.3 \quad \text{ANS.}$$

2. How many grams of sodium hydroxide must be contained in a liter of solution to give it a pH of 12?

$$\text{pH} = 12 \quad \text{means} \quad [H^+] = 10^{-12}$$

Therefore

$$[OH^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

NaOH must be 10^{-2} mole per liter. One mole = 40 g.

$$10^{-2} \text{ mole} = 0.40 \text{ g} \qquad \text{ANS.}$$

3. What is the molarity of a nitric acid solution of pH 4.2?

$$-\log [H^+] = 4.2$$

$$[H^+] = \text{antilog of } -5 \times \text{antilog of } 0.8$$
$$= 10^{-5} \times 6.3 \text{ or } 6.3 \times 10^{-5}$$

Therefore HNO_3 is $6.3 \times 10^{-5}\ M$ ANS.

Hydrolysis of Salts

In terms of the Bronsted-Lowry concept of acids and bases, we can recognize a logical relationship between the ability of the conjugate base of an acid (the anion from the acid) to donate an electron pair to a proton and the strength (degree of ionization) of the acid. The ionization of any acid in water represents a competition between the conjugate base of that acid and the water molecule, for the proton:

$$A^- + H^+ + H_2O \rightarrow HA + H_2O \quad \text{or} \quad A^- + H_3O^+$$

Since the water molecule remains constant in its electron donating property, the differences that are observed among acids must be differences, in effect, in the electron donating property of their anions. A strong acid is therefore one whose conjugate base is very weak—whose anion is not a good electron donor compared to water. A weak acid is one whose conjugate base is strong—whose anion is a good electron donor, comparable to water or even better.

Remember that in ordinary dilute solutions the concentration of water molecules is much higher than that of any anion, so that even though the anion in even competition with water might surely win the proton, the proton can to some extent be acquired by water in dilute solutions.

An anion, just because it happens to be the one that is characteristic of a given acid, does not need to come directly from that acid. It may be introduced into a water solution by adding its salt instead of the free acid. There is now no possibility of competition between water and the anion for protons introduced by the acid, but protons already present in the pure water can be acquired by the anion. If the anion is the anion of a weak acid, it will be a strong electron donor to the proton. Hence this acquisition of water protons may occur to an appreciable extent. One can imagine that the transfer of water protons to the anion occurs in much the same way as was described for the ionization of pure water (page 361). Either of the following might occur:

$$A^- + H_3O^+ \rightleftharpoons HA + H_2O$$
$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Both result in increasing the concentration of hydroxide ions, the first by decreasing the hydronium ion concentration and thus upsetting the ionic equilibrium of water, and the second directly as shown. The effect is the production of a basic solution by addition of a neutral salt to water. The pH of the solution of this salt would, from this effect, be greater than 7. This reaction of the anion from the acid, to acquire a proton, is called "hydrolysis of the ion," since it involves reaction in which water is taken apart. Since the ion came from a salt, it is called "hydrolysis of the salt." In no instance is this hydrolysis likely to be very extensive in dilute solution, because hydroxide ion is itself a very effective electron donor, and in even competition with practically any other anion in aqueous solution is likely to acquire a proton. Hence the hydrolysis only occurs until equilibrium is reached, at which the hydroxide ion formed is recovering protons as rapidly as it is being produced.

In an analogous manner, certain ions can react with water to remove hydroxide ions, thus increasing the hydronium ion concentration. To accomplish this, the ions must have vacant orbitals and thus be positive ions. The positive ions are the ions of bases. If the base is strong, the positive ion does not attract electrons strongly. This is so with the alkali metal ions, which are not highly electronegative, although they do attract water molecules sufficiently well that most of their salts are soluble. This is especially true of lithium, whose electrostatic charge is more influential because of the small size of the ion. Lithium ions cannot, however, attract a hydroxide ion away from a proton. The salts thus show no hydrolysis, so far as the cation is concerned.

A smaller and/or more highly charged cation attracts hydroxide ions more effectively. For example, to a small extent, we may expect the following reaction between magnesium ion and water:

$$Mg^{++} + 2H_2O \rightleftharpoons Mg(OH)^+ + H_3O^+$$

The above formulas are undoubtedly simplified, because these species must exist in hydrated form in aqueous solution. Probably an equation more like the following would be more appropriate:

$$[Mg(H_2O)_6]^{++} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+$$

A similar reaction, but more extensive, would be expected of the aluminum ion:

$$[Al(H_2O)_6]^{+++} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{++} + H_3O^+$$

The reaction would be more extensive because although magnesium hydroxide is a weak base, aluminum hydroxide is a very weak base.

Aluminum ions correspondingly give a more acidic reaction in water. In general, a small, highly positive cation may be regarded not only as attracting water molecules to it, but either by actual partial electron withdrawal from the water oxygen or by distortion of its electron cloud, also causing the oxygen to draw more heavily on the electrons shared with the hydrogens. In other words, the hydrogen in coordinated water is made more positive, and thus more readily released as a proton in the presence of electron-donor substances such as uncoordinated water.

Ammonium hydroxide (the solution of ammonia in water) was also described as a weak base. Ammonium ion in water reacts to some extent as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Since ammonia is a better electron donor than water, this only happens to a very slight extent and because water is present in such a large surplus. Nevertheless, it does decrease the pH of the solution somewhat.

Neutral salts thus may change the balance of hydronium and hydroxide ions in an aqueous solution in either direction. If the negative ion is the ion of a weak acid, it will hydrolyze to some extent to liberate hydroxide ions. If the positive ion is the ion of a weak base, it will hydrolyze to some extent to liberate hydronium ion. It is more useful to reason this out than to try to remember it without understanding. A salt of a weak acid tends to give basic solutions because it forms undissociated acid molecules. A salt of a weak base tends to give acidic solutions because it forms undissociated base molecules (or ions which contain undissociated hydroxide groups).

What about salts of both weak acid and weak base? Both ions will hydrolyze. The net effect on the pH of the solution depends on the relative strengths of the acid and base that made up the salt. If the base is a little stronger than the acid, although both are weak, the salt will dissolve to give a basic solution. If the acid is a little stronger than the base, an acidic solution will be formed. This applies, of course, to all strengths. You can therefore predict the direction of the effect on pH by knowing which of the acid and base that made the salt is stronger—for this is the direction in which pH will change. If both acid and base are strong, there is no hydrolysis and no change in pH. If the acid is stronger, pH will go down: acidic. If the base is stronger, pH will go up: basic.

Although hydrolysis ordinarily is incomplete, it can be caused to go to completion by taking advantage of the equilibria which exist. The hydrolysis of any ion that liberates hydronium ions can be suppressed by the addition of hydronium ions, increasing their concentration and

the speed of the reverse reaction. Hydrolysis of any ion that liberates hydroxide ions can be suppressed similarly by increasing the hydroxide ion concentration. On the other hand, such hydrolyses can be forced to completion by removing the hydronium or hydroxide ions formed, reduction of their concentration permitting only the forward, or hydrolytic, reactions. These facts will be shown, in the next and following chapters, to have important practical application.

Hydrolysis Constants

Equilibrium constants for hydrolysis of ions can be determined from the ion-product of water and the ionization constant of the acid (or base) formed by the hydrolysis. For example, consider the hydrolysis of acetate ion:

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

$$K_H = \frac{[HAc][OH^-]}{[Ac^-]}$$

For the ionization of acetic acid, HAc, (CH_3COOH)

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

$$K_I = \frac{[H_3O^+][Ac^-]}{[HAc]} = 1.8 \times 10^{-5}$$

For the ionization of water,

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_W = [H_3O^+][OH^-] = 10^{-14}$$

Then,

$$\frac{K_W}{K_I} = \frac{[H_3O^+][OH^-][HAc]}{[H_3O^+][Ac^-]} = K_H = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

One could use such a hydrolysis constant to calculate the pH of a salt solution.

EXAMPLE. What is the pH of a $1M$ NaAc solution?

$$K_H = 5.6 \times 10^{-10} = \frac{[HAc][OH^-]}{[Ac^-]}$$

All HAc must have come from acetate ion, and be equal in concentration to OH^- ion. If $[Ac^-] = 1 - X$, $[HAc] = X = [OH^-]$.

$$5.6 \times 10^{-10} = \frac{X^2}{1 - X} \quad \text{or} \quad X^2 + 5.6 \times 10^{-10}X - 5.6 \times 10^{-10} = 0.$$

This may be solved for X, using the quadratic equation:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

This gives us $X = 2.4 \times 10^{-5}$. But notice that we might have simplified the calculations by making the observation that with so small a hydrolysis constant the extent of hydrolysis X would probably be very small compared to one. That is, the denominator, $1 - X$, is approximately equal to 1. This would have given us the expression $5.6 \times 10^{-10} = X^2$, from which $X = 2.4 \times 10^{-5}$ as before. It is well worthwhile to keep in mind the possibility of such simplification, for where it can be used, it can make the solution of such problems much easier.

Since $X = [OH^-]$, then $[H^+] = \dfrac{10^{-14}}{2.4 \times 10^{-5}} = 4.2 \times 10^{-10}$

$$\begin{aligned} \log 4.2 &= \quad 0.62 \\ \log 10^{-10} &= -10 \\ &\overline{\quad 9.38 = \text{pH}} \end{aligned}$$

ANS.

Effect of Hydrolysis on Solubility

As pointed out briefly in Chapter 16, one cannot calculate the solubility of a salt from its solubility product if the ions which form when the salt dissolves react further with the water, changing their identity and therefore the concentration. Such hydrolysis can be prevented by appropriate adjustment of the pH. The example cited earlier was $CaCO_3$, which would be expected to dissolve by furnishing Ca^{2+} and CO_3^{2-} ions to the solution. The solubility product of 4.8×10^{-9} suggests that the solubility should be 7×10^{-5} mole per liter. But this would be the true solubility only if the pH were high enough to suppress the hydrolysis of carbonate ion:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

This hydrolysis reduces the concentration of carbonate ion and therefore the rate at which carbonate would rejoin the crystal, causing a greater amount of calcium carbonate to dissolve at equilibrium. The solubility of $CaCO_3$ is calculated to be actually 1.26×10^{-4} mole per

liter, or 0.013 g per liter. This agrees well with the experimental value of 0.014 g per liter. The hydrolysis raises the pH to nearly 10.

Titration of Acids and Bases

One of the most useful procedures in the analytical laboratory is the titration of acids with bases, or vice versa. This means, ordinarily, the careful addition of a solution of known concentration of acid or base to a measured sample of acid or base of unknown concentration or identity, until the latter is exactly neutralized. The volume of added reagent is measured carefully by adding it through a burette. The question is, how does one know when he has exactly neutralized the sample?

The most common method of determining this point is by use of what is called an "indicator." Ordinarily this is a water-soluble dye which is an acid or its salt, and which changes color when it changes from one form to the other. This color change is usually very intense, and a few drops of indicator are sufficient for seeing the color change in a relatively large volume of solution. The acidic or basic nature of the indicator itself does not, in such dilution, contribute significantly to the amounts of acid or base being analyzed.

The most important property of an indicator, other than its color change, is the pH at which this color change occurs. Normally, the change occurs over a range of pH, and then we need to know exactly what color it has at a given pH. Fortunately, many different indicators are known, each changing color at a pH range that is individually characteristic. One might ask, why is the pH range of the color change so important, or why do we need more than one good indicator? Why would it not be quite sufficient to find an indicator with a strong color change at pH 7?

Remember the hydrolysis of salts? When we neutralize an acid with a base in a quantitative analysis, we wish to know exactly how much of each is required to make, in theory, the neutral salt. We must take into account, however, that the neutral salt is not necessarily neutral in its reaction in water solution. We therefore wish to end the titration, not necessarily at a pH of 7, but at the pH that would correspond to that of a water solution of the neutral salt. If this pH is 9, then we need an indicator by whose color change a pH of 9 can easily be recognized. The point at which the titration is complete is called the "end point." We do not wish the end point to represent a neutral solution unless the salt alone in water would produce such a solution.

Table 25 Some Indicators, with pH and Color Changes

NAME	COLOR	pH	to	pH	COLOR
p-methyl red	yellow	3		1	red
methyl orange	yellow	4.4		3.2	red
methyl red	yellow	6.3		4.2	red
bromothymol blue	blue	7.6		6.0	yellow
litmus	blue	8.0		5.6	red
thymol blue	blue	9.3		7.9	yellow
phenolphthalein	red	9.8		8.2	colorless
alizarin yellow	violet	12.0		10.0	yellow

Applying this principle to the titration of a weak acid, we would use a strong base and an indicator that would change color at a pH higher than 7. For titration of a weak base, we would use a strong acid and an indicator that changes color at a pH lower than 7. Table 25 lists some common indicators with their characteristic color changes at appropriate pH values. For example, of their use, phenolphthalein is a good indicator for the titration of acetic acid with sodium hydroxide. Why? Titration of ammonia with hydrochloric acid would appropriately use methyl orange.

BUFFER SOLUTIONS

When one titrates an ordinary acid with a base, using an indicator that changes color over a certain pH range, one finds that unless the concentrations are extremely small in the acid and base solutions, a few drops of base (or acid) at the endpoint are sufficient to change the pH through the entire range shown by the indicator. A quantitative example should be helpful. Suppose we have added exactly an equivalent amount of base to the acid, using 0.1*N* NaOH, and now have 100 ml of titrated solution of pH 7. Two drops of the NaOH, which will have a volume of about 0.10 ml, contain $0.10 \times 10^{-4} = 10^{-5}$ equivalents of hydroxide ion. Added to the 100 ml of solution, this will give a hydroxide ion concentration of 10^{-4} mole per liter. The pH has risen, with those two drops only, from 7 to 10. Evidently pH is a very delicate property, sensitive to what seem to be very small changes. The control of pH is often experimentally very important. How can it be accomplished?

Suppose that, instead of a solution of a neutral salt, or pure water,

we had a solution of something capable of acting either as acid or base —capable both of accepting a proton and donating a proton. To find something like this, which is soluble in water, we can look to ions of polyprotic acids. Examples would be $HPO_4^=$ and $H_2PO_4^-$. Solutions of these would contain equilibria involving hydrolysis, but could react with either acid or base. If hydroxide ion is added, the reaction will be:

$$H_2PO_4^- + OH^- \rightleftharpoons H_2O + HPO_4^=$$

On the other hand, if hydrogen ion is added the following reaction will occur:

$$HPO_4^= + H_3O^+ \rightleftharpoons H_2PO_4^- + H_2O$$

A solution of salts of these ions would thus exert a compensating action tending to absorb the effects that would otherwise be noted when either acid or base were added. Any attempt to change the pH of the solution would result in an opposing reaction tending to keep the pH more nearly constant.

Simpler systems having similar properties can be any solutions of a weak acid and its salt. For example, a mixture of acetic acid and acetate ion (sodium acetate) would resist change in pH as follows:

$$HAc + OH^- \rightleftharpoons H_2O + Ac^-$$
$$Ac^- + H_3O^+ \rightleftharpoons HAc + H_2O$$

Such action is called "buffering," and a "**buffer**" is a substance or substances added to a solution to help steady the pH. Relatively large amounts of acid or of base can be added to a buffered solution without causing the very large changes in pH that would normally be expected if the solution were not buffered. Buffers are important not just in the laboratory but especially in life processes, where sudden changes in pH might be fatally destructive if buffers were not normally present in the biological fluids to prevent them.

SPECIAL HELP

Test Your Memory

1. Write an equation for the ionization of water.
2. In what way is the condition of hydrogen and of oxygen different in hydroxide ion and in hydronium ion than in water molecule?

3. How does this difference in condition affect the properties of these ions?
4. Write the fundamental equation for acid-base neutralization in aqueous solution.
5. How are hydronium and hydroxide ions able to form when they tend so strongly to react with one another?
6. What is the concentration of each of these ions in pure water at 25°?
7. Give the simplest definition of an acid.
8. Give the simplest definition of a base.
9. What is meant by "strong" and "weak" acids and bases?
10. Of what importance in determining acid strength is the nature of the anion of the acid?
11. In oxyanions, how does partial charge on oxygen affect strength of the oxyacid?
12. What is a polyprotic acid, and what can be said about its strength?
13. How can the presence of a salt of a weak acid affect the extent of ionization of that acid?
14. What is the meaning of the word "amphoteric"?
15. Write chemical equations illustrating the amphoteric behavior of zinc hydroxide.
16. What is the Bronsted-Lowry concept?
17. What are the "conjugate base" of an acid and the "conjugate acid" of a base?
18. What is the Lewis concept of acids and bases?
19. Define pH.
20. To what does "hydrolysis of salts" actually refer?
21. Give an example of a neutral salt that would give an acidic solution, and tell why.
22. Give an example of a neutral salt that would give a basic solution, and explain why.
23. What is an indicator, and how does it function?
24. What is meant by "buffer solution"? Give an example and show how it would work.

Test Your Math

1. What is the pH of a solution in which the hydrogen ion concentration is 4×10^{-6}?
2. What is the hydrogen ion concentration in a solution of pH 10.5?

3. The ionization constant of acetic acid is 1.8×10^{-5}. What is the hydrogen ion concentration when the solution is $0.05N$?
4. What is the pH of a solution containing $1M$ acetic acid and $1M$ sodium acetate?
5. Calculate the hydrolysis constant for ammonium ion. The ionization constant for $NH_3 \cdot H_2O$ is 1.8×10^{-5}.

Test Your Understanding

1. Sodium not only reacts rapidly with water at first, but continues to react rapidly. Why does this suggest that the reaction is with water molecules rather than merely with hydronium ions?
2. How do the nature of water and its ions illustrate the unfortunate limitations of oxidation numbers both to describe oxidation state and in defining oxidation-reduction?
3. Explain why the heat of neutralization is found to be essentially equal for all strong acids and strong bases.
4. In aqueous neutralization, which would be the Bronsted acid and base and which would be the Lewis acid and base?
5. The oxygen in a certain complex anion bears a relatively high negative charge. In solutions of the salts of this anion with cations of atoms relatively large in diameter in their respective periods, predict whether the pH would be greater or less than 7, and tell why.
6. A certain salt whose anion is known to hydrolyze nevertheless gives a solution of pH 7. Explain.
7. Why is the pH less than 7 in most metal chloride solutions?
8. What would you predict, and why, about the pH of solutions of neutral lithium salts of triprotic and most diprotic acids?
9. The very toxic gas, hydrogen cyanide, HCN ("prussic acid") is a very weak acid in water solution. Would you remove this compound from a gas stream by bubbling through a solution of low or high pH, or neither, and why?
10. A given salt is a complex oxide, with element 1 in the anion and element 2 the cation. Assuming that these elements are both in the same period, which has the smaller atoms? On what basis would you decide?
11. An element of low ionization energy forms oxides that behave how with strong acids, and why?
12. Would you expect the oxide of an element that in the free state is relatively volatile to be acidic or basic, and why?

13. The oxide of an element which in the free state shows closest packing of atoms unites with the oxide of another element whose binary compound with chlorine is a good chlorinating agent. Which element is in the oxyanion, and why?
14. An element that forms an extremely stable bromide forms an oxide of what kind of acid-base properties, and why?

19

Other Applications of Ionic Equilibria

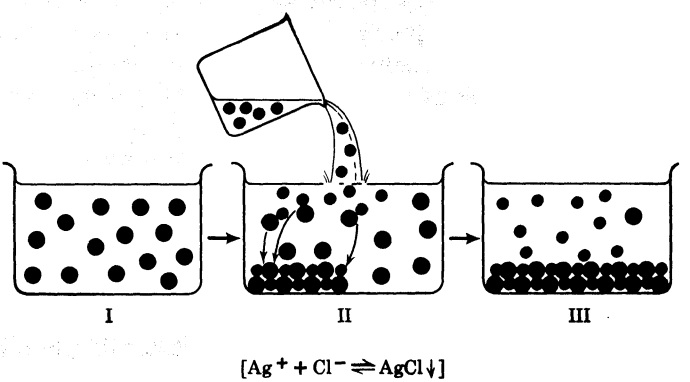
IN CHAPTER 16, the solubility product was discussed from a fundamental viewpoint. The formation of insoluble compounds from aqueous solutions has valuable practical applications. One is in analytical chemistry. Qualitative analysis makes much use of insoluble compounds, for two purposes: (1) to separate certain ions from others, and (2) to identify elements or ions. Quantitative analysis methods frequently depend on the complete, or essentially complete, precipitation of a compound in a form of high purity, which can be separated, dried, and weighed. Therefore a knowledge of ways of manipulating ionic equilibria to bring about the desired precipitations is essential to acquire for use in the laboratory. In industrial chemistry, too, these principles and methods are commonly applied, and one needs to understand them to appreciate this important part of our economic and material life.

Qualitative analysis is analysis carried out to identify the elements or ions present in a given mixture or compound. It depends on finding methods of causing an element or ion to reveal itself through properties which it alone possesses. If other elements or ions are present which

either have similar properties or in some other way would mask the properties of the element sought, these must first be removed or otherwise restrained from interference.

FORMATION OF PRECIPITATES

One of the properties by which a given ion can be recognized is its ability to combine with certain other ions, forming compounds so very slightly soluble that they precipitate essentially quantitatively. If such a compound can be formed under conditions which would prevent the formation of similar compounds by other ions present, and if it has distinguishing characteristics such as color or easily observable chemical properties, its formation can be shown to be positive proof of the initial existence of the given ion in the original mixture. For example, zinc forms the only known insoluble sulfide that is white. This sulfide will react with, and thus dissolve in, hydrochloric acid, liberating H_2S. If



I. Solution of NaCl. Only Cl^- ions shown. To reduce the concentration of Cl^- ions, another kind of ion may be added which combines with Cl^- ion to form an insoluble substance.

II. This is being done. Silver nitrate solution is being added. Only Ag^+ ions are shown. Silver chloride, AgCl, is a very insoluble substance, and as soon as Ag^+ ions collide with Cl^- ions AgCl precipitates out-and-settles to the bottom, as a white, insoluble solid. Sodium nitrate, $NaNO_3$, the only other possible combination, is very soluble and stays in solution as Na^+ and NO_3^- ions.

When more than enough Ag^+ ions have been added, the concentration of Cl^- ion has been reduced to an extremely low value by formation of insoluble AgCl shown settled on the bottom. Excess Ag^+ ions are still in solution since $AgNO_3$ is soluble.

Figure 100. Formation of a precipitate.

under controlled conditions one obtains a white precipitate by adding sulfide ion to a solution, and if this white precipitate will dissolve in hydrochloric acid, forming hydrogen sulfide, one can be reasonably sure that it is zinc sulfide. Therefore zinc was present in the original solution. However, if a black precipitate was obtained, for example, this might contain the white precipitate in a mixture of sulfides, but it would be completely hidden. If the conditions were not carefully controlled, sulfide ion might not precipitate zinc sulfide or it might precipitate other white solids that are not sulfides. It might, for example, precipitate insoluble hydroxides of ions that form soluble or hydrolyzable sulfides. Or it might be oxidized to free sulfur, which under some conditions looks more white than yellow. The sulfur, of course, would not dissolve in hydrochloric acid, but if there were a lot of sulfur and only a little zinc sulfide, you might not observe that some of the precipitate did dissolve in hydrochloric acid. In other words, one needs to be both scientific and artful to carry out qualitative analysis successfully. A thorough knowledge of precipitation is worth having.

The formation of a precipitate would seem likely to occur whenever the concentrations of the component ions are high enough to exceed the solubility product of the precipitate. This makes precipitation seem simple: you merely add, to a solution containing one of the ions, a solution containing the other of the ions in high enough concentration to cause precipitation. But it is not necessarily as easy as that, for one must take care that the conditions chosen for the precipitation do not permit partial solubility or even prevent the looked-for precipitation. We need therefore to consider the conditions under which "insoluble" precipitates dissolve, in order to avoid these conditions during the precipitation. Such information can also be very useful when we wish to prevent precipitation, or to dissolve an insoluble compound.

DISSOLUTION OF A PRECIPITATE

Let us consider a hypothetical salt, AB, of very limited solubility. The solubility product would be:

$$K = [A^+][B^-]$$

Suppose this salt AB is placed in contact with a certain amount of water, far too little to dissolve all of the salt. Since the salt is not very soluble, the saturated solution of it must be a very dilute solution. Such a saturated solution will soon form, an equilibrium being reached in which undissolved solute is dissolving at exactly the same speed with

which dissolved solute is rejoining the crystal. Most salts are strong electrolytes; some are weak. But even those that are weak must be regarded as being essentially completely ionized in extremely dilute solution. Consequently *all* of the dissolved material must be in the form of ions. This is the justification for deriving the solubility product from the equilibrium constant expression, for none of the dissolved solute exists as molecules, to change in concentration.

In this example, we are considering ways in which this insoluble compound could be dissolved. Obviously, from the equilibrium expression,

$$\text{AB (undissolved)} \rightleftharpoons A^+ + B^-$$

one needs only to decrease the concentration of either one of these ions in order to cause more of the solid to dissolve. One might, of course, decrease the concentrations of both, with the same effect. The simplest method would be to dilute the solution, which would cause more solid to dissolve. But if the solid is extremely insoluble, an enormous quantity of solvent would be needed to bring about the desired result. How else might one reduce the concentration of one of the ions?

1. Forming an Insoluble Compound

If we do not mind substituting one insoluble compound for another, we can add a solution containing some ion which will form, by combining with either A^+ or B^-, a new salt that is even more insoluble than AB. This will remove one of the original ions down to an extremely low concentration. In order for the rate of crystallization of AB to be maintained at the same rate as its rate of dissolution, when the concentration of A^+, for example, is being reduced, the concentration of B^- must be increased. The only source of B^- is the undissolved AB, which therefore continues to go into solution as long as A^+ is being precipitated.

2. Forming Complex Ions

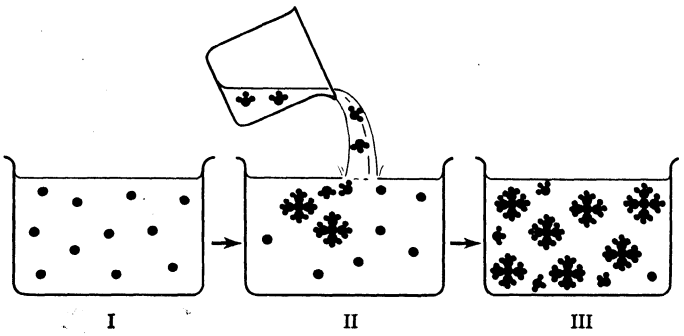
Dissolution only occurs with the simultaneous solvation of the particles. In a sense, therefore, the ions released when a salt dissolves are already to some extent coordinated to water molecules. The coordination may be loose, or it may be stable and strong, with a definite number of water molecules attached to each ion. Since the water acts

as electron donor, not acceptor, and since the donor atom is negatively charged oxygen, the ion most likely to be hydrated strongly is the cation. (However, the positive (hydrogen) end of the water dipole is attracted to the anion.)

If other electron donors are present when the salt is dissolved, or are added subsequently, they may compete with the water for positions in the sphere around the cation. One or more of the water molecules may then, at least at intervals in this dynamic system, be displaced or replaced by some other donor. The donor may be some molecular substance such as ammonia, or it may be a negative ion, for any negative ion has unshared electron pairs and negatively charged atoms capable of donating such a pair in the formation of a coordination bond.

In the equilibrium between an undissolved solute and its aqueous ions, the extent and strength of hydration undoubtedly play a role in determining the rate of recrystallization and, in effect, the solubility. The more extensive the hydration, the less easy it will be for an unhydrated ion to rejoin the crystal. But the concept of solubility product implies this result of hydration, and the concentrations of ions necessary for precipitation must include both hydrated and temporarily less hydrated or unhydrated species. The concentration of ions in the water, which we may simply term "aqueous ions" in recognition of their perhaps indefinite degree of hydration, may be reduced by the formation of relatively stable complexes with some competing electron donor. Unfortunately, the theory of coordination bonds is still in a formative state, and prediction of the relative stability of different complexes is very difficult. For example, some metal ions form stronger complexes with ammonia than they do with water, whereas others form stronger complexes with water than with ammonia. But any electron donor, which in coordination chemistry is commonly called a "ligand," may increase the solubility of a salt if it coordinates to the metal ion in the presence of water.

For example, silver ion, Ag^+, coordinates with ammonia better than it does with water. If to a solution of very soluble silver nitrate, $AgNO_3$, a source of chloride ion is added, a white precipitate of silver chloride, AgCl, quickly forms. The solubility product is only 1.6×10^{-10}, showing this to be an extremely insoluble salt. In fact, from the solubility product and the fact that only one ion of each variety is formed, we can calculate the solubility, using the expression $K_{sp} = x^2$, where x is the solubility in mole per liter. We find x to be 1.3×10^{-5} mole per liter. If we add ammonia to this mixture of saturated silver chloride solution and precipitate of undissolved silver chloride, either as a gas or as its aqueous solution, "ammonium hydroxide," the undissolved salt quickly dissolves, leaving a colorless, clear solution.



I. Solution of copper sulfate, $CuSO_4$. Only Cu^{++} ions shown. The concentration of Cu^{++} ions can be reduced by the addition of another ion or molecule which can form a stable, soluble complex with Cu^{++} ion.

II. This is being done here. Ammonium hydroxide, a solution of NH_3, is being added. Only NH_3 molecules are shown. As soon as these come in contact with Cu^{++} ions, they unite to form the beautiful blue stable complex ion in which 4 molecules of NH_3 are attached to each Cu^{++} ion.

III. The solution, when excess of NH_3 has been added, no longer readily shows the presence of Cu^{++} ions because their concentration has been reduced to a very low value by formation of the stable complex ion, $[Cu(NH_3)_4]^{++}$.

Figure 101. Formation of a soluble complex.

What happens to cause this? The ammonia forms a very stable complex with silver ion:

$$Ag^+(aq) + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + (aq)$$

An extremely high concentration of ammonia is not needed to bring this about, because the complex is so stable ($K = 1.7 \times 10^7$). The concentration of silver ion in the saturated solution of silver chloride was only 1.3×10^{-5} mole per liter, but this was ample to combine with the ammonia. As soon as it began to do so, the silver ion concentration began to drop, so that the product of its concentration times that of chloride ion no longer equalled the solubility product. Consequently, with the rate of dissolution of silver chloride now greater than the rate of recrystallization, the remaining solid silver chloride quickly dissolved.

Here all the silver ion and all the chloride ion originally present in the mixture are now present in solution. If they could become free to interact once more, the silver chloride would be reprecipitated. We can take advantage of the fact that even though the silver-ammonia complex is very stable, its formation is not irreversible, and equilibrium still

exists. If we could reduce the concentration of the ammonia, then we could increase the concentration of silver ion once more, to a value high enough to exceed the solubility product with chloride ion. How does one reduce the concentration of ammonia? If it is an electron donor, perhaps we can find a stronger acceptor than silver ion, and remove ammonia by forming it into a new complex. One of the most readily available acceptors is the proton of hydronium ion. Ammonia reacts with this very strongly, forming the very stable complex ion NH_4^+.

We have the following equilibria under consideration:

(1) $AgCl \rightleftharpoons Ag^+ + Cl^-$
(2) $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$
(3) $NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$

First, reaction (1) was brought about by introducing silver ions and chloride ions in solution. Although the concentration of silver ion in this equilibrium was very small, it was greater than it would be in equilibrium with ammonia. Therefore the addition of ammonia produced equilibrium (2), which resulted in dissolution of all the silver chloride. But ammonia forms a stronger complex with hydrogen ion than it does even with silver ion. Furthermore, it is quite capable of besting a water molecule in a competition for the proton, so it readily removes a proton from hydronium ion. Addition of acid to the solution of ammonia complex therefore upset the ammonia equilibrium with the silver complex, using up ammonia this time practically irreversibly in reaction (3), and liberating the silver ion so that reaction (1) could occur again.

If we had begun by mixing solutions of silver ion and iodide ion, we would have obtained a very insoluble precipitate of silver iodide, AgI. Addition of ammonia to this would have had no effect. Why? Because ammonia cannot form a complex with silver ion under these circumstances? No, but only because the complex ion is not sufficiently stable. Although the silver ion concentration is reduced to a very low value, it is still high enough to exceed the solubility product of the extremely insoluble iodide. In principle, then, if we could find some ligand that would form a more stable complex than the silver-ammonia complex, perhaps the concentration of silver ion could even be reduced to where the solubility product of silver iodide would not be reached. Such a ligand is the thiosulfate ion, $S_2O_3^=$, present in solutions of "photographers' hypo," which is actually sodium thiosulfate. This ligand forms so stable a complex with silver ion that even silver iodide dissolves in its presence:

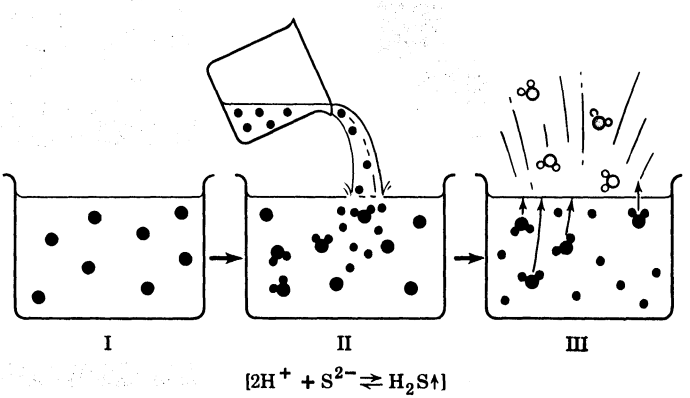
$$Ag^+ + 2S_2O_3^= \rightleftharpoons Ag(S_2O_3)_2^{\equiv}$$

3. Forming a Gas

Still another way of reducing the concentration of an ion, and thus dissolving an otherwise insoluble compound, is to introduce some reagent that will unite with the ion, forming a gas that escapes from the solution. The gases most commonly formed by such means are carbon dioxide, hydrogen sulfide, and sulfur dioxide. The first and last of these do not result directly, but are liberated because the initial product is unstable.

For example, consider ordinary limestone, or calcium carbonate, $CaCO_3$. This compound is very insoluble in water, the solubility product being 4.8×10^{-9}. The ions initially formed are Ca^{++} and $CO_3^{=}$. The calcium ion is the ion of a fairly strong base, and therefore is not expected to undergo much hydrolysis. The carbonate ion, on the other hand, is the ion of an extremely weak acid, and hydrolysis occurs as follows:

$$CO_3^{=} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-}; K = 2.1 \times 10^{-4}$$



I. Solution of Na_2S, sodium sulfide. Only S= ions shown. The concentration of S= ions can be reduced by adding an ion which will combine with S= to form a gas which can escape from the solution.

II. Here H^+ ion is being added, as a solution of strong acid. Only H^+ ion is shown. As soon as H^+ ions encounter S= ions, they unite to form HS^- ions and then H_2S molecules.

III. Hydrogen sulfide, H_2S, is of limited solubility in water and therefore soon begins to form bubbles of gas and escape from the solution. Thus the concentration of sulfide ion is reduced to a very low value.

Figure 102. Reduction of an ion concentration by the formation of a gas.

If the quantity of hydrogen ion is sufficient to convert most of the carbonate to bicarbonate the calcium carbonate completely dissolves, because the concentration of ions cannot exceed its solubility product. Calcium bicarbonate does not replace it as an insoluble phase because this acid salt is soluble. Up to this point, this example has not illustrated the formation of a gas at all, only that of the complex ion HCO_3^-, formed by coordination of a proton with the carbonate ion. But if an excess of hydrogen ion is added, further reactions occur:

$$HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$$

This occurs readily. Since bicarbonate ion is the ion of a moderately weak acid and hydrolyzes readily giving a basic solution, it can also donate an electron pair to a proton from an acid. But the undissociated carbonic acid that results is extremely unstable, and decomposes almost completely:

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

Carbon dioxide has limited solubility in water, and readily forms bubbles which rise to the surface and escape into the atmosphere.

If we drop a piece of limestone into an excess of fairly acidic solution, it will dissolve rapidly with much fizzing and bubbling as the carbon dioxide escapes.

Like the bicarbonate ion, the bisulfide ion, HS^-, is the ion of an extremely weak acid, H_2S. An ion of a still much weaker acid is the sulfide ion itself, $S^=$. Consequently, when an insoluble sulfide, such as ZnS, is placed in contact with water, hydrolysis of the ions formed by the initial dissolution occurs. Here the zinc ion too is an ion of a weak (amphoteric) base, and hydrolysis of both ions is to be expected:

$$ZnS \rightleftharpoons Zn^{++} + S^=$$
$$Zn^{++} + 2H_2O \rightleftharpoons Zn(OH)^+ + H_3O^+$$
$$S^= + H_2O \rightleftharpoons HS^- + OH^-$$
$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$

You can easily see what should be the effect of adding acid to a system containing undissolved zinc sulfide in equilibrium with its saturated solution. Hydrolysis of the zinc ion would be suppressed. Hydrolysis of the sulfide and bisulfide ions would continue, forming hydrogen sulfide. Like carbon dioxide, hydrogen sulfide is a gas having limited solubility in water, and it forms bubbles that rise to the surface and escape. The equilibria are thus continuously upset until all of the sulfide has been destroyed.

Like the acid salts of other types, such as bicarbonate (acid carbon-

ate), hydrosulfides, or "bisulfides," are much more soluble than the sulfides. It can be seen from the preceding equations that addition of hydroxide ion should suppress the hydrolysis of sulfide and bisulfide ions, and thereby increase the concentration of sulfide ions. In alkaline solution, most metal sulfides are insoluble, with the exception of the alkali and alkaline earth sulfides. Some hydroxides, however, are even less soluble than the sulfides. Such hydroxides are formed preferentially. But as the sulfide solution is reduced in pH, the concentration of sulfide ion itself is diminished, and the more soluble of the metal sulfides begin to dissolve. By careful control of the pH of the solution, certain metal sulfides can be separated from other metal sulfides, even though all would be precipitated together in an alkaline solution.

Insoluble Precipitates that Will Not Dissolve

Occasionally a very insoluble salt is encountered, to the ions of which nothing can be done to decrease their concentration. An example is barium sulfate, $BaSO_4$. The sulfate ion does not hydrolyze appreciably, and stable complexes of barium ion are relatively rare. Such salts remain essentially insoluble over a wide range of solution conditions.

CONTROL OF PRECIPITATION

From this discussion of the formation and dissolution of precipitates, it should be very clear that the use of these processes in qualitative and quantitative analysis depends on a careful and informed control of conditions. One cannot expect to form an insoluble precipitate in the presence of other ions that can form complexes, other insoluble precipitates, or gaseous products. One cannot expect to be able to identify an insoluble compound if it is formed under conditions that might precipitate other materials along with it. It is usually not sufficient, therefore, in qualitative analysis, to identify a given ion. It is also necessary to remove it, or be otherwise sure that its presence cannot interfere with the identification of other ions in the mixture. This calls for procedures which are essentially quantitative, in that they should make certain that interfering quantities of other ions are removed. But in truly quantitative analysis, where the exact amounts of pure compounds must be measured, the requirements are even more strict. This is why qualitative analysis is simpler, from the viewpoint of laboratory technique required, and therefore studied first, as a prerequisite to

quantitative analysis. But the exact care that should be used in qualitative analysis gives excellent training for more quantitative work.

Many practical applications of the principles of ionic equilibria will be discussed in detail in Part Four of this book.

SPECIAL HELP

Test Your Memory

1. How could one change one insoluble precipitate in a solvent to a different precipitate?
2. How can formation of complex ions cause dissolution of a precipitate?
3. Give an example of the production of a gas as a means of reducing the concentration of an ion.

Test Your Math

1. What is the maximum concentration of silver ion that could be in a solution of 0.01*M* NaCl?
2. To one liter of 0.1*M* $Pb(NO_3)_2$ solution is added one liter of 0.2*M* KCl solution. After filtration, one liter of 1*M* K_2CrO_4 solution is added to the filtrate. What weight of $PbCrO_4$ would thus be precipitated?
3. What weight of hydrogen ion would be consumed in dissolving 100 g of $CaCO_3$? Assume that all carbonate leaves as carbon dioxide.
4. How much 0.05*N* H_2SO_4 would be required to dissolve 10 g of ZnS? Assume that all sulfur leaves as hydrogen sulfide.

Test Your Understanding

1. Why should the formation of a complex ion commonly increase the solubility of a salt? In other words, why should a salt composed of complex ions tend to be more soluble?
2. Exactly the right amount of chloride ion is added to a solution of lead(II) ion to convert all the lead to $PbCl_2$, which, being insoluble, precipitates. Then you add a little more chloride ion, and more precipitate appears. Why?

3. How would you explain the fact that silver chloride is much more soluble in the presence of a large excess of common ion (chloride) than it is in pure water?
4. Even when no complex ions are formed, a slightly soluble compound may be somewhat more soluble in the presence of a high concentration of other ions than in pure water. Why?
5. What temperature effect, if any, would you expect to accompany the crystallization of the excess solute in a supersaturated solution, and why?
6. Why, when the solubility of sugar is a function only of sugar molecule concentration, is the solubility of silver sulfate related to both the concentration of silver and the concentration of sulfate?
7. Why, if the solubility product of silver chloride equals the product of the concentration of silver ion and of chloride ion, does the solubility product of silver sulfide equal the product of the silver ion concentration *squared* times the sulfide ion concentration?

20

Electrochemistry

ELECTROLYSIS

Fused Salts

ONE OF THE EXPERIMENTAL facts considered to support the theory of ionic bonding is that when ionic salts are heated to melting, so that the individual ions are no longer held in relatively fixed positions in the crystal, the liquid can conduct an electric current. The current does not, however, pass through this melt as it would through a metallic conductor, leaving no evidence of its passage. Simultaneously with its passing, chemical changes occur at the electrodes, indicating the decomposition of the melted salt. For example, when sodium chloride is melted and current is passed through, the electrode at which the current enters the liquid is the site of the formation of molten sodium metal, and at the electrode from which the current leaves the liquid chlorine gas is liberated.

When an electric current passes through a metallic conductor, the

valence electrons of the metal atoms are believed to be promoted to slightly higher energy levels (conduction bands) facilitating their motion through the metal. When electrons are supplied at one side of the metal, they repel the electrons already there, which, if possible, migrate out the other side. Current through a metallic conductor is thus merely a stream of electrons, those behind displacing those ahead. When the stream is stopped, the metal has the same number of electrons as before. The fact that they may not be the identical electrons initially present makes no difference, since electrons are indistinguishable from one another. The conduction of an electric current through molten salt, however, obviously has a more complicated explanation. The formation of sodium metal at the negatively charged electrode, called the "**cathode,**" can be explained as resulting from electrons leaving the cathode and joining the sodium ions in the adjacent melt:

$$Na^+ + e^- \rightarrow Na$$

The process occurring at the cathode is *reduction;* this is characteristic of cathode reactions. Similarly, the formation of chlorine at the positively charged electrode, called the "**anode,**" can be explained as resulting from the chloride ions, attracted to the oppositely charged electrode,

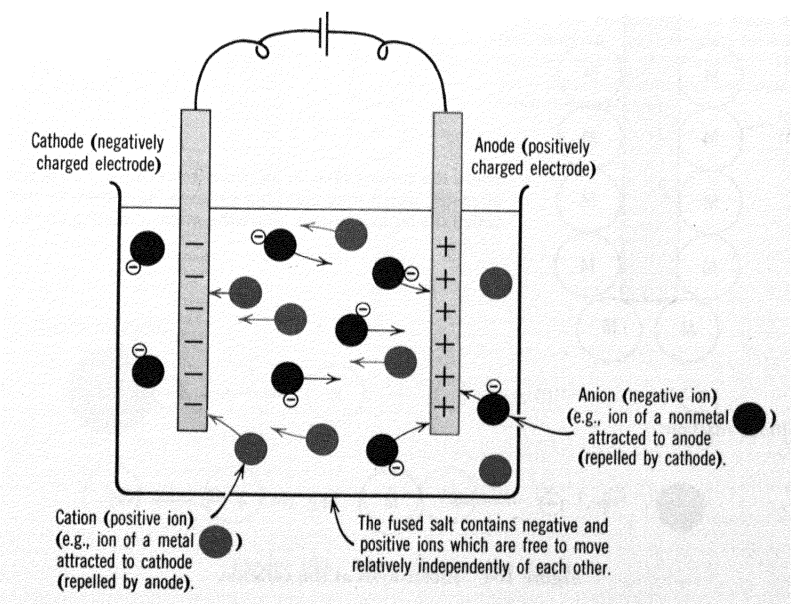
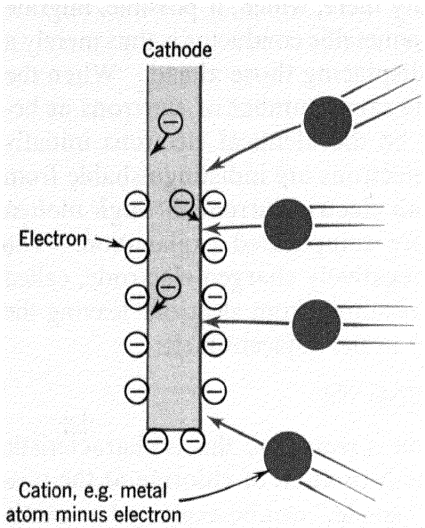
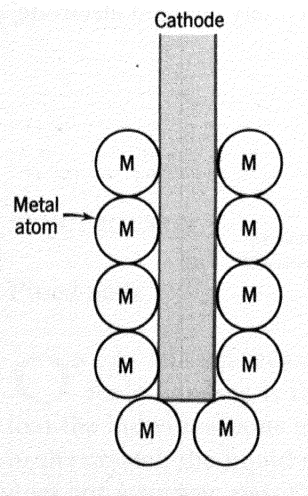


Figure 103. Electrolysis of a fused salt.



Electrostatic attraction between opposite charges causes migration of the cations (positively charged ions) to the cathode (negatively charged electrode) which is covered with extra electrons.



There the cations take on electrons to become neutral atoms of metal, which may plate the cathode, as shown, or rise or sink if the temperature is above the metal's melting point.

Cathode reaction:

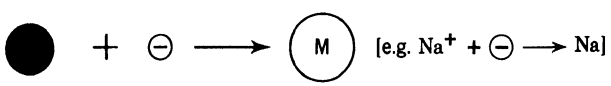
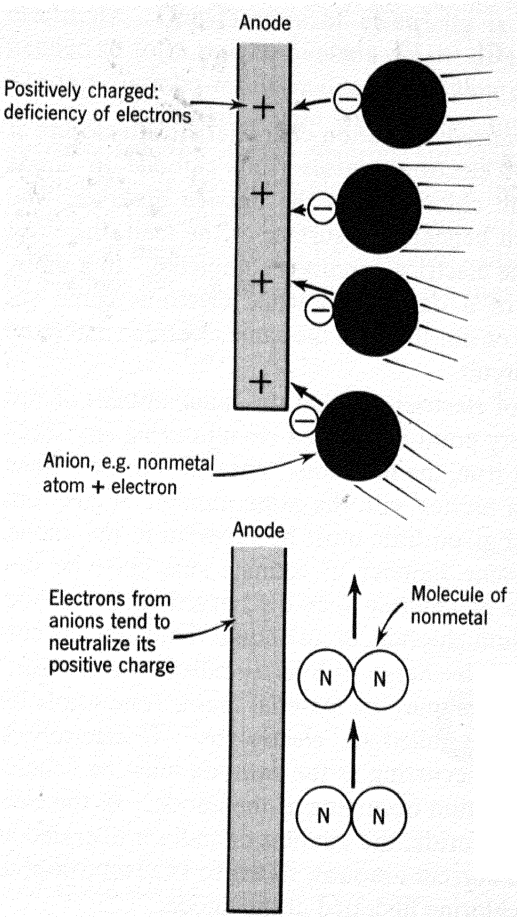


Figure 104. Electrolysis at the cathode.



By electrostatic attraction between opposite charges, anions (negatively charged ions) migrate to the anode (positively charged electrode).

There the anions give up their extra electrons to the anode, becoming neutral atoms of nonmetal. These form diatomic molecules and separate from the fused salt.

Anode reactions:

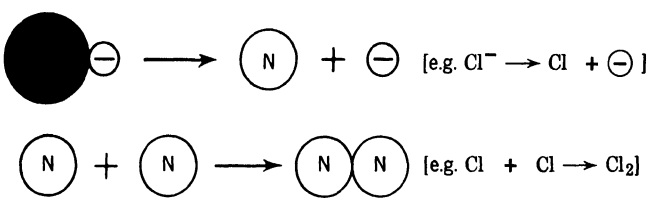


Figure 105. Electrolysis at the anode.

each giving up its extra electron to the anode, becoming thus a chlorine atom:

$$Cl^- \rightarrow Cl + e^-$$
$$2Cl \rightarrow Cl_2$$

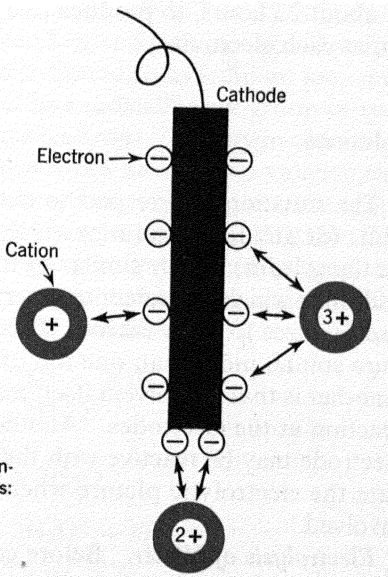
The chloride ion is thus *oxidized;* oxidation characteristically occurs at the anode. No stream of electrons passes from cathode to anode through the molten sodium chloride. To the outside observer, who cannot see what is going on beneath the surface of the melt, the effect is the same as if it did. The electrical circuit is completed. In a sense, electrons enter one door of a dark room while electrons come out another door, and whether or not they are the same electrons makes no difference in the exterior circuit.

An important principle of electricity is that the same amount of current must pass through every point in a closed circuit during any specified time. If this were not true, the flow could not continue as it does. If a current is carried by a molten salt, the same number of electrons that leave the cathode in a given time must be supplied to the anode. In sodium chloride, the same number of sodium ions must be discharged at the cathode as of chloride ions discharged at the anode. This decomposition of sodium chloride, or any liquid that conducts current through migration and discharge of ions, is called "**electrolysis.**" The conducting liquid, or sometimes the material that is responsible for the liquid being conducting, is called an "**electrolyte.**" In electrolysis, it is found that the reaction occurring at the cathode must be "chemically equivalent" to the reaction occurring at the anode. In the electrolysis of molten sodium chloride, the amount of sodium liberated at the cathode is exactly the correct amount, down to the last atom, to react chemically with the chlorine liberated at the anode.

We have already discussed (Chapter 16) the idea of equivalent weights. An equivalent weight of sodium ion is the same as the equivalent weight of sodium, and the same as one mole of sodium atoms: it is 23 grams. A mole of sodium atoms, or of any other substance, contains 6.02×10^{23} particles—here, sodium atoms. This is Avogadro's number. We can define a quantity of electricity as that quantity which contains Avogadro's number, or 6.02×10^{23}, of electrons. Knowing that it takes one electron to discharge one sodium atom, we can see that this amount of electricity is exactly the correct quantity to discharge one equivalent weight of sodium. After Michael Faraday, a great nineteenth-century experimenter, this quantity of electricity, which we may call one mole of electricity or one mole of electrons, is termed the "**faraday.**"

Each chloride ion gives up one electron to the anode during electrolysis. One mole of chloride ions would thus give up one faraday of electricity. One faraday of electricity is the amount of electricity needed to form one equivalent weight of an element at an electrode. The same faraday results in discharge of one equivalent weight of sodium and one equivalent weight of chlorine, thus giving an equivalent of chemical reaction at each electrode simultaneously.

Suppose the salt being electrolyzed is magnesium chloride, $MgCl_2$, instead of sodium chloride. Magnesium ions are doubly positive. No longer can the positive ion be completely discharged by one electron, as for sodium ion. A magnesium ion requires two electrons. While one



Ten electrons on the cathode are enough to convert 10 ions each of 1+ charge to neutral atoms:

$$10H^+ + 10\ominus \rightarrow 10H \rightarrow 5H_2$$
$$10Na^+ + 10\ominus \rightarrow 10Na$$
$$10Ag^+ + 10\ominus \rightarrow 10Ag$$

But if the ions each have a 2+ charge, then the same 10 electrons can make only 5 neutral atoms:

$$5Zn^{++} + 10\ominus \rightarrow 5Zn$$
$$5Cu^{++} + 10\ominus \rightarrow 5Cu$$
$$5Fe^{++} + 10\ominus \rightarrow 5Fe$$

And if the ions each have a 3+ charge, the same 10 electrons can only make 3 neutral atoms and begin to neutralize a fourth:

$$3Al^{+++} + 9\ominus \rightarrow 3Al$$

Therefore, $10H^+ \equiv 10Na^+ \equiv 10Ag^+ \equiv 5Zn^{++} \equiv 5Fe^{++} \equiv 3\frac{1}{3}Al^{+++}$. Or H^+ is equivalent to $\frac{1}{2}Zn^{++}$ or $\frac{1}{3}Al^{+++}$ or 1 g (1 mole) H^+ is equivalent to $^{65}/_{2}$ g (0.5 mole) Zn^{++}, or $^{27}/_{3} = 9$ g (0.333 mole)Al^{+++}.

Figure 106. Equivalent weights in electrolysis.

magnesium ion is being discharged at the cathode, therefore, two chloride ions are giving up their electrons at the anode. One faraday will produce one equivalent weight of chlorine as before, and one equivalent weight of magnesium also, but the latter is only half a mole. The equivalent weight of magnesium is therefore 12 grams, although the atomic weight in grams is 24. When we say that 12 grams of magnesium is an equivalent weight, and 23 grams of sodium is an equivalent weight, we mean that each would react with exactly the same quantity of, for example, chlorine.

The common unit of electricity is the **coulomb,** which is about 1/96,500 faraday. One **ampere** is a current flowing at the rate of one coulomb per second. From this, we could calculate that a current of one ampere would have to flow through a fused salt for 96,500 seconds, or about 27 hours, to produce one equivalent weight of any discharged ion at each electrode.

Solutions

The situation with respect to electrolytic conduction in aqueous solutions (or any liquid solutions if they conduct a current, whatever may be the solvent) is very similar to that in simple fused salts, with certain additions which are sometimes very significant. One is that the solvent itself ionizes to some extent. Thus even with pure solvent and a single pure solute, more than one ion of each charge type is usually present. Another is that the solvent itself may, in an undissociated form, undergo reaction at the electrodes. Another is that the element liberated at the electrode may be reactive with the solvent. All these additions complicate the electrolytic picture when solutions rather than fused salts are involved.

Electrolysis of Water. Before considering the electrolysis of aqueous solutions, we need to know something about the reactions of water itself at an electrode. True, water molecules are neutral and not capable of being discharged like an ion. Nevertheless, we have already seen that water can act as electron donor, through the unshared electron pairs and partial negative charge on the oxygen. We have also seen that water can act as electron acceptor, through release of a proton. A close relationship between donor-acceptor ability and oxidation-reduction has also been observed. It was pointed out that water can act as an oxidizing agent or as a reducing agent. Any body of matter, such as an electrode, which carries a large surplus of electrons, can act as a reducing agent by supplying electrons to oxidizing agents. Sim-

ilarly, any body of matter, such as an electrode, which has a large deficiency of electrons, can act as an oxidizing agent by attracting electrons from a reducing agent. It is not unreasonable to expect, then, that at least a possibility exists for water to react with electrons at the cathode and to give up electrons at the anode.

Water might take on an electron at the cathode in its capacity as oxidizing agent, or electron acceptor, through a proton. If it were to do so, hydrogen would be formed and hydroxide ion would be left behind:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

This would be quite analogous to, for example:

$$2H_2O + 2Na \rightarrow H_2 + 2OH^- + 2Na^+$$

At the anode, water might be forced to give up an electron, leaving a proton which would quickly become hydrated to hydronium ion, and a hydroxide group which would be a **"free radical"** (any group of combined atoms having an unused valence electron). This hydroxide group or radical would consist of an oxygen atom having two valence electrons but only one hydrogen atom attached. Such a radical would doubtless dimerize at once, forming hydrogen peroxide, HOOH. This compound is quite unstable with respect to water and oxygen, and might easily decompose, liberating oxygen and leaving water. These possible anode reactions are summarized as follows:

$$2H_2O \rightarrow 2e^- + 2H^+ + 2OH$$
$$2H^+ + 2H_2O \rightarrow 2H_3O^+$$
$$2OH \rightarrow HOOH$$
$$2HOOH \rightarrow O_2 + 2H_2O$$

or the net reaction: $6H_2O \rightarrow 4e^- + 2H_3O^+ + O_2$

The next question is, if these electrode reactions can indeed occur, why does not water conduct electricity easily, since the cathode reaction takes electrons from the cathode and the anode reaction supplies the same number of electrons to the anode?

The answer seems to be that very soon in the electrolysis a concentration of negative (hydroxide) ions would arise in the region of the cathode, without a corresponding concentration of positive ions, and this would somehow prevent further action of water with the cathode electrons. Similarly, at the anode, a concentration of positive (hydronium) ions would build up, without a corresponding concentration of negative ions.

It seems difficult to understand exactly how such a build-up of ions could prevent action between the electrons of the cathode and the water in contact with the cathode. We do know that when other ions are present to move in and balance the opposite charge, the electrolysis proceeds rapidly. For example, one can dissolve in the water a little sodium hydroxide, or sulfuric acid, or sodium sulfate, and the current passes much more readily, still with the production at the electrodes of only hydrogen and oxygen. It is also known from experiment that when the two electrodes are somewhat separated so that free mixing of solution is not possible, the solution, when neutral sodium sulfate is the electrolyte, does become alkaline around the cathode and acidic around the anode, just as would be predicted from the postulated reactions of molecular water. Apparently, in the solution, the electroneutrality is preserved around the electrodes by the migration of positive ions to balance the negative hydroxide ions around the cathode, and by the migration of negative ions to balance the positive hydronium ions around the anode. The function of the electrolyte seems to be to prevent electrical dissymmetries from building up within the solution.

We still need to consider why molecular water rather than its ions are considered to be mainly involved in these electrode reactions. The chief argument would be that the concentrations of the ions are extremely small. Even when the solution is made quite alkaline by addition of sodium hydroxide, in which the hydronium ion concentration is reduced to a much lower value than in pure water, hydrogen is readily formed at the cathode during electrolysis. Even when the solution is strongly acidic so that the hydroxide concentration is extremely low, oxygen is readily formed at the anode. It must be recognized that hydronium ion should surely be easier to reduce than water, and hydroxide ion easier to oxidize than water. The products would be similar, too, and the reactions might be written as follows:

$$4H_3O^+ + 4e^- \rightarrow 2H_2 + 4H_2O$$
$$4OH^- \rightarrow 4e^- + O_2 + 2H_2O$$

Each of the above reactions would have the result of leaving the opposite ion behind in excess in the region of the electrode, and we cannot overlook the possibility that reactions of water's ions may at least contribute to, if not completely account for, the reactions which now seem somewhat more logically ascribable to molecular water. Unfortunately, we cannot really see exactly what goes on at an electrode.

We also still need to consider why the sodium ion, which is positive and surely attracted by the electrons of the cathode, and the sulfate ion, which is negative and surely attracted by the positive charge of the

anode, are not discharged when electricity is passed through the aqueous solution. Although experiment is necessary to give us final answers, which may vary, depending on the conditions, a basis for rough predictions fortunately exists. (Later, more quantitative considerations may be examined.) Remember the general principle that an atom from which an electron is removed easily must form an ion which cannot attract an electron strongly, and that an atom which attracts an electron strongly cannot easily lose that electron again when it has gained it. Hydrogen is much more electronegative than sodium, and it has a much higher ionization energy. Hydrogen ion is much more electronegative than sodium ion. In any competition between sodium and hydrogen, especially positive hydrogen, for electrons, hydrogen unquestionably will win. The same reason that causes sodium to displace hydrogen from water prevents sodium ions from being discharged in preference to hydrogen ions or even the positive hydrogen in water.

Explanation of the sulfate ion reaction is not quite so easy. We do know, however, that sulfur is in its highest oxidation state and could hardly be oxidized further at the anode. Therefore, any electrons supplied to the anode must come from oxygen. A comparison between water oxygen and sulfate oxygen will indicate which is the better electron donor. Water forms hundreds of complexes, sulfate relatively few. Especially, sulfate is the ion of a fairly strong acid, HSO_4^-, which indicates that its oxygen does not supply electrons to coordinate a proton easily. We would therefore predict that the oxygen of water could supply electrons to an anode more readily than could a sulfate ion, and that water would therefore react before sulfate ion would be discharged. But, even if sulfate ion did lose its electrons to the anode, the observed results would be the same, for it would presumably form the very unstable SO_4, which would lose oxygen to leave SO_3. The SO_3 would react with the water to form sulfate ions once more, and hydronium ions, just as they were observed to form in the region around the anion.

Electrolysis of NaCl Solution

In a sodium chloride solution there are sodium ions, chloride ions, water, and small concentrations of hydronium and hydroxide ions. In the preceding section, the question was discussed of whether sodium ions or positive hydrogen would be discharged at a cathode. It was concluded that hydrogen would be discharged far more readily. At this electrode, therefore, the electrolysis of sodium chloride solution will not differ from that of water itself. At the anode, however, water might

react or chloride ion might be discharged, and we wish to understand which and why. We know that oxygen is more electronegative than chlorine and should therefore give up electrons less easily. From this, we might suspect that chloride ions would be discharged in preference to hydroxide ions or water. The experimental observation is that chlorine gas, not oxygen, is evolved at the anode under ordinary conditions. The evolution of hydrogen and chlorine leaves behind in solution the original sodium ions, plus hydroxide ions taking the place of chloride ions. In other words, electrolysis of sodium chloride solution transforms it to a solution of sodium hydroxide. Indeed, this is a commercial method of preparing sodium hydroxide as well as chlorine.

Electrolysis of Copper Sulfate Solution

This electrolysis should resemble that of sodium sulfate solution in liberating oxygen from water at the anode. At the cathode, however, the positive ions attracted are those of copper, not sodium. Copper metal is well known to be unaffected by hydronium ions, in contrast to the many metals that are readily attacked and liberate hydrogen. From this fact, it might be assumed that in a competition between copper ions and hydrogen ions for the electrons of the cathode the copper ions will win. If hydronium ions are unable to remove electrons from copper atoms, copper ions must attract the electrons more strongly than do the hydronium ions. Copper, not hydrogen, should therefore be liberated at the cathode, and it is. Since oxygen is liberated at the anode, the solution must change by increasing in hydronium ions, as well as by decreasing in copper ions. The solution of copper sulfate is thus gradually changed during the electrolysis to one of sulfuric acid, and when all the copper has been deposited the solvent will continue to be electrolyzed, giving two moles of hydrogen per mole of oxygen.

Electrodeposition of Metals

The preceding example of depositing copper serves to illustrate electrolysis of metal salt solutions in general, which has important practical applications both as a means of liberating free metal from its compounds and as a means of plating an object with a coating of the free metal.

As a means of liberating free metal, electrolysis may be used only when the metal ions are more easily discharged than the hydronium ions. Normally, this means that metals corroded by water, or by aqueous acids that can oxidize only through hydronium ion, cannot be

liberated from aqueous solution. However, under certain conditions hydrogen does not form as readily as it does normally, and it is then possible to produce electrolytically such metals as zinc from aqueous solution. The possibility of using nonaqueous solvents which will not oxidize metals has also been exploited. More will be said on electrodeposition to obtain free metals in Chapter 21.

As a means of plating objects, electrolysis is extremely valuable. In principle, any metal unaffected by water can be deposited on an object if the object conducts electricity and is made the cathode in an electrolysis of the metal salt. In practice, the nature of the deposit is extremely important, because it is useless as an ornamental or protective coating or for any mechanical purpose unless it adheres strongly to the cathode and to itself. Finding the best conditions for "electroplating" is both a science and an art. Usually such conditions include maintaining a very small concentration of the metal ion to be plated. Instead of a solution of extremely low concentration, which would soon be depleted, some complexing agent is used which keeps most of the metal ion tied up in a stable complex ion. In equilibrium with this complex is the very small concentration of free ion available to be discharged.

Also, we have up to now considered only the discharge of negative ions, or the reaction of solvent, at the anode as means of supplying electrons to it. There is another method which is especially important in electroplating or in electrodeposition in general. If the anode were to dissolve in the form of positive ions, these would leave behind the electrons they once had, and this in effect would be equivalent to supplying the anode with electrons from the solution. Any metal that could unite with oxygen liberated by the anodic oxidation of water could also dissolve, under the same oxidizing conditions, forming cations and leaving its valence electrons behind on the electrode. For example, oxygen attacks copper, forming copper(II), or cupric, oxide, CuO. Like other metal oxides, this is basic and therefore soluble in acid. When water decomposes at the anode, oxygen is liberated and acid is formed. If the anode were made of copper, it could unite with the oxygen and the oxide could dissolve in the acid, forming cupric ion, Cu^{++}. The same result would be obtained more directly, if the copper would dissolve as cupric ions in the first place.

At the cathode, then, and at the anode, the following would be the reactions during electrolysis:

$$\text{cathode:} \quad Cu^{++} + 2e^- \rightarrow Cu$$
$$\text{anode:} \quad Cu \rightarrow 2e^- + Cu^{++}$$

Thus, as fast as the copper is removed from solution at the cathode, it is replenished at the anode. The only limit to the quantity of copper

that can be deposited is the size of the copper anode. This method can be used for copper plating. It can also be used for purification of copper. Crude copper is made the anode, and under proper conditions of electrolysis very pure copper is deposited at the cathode, the impurities either remaining in solution or dropping out as an insoluble sludge.

CHEMICAL PRODUCTION OF ELECTRICITY

Up to now, we have been considering reactions that are difficult to bring about chemically, because they involve the taking apart of very stable substances. All these reactions have been brought about by electrical energy. The relationship of the energy produced or absorbed to the nature of the compounds formed or the reaction brought about has also been considered. We have recognized the general principle that reactions tending to occur spontaneously or to form very stable products do so with the evolution of energy. Electrolytic decomposition is thus a reversal of spontaneity—an artificial way of reversing what comes naturally. If a non-spontaneous reaction can be brought about by the absorption of electrical energy, then why cannot a spontaneous reaction be brought about with the evolution of electrical energy? Or, if a chemical reaction produces energy, why must this energy necessarily be in the form of heat and light? Why cannot conditions be found under which the energy produced is electrical?

The fact is that spontaneous reactions, reactions producing stable substances, can be brought about under conditions producing electrical energy. Familiar to us all are the electric dry cell, or "flashlight battery," and the lead accumulator cell, or storage battery. These are examples of the production of electricity—an electric current—by chemical reaction. In principle, any oxidation-reduction reaction—any chemical change that results in a transfer of electrons—can be brought about so that the electron transfer takes place through a wire instead of directly. This is the principle of what is called the "**galvanic**" or "**voltaic**" cell, after the Italian scientists Galvani and Volta, who independently studied these effects.

Reactions of Metals with Water

Since most of the reactions which have been made to produce electricity occur in aqueous medium, let us begin by considering the nature of the reaction of certain of the elements with water. For example, first

think of various of the metals. Sodium loses electrons so easily that it reduces water vigorously, forming hydrogen and sodium ion and hydroxide ion. We could hardly expect to maintain an electrode of so reactive a metal for any useful period of time, and the production of an electric current through a reaction of sodium in aqueous medium would seem at least extremely difficult to bring about. It may be useful to speculate on the possible mechanism of this reaction, however. The simplest mechanism would seem to be a collision between water hydrogen and the sodium crystal, the hydrogen breaking loose as a proton and simultaneously acquiring an electron from a sodium atom. But this actually is not so simple, for in the first place the sodium atom in the crystal does not possess its electron independently, and in the second place the proton is already strongly attached to a pair of electrons between it and the oxygen atom in the water. Then what is the condition of the sodium? Remember that in metals the valence electrons are relatively delocalized, not fixed between definite pairs of atoms, and the atoms are not atoms but positive ions, held together by the mobile electronic glue of the valence electrons. Now, with the concept in mind of a metal as a collection of cations, let us consider its contact with water.

We know that water tends to associate itself with cations. The bonding in sodium metal is not especially strong, as indicated by its physical properties. It might then be easy for some of the surface sodium cations to become sufficiently surrounded by water molecules that they could break loose or go into solution. This would leave the remaining sodium crystal with an excess of electrons. In other words, it would make of it the equivalent of a negatively charged cathode, by which water is decomposed as previously described, liberating hydrogen and forming hydroxide ion. This may not be the exact mechanism of the reaction of sodium with water, but it is a useful picture which can be applied to other metals in a similar way.

Magnesium. Consider placing a bar of magnesium into pure water. Again, we have magnesium ions held together by electrons that are not localized. At the surface, magnesium ions can become surrounded by attached water molecules and go into solution. The bar of magnesium thus acquires a negative charge from the electrons left behind by the magnesium ions. Water is decomposed by these electrons, as before, liberating hydrogen and forming hydroxide ion. Here we encounter an important difference, however. Sodium hydroxide is very soluble, and its ions remain in solution. Magnesium hydroxide is very insoluble, and the hydroxide ions initially formed combine with magnesium ions to form a layer of insoluble magnesium hydroxide over the surface of the metal and prevent further dissolution of the magnesium.

This difficulty could be avoided, obviously, if hydroxide ions could be

removed as fast as they are formed. Then the solubility product of magnesium hydroxide could not be exceeded, and the magnesium ions could continue to come into solution. Hydroxide ions are easily removed by reaction with hydronium ions. Consequently, if the water were acidified first, then the magnesium could continue to dissolve, and the water could continue to decompose until all the acid was depleted. It should be noted that hydronium ion in excess of that needed to keep the metal surface clean can also be reduced, and more easily than water molecules. Also, at higher temperatures $Mg(OH)_2$ is more soluble, and magnesium continues to dissolve slowly in boiling water.

Aluminum. When aluminum is placed in contact with pure water, the water molecules become quite strongly attached to aluminum ions at the surface, and some of these ions go into solution, leaving their valence electrons on the metal. These electrons accumulate in sufficient concentration to react with water. The hydroxide ions formed along with the hydrogen combine with the aluminum at once, because they are much stronger donors than water molecules. Aluminum hydroxide is extremely insoluble. It coats the metal surface, preventing further action. Thus far, the behavior is like that of magnesium. A further resemblance to magnesium is noted when the solution is acidified, for the hydronium ion combines with the hydroxide ion, removing the coating of aluminum hydroxide on the metal surface and permitting the metal to continue to dissolve as long as acid is present. Aluminum hydroxide differs from magnesium hydroxide, however, in being amphoteric rather than only weakly basic. The insoluble hydroxide can coordinate hydroxide ion to form the soluble complex ion, usually written $[Al(OH)_4]^-$, although it might more accurately be written $[Al(OH)_4(H_2O)_2]^-$. Whatever the exact state of hydration, it is called the "aluminate" ion. Its formation results in the dissolution of the protective coating of hydroxide. Just as in acid, aluminum continues to dissolve in base, with evolution of hydrogen, as long as enough hydroxide ion is present.

Aluminum can also dissolve in mercury, forming what is called an "amalgam" (a term applied to any metal-mercury combination). When the liquid amalgam is placed in contact with pure water, hydrogen is rapidly evolved, not just initially but until the water or aluminum is depleted. Here there is no chance for aluminum hydroxide to form a coating on the liquid amalgam. Although aluminum hydroxide forms, it does not prevent the fundamental reactivity of the aluminum with water. Mercury itself is inert to water.

Silver. Suppose that a piece of silver is placed in contact with water. Water molecules become attached to silver ions at the metal surface.

Some of the silver ions dissolve. Silver atoms, however, are held together quite strongly in the crystal and cannot easily be separated. Silver ions, on the other hand, readily join the silver crystal if they can acquire an electron. Consequently, only a very minute concentration of silver ions can build up in the solution before the rate at which they rejoin the now slightly negatively charged crystal equals the rate at which they dissolve. The charge on the crystal never comes close to being high enough to react with water or with hydronium ion, and no other chemical reaction occurs. No advantage is to be gained here by addition of either acid or base. No hydrogen is evolved, and the concentration of dissolved silver ion remains exceedingly small.

Copper. Copper would behave in a manner similar to that of silver. A very minute concentration of hydrated copper ions would form, but equilibrium would be reached before the charge on copper would be enough to form hydrogen.

Summary. In summary thus far, metals appear to differ from one another in the extent to which their ions can leave the metal crystal and dissolve in water. When this extent is sufficiently high, the charge of surplus electrons accumulated on the metal by the departure of cations from its surface is able to decompose water, forming hydrogen and hydroxide ions. If the metal hydroxide is soluble in water, or if it can in some other manner be prevented from coating the metal, the reaction can continue, if enough water is present, until the metal has reacted completely. If the metal hydroxide coats the metal surface as an insoluble layer, however, the dissolution of the metal must cease until the hydroxide layer is removed, whereupon it can continue as long as free metal is exposed to water. But if the extent to which ions tend to leave the metal crystal and become dispersed through the water is not sufficient to build up a high enough negative charge on the metal, water is not decomposed, and the metal remains at equilibrium with its extremely small concentration of dissolved ions. One must consider also the fact that the higher the concentration of excess electrons left upon the metal crystal by the departure of cations into the solution the lower the tendency of the cations to depart, since their departure must oppose the electrostatic attractions.

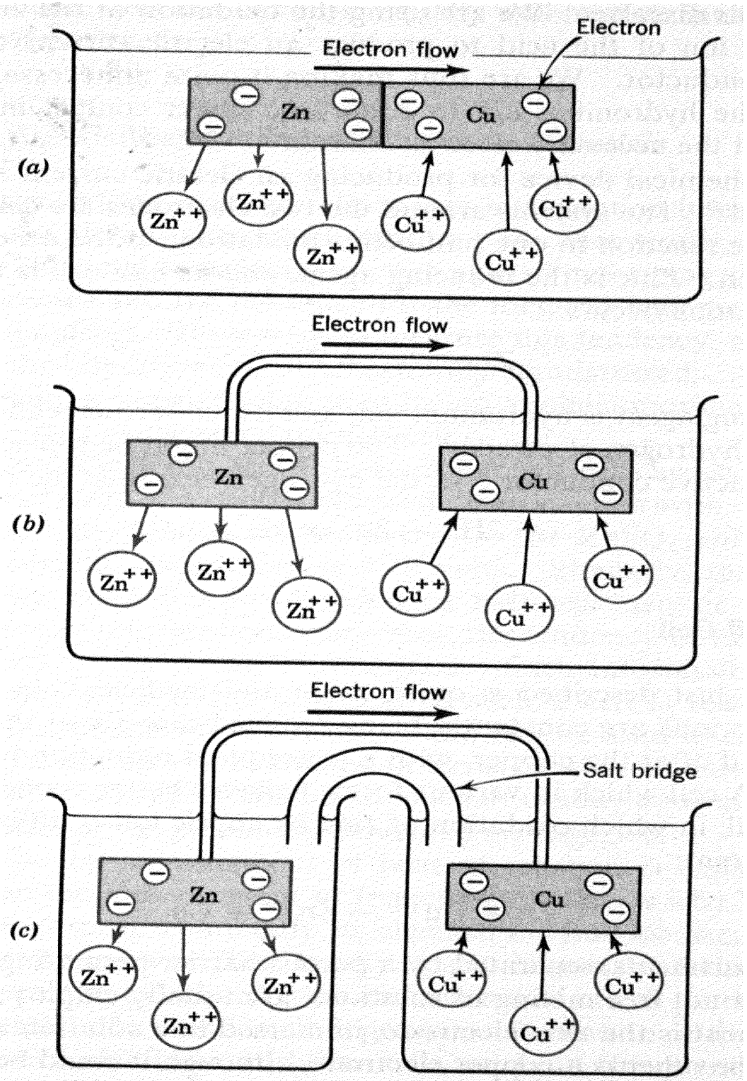
Producing a Current

If a piece of pure zinc were placed in contact with pure water, the tendency of zinc ions to become hydrated and leave the metal lattice would be inhibited, as in the case of magnesium, by the insolubility of

zinc hydroxide. This would therefore coat the surface of the metal, preventing any but the most superficial initial reaction. If acid were added to overcome this difficulty, then reaction would proceed, with liberation of hydrogen on the zinc surface. A difficulty would then arise which is perhaps more mechanical than chemical. Hydrogen gas would tend to remain adsorbed on the zinc surface, thus slowing the dissolution of the zinc. One would observe the rate of bubbling of hydrogen to diminish, becoming hardly perceptible. This would be, of course, the result of the hydrogen coating on the zinc and not of any peculiar inherent quality of the zinc.

If a piece of copper were placed in the same solution of acid, no reaction would occur except for the extremely slight dissolution of copper ions, for hydrogen could not be formed by so slight a concentration of electrons as would develop on the copper. But suppose that the copper were to be moved over to come in contact with the zinc. Then you would observe a surprising phenomenon—bubbles of hydrogen forming on the copper, and the zinc continuing to dissolve. We may account for this observation by noting that both metals would tend to acquire negative charge when placed in contact with water, but the tendency of zinc is much greater. Therefore the charge on zinc would be much greater. Copper is an excellent conductor of electrons, however, and contact with the zinc would result in an immediate flow of electrons from the zinc to the copper. Hydronium ions could now be discharged at either the zinc or the copper, liberating hydrogen, and to some extent would be discharged at both. At the zinc, however, the dissolution of positive zinc ions would tend to repel the approach of the positive hydronium ions, whereas at the copper no such repulsion would exist. Consequently the rate of hydrogen evolution would be higher at the copper, and the zinc would be less likely to become coated with hydrogen. The dissolution of the zinc would thus be facilitated notably by contact with the copper. The fundamental reason is the flow of electrons from the zinc to the copper.

Is there any reason why the electrons need to flow directly from the zinc to the copper, immersed within the solution? No. All that is required is that the electrons have some access to the copper. The fact that they are initially in much higher concentration on the zinc gives them the potential to flow to the copper if any means at all is available. Then, instead of connecting the zinc to the copper by placing them in contact, why not attach a wire to the zinc, bring it outside of the solution, and let the other end go back into the solution to attach to the copper? If this is done, the electrons flow just as freely as before. Hydrogen continues to form mainly at the copper surface, even though it



$Zn \rightarrow Zn^{++} + 2e^-$; $Cu^{++} + 2e^- \rightarrow Cu$. These are the reactions which occur because Zn has a greater tendency than Cu to form dispositive ions. Whether the electrons flow directly from Zn to Cu as in (*A*) or through an external conductor like the wire in (*B*) and (*C*) makes no difference. The current flows as long as Zn dissolves and Cu is deposited.

Figure 107. Chemical production of electrical energy.

is now quite separate from the zinc beneath the solution. The zinc continues to dissolve. We are using the oxidation of the zinc by the hydronium ion of the acid to produce an electric current through a metallic conductor. We are thus making it quite unnecessary for the zinc and the hydronium ion to come into direct contact in order to bring about the necessary electron transfer.

Such a chemical device for producing an electric current is called a "voltaic cell." The systems around the two electrodes are called "half-cells." The reaction in one half-cell is oxidation; in the other, it must be reduction. Zinc is the reducing agent, and its half-cell is the one in which oxidation occurs:

$$Zn \rightleftharpoons 2e^- + Zn^{++}$$

The oxidizing agent is hydronium ion, and its half-cell is really one containing a "hydrogen electrode." The copper might be replaced by any other unreactive conductor. In the hydrogen electrode the reaction is:

$$2H^+ + 2e^- \rightleftharpoons H_2$$

The Daniell Cell

The cell just described is quite crude and inefficient, in that some hydronium ions are constantly being reduced directly at the zinc surface instead of at the copper, with a consequent reduction in available current. A cell which in various forms behaves better is one called the Daniell cell, in which oxidation of zinc by cupric ion is utilized to produce a current:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$$

Two compartments, separated by a porous barrier permitting migration of ions but not free mixing of solutions, are usually employed. In one compartment is the zinc electrode, immersed in a solution of zinc sulfate. In the other is a copper electrode, although it could be any other unreactive conductor, immersed in a solution of copper sulfate. When the zinc and copper are connected by an external conductor zinc dissolves forming zinc ions, and the electrons left behind spread out through the external conductor to the copper. This attracts copper ions and gives them electrons, forming copper atoms at its surface. The sulfate ions tend to migrate from the copper sulfate compartment, where they are now too numerous in comparison with the depleted copper ions, to the zinc sulfate compartment, where they balance the

now greater concentration of positive zinc ions in the solution. Zinc ions and sulfate ions can of course equally well migrate into the copper half-cell compartment.

Standard Half-Cells and Standard Electrode Potentials

The tendency for a metal to release ions into solution is less, in effect, if its ions are already present in solution. In other words, as the concentration of metal ions increases, the rate of reforming the metallic lattice increases and the tendency for the metal to become negatively charged diminishes. If we wish to measure this tendency, or electrode potential, the conditions must be carefully standardized. An element in contact with a 1-molar solution of its ion at one atmosphere pressure and 25° is taken as the standard half-cell.

In the Daniell cell discussed above, if the half-cells are assembled as standard half-cells, the copper electrode is in contact with $1M$ $CuSO_4$ solution, and the zinc is in contact with $1M$ $ZnSO_4$ solution. At 25°, the potential of this cell is 1.10 volts. Similarly, the potential of any other combination of standard half-cells can be measured, and in this way information concerning the tendency of many chemical reactions to occur can be obtained. Such information is especially valuable because the potential of such a cell is related to the equilibrium constant for the reaction and can be used to calculate it. The potential can also be evaluated in terms of what is known as "free energy," which is roughly similar to, but not exactly equivalent to, the "heat of reaction," as previously explained on page 300.

Ordinarily, the measurement of heat of reaction is experimentally simpler than the measurement of free energy. This is why heat of reaction is used more commonly in chemistry. But for accuracy, free energy must be known. This is why it is so important and useful that free energy can be calculated from measurements of cell potentials.

The potential of a voltaic cell depends on the nature of the chemical change at each electrode, and thus tells us about the overall reaction but not about the relative tendencies at each individual electrode. As yet, there seems to be no way of measuring the separate contribution of one half-cell on an absolute basis. Arbitrarily, however, one particular half-cell has been chosen to represent zero potential. This does not mean that it actually has zero potential, but only that it can be used to establish a relative scale of individual half-cell potentials. The standard chosen is the hydrogen electrode at 25°. This can consist of an inert conductor, such as platinum, immersed in a solution which is

1*M* with respect to hydrogen ion, with a stream of hydrogen gas at one atmosphere pressure bubbling up around this conductor. The reaction whose potential is thus arbitrarily called zero is:

$$H^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2$$

If the hydrogen electrode is made half of a voltaic cell, with some other half-cell, then the potential of the cell is taken as the sum of the two half-cell potentials. Since one of these has arbitrarily been selected as zero, the relative value of the other is the same as the potential measured for the cell. It is found that certain half-cells when combined with the hydrogen electrode send current in one direction, and others in the other direction. For example, if the second half-cell is a zinc electrode, electrons will flow from the zinc, externally to the hydrogen. If the second half-cell is a chlorine electrode (chlorine gas at one atmosphere bubbling around an inert conductor), then the chlorine must take on electrons from the hydrogen, and the external current flows from the hydrogen to the chlorine. Obviously, the direction of the chemical potential of the zinc is the opposite of that of the chlorine. It is not enough to measure half-cell potentials: they must be differentiated as to direction. This is done in America by applying the negative sign to the relative potential of half-cells giving an external flow of electrons from hydrogen to the half-cell, and the positive sign to the half-cells producing an external flow of electrons to hydrogen. Thus we speak of zinc as having a positive chemical potential, and chlorine as having a negative chemical potential.

Nearly everywhere else, the convention is the opposite, which is one of those unfortunate states of affairs arising from honest differences of opinion about a matter which, being arbitrary, cannot be decided on scientific grounds but only on an arbitrary basis. Science should, of course, adopt the same conventions worldwide, so that every scientist reading the work of another could be sure at once what the writer meant.

As described above, it is possible to establish a table of values of half-cell potentials involving various electrode reactions, which will give the relative tendencies for these individual electrode reactions to occur. From such a table, one can determine simply by subtracting one half-cell potential from the other what should be the potential of the complete cell. Thus it is possible also to measure the potential of a cell consisting of one half-cell for which the potential is known and another for which the potential is not known, and so to determine the new half-cell potential and extend the table. Such a table (Table 26), which gives some representative values out of a much more extensive compilation, tells, since all such reactions involved oxidation-

Table 26 Some Half-Cell Potentials

ELECTRODE REACTION	E° (VOLTS)
$Li = Li^+ + e^-$	3.02
$Cs = Cs^+ + e^-$	3.02
$Rb = Rb^+ + e^-$	2.99
$K = K^+ + e^-$	2.92
$Ba = Ba^{++} + 2e^-$	2.90
$Sr = Sr^{++} + 2e^-$	2.89
$Ca = Ca^{++} + 2e^-$	2.87
$Na = Na^+ + e^-$	2.71
$Mg = Mg^{++} + 2e^-$	2.34
$Be = Be^{++} + 2e^-$	1.70
$Al = Al^{+++} + 3e^-$	1.67
$Zn = Zn^{++} + 2e^-$	0.76
$Fe = Fe^{++} + 2e^-$	0.44
$Sn = Sn^{++} + 2e^-$	0.14
$H_2 = 2H + 2e^-$	0.00
$Cu = Cu^{++} + 2e^-$	−0.34
$2I^- = I_2 + 2e^-$	−0.53
$Ag = Ag^+ + e^-$	−0.80
$Hg = Hg^{++} + 2e^-$	−0.85
$2Br^- = Br_2 + 2e^-$	−1.06
$H_2O = \frac{1}{2}O_2 + 2H^+ + 2e^-$	−1.23
$2Cl^- = Cl_2 + 2e^-$	−1.36
$2F^- = F_2 + 2e^-$	−2.85

reduction, the relative strengths of oxidizing and of reducing agents, under the standard cell conditions. It is therefore called a table of Redox Potentials, or Oxidation-Reduction Potentials.

The Effect of Concentrations; pH Measurement

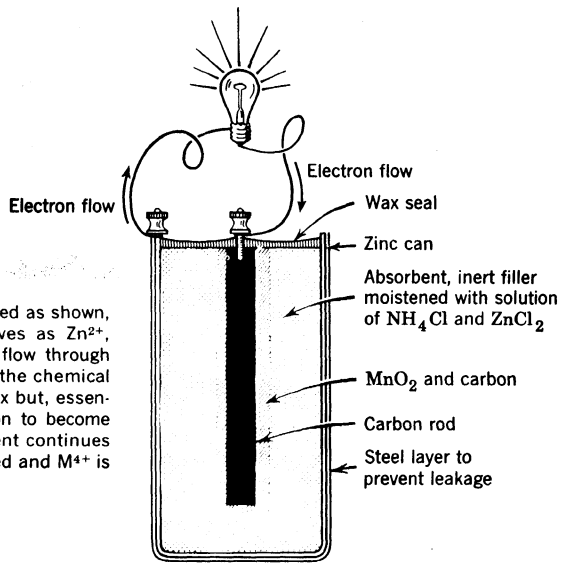
Remember that the potentials listed in Table 26 are for one-molar solutions only. These potentials are measured when the cell is operating essentially reversibly, and therefore reflect equilibrium conditions at the electrodes. These conditions, in turn, reflect the concentrations of ions. In general, the higher the concentration of ions in solution, the greater the speed of rejoining the electrode, and thus the smaller the tendency for the electrode reaction to occur. The electrode potential is therefore somewhat lower when the concentration of ions is higher, and vice versa.

For example, the standard potential, $E°$, for the zinc electrode is 0.76 volt. This represents the situation when the zinc ion concentration is 1 molar. If the zinc ion concentration is higher than that, the potential will be lower. This suggests that if two half-cells, having the same electrode but with different concentrations of solutions, were assembled to form a voltaic cell, current might be obtained from the difference in chemical potential of the two electrodes. This is true, the electrons in the external circuit flowing from the zinc that is in contact with the more dilute solution to the zinc that is in contact with the more concentrated solution. Such a combination is called a "concentration cell." Potentials obtainable are generally substantially lower than can be produced by a combination of different electrode materials in half-cells. Concentration cells thus have little practical importance in producing usable current.

The principle of concentration cells is very useful, however. One important application is to the measurement of pH. Instead of using an indicator, one can use a hydrogen electrode, making the solution in question the other half-cell by inserting a platinum electrode and connecting the two by a salt bridge. Since the potential of the standard hydrogen electrode depends on the concentration of hydrogen ion being one molar, if the solution has a different hydrogen ion concentration, the cell potential will be measureable and the pH can be calculated from it. In a titration of an acid with a base, or vice versa, the change in pH with addition of standard solution can be observed continuously, and the end point, in the region of which the pH change with addition of solution is by far most rapid, can thus be determined very accurately from the curve. Acid-base neutralizations can thus be carried out completely automatically if desired. Similar applications to numerous other solution reactions can be made.

Dry Cells

The construction of an effective combination of half-cells in a practical form for the production of useful current is far more difficult than the experimental assembling of the same half-cells for measurement of their potential. Of the thousands of possibilities that have been investigated, the most widely successful has been the LeClanche dry cell, used in ordinary flashlight batteries and similar applications. This cell as ordinarily constructed consists of a zinc can (in a steel case to prevent leakage) containing a solution of ammonium chloride which is made "dry" by absorbing it in a porous material such as sawdust. The can is the producer of electrons, for the usable current. At the center is



When the external circuit is closed as shown, zinc from the container dissolves as Zn^{2+}, leaving behind electrons which flow through the wire to the carbon. There the chemical reactions are somewhat complex but, essentially, Mn^{4+} takes on an electron to become Mn^{3+}. Thus the external current continues to flow while Zn is being oxidized and M^{4+} is being reduced.

Figure 108. Cross section of a dry cell.

a carbon electrode, surrounded by a paste of manganese dioxide, MnO_2, the whole being surrounded by the absorbent material containing the ammonium chloride solution. In operation, electrons flow from zinc externally to the carbon, where they result in reduction of the manganese dioxide to, presumably, some form equivalent to Mn_2O_3. Zinc goes into solution as zinc ions, in order to liberate these electrons.

This dry cell has the great advantage of being cheap, and for this reason it is the most widely used of such cells. Each cell supplies current at a potential of a little more than one volt, and by interconnection of such cells in series much higher potentials can be obtained.

The complete chemistry of the dry cell is quite complex, evidently complicated by the fact that reactions differ depending on the rate at which current is being withdrawn. Basically, the reaction of zinc with ammonium chloride solution, which is slightly acidic through hydrolysis of the ammonium ion, involves the displacement of hydrogen by zinc. This must result in liberation of ammonia, which is then free to form stable complexes with the zinc ion $[Zn(NH_3)_4]^{++}$. The hydrogen, however, if liberated as the free gas, would need to escape from the cell and would tend to coat the carbon electrode, preventing adequate contact with the solution. The purpose of the manganese dioxide appears to be to oxidize the hydrogen to water, preventing its accumulation where

it would interfere with cell reaction. Even so, when the cell has been permitted to produce current for some time, the manganese dioxide becomes less effective in preventing hydrogen liberation, and the cell potential goes down. After the cell has stood idle for a while, more favorable conditions are restored, at least temporarily. Even a nearly "dead" cell may light a flashlight bulb brightly at first, although the light soon dims.

Accumulator Cells; the Storage Battery

In principle, oxidation-reduction reactions can be reversed by the use of electrical energy, and one should be able to reform, through electrolysis, the original electrode materials of a voltaic cell after the cell has operated to the limit of its capacity. In practice, it is very difficult to carry out such a reversal under conditions producing a satisfactory physical state of the electrode materials, which would enable the cell to be exhausted and replenished over and over again, indefinitely. Again, many possibilities exist, but few have proven economically successful. The most successful thus far has been the lead storage battery—a "battery" being actually an assembly of individual voltaic cells.

The lead storage battery cell consists, fundamentally, of two lead—lead sulfate electrodes immersed in sulfuric acid, containing water. As such, the cell can create no potential, for each lead electrode has the same tendency to form lead ions. When an outside source of current is applied, however, making one electrode a cathode and the other an anode, lead of the lead sulfate is converted to free lead at the cathode, by discharge of lead ions. Lead sulfate is converted to lead dioxide, PbO_2, at the anode, by removal of electrons. This electrolytic process is called "charging" the cell. When it has been completed, one electrode consists of lead in contact with the aqueous sulfuric acid. The other electrode consists of lead dioxide in contact with the acid. When the electrodes are connected externally by a metallic conductor, the lead goes "into solution" in the sulfuric acid, and the electrons flow from the lead electrode through the conductor into the lead dioxide electrode, where they reduce hydronium ions, and the lead(IV), to water and lead(II). But, since lead sulfate is insoluble, it forms in the solid phase at both electrodes. When the cell's electrodes have both been converted to lead sulfate, the current ceases, and the cell is "discharged." It needs charging again before it will produce additional current.

We may consider the aqueous sulfuric acid, which in the discharged cell has a concentration of about 12%, to consist mainly of hydronium ions and bisulfate ions. In the charging process, the hydronium ions

are attracted to the cathode, but lead is above hydrogen in the electromotive series, and is more easily discharged than hydronium ions. The lead is thus deposited from the lead sulfate, leaving the sulfate ion. At the anode, electrons are attracted away from the water molecules, which are more easily oxidized than bisulfate ions or sulfate ions, forming lead dioxide from the water oxygen and leaving hydronium ion to balance the sulfate ion liberated at the cathode:

$$\xrightarrow[\text{charging:}]{} \quad \text{cathode: } PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^=$$

$$\xleftarrow[\text{discharging:}]{} \quad \text{anode: } PbSO_4 + 2H_2O \rightleftharpoons 2e^- + PbO_2 + H_2SO_4 + 2H^+$$

Notice that discharging dilutes, and charging concentrates, the acid. This is the basis for testing the condition of the acid with a hydrometer, which measures the density. The discharged cell has acid of lower density. Being more dilute, it also freezes more easily, another reason for keeping a battery charged in the wintertime.

SPECIAL HELP

Test Your Memory

1. What is the name of the electrode at which positive ions are discharged? Negative ions?
2. Write equations for the reactions at each electrode when fused sodium chloride is electrolyzed.
3. How do metallic and electrolytic conduction differ?
4. How many electrons are in one faraday? How many coulombs?
5. Write equations for the electrode reactions during electrolysis of water, (*a*) if water molecules react directly, and (*b*) if water's ions are discharged.
6. How does sodium hydroxide result from electrolysis of salt solution?
7. Which electrode should be the impure metal when electrolytic purification is carried out? Why?
8. What is a voltaic cell, and how does it differ from an electrolytic cell?
9. What is meant by "half-cell"?
10. What is the Daniell cell?
11. Describe the standard hydrogen electrode. For what purpose is it used?
12. What are electrode potentials? Cell potentials?

13. What is a "concentration cell," and why does it work?
14. What is the electron source in a dry cell?
15. Write equations for the electrode reactions during charge and discharge of a lead accumulator cell.

Test Your Understanding

1. What would be the probable result of using as an anode in electrolysis of a fused salt the same metal as in the salt?
2. Would a bromide which gives a strongly acidic water solution be likely to conduct electricity well in the molten state?
3. What does the easy conduction of an electric current through a melted fluoride seem to tell us about the ionization energy of the other element?
4. A device for measuring quantities of electricity is an electrolytic cell called a "silver coulometer." It consists of silver electrodes immersed in $AgNO_3$ solution, the cathode being detachable so that it can be weighed carefully. Describe how you would use it.
5. A distinction has long been made between "ionic" and "covalent" compounds on the basis of their electrical conductivity in the fused state. High conductivity has been accepted as proof of free ions, and low conductivity as proof of undissociated molecules in the melt. In the light of the discussion of the electrolysis of water, what could be said about the validity of this distinction?
6. The oxidation potentials for the following metal ionizations are given in random order. Arrange the metals in order of increasing reducing ability. Li 3.045, Pb 0.126, Mn to Mn^{++} 1.18, Cu to Cu^{++} -0.337, Ag -0.7991, Na 2.714, Ca 2.87.
7. Why would the alkali and alkaline earth metals, which give up electrons so readily, be poor materials for an ordinary aqueous voltaic cell?
8. Metallic corrosion frequently involves metallic couples—junctions of two different metals. Explain why. Then suggest how a chunk of magnesium buried near an iron pipeline and connected to it by a wire can protect the pipeline against corrosion.
9. A "fuel cell" is a voltaic cell especially designed to derive electric current from the oxidation of normally nonconducting or nonelectrolytic reducing agents such as hydrocarbons. In the external circuit, would you expect electrons to flow from hydrocarbons to oxygen or vice versa, and why?

PART FOUR

Principles and Practice

21

Production of Metals

THE METALLIC STATE of matter imparts properties unequalled by any other form of matter, thus making metals indispensable to us. In some areas of application other materials, such as plastics, have provided a cheap and sometimes superior substitute for metals. For certain uses, however, it seems unlikely that any future substances will ever replace metals. The properties that seem especially difficult to approach by any other than a metallic structure are thermal and electrical conductivity and malleability and ductility. These properties, combined with those of density, physical strength, thermal stability, and chemical properties, have made metals the backbone of our material civilization.

Metals occur in nature either "native" (in the uncombined state) or chemically united with other elements. Their occurrence in the free state is only possible if they are extremely resistant to corrosion by the atmosphere and water. This eliminates all but platinum and its closely related neighbors, silver, gold, some copper, and some mercury and bismuth. All other metallic elements seldom or never occur in the uncombined condition. Even when native, the metals are usually thoroughly dispersed through rock or similar material. When they occur as compounds, these are often far from pure, and frequently also

dispersed through rock or other material. Material that contains metal in whatever form, *if* the metal can be isolated from it economically, is called "ore." Many materials contain metals either in too small a concentration, or in too difficult a form to isolate, to serve as economic sources of the metal; such materials are not called ores. For example, practically all ordinary clay in the soil contains relatively large concentrations of aluminum, but this metal at the present time is so much more cheaply obtained from other materials that soil is not called an aluminum ore. On the other hand, very small concentrations of uranium compounds in rock are considered worthwhile sources of uranium, and such rock is called uranium ore.

NATIVE METALS

Recovery of native metals from their ores is often just a physical process of separating the metal from the rock. Bismuth, for example, is relatively low melting, and its ore can be heated until the bismuth melts and runs out. But sometimes chemical assistance is needed. For example, gold and silver sometimes occur so thinly distributed through the rock that they must be separated by chemical means. The ore is ground to a fine powder and placed in shallow trays and covered with sodium cyanide solution. Silver and gold are oxidized by the air only extremely superficially, but in the presence of cyanide ion this is enough to cause them to dissolve in the solution, because the cyanide complexes formed are very stable. In contact with the air, the metal is continuously kept clean of superficial oxide layer by the dissolution of the oxide in the cyanide solution, and slowly the air oxidation is thus maintained. After several days, extraction of the metal from the ore by this chemical means may become essentially complete:

$$4Ag + 8CN^- + 2H_2O + O_2 \rightarrow 4Ag(CN)_2^- + 4OH^-$$

The metal can then be liberated by electrolysis of the solution of complex, or by action of a strong reducing agent.

One could predict the difficulty of oxidizing silver by noting the oxidation potential of silver ion:

$$Ag^+ + e^- \rightarrow Ag; \ -0.799 \text{ volt}$$

On the other hand, with cyanide ion:

$$Ag(CN)_2^- + e^- \rightarrow Ag + 2CN^-; \ 0.31 \text{ volt}$$

Silver metal is a much better reducing agent in the presence of cyanide ion.

ELECTROLYTIC REDUCTIONS

When metals are especially difficult to obtain through chemical reduction, or when the less expensive reducing agents available react further with the metal when it is liberated, thus preventing its isolation in acceptably pure form, electrolytic reduction is usually employed. This may be carried out in aqueous solution, in nonaqueous solution, or by using only the fused salt. The simplest method is to deposit the metal electrolytically from an aqueous solution of its ions. This method is quite satisfactory for metals less active than hydrogen—below it in the electromotive series. Such metals, however, are also the easiest to isolate by chemical reduction, which is often cheaper. Electrolysis of an aqueous solution cannot be employed for metals more reactive than hydrogen without devising special conditions whereby the deposition of hydrogen is greatly restricted or prevented. Such conditions have been devised successfully for a number of metals. Also, to avoid the difficulties of trying to reduce active metal ions from an aqueous solution, considerable attention has been directed toward finding nonaqueous solvent systems from which the metals could be electrodeposited. Some special methods have been discovered. But to avoid the ordinary solvent difficulties entirely, fused salts are electrolyzed. One of the attendant disadvantages is that if the salt is sufficiently polar to conduct electricity well in the fused state, it is likely to have, for that very reason, a high melting point. This disadvantage is sometimes partly overcome by introducing other salts, a mixture of salts often having a much lower melting temperature than any of the pure components.

Electrodeposition from Aqueous Solutions

Some of the metals which are easily electrodeposited from aqueous solutions containing their ions are copper, silver, gold, zinc, cadmium, chromium, rhodium, and lead. The most common application of this method, however, is to the final purification, after the crude element has been obtained through chemical reduction. Copper especially, and also some lead, is purified in this manner. By making the crude metal the anode and carefully controlling the conditions of the electrolysis, the copper or lead can be oxidized at the anode and redeposited in a very pure state at the cathode. Impurities such as iron are oxidized at the anode, and, not being reduced at the cathode as easily as are the ions of the desired metal, remain in the solution. Impurities such as silver, gold, bismuth, and other less reactive metals may not be oxidized at the anode, but when the supporting metal dissolves, these metals

drop to the bottom of the electrolytic bath as a solid sludge. The entire costs of the electrolytic refining of copper can commonly be recovered by isolating more valuable metals from the sludge.

The electrodeposition of metals such as zinc and even iron is occasionally accomplished from aqueous solution, under conditions of high current density that have the effect of creating an "overvoltage" for hydrogen, increasing the voltage necessary for hydrogen ion discharge at the cathode. Even though, under ideal conditions, the hydrogen would form, rather than the metal, satisfactory deposition of the metals can be effected under these special conditions.

Electrodeposition from Nonaqueous Solutions

On a relatively small scale, separation of some of the more active metals has been accomplished by electrolysis of solutions of their salts in nonaqueous solvents. Possibly further research will result in improved applications of this general type of technique.

The Hall Process for Aluminum Production. What might be termed an electrolysis of a fused salt mixture, as well as being called an example of electrolysis of a salt in a nonaqueous solvent, is the industrial large-scale preparation of aluminum, invented by Charles Hall in America and almost at the same time independently by Heroult in France. Aluminum oxide is found to dissolve in the easily fused complex salt, Na_3AlF_6, found as a natural mineral called "cryolite." Aluminum oxide, Al_2O_3, partially hydrated, is found in nature in a crude form called "bauxite." Although this could be dissolved in molten cryolite and then electrolyzed, the aluminum produced would be very impure, and too difficult to purify economically. For this reason, purification of the bauxite first is necessary. It is dissolved in hot sodium hydroxide solution, which forms soluble complex "aluminate" ions (page 414). Hydrous oxides of iron do not form such complexes, and remain insoluble. Silicon dioxide, since it is acidic, does dissolve, forming silicates. Filtration separates the iron oxides, and cooling separates aluminum hydroxide again, the silicates remaining in solution.

Electrolysis is ordinarily conducted by dissolving the purified bauxite in molten cryolite containing some calcium and sodium fluorides, at 1000°. The container is an iron box lined with graphite, which serves as the cathode. Graphite rods dipping into the melt serve as the anode. Reactions during electrolysis are complex and imperfectly understood, but they do lead to the deposition of pure molten aluminum at the cathode. Oxygen, fluorine, and some products of their attack on the

carbon anode are formed at the anode, with the result that periodically the anode must be replaced.

Electrodeposition from Fused Salts

If a salt is sufficiently polar, its melt generally conducts electricity relatively easily, and its ions are considered to be the current carriers. As mentioned earlier, polarity also produces high melting points, and mixtures of salts are often used to gain the advantage of lower fusion temperatures. Sodium chloride, mixed with some calcium chloride, can be electrolyzed as a melt at 600°, although the melting point of pure NaCl is two hundred degrees higher. In a cell designed to keep the products separate, which is of course highly important here, sodium is produced at the cathode and chlorine at the anode.

Fused salt electrolysis is applied chiefly to the production of magnesium. Sea water is brought into pools where calcium hydroxide, obtained from the thermal decomposition of oyster shell calcium carbonate dredged up nearby, is added. Magnesium ions are precipitated as the hydroxide, which is much less soluble than calcium hydroxide. The hydroxide is converted by hydrochloric acid to the chloride, which is fused and electrolyzed at about 700°.

Other metals obtained by electrolysis of fused salts include beryllium, potassium, and metals of the lanthanide series.

CHEMICAL REDUCTIONS

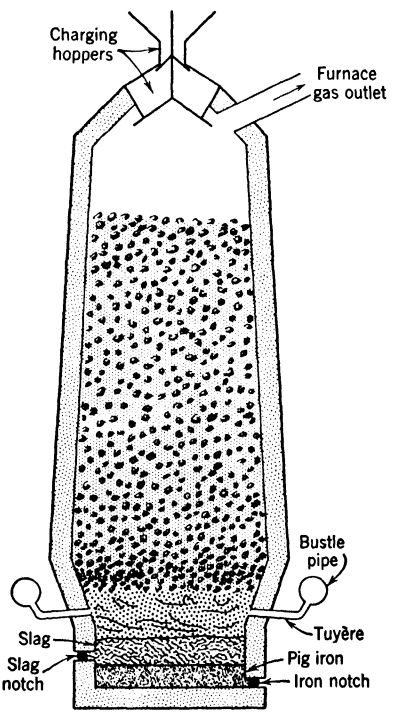
The cheapest and most common chemical reducing agent for obtaining free metals is carbon, in the form of coke prepared by heating coal to drive off volatile components and products. Other reducing agents sometimes used are hydrogen, aluminum, sodium, silicon, iron, magnesium, calcium, and zinc. Some of the metallic elements produced by chemical reduction include iron, magnesium, nickel, cobalt, manganese, molybdenum, tungsten, titanium, beryllium, lead, zinc, antimony, mercury, and copper.

The use of carbon is restricted to preparation of metals which do not easily form stable carbides or in which carbide formation is not wholly undesirable. It also requires the conversion of the compound in the ore, if it is not already present, to the oxide. Most ores contain the metals as sulfides if not oxides. Sulfides can be converted to oxides by heating the ore in the air. This process, called "roasting," is an important preliminary to reduction in many metallurgical processes.

Iron and Steel

By far the most important metal in modern civilization is iron, in any of its various usable forms. Yet pure iron is soft, relatively weak, and easily corroded, and therefore of little practical use. Introduction of carefully controlled concentrations of carbon and other impurities, however, converts iron to steels of many types and applications, much superior to pure iron.

The blast furnace, Figure 109, is a brick tower nearly one hundred feet tall, in which the main reduction of iron ore to crude iron is carried out. The principal naturally occurring ores of iron are "haematite," largely Fe_2O_3, and "magnetite," Fe_3O_4. These contain silicon as sand and silicates and also other impurities, but fortunately are so rich in iron oxides that they do not require preliminary concentrating before they are ready for reduction. At the top of the furnace is introduced a mixture of iron ore, limestone, and coke. Near the bottom, a blast of



Howard L. Ritter, *An Introduction to Chemistry,* John Wiley and Sons, 1955.

Figure 109. Blast furnace for reduction of iron ore.

hot air is blown in. This air heats and ignites the coke, forming carbon monoxide and carbon dioxide, but chiefly the former under the operating conditions. The heat of the burning coke decomposes the limestone, liberating carbon dioxide and forming lime. The carbon dioxide reacts with hot carbon, forming carbon monoxide. The lime reacts with silica forming calcium silicates, which are liquid at the furnace temperatures and run downward to form a liquid slag layer near the bottom. The carbon itself to some extent, but largely the carbon monoxide, act as reducing agents toward the iron oxides. These are reduced, probably in steps, eventually to form free iron, which is not only liquid at these temperatures but also relatively dense. The liquid iron flows downward, forming a layer at the very bottom underneath the layer of less dense liquid slag. The slag protects the iron from further oxidation by the incoming blast of hot air. Periodically, both slag and liquid iron are withdrawn. The iron is cast in molds, forming it into shapes which, for obscure reasons, are called "pigs." Continuous feed of materials to the top of the furnace, and continuous blast of hot air at the bottom, keep the operation going. A single blast furnace, producing about 1000 tons of pig iron a day, may operate for months without shutdown.

Some of the chemical reactions presumably occurring within the furnace are:

$$C + O_2 \rightarrow CO_2$$
$$2C + O_2 \rightarrow 2CO$$
$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$CaO + FeSiO_3 \rightarrow FeO + CaSiO_3$$
$$CO_2 + C \rightarrow 2CO$$
$$CO + Fe_2O_3 \rightarrow 2FeO + CO_2$$
$$CO + FeO \rightarrow Fe + CO_2$$

The great bulk of the pig iron is converted to various kinds of steel. The manufacture of steel is both an art and a science, originating as an art and gradually, as more and more fundamentals became known and applied, becoming more and more of a science. The process accounting for most of modern steel production is called the "open hearth" process. The iron is melted in huge shallow trays, which are lined with materials that react with some of the impurities and thus remove them. When those of the undesirable impurities that have not reacted with the hearth lining have been destroyed by oxidation, the last major traces of impurities like sulfur and phosphorus are removed by addition of other substances, such as manganese, which readily forms a sulfide exceedingly insoluble in the molten iron. The carbon content is adjusted—usually

kept in the neighborhood of 2 to 4 per cent—and finally any alloying materials are added and the melt is removed to be shaped as desired.

Alloys constitute an exceedingly complex area in the whole field of the solid state of matter, and much of what is known about them was learned empirically, by trial and test. The structure of an alloy is not merely a direct result of its composition, although composition is an important factor. Structure also depends on treatment, for as a melt cools the structure in the liquid changes, and the first crystals to separate are not representative of the overall composition, any more than would be the case on cooling any complex solution. Furthermore, the size and shape of the crystals formed on cooling depend on the conditions of cooling. In the cold, the rate at which equilibrium in material such as steel can be reached is extremely, even negligibly, slow. One can therefore produce "metastable" structures by cooling the melt too rapidly for equilibrium to be reached or maintained. Also, the mechanical treatment, such as hammering or rolling, can affect the structure, and to different degrees depending on the temperature of the mechanical treatment. Experience has shown that extraordinarily large differences in the ultimate qualities of a mixture of metals in the solid state at ordinary temperatures may result from seemingly minor changes in composition, or in heat or mechanical treatment of the metal. We cannot expect, therefore, any simple exposition of alloys in general or steels in particular. The subject is too complex. Many different alloying metals are added to iron in the production of special steels.

Tin

Tin occurs in nature largely as the dioxide SnO_2, in a mineral called "cassiterite." From this ore the production of tin is relatively simple. It is sometimes carried out by heating a mixture of the ore with carbon (coke or charcoal) on a sloping hearth. The tin formed is molten, and runs to one side where it is collected. Some tin is used in alloy with lead as solder. Most of it is applied in an extremely thin coat to sheet iron used for making "tin" cans, which are only iron cans with the iron thinly protected from rust by the tin plate. By comparison of the half-cell potentials,

$$Fe \rightarrow Fe^{++} + 2e^{-};\ 0.440 \text{ volt}$$
$$Sn \rightarrow Sn^{++} + 2e^{-};\ 0.136 \text{ volt}$$

one can recognize that actually tin is less reactive than iron and can give it protection against rust only by shielding the iron completely from the air. If so much as a tiny hole appears in the tin plate, exposing the

iron, the iron rusts much more rapidly as an iron-tin couple than it would as pure iron.

Alloyed with copper, tin forms the valuable alloys known as bronzes.

Zinc

Zinc occurs in different crystalline forms of the sulfide, called "sphalerite" or "zinc blende," and "wurtzite." The sulfide is roasted in air, which converts it to oxide, and then reduced by heating with carbon:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$ZnO + C \rightarrow Zn + CO$$

With more careful roasting, most of the sulfide can be converted to the sulfate, which, being water soluble, can then be extracted from extraneous parts of the ore. If desired, it can be reduced electrolytically in aqueous solution under conditions inhibiting the production of hydrogen.

Zinc is very important as a corrosion-resistant protective coating on iron, which is called "galvanized iron." It also forms the alloys with copper known as brasses.

Lead

The principal lead ore is the sulfide, PbS, "galena." This can be converted to oxide by roasting, and the oxide reduced by heating with carbon, in a combination of processes very similar to those described for zinc. Sometimes the original roasting is carried out only part way, forming a mixture of the sulfide, oxide, and sulfate. This mixture then interacts when heated further in the absence of air:

$$PbS + 2PbO \rightarrow 3Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

Lead so obtained is likely to contain impurities that are removed by electrolytic refining.

Copper

The winning of copper from its ores illustrates a case where the amount of copper, usually less than 2 per cent, would make it uneconomical to try to recover the copper without first concentrating the

copper-bearing part of the ore. Copper ores commonly contain the copper as the sulfide: "covellite," CuS, "chalcocite," Cu_2S, or more complex minerals. The ore is ground and mixed with water to which wetting agents have been added. The silicaceous materials are preferentially wetted by the water and sink as "gangue," but the sulfide is not wetted and can be removed from the top as a froth. This process is called "flotation."

Roasting and smelting of the concentrated sulfides converts the sulfur to sulfur dioxide and some of the impurities to oxides, leaving the metallic copper in a fairly pure form, which is usually further purified by electrolytic refining.

Other Chemical Reductions

Magnesium compounds can be converted to its oxide, instead of electrolyzing the fused chloride, and then heated to a very high temperature with an alloy of iron and silicon. The silicon takes away the oxygen, and magnesium vapor is separated and cooled. The oxide can also be reduced by carbon, under conditions where the metal is separated before it can react again with the carbon dioxide, reforming the metal oxide. Hydrogen is also used.

Lead and antimony sulfides can be reduced to the metals without first roasting to oxides, by heating with scrap iron, which combines with the sulfur.

Oxides of manganese can be reduced by heating with powdered aluminum. Indeed, the "thermite" process of welding steel rails in place depends on the ability of aluminum to take oxygen away from iron. A mixture of iron oxide and powdered aluminum is placed over the rail and heated, to initiate the reaction. This is highly exothermic, and forms molten iron on the spot. Magnesium or sodium can be used to convert chlorides of other metals to free metal, for example in the preparation of titanium. Silicon, which although not strictly metallic does have metallic properties, can be formed from its chloride by the action of sodium.

Hydrogen is used in reduction of oxides of molybdenum and tungsten to the metals, as well as in similar reduction of other metal oxides.

REDUCTION BY THERMAL DECOMPOSITION

In a few instances, simple thermal decomposition of a metallic compound will produce the free metal. For example, mercury sulfide roasted

in air is converted to the unstable oxide which liberates mercury. Complex ammonium chlorides of iridium and platinum decompose thermally to yield the free metals.

SPECIAL HELP

Test Your Memory

1. What must be accomplished, fundamentally, to prepare a metal from its compound?
2. What is a "native" metal?
3. How does cyanide assist in recovery of silver from its ores?
4. Is it impossible to electrodeposit from aqueous solution a metal more active than hydrogen? Why?
5. Name seven metals that are sometimes electrolytically prepared from aqueous solution.
6. Describe the Hall process for aluminum.
7. How is bauxite purified? What principles are involved?
8. What device is used to reduce temperatures required for electrolysis of fused salts?
9. Name six common chemical reducing agents used for metal production.
10. Name six metals commonly prepared by chemical reduction.
11. What is an ore?
12. What is the purpose of roasting an ore?
13. What is a blast furnace? Describe its operation, writing appropriate chemical equations.
14. What are the formulas of "haematite" and "magnetite"?
15. Write an equation for the reduction of "cassiterite."
16. In terms of electrode potentials, explain how an imperfect tin plate speeds rusting of iron.
17. Identify "wurtzite," "sphalerite," "zinc blende," "chalcocite," "covellite," and "galena."
18. What is "flotation"?
19. What is the "thermite" process and why does it work?

Test Your Math

1. How many faradays are required to produce one ton of aluminum?
2. What amount of coke, if it is 15% ash, would be needed to reduce a

ton of magnetite ore of 65% purity, if the carbon were all oxidized to CO and this were the sole reducing agent?
3. What volume of CO, at standard conditions, would result from the reduction of 100 lb of ZnO to free metal?
4. In the electrolytic refining of copper, assuming 2% impurities all separating as anode sludge, how long would a 4-amp current take to deposit 1 kg of sludge?
5. By heating with limestone an ore containing 30% sand, what weight of slag (assuming $CaSiO_3$) would be formed per ton?

Test Your Understanding

1. Why does it seem improbable that any combination of nonmetal atoms will ever rival metals in characteristically metallic properties such as electrical conductance?
2. Under what conditions if any would you expect a metal to be liberated from a mixture of its sulfide with its oxide?
3. What means would you suggest for isolating a metal from its halide if the metal atoms are very low in ionization energy and have a high ratio of outermost vacancies to electrons?
4. How would you isolate a free metal from its sulfide if the hydride of the metal is not highly polar?
5. A certain ore contains metal as the carbonate. How might you isolate the metal if its carbonate is very stable thermally?
6. A certain metal occurs in small traces, native in the rocks. It is soluble in mercury. How might you isolate it?

22

Some Important Bases

CALCIUM HYDROXIDE

THE CHEAPEST and most available source of hydroxide ions on a large scale is calcium hydroxide, or slaked lime, $Ca(OH)_2$. This in turn comes from quicklime, CaO, by the addition of water:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The reaction is highly exothermic. When the supply of water is relatively small, enough local heat is generated to boil the water or even to set fire to wood. The process of adding water to quicklime is called "slaking."

Quicklime itself—both it and slaked lime are frequently called simply "lime"—is obtainable in enormous quantities from vast deposits of limestone or related minerals. The ingredients for limestone are also extracted from the sea water by shell fish and converted into limestone for their protective shells. Vast accumulations of old shells exist which can serve as a source of calcium carbonate. Limestone, and a much harder crystalline form known as marble, are both essentially calcium carbonate, $CaCO_3$. Like calcium hydroxide, calcium carbonate may be regarded as derivable by the addition of a more acidic oxide to calcium

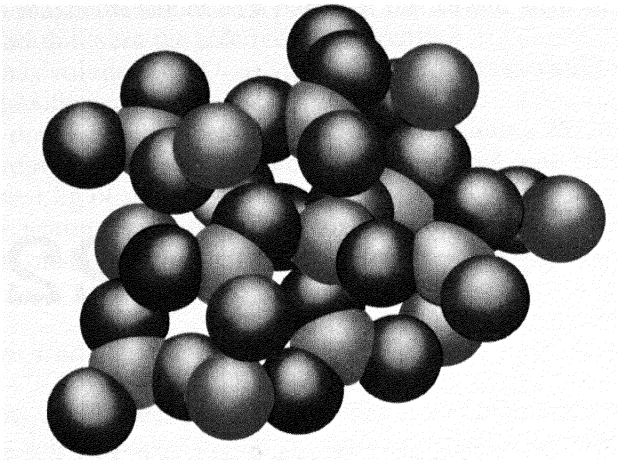
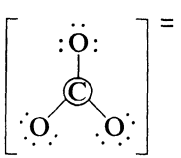


Figure 110. Calcium carbonate structure.

oxide. The oxygen in calcium oxide is sufficiently negative to serve as electron donor. In the reaction with water, it donates electrons to a proton of the water. In the reaction with carbon dioxide, it donates electrons to the carbon. In both instances, the oxygen becomes part of the anion (hydroxide or carbonate), forming a complex oxide. In calcium carbonate, the distribution and orientation of ions is such that each calcium atom is surrounded at equal distances by six oxygens, each from a different carbonate group, and each oxygen is close to two calciums as well as its own carbon. The coordination number of oxygen is three, and the grouping about it is planar; the coordination of calcium is six, and the grouping octahedral.

In general, the stability of a crystalline complex oxide appears to increase with the ability of the anionic group to acquire greater control of the electrons which give it its characteristic charge, and to decrease with increased polarizing ability of the cation. In other words, salts of complex oxyanions tend to be more stable, the less electronegative the metal and the larger the cation and lower the cationic charge. A cation has less polarizing (deforming) action on the anion, the larger the cation and the lower its positive charge. As shown on page 169, we can represent the carbonate ion in the following way:



This indicates that the three oxygen atoms are equally attached to the carbon. The carbon is joined to each oxygen by a single covalent bond supplemented by a third of an electron pair of the oxygen. When the metal ion has high attraction for electrons and high polarizing ability, and is small enough to exert its powers at close range, the symmetry of the complex ion tends to be destroyed through distortion of its electronic cloud. The more distorted it becomes, the more readily carbon dioxide is liberated, leaving behind the metal oxide.

In the series of Group IIA metal carbonates, we see the effects of increasing size and decreasing electronegativity of the metal from beryllium down the group. Beryllium carbonate is unstable even at 0°, reverting to BeO and CO_2. The dissociation pressure of carbon dioxide reaches one atmosphere when magnesium carbonate is heated to 540°. For calcium carbonate, the temperature is 900°, and for barium carbonate, 1360°. This means that although calcium carbonate is very stable at ordinary temperatures, by heating it one can drive out carbon dioxide, leaving calcium oxide behind. Industrially, this process is carried out in huge kilns. The escaping carbon dioxide may be used for dry ice or for other purposes.

$$CaCO_3 \rightarrow CaO + CO_2$$

Remember that the effective concentrations of solids cannot be altered by changing their relative amounts. Therefore, the only variable concentration here is that of carbon dioxide. The concentration of a gas and its pressure are essentially synonymous. The equilibrium constant for the decomposition of limestone is therefore merely the equilibrium pressure of carbon dioxide:

$$CaCO_3 \rightleftharpoons CaO + CO_2;\ K = p_{CO_2}$$

The decomposition is endothermic, and from this we can predict that the constant becomes smaller at lower temperatures and larger at higher temperatures. This prediction is entirely correct. Lime will absorb carbon dioxide from the air at ordinary temperatures, forming limestone.

Calcium carbonate itself is basic, because it is the salt of a fairly strong base, calcium hydroxide, with the weak carbonic acid. Even though it is extremely insoluble ($K_{sp} = 4.7 \times 10^{-9}$) in water, it can neutralize aqueous acids by acquiring their protons. Even solutions of carbon dioxide in water can be neutralized:

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2$$

Thus, a natural water can contain enough dissolved carbon dioxide to exert a solvent effect on limestone, because the bicarbonate of calcium is much more soluble than the carbonate:

$$CO_3^{=} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O$$

However, calcium bicarbonate is quite unstable, and when its solution is heated, or merely evaporated, it decomposes to liberate carbon dioxide and water and form the carbonate again. These facts lead to some interesting natural phenomena. One is the "limestone sink," a depression in the ground where the earth has sunk in, collapsing after its substructure of limestone was dissolved away by underground waters. Others are the stalagmites and stalactites of limestone caves—the caves themselves being potential sinks that have not yet sunk. Slowly dripping solutions of calcium bicarbonate have fallen from the ceiling to the floor and then evaporated, building up calcium carbonate deposits projecting upward from the floor. They have also evaporated from the ceiling before they could drop, building up similar deposits that hang from the ceiling.

Water Hardness

Still another phenomenon caused by calcium carbonate-bicarbonate equilibria is that of "temporary hardness" in water. The "hardness" of water is caused by the presence of metal ions such as those of calcium, iron, and magnesium. A soap is a salt of a metal with an organic (carbon and hydrogen) acid having a long chain structure. Alkali metals give soluble salts and thus soluble soaps. Ordinary household soaps are usually sodium salts. Insoluble soaps are formed by the ions of calcium, iron, and magnesium. Hard water wastes soap by precipitating insoluble curds of calcium and other metal soaps that have no detergent action. The sodium soap in effect must first "soften" the water before it can go into solution itself in high enough concentration to be effective.

Water hardness is conveniently classified as "temporary" and "permanent." Temporary hardness is caused mainly by the soluble bicarbonates of magnesium and calcium. These are easily removed merely by boiling the water. The resulting precipitates of carbonates form the hard water sediment on cooking and drinking vessels. The other metal ions must be precipitated out by some other reagent—for example, by calcium hydroxide added in carefully controlled quantities—or by ion exchange. Certain minerals, notably the silicates called "zeolites," and certain synthetic products called "ion exchange resins," are solids of open structure containing negative sites and positive ions to balance the charge. The positive ions are, in the minerals, ordinarily those of sodium. They are easily accessible to solutions placed in contact with the mineral, and can thus exchange places with ions introduced in the

solution. If the ions from the solution, like magnesium, calcium, and ferrous ions, are more strongly held by the mineral than are the sodium ions, they tend to displace sodium ions into the solution and remain attached to the mineral in their place. Thus a hard water making contact with the zeolite containing sodium ions becomes soft water containing sodium ions, while the zeolite acquires the offending metal ions. When the zeolite has become so filled with these ions that at equilibrium with a solution significant concentrations of undesirable ions still remain in the solution, it is no longer useful as a water softener, and must be refreshed. The procedure is to place the mineral in contact with a strong sodium chloride solution, passing this solution through the mineral to flush out displaced ions. Although in even competition the other ions would be favored for positions on the mineral, the extremely large excess of sodium ions assures that at equilibrium most of these other ions are displaced by sodium. The mineral is now ready to serve as a softening agent once more.

The ion exchange resins are of two principal types, those that absorb metal ions or positive ions and those that absorb anions. When water containing ions of any variety is passed through a cation exchange resin that has first been saturated with hydrogen ions, the metal ions from the water are practically quantitatively taken out, displacing hydrogen ions from the resin into the solution. When the same water solution is now passed through an anion exchange resin that has been saturated with hydroxide ions, its anions are taken out, displacing hydroxide ions from the resin into the solution. Since the ions originally in the water were of equal total positive and negative charge, the final water must have had displaced into it equal numbers of hydrogen and hydroxide ions, which unite, of course, to form water. By this means, remarkably pure water can be obtained. The ion exchange resins can be rejuvenated, when they are saturated with other ions, by treating them with acid or base, as required.

Uses of Calcium Hydroxide

Although calcium carbonate does have a basic reaction, in the absence of ideal conditions this reaction is very slow. Calcium carbonate might be spread over or mixed with acidic soils, for example, but its reaction would not be rapid enough for immediate agricultural advantage. This is why calcium hydroxide, which is much more soluble, is used for "liming" fields. One of the largest uses of calcium hydroxide is as "agricultural lime." The decay of organic matter in the

soil frequently produces acidic conditions, whereas many vegetables grow best when the pH is somewhat above 7. Hence lime is a very valuable addition to many soils at appropriate times.

Calcium hydroxide is also very important in the chemical industry. Solutions are not very concentrated, since the solubility of calcium hydroxide is only 1.85 g per liter at 0°, and decreases with rising temperature. However, a slurry of solid hydroxide with its saturated solution is just as effective in neutralizing acids as it would be if it were all initially dissolved. It is used in the paper industry, absorbing sulfur dioxide gas to become a solution of calcium bisulfite, $Ca(HSO_3)_2$, which is then used to dissolve lignin from wood fibers to leave the cellulose. In the petroleum industry, it can absorb hydrogen sulfide and other acidic gases from petroleum process gases. Wherever a cheap, abundant source of hydroxide ions is needed, and high water solubility is unnecessary, calcium hydroxide may fill the need. Its specific application in the industrial preparation of other chemicals will be discussed in the sections to follow.

SODIUM CARBONATE

One of the very important chemicals of commerce is "soda ash," which is sodium carbonate, Na_2CO_3. This is the salt of a strong base and weak acid, and thus gives alkaline solutions through hydrolysis of the anion:

$$CO_3^{=} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-}$$

Addition of hydronium ion causes the further reaction:

$$HCO_3^{-} + H_3O^{+} \rightleftharpoons H_2CO_3 + H_2O$$

By virtue of the instability of carbonic acid and the escape of carbon dioxide from solutions, the carbonate ion can serve very effectively as a base. Sodium carbonate is quite soluble in water, and thus forms solutions that can be very useful for absorbing acidic materials. It also has other important uses not dependent specifically on its basicity.

The most important source of sodium carbonate is synthetic, by the Solvay process. This process makes use of several familiar principles of general chemistry. Essentially, it consists of saturating brine (saturated sodium chloride solution) with ammonium bicarbonate (NH_4HCO_3). Ammonia and carbon dioxide gases are passed into the brine, forming ammonium and bicarbonate ions through interaction of

the ammonia and the carbonic acid. The resulting solution contains, therefore, chiefly sodium ions, chloride ions, ammonium ions, and bicarbonate ions.

The least soluble possible combination of ions in such a mixture is the one that will precipitate out first. Here it happens to be that of sodium and bicarbonate ions. Their solubility product is exceeded, and sodium bicarbonate, $NaHCO_3$, is precipitated. This is filtered off and heated. Like most other acid salts, it changes to free acid and normal salt when so treated:

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + (H_2CO_3)$$
$$(H_2CO_3) \rightarrow H_2O + CO_2$$

The success of any industrial operation depends ultimately on its being profitable. This means, especially in the face of competition from other manufacturers, that every effort must be made to avoid waste, to use all of the starting materials, and to recover all the products without loss. The carbon dioxide from the preceding operation is therefore saved and used again to saturate additional brine solution.

But where did the carbon dioxide come from in the first place? It came from calcium carbonate, by thermal decomposition. This left calcium oxide, which was slaked with water, forming calcium hydroxide. This is also important to the operation, because the most expensive reagent in the process is ammonia. The process cannot succeed economically if the ammonia cannot be recovered. Calcium hydroxide is essential to the recovery of ammonia.

When the sodium bicarbonate was precipitated and filtered, the filtrate must have retained the ammonium ions and the chloride ions. In effect, then, the precipitation of sodium bicarbonate brought about a metathetical or double decomposition reaction, producing ammonium chloride:

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3\downarrow + NH_4Cl$$

Remember that ammonium ion is the cation of a weak base. It therefore hydrolyzes to some extent in water, forming hydronium ions:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

As written, at equilibrium the reaction to the left is highly favored, for ammonia is a much better electron donor than water. However, the addition of hydroxide ions would remove most of the hydronium ions, upsetting this equilibrium and causing the forward reaction to be

favored. Furthermore, although ammonia is a better donor than water, hydroxide ion is a better donor than ammonia. In a competition between ammonia and hydroxide ion for a proton, even though the proton may already reside on the ammonia nitrogen, the hydroxide ion must win:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

In the presence of an excess of hydroxide ions, this reaction is speeded toward the right, until the concentration of ammonia in the solution exceeds its solubility, and ammonia gas is liberated.

The calcium hydroxide is used, therefore, to mix with the ammonium chloride solution, liberating the ammonia, which is saved to be passed into additional brine. This leaves calcium ions in place of ammonium ions in the solution, together with the chloride ions from the original brine. In effect, the solution is now one of calcium chloride. By evaporation of the water, the calcium chloride is recovered. Calcium chloride, when made anhydrous, has a high affinity for water, removing it from the air to form stable hydrates. It is therefore a good drying agent, useful in dehumidifying damp basements and for keeping dust down on dirt roads. But its value is not nearly as great as that of the sodium carbonate. When two or more products of a reaction are formed, the one of greatest economic value, for which the reaction was primarily run, is called the chief or major product, and the others are called "byproducts." Calcium chloride is the byproduct of the Solvay process, which is operated to make sodium carbonate.

In summary, the Solvay process starts with sodium chloride, limestone, and ammonia, and forms sodium bicarbonate and calcium chloride. Although the reaction does not proceed directly in the following way, the equation shows the overall picture of the chemical conversions that occur:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

In addition to its uses as a base, sodium carbonate is a valuable source of sodium oxide. Large quantities of it are used in the manufacture of sodium silicates and especially of glass, which consumes one-third of the total soda ash production. The rest finds use in soap powders, water softening, textile processing, welding fluxes, flotation, aluminum production, desulfurization of iron and steel, and manufacture of pulp and paper. As the decahydrate, sodium carbonate is "washing soda"—poisonous through its alkalinity, and by no means to be confused with "baking soda," which is sodium bicarbonate.

SODIUM HYDROXIDE

When a very high concentration of hydroxide ions is needed, the high solubility of the strong base, sodium hydroxide, NaOH, makes it very useful. In lower concentrations, too, it has many valuable applications, although it is much more expensive than lime.

One way of making sodium hydroxide is to take advantage of the insolubility of calcium carbonate as well as the ease with which it is converted to calcium hydroxide. Calcium hydroxide is added to sodium carbonate solution. Calcium carbonate, of course, precipitates, leaving sodium hydroxide in solution:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

The calcium carbonate can be filtered off, leaving the solution of sodium hydroxide to be concentrated, if desired, to the point of separating solid NaOH.

Another, and much more important, method of making sodium hydroxide is by electrolysis of sodium chloride solution. This electrolysis may be carried out primarily to produce chlorine, in which case sodium hydroxide is the byproduct. Or the relative importance of the products may be reversed.

Sodium hydroxide is variously supplied in the laboratory as sticks or pellets. In either form, it absorbs moisture from the air so readily that a saturated solution of sodium hydroxide is quickly formed on the surface, imparting caustic properties not so obvious in the dry solid. Large quantities of sodium hydroxide are used industrially, in petroleum refining, for soap and other detergent manufacture, in the production of rayon and cellophane, and for textile treatment, rubber reclaiming, vegetable oil refining, and in the pulp and paper industry.

AMMONIA

Solutions of ammonia in water are basic, through removal of protons by the ammonia to form ammonium ions, leaving a surplus of hydroxide ions:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

We therefore find it convenient to study this compound under the heading of bases, even though it has many other uses.

Ammonia is a gas, boiling at $-33.4°$ and liquefied at 25° under a

pressure of about ten atmospheres. Its main source is by synthesis from the free elements. This involves considerable difficulty, for nitrogen molecules are exceedingly stable and not easily persuaded to break apart in order to react with other elements. The synthesis of ammonia is frequently cited as an excellent example of the application of the principle of LeChatelier. We may find it useful to consider the nature of the equation describing the synthesis:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$$

Since the synthesis reaction is exothermic, we can predict that elevation of the temperature will cause a shift of the equilibrium to a position counteracting the temperature rise—in other words, favoring the endothermic reaction which is the opposite of the desired synthesis. Therefore one would expect that the reaction should be run at as low a temperature as practical.

On the other hand, the extreme stability of nitrogen molecules and the obvious requirement of breaking them apart before a single molecule of NH_3 can form suggest that drastic means must be employed. A high temperature would appear to be needed, but we know that although equilibrium would be reached more rapidly at such a temperature, the equilibrium concentration of ammonia would be too low to be worthwhile. Obviously, this calls for a compromise, and some additional help. The additional help was provided by the famous German chemist, Fritz Haber, who discovered that certain iron-containing materials could greatly assist the reaction, permitting equilibrium to be attained at a low enough temperature, and rapidly enough, for the practical production of ammonia. The iron catalyst evidently lowered the activation energy greatly, presumably by holding the nitrogen molecules in positions more receptive to reaction with the hydrogen, perhaps by forming nitrides of the catalyst.

Inspection of the synthesis equation reveals still another important way in which the equilibrium yields of ammonia might be affected. The number of moles of reactants is four; the number of moles of products is two. These are all in the gas phase, and hence the reduction in total number of moles of gas means reduction in pressure. The principle of LeChatelier tells us that if the pressure on such a system at equilibrium is increased, the position of the equilibrium will shift in the direction of opposing the pressure increase—in other words, toward forming fewer molecules. Higher yields of ammonia at equilibrium are therefore to be expected at higher pressures, which will increase the rate of the forward reaction more than the rate of the reverse reaction.

Knowing the fundamentals of obtaining good equilibrium yields of a

desired product is not necessarily enough, however, for a process to have maximum economic efficiency. In this Haber synthesis of ammonia, it has been found more productive on a time basis to separate ammonia before equilibrium is reached, not thus obtaining maximum yields but obtaining more ammonia per day. Furthermore, reactions with hydrogen at high pressures, and especially at elevated temperatures, present engineering problems because of the ease with which hydrogen diffuses into and through many metals under such conditions. This would be bad enough in itself, but in steels the iron is made tough and strong by the presence of carbon. This is hydrogenated by the hydrogen to form methane, leaving the iron relatively soft and weak and no longer the original strong steel capable of holding the desired high pressures. Ordinarily, there is plenty of work for the chemical engineer to do after the chemist has worked out the fundamentals of a chemical manufacturing process. Sometimes the engineering is the most difficult part of the development of an economical process for large-scale production.

SPECIAL HELP

Test Your Memory

1. How is slaked lime made from limestone?
2. What is the equilibrium constant expression for the initial reaction?
3. How can a base that is not very soluble serve as a good source of hydroxide ions in solution?
4. Write an equation showing how limestone can dissolve in "carbonated" water.
5. How does zeolite function in water treatment?
6. How do ion exchange resins soften water?
7. What is the major use of calcium hydroxide? Why is it needed for this use?
8. What is "soda ash"?
9. How can this neutral salt perform as a base?
10. Describe in detail the Solvay process.
11. How can ammonia be recovered from its salts? What fundamental principles are involved?
12. What is the net conversion reaction covering the Solvay process?
13. How can sodium hydroxide be prepared from slaked lime?
14. Describe the electrolytic preparation of sodium hydroxide.

15. Write an equation showing how ammonia can serve as a source of hydroxide ions in water.
16. Discuss the Haber process from the viewpoint of obtaining maximum yields.

Test Your Understanding

1. How and why would you expect H_2SO_4 to differ in stability from Na_2SO_4?
2. In a major group of the periodic table, how would you expect the stability of nitrates to vary? Why?
3. A certain element forms a very stable carbonate. What would you predict for the physical properties of the iodide of this element and the chemical properties of the binary hydrogen compound of this element?
4. What would be the effect of pH on preserving a complex anion that is not very stable?
5. How might one decompose limestone thermally at temperatures lower than 900°?
6. Explain how the liming of fields may destroy ammonium salts in the soil.
7. Why the indirection in the Solvay process? Why are not NaCl and $CaCO_3$ caused to react directly?
8. Why is the production of NaOH from slaked lime and soda ash wasteful of potential basicity?

23

Some Important Acids

THE ACIDS used in largest quantities in industrial chemistry are the same as those used in the laboratory: sulfuric acid, nitric acid, and hydrochloric acid. It is not always necessary for industrial processes, however, that these acids be prepared in as high a purity as for laboratory reagent use. Sometimes chemicals manufactured on a very large scale are quite pure, on the other hand, and can be used directly as laboratory reagents.

SULFURIC ACID

With considerable justification, it has been said that the standard of living of a country can be judged by the per capita consumption of sulfuric acid. The truth of this statement lies in the fact that sulfuric acid is one of the most important and essential foundations of industrial chemistry, and hence of industry. The per capita consumption of sulfuric acid in the United States is about one pound per day.

Sulfur

One reason for the rapid growth of chemical industry in America is the abundance of the element sulfur in natural deposits having a remarkably high degree of purity, often better than 99 per cent. This sulfur occurs chiefly in geological structures called "salt domes," found mainly in Texas and Louisiana. The sulfur occurs in layers from several hundred to several thousand feet below the surface. Mining it by conventional methods would have added to its cost enormously. This has been unnecessary, owing to the ingenuity of an engineer named Herman Frasch. Frasch devised a method of bringing sulfur to the surface without going down after it. A hole is drilled down to the sulfur-bearing stratum. This serves as an entrance for a system of three concentric pipes. Superheated water is pumped down the outside pipe into the sulfur bed, where it melts the sulfur (m p about 115°). Compressed air is forced down the center pipe where it forces the molten sulfur up the middle pipe. The sulfur stays in the molten state all the way up because its pipe is jacketed with the superheated water pipe. It flows into huge outdoor bins where it solidifies as part of an enormous block. For shipment either by train or ship, it is dynamited loose from the block.

The Contact Process

Sulfur as it comes from the wells is ordinarily pure enough for successful application in the manufacture of sulfuric acid. It is burned in air, forming sulfur dioxide. Curiously, sulfur trioxide is more stable at ordinary temperatures than a corresponding mixture of sulfur dioxide and oxygen. From this fact, one would predict that sulfur trioxide should be the product of burning sulfur in air. Actually, only very small amounts of sulfur trioxide are found to be present in the sulfur dioxide that forms as the principal product. To understand this, we must consider the nature of the reactions:

$$S + O_2 \rightarrow SO_2$$
$$2S + 3O_2 \rightarrow 2SO_3$$
$$2SO_2 + O_2 \rightarrow 2SO_3$$

Without knowing the exact mechanisms of these reactions, we can still see that it would be possible for sulfur to react with a single molecule of oxygen in forming SO_2, but that the O_2 molecule must be atomized

to form SO_3. This suggests that the activation energy for the formation of SO_3 might be much higher than it is for the formation of SO_2, making the latter the chief reaction under ordinary conditions.

We know that a catalyst appears to function by reducing the requirement of activation energy, and if sulfur trioxide should be the favored product a catalyst should assist in its formation. A higher temperature should also help in providing the needed energy, but here we encounter the difficulty that the equilibrium constant is lower at higher temperatures. In other words, the formation of sulfur trioxide is exothermic. Heat speeds its decomposition more than it speeds its synthesis. As in the Haber synthesis, a compromise must be found, in the form of a catalyst which reduces the activation energy requirement and thus permits good yields of sulfur trioxide to be produced at temperatures where such yields are possible and at rates that are practical. The two best known catalysts for this reaction are platinum metal and vanadium(V) oxide, V_2O_5.

The sulfur dioxide from the burning of sulfur must be purified of traces of arsenic which are present in the original sulfur, and which form a dust of oxide when the sulfur is burned. Otherwise the final sulfuric acid will contain this arsenic, which is very undesirable. Arsenic oxide is separated from the gases by electrostatic precipitation, which discharges the tiny particles allowing them to coalesce and settle out. Traces of arsenic that may slip through the precipitator are very harmful in poisoning the platinum catalyst so that it no longer functions. For this reason, as well as the lower cost, the vanadium oxide catalyst is more commonly used.

Because these catalysts are heterogeneous in their action rather than homogeneous, providing a solid phase to promote a gas phase reaction, which then occurs at the solid surface, they are called "contact" catalysts. The process for manufacturing sulfuric acid is therefore called the "contact process."

In principle, sulfur trioxide has a high affinity for water and should dissolve in it rapidly with the evolution of much heat. In practice, the gas appears to react with the water vapor before it reaches the liquid surface, forming a fog of sulfuric acid which does not mix easily with the water and greatly slows down the absorption of sulfur trioxide. This difficulty is overcome by dissolving the sulfur trioxide in sulfuric acid, wherein it is readily soluble, since sulfur trioxide and water are miscible in all proportions. The compound, pyrosulfuric acid, $H_2S_2O_7$, although unstable, is probably the principal product of the dissolution of sulfur trioxide in sulfuric acid. It readily loses sulfur trioxide to the

air, in the form of dense white fumes, traces of which, when inhaled, cause an irresistible impulse to cough. Commercially solutions containing more than enough sulfur trioxide to water to produce H_2SO_4 are called "fuming sulfuric acid," or "oleum" because they are dense, oily liquids.

Oleums can be diluted with water to give sulfuric acid solutions of any desired concentrations. The CP concentrated sulfuric acid of the laboratory is about 98 per cent H_2SO_4 and the rest water, by interaction, containing several species. More concentrated solutions—e.g. 100 per cent H_2SO_4—contain a number of ionic and molecular species including some relatively free sulfur trioxide. Industrially, the sulfuric acid most commonly used as "concentrated sulfuric acid" is about 93.2 per cent H_2SO_4. The composition corresponding to $H_2SO_4 \cdot H_2O$ is 84.5 per cent H_2SO_4.

The concentrated acid undergoes autoionization to a greater extent than pure water:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

In dilute aqueous solutions, sulfuric acid is a strong acid, the first proton being essentially completely removed by water. The second ionization, that of the bisulfate ion, is understandably weaker, for a proton must be separated from a doubly negative ion instead of a singly negative ion. Also, the oxygen on the bisulfate ion is much less negative than that on the sulfate ion, giving the latter a stronger attraction for a proton. The dissociation constant for bisulfate ion is 1.3×10^{-2}. This suggests that a solution of sodium sulfate, for example, should be slightly basic by hydrolysis of the sulfate ion. Actually, the hydrolysis constant is very small (7.7×10^{-13}) and sodium sulfate solutions are very nearly neutral.

Sulfuric acid is not only very useful as an acid, but it also is an excellent dehydrating agent, having a high affinity for water. Concentrated sulfuric acid will absorb moisture from the air, and it will also help the progress of other chemical reactions in which water is formed. For example, it helps to bring about the formation of diethylether from ethyl alcohol, as will be described in Chapter 24, and it is extremely useful in nitrating reactions, as will be discussed later. Its solutions can of course absorb alkaline gases, and ammonium sulfate is formed in large quantities by the absorption of ammonia gas from the decomposition of coal. In concentrated form, sulfuric acid is an oxidizing agent, relatively weak in the cold but much stronger at elevated temperatures. In oxidation, the acid may be reduced to sulfur dioxide, or even to elementary sulfur or hydrogen sulfide.

HYDROCHLORIC ACID

Concentrated sulfuric acid acts on sodium chloride to liberate hydrogen chloride, because this is volatile:

$$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$$

This reaction occurs at ordinary temperatures. At higher temperatures, the second hydrogen is effective:

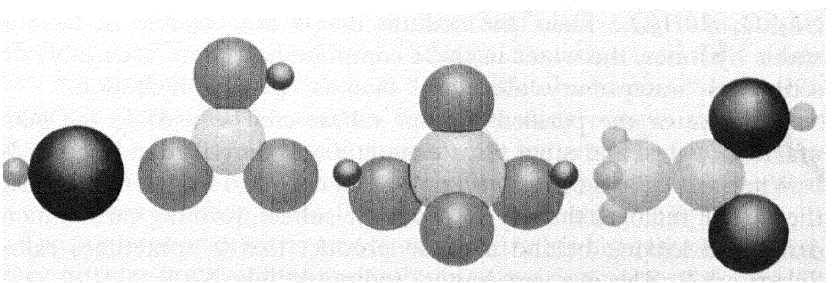
$$NaHSO_4 + NaCl \rightarrow HCl + Na_2SO_4$$

One industrial method, perhaps the oldest such method, of making hydrochloric acid uses the above reactions. Hydrogen chloride is a gas, boiling at $-85°$. It reacts with water very rapidly:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The chloride ion is a poor electron donor to a proton. The solution is therefore a strong acid, hydrochloric acid, which is frequently referred to by formula HCl, disregarding the fact that the actual compound HCl is a gas. In a solution that is saturated at room temperature, the percentage of HCl is about 36. At this concentration, not all the hydrogen chloride has reacted with water, for at equilibrium a considerable quantity of molecular hydrogen chloride is evidenced by its escape when the stopper is removed from the bottle.

Hydrochloric acid is so corrosive to metals that it must be pumped and stored in glass or plastic pipes and vessels. It is used to help clean mortar from masonry, for although ordinarily it has little effect on clay brick it attacks concrete. Commercial hydrochloric acid is usually colored a brownish yellow by iron and other impurities, and is called



HCl HNO_3 H_2SO_4 CH_3COOH acetic acid

Figure 111. Models of some useful acid molecules. These form acids in water solutions. The first three are strong acids, the last is weak.

"muriatic acid." "Muriate of soda" is an old-fashioned name for sodium chloride. The impurities are not harmful in the use of the acid for "pickling" iron—removing rust, as from scrap iron before melting.

The sulfuric acid-salt method of making hydrochloric acid is not needed where hydrogen chloride is formed as a byproduct of other reactions. For example, if the electrolysis of sodium chloride solution is carried out primarily to prepare sodium hydroxide, the byproducts are hydrogen and chlorine. Hydrogen readily burns in chlorine, forming hydrogen chloride. Chlorination of compounds containing carbon and hydrogen results in the displacement of hydrogen from the carbon by chlorine, and combination of the displaced hydrogen with additional chlorine:

$$-\text{C}-\text{H} + \text{Cl}_2 \rightarrow -\text{C}-\text{Cl} + \text{HCl}$$

Chlorination of hydrocarbons is conducted on a large scale, yielding so much hydrogen chloride as a byproduct that the need for hydrochloric acid is nearly filled, in some areas, by this process alone.

Salt Cake and Sodium Sulfide

The crude sodium sulfate resulting from the action of hot sulfuric acid on sodium chloride in the manufacture of hydrochloric acid is called "salt cake." It normally contains small amounts of sodium bisulfate and sodium chloride, as well as iron and other minor impurities. These can be removed by recrystallization from water, which can be carried out under various conditions producing various products. Commercially available in pure form from such recrystallization are anhydrous sodium sulfate, the hepta-hydrate $Na_2SO_4 \cdot 7H_2O$, and "Glauber's salt," $Na_2SO_4 \cdot 10H_2O$. Since the sodium ion is not capable of forming stable hydrates, the water in these compounds is more accurately described as "water of crystallization" than as "water of hydration."

Salt cake or the purified sodium sulfate can be used in the manufacture of glass and other silicate materials, as described in Chapter 24.

When salt cake is mixed with powdered coke and heated in a furnace, the carbon removes the oxygen from the sulfate, forming carbon monoxide and leaving behind a crude product that is sometimes called "black ash." This is a very impure sodium sulfide, Na_2S:

$$Na_2SO_4 + 4C \rightarrow 4CO + Na_2S$$

It is extracted with water. Relatively pure hydrates of sodium sulfide can be obtained by evaporation and crystallization. Sodium sulfide

has numerous applications, including synthesis of dyes and use in the dehairing of hides in the leather industry.

The term "black ash" is more commonly applied to a similar product obtained from barium sulfate. Barium sulfate is extremely insoluble and unreactive, and the conversion to sulfide, which is soluble, is useful as a means of obtaining barium in solution for the formation of other barium salts. By mixing barium sulfide solution with zinc sulfate solution, double precipitation is caused. The precipitate, an equimolar mixture of ZnS and $BaSO_4$, is used as the white pigment, "lithopone."

NITRIC ACID

When sodium nitrate, $NaNO_3$, is heated with concentrated sulfuric acid, nitric acid, HNO_3, can be distilled away, its boiling point being 84°. In this respect, the synthesis of nitric acid closely resembles that of hydrogen chloride. However, nitric acid is much less stable than hydrogen chloride, and the additional heating needed to use the second hydrogen of the sulfuric acid would decompose it. Therefore the reaction goes only half as far:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$$

The crude sodium bisulfate formed in this reaction is called "niter cake." It has a variety of uses, including the cleaning of toilets, for which a preparation of sodium bisulfate is commonly used.

Pure nitric acid slowly decomposes. In addition, it is a powerful oxidizing agent and somewhat hazardous, reacting vigorously and spontaneously with oxidizable materials. For ordinary use, therefore, it is mixed with water to make "concentrated nitric acid," which is between 65 and 70 per cent HNO_3. This acid solution is initially colorless, but on standing, especially in sunlight, it decomposes slowly, liberating oxygen and the reddish brown gaseous compound nitrogen dioxide, NO_2. In dilute solution, this oxide imparts a brownish yellow color, which is thus the characteristic color of concentrated nitric acid that has been standing in the laboratory for some time.

The preparation of nitric acid from the nitrate is not extensively used, since nitrates are found abundantly in only a few parts of the world, notably Chile, and are themselves so useful in agriculture. Most nitric acid is prepared from synthetic ammonia. When ammonia gas is passed through a flame, the hydrogen burns, forming water and releasing the nitrogen, which remains as N_2. If, however, ammonia and

oxygen are passed over a heated platinum catalyst, the nitrogen too is oxidized:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The catalytic oxidation of ammonia is called the "Ostwald process." It is the most important source of oxides of nitrogen. The oxide formed initially, NO, is called "nitric oxide." At the high temperature of the reaction, this is the most stable oxide of nitrogen, but when it is cooled and mixed with air or oxygen it unites with more oxygen spontaneously, forming nitrogen dioxide, the reddish-brown gas mentioned above. Nitrogen dioxide becomes colorless at low temperatures, owing to dimerization to N_2O_4.

To prepare nitric acid, nitrogen dioxide is mixed with water in specially designed towers. The reaction involves oxidation and reduction of the nitrogen:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The nitric oxide byproduct is again mixed with air to reform NO_2, and the NO_2 mixed with water as before. Ultimately all the nitric oxide from the oxidation of ammonia is converted to nitric acid.

Nitric acid has three important types of reaction. In dilute solution it is a very strong acid, and gives all the reactions characteristic of hydronium ion. In more concentrated solutions it has oxidizing powers, not merely through hydronium ion but by the ease of reduction of the nitrogen. In very concentrated solutions, especially when mixed with concentrated sulfuric acid, it is a nitrating agent as well as a powerful oxidizing agent.

As a consequence of its oxidizing power, nitric acid can attack metals too unreactive to be dissolved or appreciably affected by hydronium ion. Such metals are weak reducing agents, and therefore the nitrogen is not greatly reduced, nitric oxide or nitrogen dioxide being the major products. If the nitric acid is concentrated, nitrogen dioxide is the chief reduction product, because any more highly reduced product would be re-oxidized by the nitric acid. If the nitric acid is somewhat diluted, the chief reduction product is then nitric oxide. These reactions may be illustrated by the action of nitric acid on copper, which dissolves in it readily although it is unaffected by hydronium ion:

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

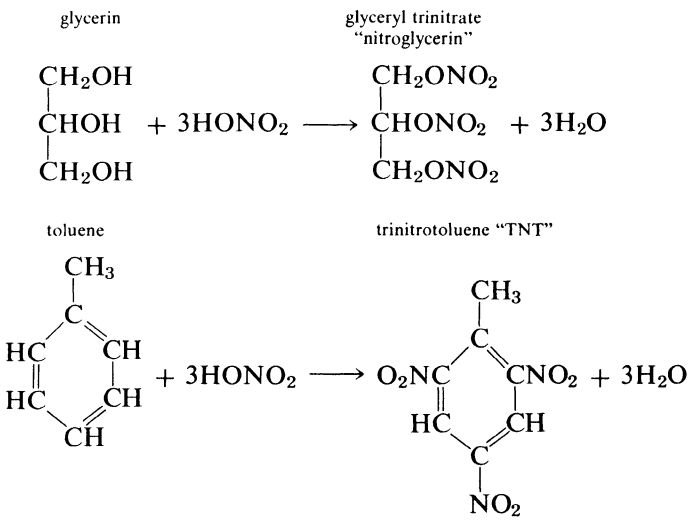
When strong reducing agents are employed and the nitric acid is rather dilute, it may be reduced to elementary nitrogen or to ammonia, which of course would form ammonium ion.

The oxidizing power of nitric acid is enhanced when it is saturated

with nitrogen dioxide. Such an acid, which is reddish-brown in color, is called "fuming nitric acid." Like pure nitric acid, this is a powerful oxidizing agent, and its action can easily set fire to wood and other combustibles.

All nitric acid is extremely corrosive to the flesh, causing ugly burns that heal very slowly. When the nitric acid is very dilute or has only a very short time in which to react, it reacts with the skin proteins to form what is called "xanthoproteic acids," staining the skin a brownish yellow. The oxides of nitrogen, especially nitric oxide and nitrogen dioxide, are extremely poisonous, being lung irritants that cause "pleural edema," the filling of the lungs with fluid, causing suffocation and death hours after exposure. The exposure may not even have been recognized, so insidious is the action of traces of these gases. No sensible chemist works with nitric acid outside of a good hood when it is being used as an oxidizing agent.

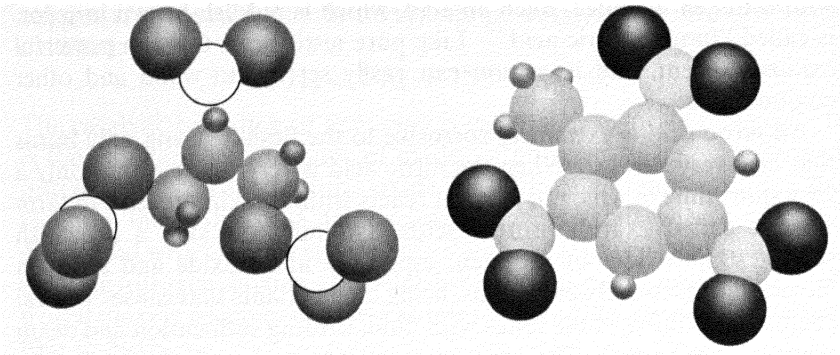
Two ways in which nitric acid can function as a nitrating agent are illustrated by the industrial preparation of the explosives nitroglycerin and trinitrotoluene (TNT):



Nitrous Acid and Nitrites

When nitric oxide and nitrogen dioxide are mixed at low temperatures, they form a pale blue liquid having the composition N_2O_3. This should be the anhydride of nitrous acid, HNO_2:

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$



"nitroglycerine" "TNT" trinitrotoluene

Notice the high positive charges on carbon in both of these compounds. In part, at least, their instability and explosiveness may result from weakening of the bonds between the carbon atoms, caused by electron withdrawal by the nitrogen and oxygen atoms. Major contributions are of course made by the high stability of N_2, H_2O, and CO_2, the chief final products, all formed as hot gases under high pressure.

Figure 112. Models representing "nitroglycerin" and "TNT."

Below room temperature, however, this oxide decomposes, forming an equimolar mixture of NO and NO_2. This mixture of compounds behaves chemically as if it were N_2O_3. With water it forms solutions of nitrous acid, and in sodium hydroxide solution it forms sodium nitrite, $NaNO_2$. The alkali metal nitrites can also be formed by heating the nitrates, which lose oxygen above their melting points. These nitrites are thus very stable.

Nitrous acid itself is a very unstable substance and has not been isolated from solution. Only dilute solutions are reasonably stable, the more concentrated solutions decomposing fairly rapidly. Nitrous acid is a weak acid, having a dissociation constant of 4.5×10^{-4}. The decomposition appears to be complex, giving nitric oxide and nitrogen dioxide, and the latter reacting with water, giving nitric acid and nitric oxide.

SPECIAL HELP

Test Your Memory

1. Describe the Frasch process.
2. Why is a catalyst needed in the "contact process"?

3. What are the two principal methods of preparing hydrogen chloride?
4. Why is hydrochloric acid a strong acid?
5. What is "salt cake"?
6. How is sulfide made from salt cake?
7. What is "nitre cake"?
8. How is nitric acid prepared from ammonia?
9. For what three types of reactivity is nitric acid noted?
10. Write equations for the oxidation of copper by nitric acid, first very concentrated, second more dilute.

Test Your Understanding

1. Why should superheated water be superior to steam in the Frasch process?
2. How are the Haber process and the contact process fundamentally similar?
3. Consider the possible electronic structures of the sulfate and bisulfate ions, and see whether there is any reason why sulfate ion might be enough more stable than bisulfate ion to make the second acid ionization of H_2SO_4 more extensive than would otherwise be expected.
4. If HNO_3 should react with H_2SO_4 as though HNO_3 were basic, splitting off water, what species of ions might form?
5. Complete by the electron transfer method the equation for the oxidation of ammonia to nitric oxide, and check with the text.

24

Introduction to Organic Chemistry

THE CHEMISTRY of life is intimately bound up with that of carbon and hydrogen compounds. To such an extent is this true that it was once believed to be a chemistry quite distinct from that of the inanimate and mineral world, distinguished by a "vital force" associated somehow with the mystery of life. Compounds that appeared to be derived from and associated with biological processes were therefore called "organic" compounds. Their chemistry is still called "organic chemistry." In 1828, a German chemist named Wohler discovered that the heating of ammonium cyanate, NH_4CNO, which was recognized to be an "inorganic" compound, converted it to "urea," NH_2CONH_2. Urea had long been known as a constituent of urine, and thus as a typical organic compound. If an organic compound could thus be formed without the agency of some mysterious life force, the distinction between organic and inorganic compounds was no longer valid. This was a startling discovery in Wohler's time, but experience since then has shown that there is indeed no fundamental separation between the

chemistry of carbon and hydrogen and that of the other elements. Thousands of carbon-hydrogen compounds have been synthesized from "inorganic" substances, without the slightest assistance from a "vital force" other than that of the chemist mixing the reagents.

Nevertheless, excellent reasons other than precedent remain for classifying and studying the chemistry of carbon-hydrogen compounds and their derivatives as a separate branch of the science, even though no definite or fundamental boundary can be drawn. Chief among these is the fact that about ten times as many carbon-hydrogen compounds as non-carbon-hydrogen compounds are known. Furthermore, although these compounds containing carbon and hydrogen cover a wide range of properties, they have certain fundamental similarities to each other that find no counterpart in the chemistry of the other elements. In order to understand these facts, we need to consider carefully the inherent nature of carbon and hydrogen.

The atomic structure of carbon includes four electrons in the four outer orbitals, and for purposes of bonding these are easily distributed, one to an orbital. With four unpaired electrons, and correspondingly four vacancies capable of accommodating outside electrons, the carbon atom can form four single covalent bonds. When it has formed these bonds it has no additional electrons that could become involved in bonding, and it has no orbital vacancies that could become involved in bonding.

The atomic structure of hydrogen includes but one electron in the single outer (and only) orbital. With one unpaired electron and one orbital vacancy, the hydrogen atom can form one single covalent bond. When it has formed this bond, it has no additional electrons and no orbital vacancies that could become involved in bonding.

Very significantly, carbon and hydrogen atoms are the only kinds of atoms, of all the chemical elements, for which the above is true. All other atoms, when they have formed as many single covalent bonds as they can, still have either outer orbital vacancies or unshared electrons. These are potentially vulnerable to further chemical attack. In the elements of the carbon group, it is the outer *d* orbitals that are vacant and available. Carbon does not have such orbitals. This means that in carbon compounds, especially where the carbon atoms form four single covalent bonds, neither the hydrogen nor the carbon are easily susceptible to chemical reaction with other substances. On this account, carbon-hydrogen compounds should tend to be unreactive.

Another important fact about carbon and hydrogen atoms is that they are very similar in electronegativity. This means that carbon-hydrogen bonds, unless influenced otherwise by other substituents, are

essentially nonpolar. For this reason also, the bonds are less susceptible to chemical attack by outside reagents. Furthermore, the nonpolarity of a hydrogen-carbon bond means that relatively little distortion of a carbon bond to another atom is caused by the hydrogen. Especially, carbon atoms holding attached hydrogen atoms can complete their valence by joining to other carbon atoms, the carbon-carbon bonds being practically the same as if the hydrogen were not present. Carbon atoms can thus join together in indefinitely extended arrays, not merely when alone, as in diamond or graphite, but also when attached to hydrogen. This means that an indefinitely large number of compounds, depending on the number of carbon atoms per molecule and on the geometrical arrangement of the carbon and hydrogen atoms, is possible. For very few other combinations of elements could this indefinitely extensive bonding be possible, especially with hydrogen attached, because very few elements are as near to it in electronegativity.

A further important fact about carbon-hydrogen bonds is that they are very strong, their strength being aided by the fact that carbon atoms are, compared to atomic sizes of the other elements, relatively very small. The strength of bonding to hydrogen falls off rather rapidly as the other atom increases in size. This tendency is in addition to the fact that large atoms do not join as strongly to each other as do smaller atoms.

Still another important factor contributing to the variable nature of carbon-hydrogen compounds is the ability of carbon, which it shares mainly with only nitrogen and oxygen, to form multiple bonds. None of the heavier atoms, using the *s* and *p* orbitals, come close to carbon in this ability.

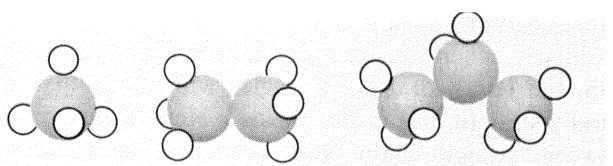
Taken together, these facts impart a "uniqueness" to carbon-hydrogen chemistry that is not approached closely by any other combination of elements. These facts, taken together, permit a vastly larger number of possible compounds of carbon with hydrogen than of any other combination of elements. Thus the chemistry of carbon and hydrogen, which is the fundamental basis of organic chemistry, is more extensive by far than that of any other elements, not because carbon atoms are inherently different from those of the other elements except in the expected way, but because of the *combination* of circumstances outlined above. In the periodic table, carbon fits in just as smoothly as any other element. The common implication that organic chemistry exists because carbon atoms themselves can do things no other atoms can do is quite misleading.

SOME VARIETIES OF HYDROCARBONS

Paraffins, or Alkanes

A molecule of methane, CH_4, is the simplest compound of carbon with hydrogen. If one hydrogen atom with its electron is removed from a molecule of methane, the remaining free radical, $—CH_3$, is called the "methyl" group. With its free electron and vacancy, the methyl group can form one single covalent bond. Therefore two methyl groups could unite by a covalent bond, forming a molecule having the formula $H_3C—CH_3$, or C_2H_6. This is a compound called "ethane." It is the result of substituting a methyl group for a hydrogen atom of methane.

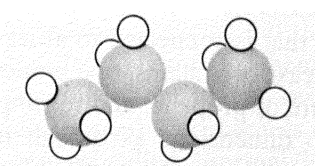
Suppose now a second methyl group is substituted for one of the three remaining hydrogens of the already methyl-substituted methane. This would result in a formula $H_3C—CH_2—CH_3$, or C_3H_8. This represents a compound called "propane." Notice that C_3H_8 is greater than C_2H_6 by CH_2, and that C_2H_6 is greater than CH_4 by CH_2. We have here the beginning of a series of hydrocarbons, each differing from



CH_4
methane

C_2H_6
ethane

C_3H_8
propane



C_4H_{10}
n-butane

(This is the first in the series for which isomeric structures are possible—hence the "*n*" to designate the "straight" chain structure.)

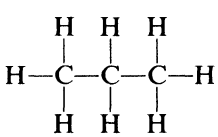
Figure 113. Homologous series of normal alkanes.

the one before by the addition of one carbon and two hydrogen atoms per molecule. We can recognize a type formula for these compounds: all correspond to C_nH_{2n+2}. For each molecule, the number of hydrogen atoms is twice the number of carbon atoms, and two more besides. Such a series of similar compounds, differing by some constant increment such as CH_2, is called a "**homologous series.**" Many such series occur in organic chemistry. Their importance lies in the fact that they permit a systematic grouping of compounds by similarities in formula and properties. Once you understand what one member of a homologous series is like, you can judge fairly well what each of the other members is probably like.

The particular homologous series introduced above is called the "alkanes," or "paraffins." We can predict that with four carbon atoms per molecule there must be twice four plus two, or ten hydrogen atoms. The formula would be C_4H_{10}. This is a compound called "butane." Similarly, if there are twenty carbon atoms per molecule, there must be twice twenty plus two, or 42 hydrogen atoms, with formula $C_{20}H_{42}$. A compound of this formula is called "eicosane."

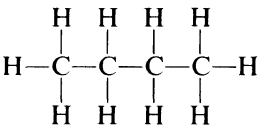
We know that all four positions around a carbon atom are equivalent, and that the angle between any two bonds is 109°28′. When two carbon atoms are attached to the same third carbon, as in propane, the chain of three carbons must therefore be bent, forming the proper bond angle. Similarly, when four or more carbon atoms are joined together in a chain, the tetrahedral bond angles will insure that the chain is never literally straight, but rather zigzag. Nevertheless, a distinction is made between "straight chain" and "branched" hydrocarbons. In this terminology, "straight chain" means that the carbon atoms are attached consecutively in a row, so that no one carbon atom is connected to more than two other carbons. "Branched" hydrocarbons contain at least one carbon atom that is connected to at least three other carbons, and thus is part of at least two chains, one branching from the other.

Consider the structure of propane, and to simplify visualization let it be represented in two dimensions as though the chain were indeed straight.

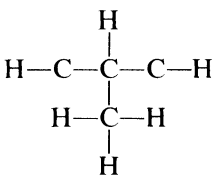


Notice that there are two methyl groups, each having three hydrogens. Since all three must be exactly alike on each methyl, and the methyl groups themselves are indistinguishable from one another, all six hydro-

gens are in exactly equivalent positions. A methyl group might be substituted for any one of the six hydrogens with exactly the same result, a butane represented by the schematic structure:



However, the central carbon of propane is not a part of a methyl group. It has attached to it not three hydrogens, but only two hydrogens and two carbons. To substitute a methyl group for one of these two hydrogens—and since they are exactly equivalent to one another, it would make no difference which—would produce a structure obviously quite different from the "straight" chain structure above:



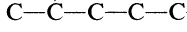
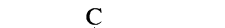
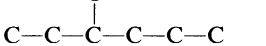
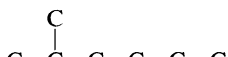
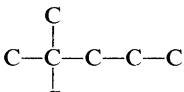
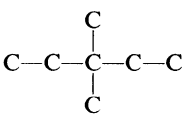
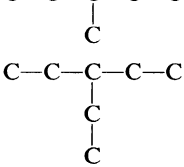
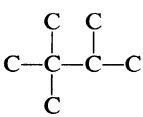
This is a branched butane. It has exactly the same formula, C_4H_{10}, as the straight chain butane. Two or more compounds differing structurally but having exactly the same molecular formula are called **"isomers."** Isomers are especially important in organic chemistry.

The Naming of Alkane Isomers

Unless one takes the trouble to sketch out the schematic structure of each isomer, one needs different names for them in order to write clearly about them. For speaking about them, such names are essential. When only two isomers exist, the problem is easily solved. Straight chain isomers are in general called "normal," abbreviated "*n*-." The butane isomer having the straight chain is called "normal butane," or simply "*n*-butane." The other isomer, since there is only one, is called "isobutane." Every chemist knows the correct structure of each when he sees or hears the name.

The possibilities for isomers, however, increase rapidly as the number of carbon atoms in the molecule increases. Some examples are listed in Table 27. Obviously, the naming of these isomers, in a simple way that tells entirely unambiguously the exact structure of each, demands

Table 27 Hydrocarbon Properties: Homologous Series, and Isomers

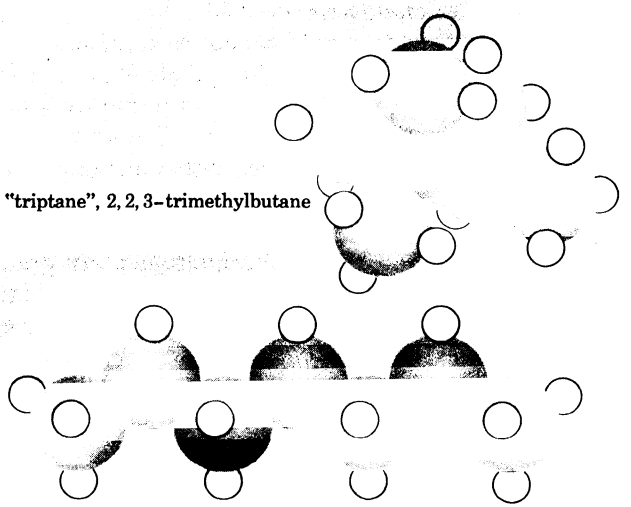
NAME	FORMULA	SKELETON	MELTING POINT, °C	BOILING POINT, °C
methane	CH_4		−182.6	−161.4
ethane	C_2H_6		−172	−88.6
propane	C_3H_8		−187.1	−42.2
n-butane	C_4H_{10}		−135	−0.6
n-pentane	C_5H_{12}		−129.7	36.3
n-hexane	C_6H_{14}		−94	69
n-heptane	C_7H_{16}		−90.6	98.4
2-methylhexane	C_7H_{16}		−118.2	90.0
3-methylhexane	C_7H_{16}		−119.4	91.8
2,2-dimethylpentane	C_7H_{16}		−125	79.1
2,3-dimethylpentane	C_7H_{16}		(glass)	90.0
2,4-dimethylpentane	C_7H_{16}		−119.4	80.8
3,3-dimethylpentane	C_7H_{16}		−135.0	86.0
3-ethylpentane	C_7H_{16}		−118.7	93.5
2,2,3-trimethylbutane	C_7H_{16}		−25	80.8

careful systematization. The system now generally adopted is to name each alkane as a **derivative**—meaning a compound derived from—of the alkane represented by the longest consecutive chain in the molecule. The carbon atoms in this chain are numbered consecutively from 1. The positions of branches on this chain are then designated by number, and the

branches are named according to the number of carbon atoms in *their* longest chain. The isomer is named by giving first the lowest number where a branch occurs, then naming the branch, then giving the next lowest number where branching occurs, then naming this branch, and so on, and finally naming the alkane from which this hydrocarbon is considered to be derived.

For example, the straight chain butane would still be "*n*-butane." The branched butane would be considered a derivative of propane, since the longest consecutive chain of carbon atoms in the molecule is 3. This is true no matter at which carbon you begin to count. Again, no matter how you begin to number the chain, you will find that there is a methyl group attached as a branch on carbon number 2 of the propane chain. The isomer thus receives the systematic name "2-methylpropane."

The common, unsystematic name of any compound is called its "trivial" name. For this particular compound, the trivial name of "isobutane" is so universally used that even a chemist specializing in hydrocarbons might need to pause to think what you meant if you referred to it as "2-methylpropane." This is not strange. Who ever calls water "hydrogen oxide"? But since trivial names do not even exist for



Although identical in molecular formula, these two isomers burn very differently in an internal combustion (automobile) engine. The straight chain compound knocks very badly; the branched one burns more smoothly (has higher "octane rating") than any other known hydrocarbon.

Figure 114. Alkane isomers.

most of the isomers beyond five carbon atoms per molecule, systematic names are indispensable. For instance, the following isomers of C_7H_{16} exist: *n*-heptane, 2-methylhexane, 3-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3-ethylpentane, and 2,2,3-trimethylbutane. Only the last has a trivial name, "triptane." This is because of its special importance as the smoothest burning, most powerful hydrocarbon fuel for an internal combustion engine.

Among the eleven possible isomers of octane, C_8H_{18}, one is called by the trivial name "isooctane" because it is used in testing the antiknock qualities of gasoline. This isomer is actually 2,2,4-trimethylpentane. It has the quality of performing very well in an internal combustion engine, especially with respect to burning without "knocking." Since it can be made in quantity, it is used as the quality standard in the familiar "octane rating" of gasoline. Straight chain alkanes beyond five carbon atoms per molecule are notoriously bad in causing engine knock, and *n*-heptane, which is also available in quantity, is used for the bottom of the rating scale. It is assigned the "octane number" of 0, and isooctane, 100. Fuels are rated by comparing their knocking tendencies under standard conditions with synthetic blends of *n*-heptane and octane. For example, a gasoline which has knocking characteristics similar to a blend of 80 per cent "isooctane" and 20 per cent *n*-heptane is assigned the octane number of 80.

The naming of organic compounds in general follows a system quite similar to that described for hydrocarbons. Details are outside the intended scope of this book, but a few other examples will be given in following sections.

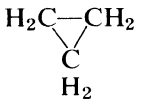
The number of possible alkanes is obviously enormous. In theory, any alkane can exist for which you can write out a structure, keeping in mind that every carbon atom must form four single bonds and all that are not to other carbon atoms must be to hydrogen. In practice, only a tiny fraction of the possibilities have been isolated and identified and characterized, but there is no reason to suspect that any of the possibilities could not actually exist.

Cycloalkanes, Cycloparaffins, Naphthenes

One restriction must be stated to limit the possibilities for alkanes in the preceding paragraph. This restriction is that if closed rings should be formed these would decrease by two hydrogen atoms for each ring, the number of hydrogens in the formula, and therefore change the type formula from that of alkanes, C_nH_{2n+2}, to a different formula,

$C_nH_{2n+2-2r}$, where r is the number of rings in the molecule. The simple rings themselves are called "cycloalkanes" or "cycloparaffins," and have the formula, C_nH_{2n}. The preceding more general formula applies to compounds which contain rings but also have open chains. Such hydrocarbons are called "naphthenes."

The simplest possible ring must contain three carbon atoms, joined as a triangle. Such a compound is C_3H_6, cyclopropane. Its molecule consists of three CH_2 groups joined as follows:



Notice that such a ring requires bond angles of 60° whereas the usual tetrahedral angle is 109°. Such bonding is therefore weaker than normal, and the ring breaks open rather readily.

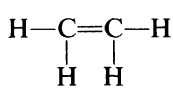
Also known are cyclobutane, cyclopentane, cyclohexane, and less commonly some of the larger ring molecules. Five- and six-membered rings, however, are most stable, the bond angles no longer being the result of strain. Hydrocarbons and their derivatives having cyclohexane rings are especially common and important.

Such rings can, of course, be incorporated in alkane type molecules, in a practically infinite variety of ways, forming thousands of compounds grouped under the heading of "naphthenes."

Alkenes or Olefins

Isomeric with the cycloalkanes are hydrocarbons resembling alkanes except for lacking a hydrogen atom on each of two adjacent carbon atoms. In the absence of these hydrogens the electrons become involved in bonding between the two adjacent carbons, supplementing the single covalent bond already there, to form a double bond. As for the cycloalkanes, the type formula is C_nH_{2n}. These hydrocarbons with a double bond are called "alkenes" or "olefins," the latter being the more trivial name, derived from words meaning "oil-forming," a property of alkenes.

The simplest alkene is known by the trivial name of "ethylene." Its systematic name is "ethene," corresponding to the fully hydrogenated "ethane." The formula may be written $H_2C{=}CH_2$. The schematic structure is:

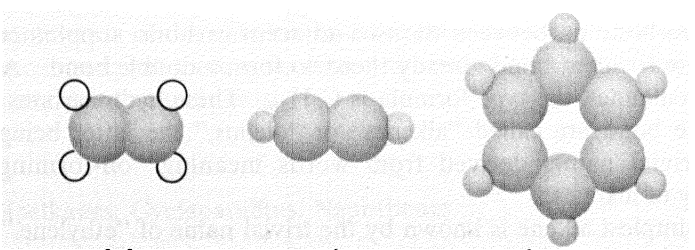


A double bond can occur between any two carbons, to each of which no more than two other carbon atoms are attached. Within this limitation, the number of alkene isomers may equal that of the corresponding alkene, and in addition include structures where the basic arrangement or carbon skeleton is unchanged but the position of the double bond differs. For example, only one alkene corresponding to the alkane ethane can exist, and one corresponding to propane. Corresponding to butane, however, two different isomeric alkenes can arise from *n*-butane, and still a third from "isobutane." The double bond can be between the first and second carbon atoms of *n*-butane or between the second and third. All three possible positions in isobutane are equivalent. The position of the double bond is also represented by number in the chain, corresponding to the carbon which the double bond *follows*. Thus, the isomers derived from the straight chain structure would be called "1-butene" and "2-butene," depending on whether the double bond follows the first or second carbon: C=C—C—C and C—C=C—C.

The number of isomeric alkenes, corresponding to a given number of carbon atoms per molecule, is generally greater even than the number of alkane isomers. Thus the number of possibilities for different compounds of carbon and hydrogen becomes even more vast.

Acetylenes or Alkynes

When each of two adjacent carbon atoms is joined to only one other atom by a single bond, two electrons and two vacancies on each would



ethylene C_2H_4 "alkene"

acetylene C_2H_2 "alkyne"

benzene C_6H_6 "aromatic"

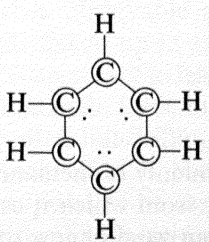
Figure 115. Ethylene, acetylene, and benzene.

be left uninvolved, but for their ability to supplement the single bond between the two carbons. Thus is formed a triple bond. The simplest example is "acetylene," HC≡CH. This is its trivial name. The systematic name would be "ethyne." Hydrocarbons in general that contain triple bonds are called "alkynes." If they have but one such bond per molecule, and otherwise resemble alkanes, their type formula is C_nH_{2n-2}.

Triple bonds can in principle exist between any two adjacent carbon atoms in a molecule, each of which is attached to only one other atom by a single covalent bond.

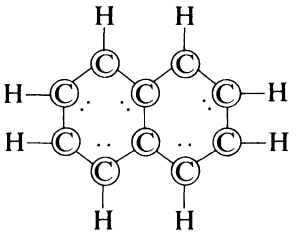
Aromatic Rings: Benzene

We have already seen in graphite how carbon atoms can form six-membered rings. A whole class of hydrocarbons distinguished by such six-membered rings begins with, and may be considered to be derived from, benzene, C_6H_6. This molecule is a planar hexagonal ring, of carbon atoms, each holding one hydrogen atom and attached to two other carbon atoms. One electron and one vacancy of each carbon atom is thus superfluous if the three bonds formed are single covalent bonds. They are not, however, single bonds, nor are they alternate single and double bonds. Instead, the six extra electrons and vacancies appear to supplement the single bonding in a very symmetrical manner, holding the ring together more strongly than single bonds alone could do and making the bonds between carbon atoms all exactly equal. We recognize this system as a system "in resonance," and represent it as follows:



The six extra electrons are equally involved with all six orbital vacancies and give the ring extra stability, so that it holds together as a unit through many kinds of chemical reactions. Hydrocarbons may also have "condensed rings" analogous to those of graphite, in which two or more benzene rings share sides in common. For example, "naphtha-

lene," $C_{10}H_8$, consists of two such rings with two carbons in common, and therefore hydrogen is attached only to the unshared carbon atoms:



All such compounds show "resonance" in their structures, which gives them similar characteristics. They are classified, together with hydrocarbons derived from them by substitution of alkyl groups in place of hydrogen, as "aromatic hydrocarbons," or simply "aromatics."

If one considers now the possibilities for combinations of aromatic rings, cycloalkane rings, double bonds, triple bonds, and alkanes as alkyl groups, one begins to recognize that organic chemistry could consist of millions of different compounds even if only carbon and hydrogen were involved. But, as we shall see, other elements can also be included.

SOURCES OF HYDROCARBONS

The greatest sources of hydrocarbons in nature, actual or potential, are natural gas, petroleum, oil shale, and coal. Together they form an immense resource of raw materials for fuels and organic chemicals of all kinds.

Natural Gas

Natural gas, consisting mainly of methane, occurs in tremendous underground accumulations, from which it can be tapped by wells. Its exact origin is unknown, but we do know that methane is the principal product from the anaerobic ("in the absence of oxygen") decomposition of organic matter by microorganisms, especially certain species of bacteria. Its natural occurrence in America is mostly in the Southwest, from which pipelines carry it to all parts of the country. Although chiefly used as a fuel it could, on demand, serve also as a source of all kinds of organic chemicals.

Petroleum

Petroleum is a mixture of hydrocarbons, mostly liquid or solid, that may range in appearance from clear liquid to tar, depending on its source. It occurs in underground accumulations often associated with certain types of geological formations known as stratigraphic traps, where internal pressures have caused layers of rock to break and slide over one another, forming relatively impervious caps beneath which oil can accumulate without serious leakage. In many instances, petroleum seems to have migrated from other locations to form these accumulations, or reservoirs. The exact origin of petroleum has been the subject of much research and speculation, but the final answers are not yet available. Probably the origins in different locations are somewhat different, although there are certain basic similarities. Such basic similarities are not easily apparent, and petroleums have been classified as "paraffinic," "naphthenic," "aromatic," or "mixed" base crudes, depending on their dominant chemical character or composition. In all types, the mixtures are almost unimaginably complex. One petroleum sample has been the subject of continuous analytical research since 1928. Thus far it has yielded 175 different pure hydrocarbons, but these account for only about 46 per cent of the whole.

The search for petroleum makes a fascinating story by itself. The surest test of its presence still remains the drill, but even this is not certain. The popular concept of petroleum reservoirs as pools of liquid oil under pressure, ready to form uncontrolled "gushers" as soon as the drill penetrates the restraining caprock, is seldom valid. Usually the oil must be pumped to the surface from a well. Sometimes the drill can go right through an accumulation of oil that is commercially useable without any obvious evidence observable at the surface. This may happen when the oil is well soaked up in sand or shale. Continuous analysis of the drill cuttings is necessary to learn when oil is encountered. Drillers have performed remarkable feats, including obtaining oil from depths of more than three miles, but drilling is far too expensive to be used alone to find oil. Much effort is exerted toward finding likely places to drill. Often, oil appears to be associated with the shores of ancient seas, long ago buried. The location of these gives clues about where to drill. Seismic exploration, by setting off explosions and charting the shock waves as they are reflected back from the various layers of rock, helps to locate geological structures which would be capable of holding oil. Different layers of rock differ in their uranium content, and hence in their natural radioactivity, which means that "radioactive well logging" (measuring the variation of radioactivity with depth, in

the well) can give helpful information. But the drill remains the final test, and even here, when a "dry hole" results, one always wonders whether oil may actually be there but just a little deeper than they decided to drill.

Oil Shale

Enormous deposits of "oil shale" occur, notably in Colorado and Utah, in the form of entire mountain ridges of oil shale rock. This is not shale that contains oil, as the name seems to imply, but rather layers of shale intermingled with very thin layers of organic matter of great chemical complexity. This material, a yellowish or tannish solid, is called "kerogen." Only when it is heated to its decomposition does it form gaseous and liquid hydrocarbons. Kerogen also contains appreciable quantities of nitrogen and sulfur, as well as the carbon and hydrogen, with the result that the hydrocarbons formed by pyrolysis are not very pure. They require much more careful refining to produce materials competitive with those obtainable from petroleum. Furthermore, no simple way of separating the kerogen from the rock before pyrolysis is available. This means that about a ton of waste rock must be handled and ground and heated and then disposed of for every barrel or two of hydrocarbon products. Consequently, oil shale remains a largely undeveloped resource, one more likely to be used after the natural gas and petroleum supplies have been largely depleted.

Coal

Coal is a familiar black carbonaceous material containing substantial amounts of mineral substances such as silicates and smaller amounts of hydrogen, oxygen, nitrogen, and sulfur. It appears definitely to be the product of long pressure of rock on vegetable matter. It occurs in enormous quantities, and has long been an important source of carbon and energy in the development of modern civilization. Although it contains some hydrogen, this is not enough to make it, alone, a useful source of many hydrocarbons. However, processes have been developed for heating coal with hydrogen gas, under conditions causing "hydrogenation of the coal," breaking carbon-carbon bonds and forming carbon-hydrogen bonds. By this means, gaseous and liquid hydrocarbons can be made. Some day this, too, may be an important substitute for petroleum.

Synthesis of Hydrocarbons

Two important methods for producing hydrocarbons from inorganic materials are especially worth mentioning. One is the production of calcium carbide by high temperature reaction between limestone and coke:

$$CaCO_3 + 3C \rightarrow CaC_2 + 3CO$$

This may well go through the intermediate decomposition of the carbonate, followed by the reduction and carbidation of the calcium oxide. Calcium carbide is the calcium salt of the very weak acid acetylene. It therefore hydrolyzes completely, liberating free acetylene and forming calcium hydroxide:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HCCH$$

Acetylene can be polymerized and hydrogenated and caused to undergo various reactions with other elements, to the extent that one could, if necessary, obtain almost any needed organic compound from this source.

The other method depends on the original developments of the German chemists Fischer and Tropsch. Carbon monoxide (for instance obtained by reduction of carbon dioxide with hydrogen) reacts with hydrogen under the influence of a catalyst (often containing cobalt) to form hydrocarbons. Innumerable modifications of this process result not only in hydrocarbons but also in many derivatives of hydrocarbons, so that here again is a means of organic synthesis of very wide scope.

SOME DIRECT APPLICATIONS OF HYDROCARBONS

Most hydrocarbons today are obtained from petroleum. This mixture contains compounds ranging in molecular weight from relatively low to very high. Since hydrocarbons are inherently low in polarity, the chief factor determining their physical properties, such as melting point and volatility, is the van der Waals forces between molecules. These forces in turn are influenced by structure, molecules that can pack closely together showing greater effects of such forces than those that cannot. Van der Waals forces are also dependent on the number of electrons in a molecule. The results of these factors are that in general (1) the higher the molecular weight the higher the melting point and the lower

the volatility, and (2) when the molecular weight remains constant, as for a set of isomers, chain branching tends to lower the melting point and increase the volatility, except when it results in the kind of symmetrical structure where closer than ordinary packing of molecules is possible. Some examples of both these effects are listed in Table 27.

The differences in boiling point are of greatest importance in separating the hydrocarbons from petroleum. Relatively few pure compounds can be separated by ordinary fractional distillation, but fractions that are similar in boiling point can be obtained. Below C_5, hydrocarbons are all gaseous, but can be separated by fractional distillation at lower temperatures and/or under pressure. The propane and normal butane are mainly used as fuels. A mixture of them condenses under moderate pressure and is used as "bottle gas" fuel. The pentanes are very volatile liquids, but may to a limited extent be incorporated in gasoline, especially for cold weather use. The gasoline fraction from petroleum contains chiefly hydrocarbons from C_6 through about C_{10}, with some heavier. Next higher come kerosene, light and heavy gas oils, lubricating oils, waxes, and asphalts.

But petroleum rarely if ever has the needed proportions of these components. To take gasoline, for example, not only is the gasoline fraction (called "straight-run") far too small to meet the needs, but it is usually inferior as a fuel and can only be used satisfactorily when blended with a larger amount of much better compounds. Therefore many processes, mostly catalytic, have been devised to convert large hydrocarbon molecules to small ones, small ones to large ones, alkanes to their isomers, alkanes to alkenes, and so on. Most petroleum products on the market are not isolated directly from the petroleum but are obtained from direct petroleum products by one or more of these "refining" processes. If you have had a close view of a modern oil refinery, you have doubtless been impressed by the multitude of intricate devices, some towering many feet into the air, which make up most of its physical equipment. These devices are only to a small extent concerned with separating the natural components of petroleum. To a much larger extent they are essential for chemical rearrangement of these natural components, giving superior and therefore more profitable products.

Among direct applications of hydrocarbons, then, may be included fuels, lubricants, waxes, and asphalts, as mentioned, and in addition high polymers such as the new and very useful transparent films of polyethylene, and synthetic rubber. But more and more, as the chemical industry continues to expand, hydrocarbons from petroleum or other sources are being used for the manufacture of all kinds of other

organic compounds, containing, in addition to hydrogen and carbon, oxygen, nitrogen, sulfur, phosphorus, chlorine, fluorine, and/or many other elements.

FUNCTIONAL GROUPS

As explained earlier, hydrocarbons tend to be unreactive chemically, because they are thermally stable and have no outer electrons or vacancies vulnerable to attack by outside reagents. Except for drastic treatment such as pyrolysis or burning, therefore, hydrocarbon groups tend to remain intact. It is possible, however, to substitute for the hydrogen of a hydrocarbon, other atoms or groups which will be chemically reactive. The result of such a substitution is called a "**derivative**" of a hydrocarbon. The active atoms or groups are called "**functional groups.**"

The most common functional groups consist of atoms originally more electronegative than the hydrocarbon group. They are thus electron-withdrawing groups, leaving partial positive charge on the hydrocarbon group and becoming partially negative themselves. It is a curious but quite reliable generalization that although all parts of a molecule must have some effect on its reactivity, one can study this reactivity very helpfully, as a rule, in terms of the nature or condition of the negative part only. We have already seen that this is true for oxides and chlorides, in which the identity of the other element could practically be ignored, the property of the compound being interpretable in the light of the condition of the combined oxygen or chlorine. The one exception is hydrogen, which, although it adheres to the rule when negatively charged, has significant protonic activity when positive, and especially when joined to some atom other than carbon. This quality is not shown by other elements. We can thus, in the hydrocarbon derivatives, afford to focus closest attention on the functional group (although we should not wish to ignore the hydrocarbon group entirely) in understanding their chemistry.

In so doing, we must recognize that in compounds where the hydrocarbon group is the more electronegative our rule holds only if the hydrocarbon group is considered the functional group, as indeed it is. This applies to those active compounds formed by joining an active metal to a hydrocarbon group directly through a metal-carbon bond. When the hydrocarbon group is partially negative, it behaves much like negative hydrogen in the hydrides, being easily oxidized and readily

hydrolyzed by water. But organometallic compounds, as these are called, are outside the intended scope of this chapter. The functional groups of most immediate interest are all partially negative in their combination with the hydrocarbon group.

Halides

One of the most useful ways of beginning the synthesis of some other organic compound from a hydrocarbon is to take advantage of the fact that the halogens can react with the hydrocarbon, substituting for hydrogen without disrupting the carbon structure. The resulting halides, by virtue of their halogen functional group, can then undergo further reactions, yielding other derivatives. For example, methane, by carefully controlled chlorination, becomes methyl chloride:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

Further chlorination would yield, successively, CH_2Cl_2 (methylene chloride, or dichloromethane), $CHCl_3$ (chloroform, or trichloromethane), and CCl_4 (carbon tetrachloride, or tetrachloromethane).

Many compounds derived from hydrocarbons by substitution of halogen (especially chlorine) for one or more hydrogen atoms per molecule are valuable not only as chemical intermediates in the synthesis of other compounds, but in their own right, as solvents for greases, fats, waxes, plastics, and other substances. Carbon tetrachloride is perhaps the most familiar example.

Relatively recently it has been found possible to replace all the hydrogen atoms of hydrocarbons by fluorine atoms. This cannot be accomplished usefully with the other halogens, but the fluorine compounds are very stable. They form, with their derivatives, a new class of com-

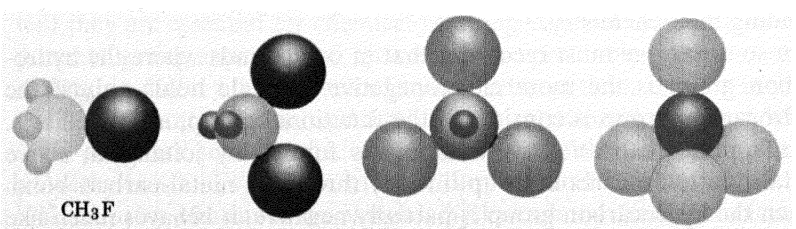


Figure 116. Successive substitution of fluorine for hydrogen on methane.

pounds that promises to rival the hydrocarbons and their derivatives in variety and number of possibilities. Research on these "perfluoro" compounds is currently very active, and has resulted already in some highly useful substances, including some extraordinary plastics. Best known of these is "teflon."

Alcohols and Phenols

Functional halide can frequently be hydrolyzed to give hydrogen chloride, or its salt, and leave hydroxyl group in its place on the hydrocarbon. If this hydroxyl group oxygen is attached to a non-benzene-ring carbon, the compound is called an "**alcohol.**" If it is attached to a benzene-ring carbon, it is called a "**phenol.**"

The simplest alcohol is methyl alcohol, or methanol, CH_3OH. There are also ethyl alcohol, or ethanol, CH_3CH_2OH, propyl and isopropyl alcohols (the second having the hydroxyl attached to the middle carbon), various isomeric butyl alcohols, and so on. The alcohols thus form a homologous series of type formula ROH, where R is some hydrocarbon group other than an aromatic ring. The most familiar of the series, ethyl alcohol, is most commonly called simply "alcohol," as though this name were sufficient to identify it. People who go blind drinking methyl alcohol, or become totally paralyzed drinking isopropyl alcohol can, if they survive, appreciate the need to be more specific. All alcohols are poisonous, but ethyl alcohol happens to be least so. We thus see at once that the nature of the hydrocarbon group *is* significant, especially physiologically. However, the similarities of alcohols that justify their consideration as a group of closely related compounds depend largely on their common content of hydroxyl group attached to non-aromatic carbon.

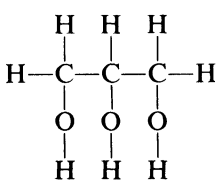
The hydroxyl group in all these alcohols is very slightly acidic, enough to react slowly with sodium, for example, forming the sodium salt or "alcoholate" and liberating hydrogen. In all, the hydroxyl group tends to make the compound water soluble, because of the possibility of protonic bridging between water and alcohol hydroxyl group. However, the larger the hydrocarbon group, the less water-soluble the alcohol. Although methyl and ethyl alcohols are completely miscible with water, the higher alcohols tend toward limited miscibility and finally very low solubility. Alcohols in general are excellent solvents for organic chemicals—other hydrocarbon derivatives—and often serve as reaction media for organic reactions in which the hydroxyl group does not participate.

The presence and mobility of the extra electrons and vacancies on the benzene ring appear to impart greater acidity to the hydroxyl group when it is attached directly to the ring. The simplest compound of this type, hydroxybenzene, or "phenol," is also called "carbolic acid," which is the trivial name. Phenols are only very weakly acidic even though more so than alcohols. Unlike the alcohols, they are very corrosive to the body tissues. Phenols have greater antiseptic properties than alcohols, and some are used in disinfectants. "Bakelite" is an example of a plastic the manufacture of which consumes large quantities of phenol. Many other chemical applications make this an important class of compounds.

Polyhydroxy Compounds

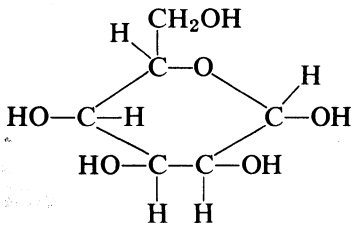
Ethyl alcohol may be considered to be derived by substituting a hydroxyl group for a hydrogen atom on ethane. If a second hydroxyl group is substituted for a hydrogen on the other methyl group of ethane, the compound CH_2OHCH_2OH results. This "dihydroxyethane" or "ethanediol" is commonly called "ethylene glycol." It is miscible with water in all proportions—a property that tends to be enhanced by increasing the number of hydroxyl groups—and gives solutions of low freezing points. The most familiar use of ethylene glycol is as the main constituent of "permanent antifreeze," which also contains corrosion inhibitors. Ethylene glycol is also a valuable solvent, and a useful intermediate in organic syntheses. Any dihydroxy-hydrocarbon is called a "**glycol**"; many are known.

Two or more hydroxyl groups appear to be very unstable on the same carbon, for water is split out whenever a reaction would produce such an arrangement. However, any or all carbons in the same molecule may hold one hydroxyl group each. When this happens to propane, the trihydroxyalcohol called "glycerin" or "glycerol" results. This has the structure:



A large number of compounds are known in which the number of hydroxyl groups (assuming all oxygens to be part of hydroxyls) equals the number of hydrogens attached directly to carbon. Since this gives

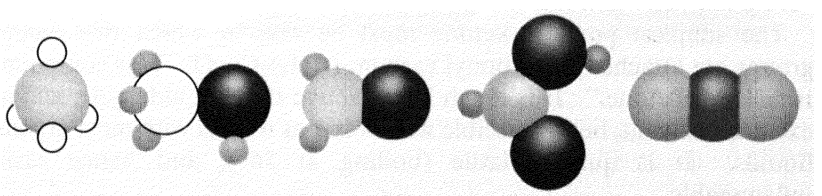
the equivalent of water plus carbon these compounds are called "**carbohydrates,**" although the water is certainly not present as a hydrate of carbon. For example, the sugar called "glucose" has the formula $C_6H_{12}O_6$. This corresponds to six water molecules to six carbon atoms, but here not all oxygens are present as hydroxyl:



Similarly, cane sugar, $C_{12}H_{22}O_{11}$, is a carbohydrate. The term includes sugars and starches and cellulose, the starches being somewhat polymeric and cellulose being highly polymeric. Except for a little elementary carbon applied to its surface in a manner alleged to be significant, this page before your eyes is mainly cellulose.

Aldehydes and Ketones

An alcohol can be regarded as the first intermediate product in the oxidation of a hydrocarbon, in which one hydrogen is displaced by a hydroxyl group. As stated, the same carbon atom cannot hold two hydroxyl groups without splitting out water. The second step of the



CH_4	CH_3OH	H_2CO (HCHO)	HCOOH	CO_2
methane	methyl alcohol	formaldehyde	formic acid	carbon dioxide

Note that these products correspond to successive replacement of H by OH, with splitting out of water whenever two OH groups would be attached to one carbon—such structures almost always tend to be unstable with respect to $-\overset{|}{C}=O + H_2O$. Thus HCHO could result from loss of H_2O from $CH_2(OH)_2$, and CO_2 from loss of H_2O from carbonic acid, $O=C(OH)_2$.

Figure 117. Progressive oxidation of methane.

oxidation then might place a second hydroxyl on the same carbon that holds the first, but if so water would split out, leaving behind then a "carbonyl" group, which is simply a carbon doubly bonded to oxygen, =C=O. Two classes of compounds may result. If at least one of the other two bonds of the carbonyl carbon is to hydrogen, the compound is classed as an "**aldehyde,**" for which the characteristic functional group is —CHO (—CH=O). If both of the other two bonds on carbonyl carbon are to other carbon atoms instead of to hydrogen, the compound is classed as a "**ketone,**" $R_2C=O$, where both R's represent hydrocarbon groups.

The reason for distinguishing aldehydes from ketones is that the hydrogen on the aldehyde group is relatively reactive, much more so than a hydrocarbon group would be, especially toward further oxidation. Aldehydes also polymerize much more readily than ketones.

The simplest aldehyde is the one with both remaining bonds of the carbonyl carbon attached to hydrogen: $H_2C=O$ or HCHO. This is a gaseous compound called "formaldehyde." It is easily polymerized to a solid called "paraform," which, when heated, gives off formaldehyde monomer again. It dissolves readily in water giving solutions called "formalin." Formaldehyde kills microorganisms, and is used as a disinfectant and in embalming. The bakelite plastic mentioned earlier as being derived mainly from phenol is actually a copolymer of formaldehyde and phenol, which combine, splitting out water, to form indefinitely extensive structures.

The next aldehyde has one of the carbonyl carbon bonds to hydrogen and the other to methyl. A homologous series of aldehydes thus exists, with increasing size of the alkyl group. The methyl compound is called "acetaldehyde," and has the formula CH_3CHO.

The simplest possible ketone must be that in which two methyl groups are attached to carbonyl carbon: $(CH_3)_2C=O$. This compound is called "acetone." It is much less reactive than an aldehyde, and an excellent solvent, being miscible with water as well as with most organic liquids. It is quite volatile (boiling at 56°), and hence easily inflammable.

Other ketones form homologous series with acetone, the size of the alkyl groups increasing separately or simultaneously—i.e., methylethylketone or diethylketone.

Carboxylic Acids

Oxidation of formaldehyde, by substituting a hydroxyl group for one of the hydrogen atoms, produces the compound HC(OH)=O, usually

written HCOOH. This is "formic acid." The —COOH group is called the **"carboxyl"** group. It is the functional group characteristic of a class of organic acids called **"carboxylic acids."** These are ordinarily weak acids, formic acid being the strongest. That they are much more acidic than alcohols can be readily understood from the facts of inorganic acids previously considered. Just as HNO_3 is stronger than HNO_2, and H_2SO_4 stronger than H_2SO_3, the addition of oxygen to the hydroxyl carbon increases the hydroxyl acidity by withdrawing charge from the hydroxyl, making the hydrogen more positive. The difference between methyl alcohol and formic acid is simply that two of the hydrogens from the methyl carbon in the alcohol are replaced by one oxygen, which is much more electronegative, in the acid.

The odd trivial names of the aldehydes can now be explained. Formaldehyde is the aldehyde which oxidation converts to "formic acid." Acetaldehyde is the aldehyde which is converted by oxidation to "acetic acid," CH_3COOH.

Formic acid is a constituent of certain ant and bee stings, making them far more painful than the mere insertion of a sharp instrument. Formic acid is so named from the Latin word for ant, for it can be obtained by what is aptly termed the "destructive distillation" of ants. Acetic acid is the product when the fermentation of sugars continues beyond alcohol, the oxidation series being ethane, ethyl alcohol, acetaldehyde, and acetic acid. Further oxidation would lead to carbon dioxide and water. Fermentation of apple cider beyond the "applejack" stage leads thus to "cider vinegar," far less exciting as a beverage. Vinegar in general is a very dilute solution of acetic acid. Homologous series of carboxylic acids can include all compounds of type formula RCOOH, R representing a homologous series of alkyl groups. These acids are especially unpleasant in the lower part of the series, having strong, acrid odors. The C_4 acid is a characteristic component of rancid butter and of the atmosphere in poorly ventilated gymnasiums. Higher acids impart an aesthetic unpopularity to the billy goat. Salts of long chain acids are called **"soaps."** They are valuable not only in cleansing but also mixed with oil to form lubricating greases.

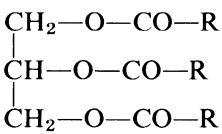
Esters

Carboxylic acids react with alcohols to form compounds of generally sweet and agreeable odor called **"esters."** Water is split out in this reaction, which is called "esterification":

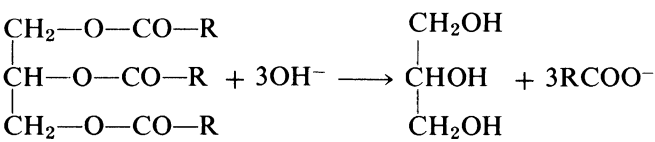
$$ROH + R'COOH \rightarrow R'COOR + H_2O$$

Formally, esterification seems to resemble acid-base neutralization in water, the ester being analogous to the salt. However, the reactions are quite dissimilar. Acid-base neutralization in aqueous solution occurs almost instantly, by the interaction of ions. The water is formed by combination of hydroxide from the base with proton from the acid. Esterification occurs very slowly, even with a catalyst present, which is essential. The ester is in no sense as ionic as a salt, and the water split out, experiments have proven, consists of hydrogen from the alcohol and hydroxyl from the acid.

Esters are not easily hydrolyzed back to their original alcohol and carboxylic acid, merely by water, but alkaline solutions are quite effective, liberating the alcohol and forming the carboxylate anion. A very important application of this reverse of esterification is found in the manufacture of soap. Important naturally occurring esters are the substances called **"fats."** Fats consist mainly of "glycerides"—esters of glycerin—with long chain carboxylic acids:



Soap consists of metal salts, usually sodium salts, of these monobasic acids. Since fats are the most readily available source of the acids, soap is made by "de-esterification" of the fats with sodium hydroxide. The glycerin is liberated as a byproduct, and the soap is the sodium salt of the carboxylic acids:



This process is called **"saponification,"** which means "making into soap." Any ester can be hydrolyzed, of course, whether or not the acid portion is of the right nature to make soap.

Esters of many alcohols and relatively low molecular weight carboxylic acids find numerous applications in flavoring and perfumery.

Ethers

The removal of one mole of water from two moles of alcohol produces a compound in which two alkyl groups are bridged by one oxy-

gen atom. Such compounds are called "**ethers.**" The simplest ether is dimethylether, CH_3OCH_3. It can be formed from methyl alcohol as follows:

$$CH_3OH + CH_3OH \rightarrow CH_3—O—CH_3 + H_2O$$

You may notice that this is an isomer of ethyl alcohol, having the same formula, C_2H_6O. It is very different in its properties, being gaseous and lacking a hydroxyl group. This absence of hydroxyl group means inability to associate through protonic bridging, which results usually in much greater volatility of ethers than for the isomeric alcohols.

The ether that is called "ether," although this is actually only a generic term, is "diethylether," $C_2H_5—O—C_2H_5$. Diethylether (as well as dimethylether) is familiar as an anaesthetic widely used in hospitals. Its high volatility (b.p. 35°) and high inflammability, producing explosiveness when mixed with air, require extreme care in avoiding sparks of static electricity (or lighted cigarets) when ether is being used. The liquid ethers are also excellent solvents, being relatively unreactive chemically, and thus suitable as reaction media for a great variety of organic reactions.

Polyethers result when water is similarly split off from glycols, because of their two functional groups which permit ether formation at two different points of the molecule. They have applications as lubricants, hydraulic fluids, and other products.

Mercaptans

Sulfur can substitute for oxygen in most organic compounds. The most familiar example is perhaps the sulfur analogs of alcohols, which are called "**mercaptans,**" of formula RSH. The simplest mercaptan is methyl mercaptan, CH_3SH. Sulfur lacks the capacity to form protonic bridges, which is so significant in oxygen. Consequently, mercaptans in general are much more volatile than the corresponding alcohols. Methyl mercaptan, instead of being a liquid like methyl alcohol, is a gas (b.p. 6°). The mercaptans, like the alcohols, are slightly acidic. Unlike the alcohols, those that are appreciably volatile have exceedingly disagreeable odors. As a result, mercaptans as a class are notorious for unpleasant odors. Their reputation is unfair, since the higher mercaptans in pure state are rather sweet and agreeable in odor. These odors, of the lower molecular weight mercaptans, are extremely impressive on the olfactory nerves of humans, and can be detected in astonishingly small concentrations. Traces of ethyl mercaptan, C_2H_5SH, are delib-

erately included in manufactured gas used for home cooking fuel, for its carbon monoxide and hydrogen are both odorless and leakage might be discoverable otherwise only by death. The mercaptan makes it easy to recognize that leaking is occurring, and also makes one anxious to do something to stop it. Butyl mercaptan, C_4H_9SH, seems to be a principal ingredient in the protective fluid of the skunk. No easy way of thoroughly destroying this odor in a quick and harmless way seems to be known. Fortunately, however, tomato juice, applied over the sprayed area, will for unknown reasons (possibly associated with its acidity) reduce the odor to just within the limits of human tolerance. This, compared to full strength, is a very substantial reduction, indeed.

Amines

Substitution of alkyl groups for hydrogen on ammonia gives organic compounds known as "**amines.**" These are "primary," RNH_2, "secondary," $RR'NH$ or R_2NH, and "tertiary," $RR'R''N$ or R_3N. These amines are fairly volatile, although less so than ammonia, and have characteristic fishy odors. Like ammonia, they can act as electron donors, in the formation of coordination compounds.

Amides

When the ammonium salt of a carboxylic acid is heated, water is lost, and the product is an "**amide,**" which resembles a carboxylic acid but has an "amino," NH_2, group instead of a hydroxyl group:

$$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

Polymers

Small organic molecules can join together to form indefinitely large organic molecules in two ways. The process is called "**polymerization.**" The individual types are called "addition polymerization" and "condensation polymerization."

Addition polymerization results from the joining together of unsaturated molecules through their multiple bonds. For example, ethylene can be caused to polymerize by adding molecules together through the double bonds, forming long chains, $—CH_2—CH_2—CH_2—CH_2\ldots$

indefinitely. Of this nature are such useful materials as "polyethylene" plastics.

Condensation polymerization involves a reaction between the functional groups of each of two molecules in which a small molecule, usually water, is split out and the residues join together. For instance, the splitting of water in the formation of ethers could be called a condensation polymerization. However, polymerization implies more than just dimerization: it implies indefinitely extensive condensations. Such can only occur if each original molecule possesses not just one but two or more functional groups. For example, if water is split out of glycol instead of alcohol, polyethers result. If water is split out of glycols and dicarboxylic acids, polyesters result. If water is split out of diamines and dicarboxylic acids, polyamides result. Difunctional compounds alone tend to form chains, but tri- or polyfunctional compounds can produce three-dimensional cross-linking. All these and similar reactions can be employed to produce a wide variety of enormously useful liquid and solid products of high molecular weight, often good mechanical properties, and sometimes astonishingly high resistance to chemical reagents.

Polymers have great importance in nature as well as in synthetic products. Proteins, for example, are polyamides, condensation products of amino acids, which can polymerize by virtue of possessing in one molecule both kinds of functional groups needed. Fortunately, we do not need to rely solely on van der Waals forces to hold us together, great strength being contributed by covalent bonding in highly polymeric compounds within our bodies.

SUMMARY

Within certain limitations and restrictions, which are not very narrow or confining, an almost infinite number of possible compounds could be made, starting with hydrocarbons and substituting various functional groups for the hydrogen atoms. The wonder, when we understand how vast the possibilities, is not why there are so many organic compounds, but rather why there are not more. As this is being written and printed, hundreds more *are* being made. The future shows not even the slightest suspicion of any ultimate limit. We may be thankful that the fundamentals remain, and presumably will remain, relatively fixed. Progress in the study of fundamentals will probably be mainly in the direction of greater depth of understanding, leaving us with at least a reasonably possible start on the impossible task of learning all that can be known

about chemistry. The empirical knowledge of new reactions, new compounds and their properties, will continue to expand, farther and ever farther beyond any individual human capacity to absorb it.

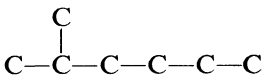
SPECIAL HELP

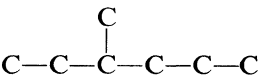
Test Your Memory

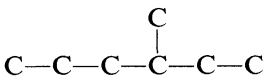
1. Why are compounds of carbon and hydrogen so unusually numerous?
2. What is the type formula for alkanes?
3. What is meant by "homologous series"?
4. Write out structural formulas for all possible C_{10} alkanes (decanes) and give the systematic name to each.
5. What is a "naphthene"?
6. What is the type formula of an olefin?
7. What is the structural formula of acetylene?
8. What is "benzene"? What are "aromatic" hydrocarbons?
9. What are the four principal natural sources of hydrocarbons?
10. How can hydrocarbons be synthesized from inorganic materials? Name and describe two methods.
11. What are the chief usable fractions of petroleum, in order of increasing boiling temperatures?
12. What is meant by "functional group"?
13. Name some organic halides and their uses.
14. Distinguish among an "alcohol," a "phenol" and a "glycol."
15. Distinguish between "aldehydes" and "ketones."
16. What are the similarities and differences between neutralization and esterification?
17. What is a "fat" and how is it "saponified"?
18. Identify "ethers," "amines," "mercaptans," and "amides."
19. What is the relationship between "polyfunctional" molecules and "condensation polymers"?

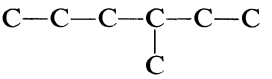
Test Your Understanding

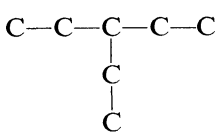
1. Proceeding along any homologous series of compounds in the direction of increasing molecular weight, what do you predict will happen to the melting point and volatility, and why?
2. Which of the following carbon skeleton structures represent identical, and which isomeric, compounds?

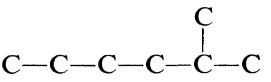
(*a*) 

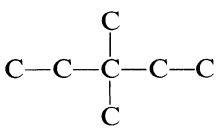
(*b*) 

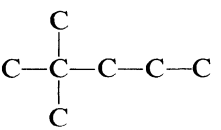
(*c*) 

(*d*) 

(*e*) 

(*f*) 

(*g*) 

(*h*) 

3. What reasons can you suggest for diminished stability of bonding when a propane chain is closed to form cyclopropane?
4. Suggest a typical chemical reaction of an olefinic double bond.
5. Predict the products of reaction between dimethyl magnesium and water, and explain.
6. Predict the products of a reaction between an alkyl halide and sodium metal, and explain.
7. Predict the products of a reaction between a sodium alcoholate and an alkyl halide, and explain.
8. Predict the products of a reaction between sodium hydroxide and chlorobenzene, and explain.
9. Adopting the conventions of oxidation number, including $+1$ for hydrogen, determine the oxidation state of carbon in each of the following: CH_4, CH_3OH, CH_2O, HCOOH, CO_2.
10. Predict and explain the effect on the strength of acetic acid of substituting fluorine atoms for hydrogen on the methyl group.
11. What analogy can be drawn between the pairs of compounds, (*a*) HNO_2 and HNO_3, and (*b*) CH_3CH_2OH and CH_3COOH?
12. What kind of product would you expect to form when water is removed from a mixture of glycol and dicarboxylic acid?
13. Two hydroxyl groups on the same carbon atom in an organic compound appear to be very unstable, water being lost at once. For example, attempts to prepare $CH_2(OH)_2$ result only in H_2O and CH_2O. What inorganic analogy can you think of?

25

Survey of the Major Group Elements

CHAPTER 7 consisted of an introduction to the periodic table, emphasizing the relationships of the atomic structure of the elements to their physical properties. Periodic changes in the chemical properties of the elements were stressed in Chapters 11, 12, and 13. The purpose of this chapter is to survey systematically the properties of the "inert-shell" and the "18-shell" elements, which in the periodic table are to be found comprising the "major groups," and also the zinc-cadmium-mercury family. The latter are conventionally included with the subgroups primarily because no other place for them seems open. In fact, however, they differ from all other subgroup elements in never utilizing their underlying *d* orbitals for bonding, but using only the outer shell. Electronically, they are just as truly "major group" elements as the gallium, indium, thallium, and germanium, tin, lead that follow them. Figure 118 presents the "major group" part of the periodic table, and makes a place, although of necessity somewhat awkwardly, for zinc, cadmium, and mercury.

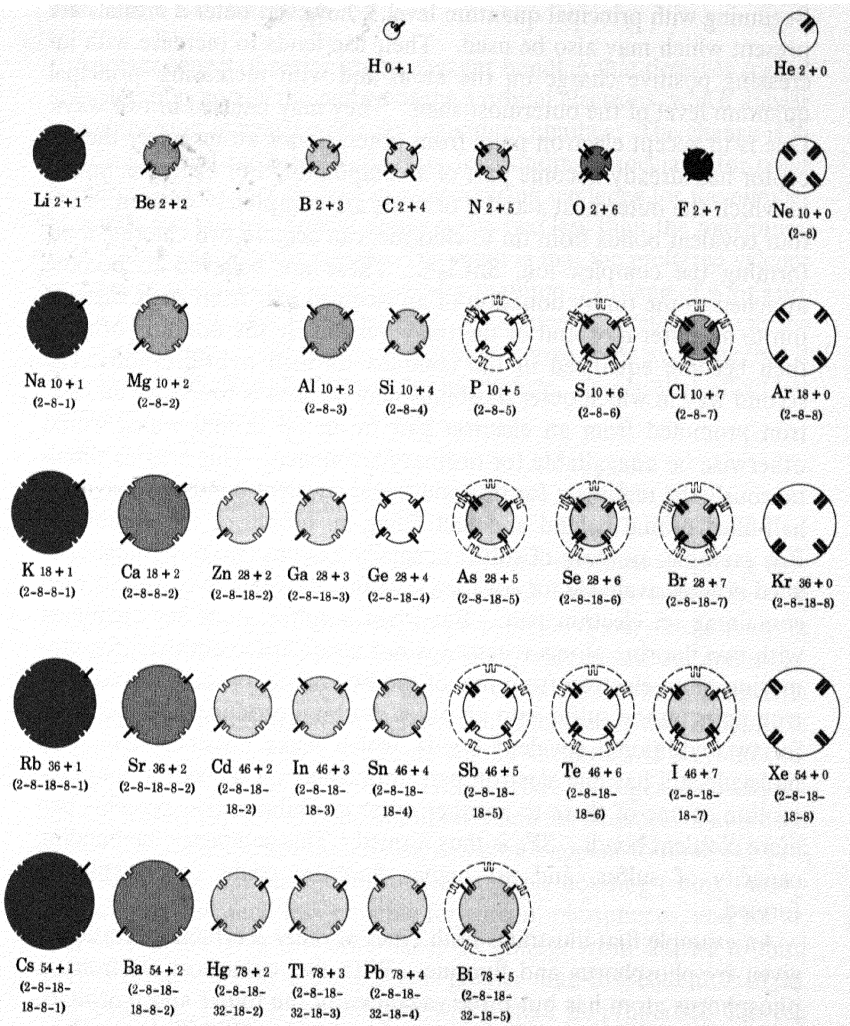


Figure 118. Schematic representation of major group valence structures.

General Bonding Characteristics

The major group elements are characterized by their bonding, which makes use of orbitals and electrons of the outermost shell only. The orbitals of lowest energy are the *s* and *p* orbitals, which are therefore most commonly involved in the chemical combination of these elements.

Beginning with principal quantum level 3, however, outer *d* orbitals are present which may also be used. Their use tends to increase with increasing positive charge on the atom and with increasing principal quantum level of the outermost shell. They may be used in two ways. One is to accept electron pairs from other, donor atoms, after the acceptor has already become part of a compound. For example, $SnCl_4$, in which the outermost *s* and *p* orbitals are completely utilized in the four covalent bonds from tin to chlorine, can acquire two chloride ions, forming the complex ion, $SnCl_6^=$. These are believed to become attached to the tin by donation of an electron pair from each chloride ion to an outer *d* orbital of the tin. Very likely the bonding orbitals then become equalized in the complex through hybridization. The second way in which outer *d* orbitals may be used is to receive an electron promoted from an electron pair in an *s-p* orbital which would otherwise be unavailable for ordinary covalence. This creates simultaneously the requisites for two additional covalent bonds, by leaving a half-filled orbital behind and half filling an orbital of the *d* sublevel. For example, an atom of sulfur normally has but two outermost half-filled orbitals available for covalent bonding, the other two orbitals each containing an electron pair. But when a sulfur atom has combined with two fluorine atoms reaction is not necessarily complete, for promotion of an electron from one of the two otherwise uninvolved electron pairs on the sulfur into an outer *d* orbital produces the requisites for two additional covalent bonds, which make possible SF_4. This molecule still has one electron pair untouched, on the sulfur, and promotion of one of these to another outer *d* orbital makes possible two more covalent bonds. SF_6 is thus formed. This completes the bonding capacity of sulfur, and no higher fluorides could conceivably be formed.

An example that illustrates both types of outer *d* orbital utilization is given by phosphorus and fluorine. With five outermost electrons, a phosphorus atom has but three vacancies in the four *s* and *p* orbitals, and can normally form but three covalent bonds. With fluorine, phosphorus can form PF_3. Promotion of one of the remaining uninvolved electron pair to an outer *d* orbital of the phosphorus creates the requisites for two additional covalent bonds, and thus PF_5 can result. Although this is the limit of ordinary covalence for phosphorus, since no other electrons are available, the five fluorine atoms do not cover up the phosphorus atom completely, as do the six in SF_6. A fluoride ion, by donating a pair of its electrons, can therefore become coordinated to the PF_5 through another of the outer *d* orbitals of the phosphorus atom, forming the complex ion PF_6^-.

The "Inert Pair Effect"

Another aspect of major group element bonding that deserves special consideration here is the nature of the *s* orbital electrons, which appear to change with increasing principal quantum number. The change is in the direction of reduced availability for bonding, especially for polar bonding. It becomes evident in an increasing tendency for the number of bonds formed by 18-shell atoms to be two less than the maximum, going down the periodic group. The result is that the preferred valence in polar compounds is 1 instead of 3 for thallium, 2 instead of 4 for lead, and 3 instead of 5 for bismuth. This phenomenon is referred to as the "inert pair effect." No simple explanation seems to be available, but it is a well-established experimental observation. No similar effect has been noted in the transition elements.

Electronic Variations within Groups

Helium atoms differ from all the other inert elements in having only 2 electrons in the outermost quantum level. All the others have 8. Similarly, all the active elements of period 2 have only 2 electrons in the shell directly beneath the valence shell, whereas all the active elements of period 3 have 8. The most obvious difference in properties that seems to be related to this electronic difference is that of multiple bonding, and applies only where no wholly vacant *s* and *p* orbitals remain (C, N, O, versus Si, P, S). Thus, carbon, nitrogen, and oxygen appear readily capable of bond multiplicity and the closeness of approach which this requires, but underlying shells of 8 appear to hinder or prevent such close approach, and similar multiple bonding (using *s* and *p* orbitals) seems much less possible for silicon, phosphorus, and sulfur. But even apart from this difference, the change from second to third period element wthin a group seems greater than subsequent changes. For example, there is probably a wider span in properties between lithium and sodium than between sodium and potassium, wider between oxygen and sulfur than between sulfur and selenium, or between fluorine and chlorine than between chlorine and bromine.

GROUP IA

Some properties of these elements are listed in Table 28. As would be inferred from their possession of only one outermost electron per atom, and from the relative ease of its removal (ionization energy),

these elements are all active metals. They crystallize in the body-centered cubic structure, in which every interior atom is surrounded by 8 nearest neighbors at the corners of a cube surrounding it, and by 6 more neighbors 15 per cent farther away at the centers of the 6 adjacent cubes. The relative weakness of metallic bonding, when each atom provides but a single valence electron and only *s* and *p* orbitals for sharing, and when the atoms themselves are not very compact, gives these metals softness and weakness unusual in metals. Lithium is hardest, and the hardness diminishes down the group, sodium being easily cut with a knife and cesium being about as soft as beeswax. All are good conductors of electricity.

Lithium, about 0.05 per cent, improves the tensile strength, hardness, and corrosion resistance of magnesium, aluminum, and lead. Sodium

Table 28 Some Properties of the Alkali Metals (Group IA)

	Li	Na	K	Rb	Cs
atomic number	3	11	19	37	55
electronic structure	2-1	2-8-1	2-8-8-1	2-8-18-8-1	2-8-18-18-8-1
or, one electron beyond:	He	Ne	Ar	Kr	Xe
atomic weight	6.939	22.990	39.102	85.47	132.905
atomic volume, ml/mole	13.1	23.7	45.3	55.9	70.0
density, g/ml	0.53	0.97	0.86	1.53	1.90
melting point, °C	180.5	97.8	63.2	39.0	28.6
heat of fusion, kcal/mole	0.72	0.62	0.55	0.52	0.50
boiling point, °C	1331	890	766	701	685
heat of vaporization, 25°, kcal/mole	32.19	21.28	18.53	16.54	15.75
covalent radius, Å	1.34	1.54	1.96	2.11	2.25
ionic radius, M^+, Å	0.60	0.95	1.33	1.48	1.69
heat of atomization, kcal/mole	37.1	26.0	21.5	20.5	18.8
electronegativity	0.86	0.85	0.80	0.77	0.76
ionization energy, first, kcal/mole	124	119	100	96	90
same, second	1738	1086	732	632	540
electrode potential, volts	3.045	2.714	2.925	2.925	2.923

Notes: (1) The weaker bonding of larger atoms is shown, from Li to Cs, by decrease in heat of atomization, melting point, heat of fusion, boiling point, and heat of vaporization; ionization energy and electronegativity also decrease.

(2) The second ionization energy, so much larger than the first, shows how difficult it is to break into the closed inert-shell beneath the valence shell.

(3) The higher electrode potential for Li is probably the result of higher heat of hydration of the much smaller Li^+ ion.

metal has some application as a heat exchange medium, since it is both very low melting and excellent as a conductor of heat. As such, it has some application in power plants, and serves as a liner in exhaust valves of aircraft and heavy duty bus and truck engines, to help prevent overheating and valve sticking. Cesium has limited application in photoelectric tubes, as does rubidium, since the mobility of their valence electrons is easily influenced by the absorption of light. Otherwise, the metals of this group have essentially no applications as metals on a commercial scale.

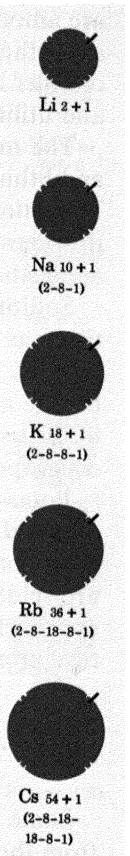


Figure 119.

Chemically, these metals are extremely reactive, reactivity increasing from lithium to cesium. They are lowest in ionization energy and in electronegativity, and thus readily lose electrons to more electronegative atoms, frequently forming positive ions. With oxygen they react readily. Lithium is only slowly attacked by dry oxygen but still too readily to be stored without protection, as by immersion in an inert liquid. A freshly cut surface of sodium has a bright, pinkish metallic luster but quickly fogs over on exposure to the air. Potassium is more rapidly oxidized, even catching fire, especially if the air is slightly moist. Rubidium and cesium are spontaneously inflammable. All these metals also react vigorously, if not almost explosively, with water, liberating hydrogen from the water and forming strongly alkaline solutions of the metal hydroxide. For this reason, the family name of the metals of this group is the **"alkali metals."**

Naturally, the alkali metals would not be expected to be found uncombined. They occur as salts, mainly where former seas or salt lakes have evaporated. Sodium chloride is most abundant. Potassium chloride is found mixed with other salts but only in moderate supply, Lithium, rubidium, and cesium salts are much rarer. Being themselves such strong reducing agents, the alkali metals cannot easily be reduced from their salts. Their principal method of production is electrolysis of a molten salt. Sodium, which is by far the most available, is frequently used as a reducing agent, often in the production of other metals, such as titanium.

The alkali metal cations are among the largest of cations and possess, along with their unit positive charge, the stable electronic structure of the inert element atoms. Consequently, they are not themselves easily influenced by external electrical fields, nor do they exert a strong

polarizing influence on negative ions. They therefore tend to be least active toward electron donors, forming fewer stable complexes than almost any other simple cations. Furthermore, their salts with anions are among the most stable. Most such salts are quite soluble in water and other polar solvents. In general, they are more soluble than salts of other metals with the same anions. This property gives special value and utility to the compounds of the alkali metals.

The most important compounds of lithium include lithium hydride and lithium aluminum hydride, $LiAlH_4$, both excellent reducing agents. The latter is especially valuable because of its solubility in ether, wherein it is extremely useful in organic syntheses. Lithium chloride has some application in solution in controlling humidity for air conditioning.

Sodium compounds are extremely important in large scale applications, as well as in the research laboratory. The great raw material for these is sodium chloride, most of which is converted to sodium carbonate and sodium hydroxide, as explained in Chapter 22. In addition to the uses detailed there, sodium compounds are used in production of drugs, perfumes, dyes, and for many other applications.

Potassium compounds are especially important in agriculture as an essential to plant growth, where the chloride, carbonate, and nitrate are most commonly applied. In other applications, potassium compounds are seldom superior to the corresponding sodium compounds, which are much cheaper. Rubidium and cesium compounds have little practical application.

GROUP IIA

Some properties of these elements are listed in Table 29. They differ from the alkali metals in having two instead of one outermost electron, surrounding an electronic configuration like that of an inert element. With still an excess of vacancies over electrons in the outer orbitals, these elements are all metallic, this quality increasing with increasing atomic radius and decreasing ionization energies down the group. The atoms are somewhat more compact than those of the preceding alkali metals, and have correspondingly higher electronegativity. The larger number of valence electrons, together with the smaller size that permits closer interaction, give to these elements stronger metallic bonding, with correspondingly higher melting and boiling points. As in the alkali metal family, the hardness of the metal is greatest for the smallest atoms, and diminishes from beryllium, which is quite hard, to barium (and presumably radium) which are relatively soft. The melting points follow a trend in the same direction.

These elements are chemically somewhat less reactive than the alkali metals, but are still very reactive. Not only do they react with oxygen of the air, as do the alkali metals, but they also combine readily with nitrogen, especially when heated with it, forming nitrides, of general formula M_3N_2. These hydrolyze readily in the manner expected for binary compounds of elements so different in electronegativity, the hydrogen becoming attached to the more electronegative and the oxygen of the hydroxyl becoming attached to the less electronegative element, thereby forming the most polar bond possible:

$$M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3$$

Such reactivity with both major constituents of the atmosphere suggests that these metals cannot be used where exposed to the air. However, the oxide and/or nitride coating which is initially formed is quite effective in protecting the metal from further corrosion, especially for the lighter members of the group, which is not true for the alkali metals.

Beryllium finds application in alloys, especially with copper. It is also an important source of neutrons, which are emitted when the element is bombarded by alpha particles. Beryllium atoms change thus to carbon 12 atoms, with the emission of one neutron. A yield of 30 neutrons per million alpha particles (He^{++} ions) can be obtained. Magnesium, of course, is well known as a light-weight structural metal. This is a practical application only because the superficial corrosion by the atmosphere is very effective in protecting the mass of metal against further action. Calcium, strontium, and barium are too easily corroded and too soft and weak to have much use as materials of construction.


Be 2+2


Mg 10+2
(2-8-2)


Ca 18+2
(2-8-8-2)


Sr 36+2
(2-8-18-8-2)


Ba 54+2
(2-8-18-
18-8-2)

Figure 120.

As expected of metals having low electronegativity and low ionization energy, these metals are good reducing agents. Magnesium and calcium especially are sometimes applied in the production of less active metals from their compounds. Being good reducing agents, they give up electrons to oxygen quite readily, with the liberation of much energy. The oxides thus formed react with water to form stable hydroxides which are basic. For this reason, the metals of this entire group, but especially calcium, strontium, and barium, are called the "**alkaline earth**" metals. Beryllium oxide and magnesium oxide are less conspicuously alkaline earths, but are included in the term "alkaline earth group."

Table 29 Some Properties of Group IIA Metals

	Be	Mg	Ca	Sr	Ba
atomic number	4	12	20	38	56
electronic structure	2-2	2-8-2	2-8-8-2	2-8-18-8-2	2-8-18-18-2
or, two electrons beyond:	He	Ne	Ar	Kr	Xe
atomic weight	9.012	24.312	40.08	87.62	137.34
atomic volume, ml/mole	5.0	14.0	25.9	33.7	39.2
density, g/ml	1.86	1.74	1.54	2.60	3.74
melting point, °C	1285	650	845	757	710
heat of fusion, kcal/mole	2.8	2.1	2.1	2.2	1.8
boiling point, °C	2477	1120	1492	1370	1638
heat of vaporization, kcal/mole	70.4	30.8	35.8	33.2	36.1
covalent radius, Å	0.90	1.30	1.74	1.92	1.98
ionic radius, M^{++}, Å	0.31	0.65	0.99	1.13	1.35
heat of atomization, kcal/mole	77	35.9	46	39.2	42
electronegativity	1.37	1.21	1.06	1.00	0.96
ionization energies, kcal/mole: first:	215	176	141	131	120
second:	417	345	272		
third:	3545	1847	1181		
electrode potential, volts	1.85	2.37	2.87	2.89	2.90

Notes: (1) Despite the relatively large atoms (shown by its density), Ca has a higher melting point, higher boiling point, heat of vaporization, and heat of atomization than either of its group neighbors, suggesting that in the metallic bonding Ca may begin to use its 3*d* orbitals.

(2) Observe the parallel between boiling points and heats of vaporization.

(3) The large increase from second to third ionization energy shows how stable the underlying closed shell is, relative to the valence shell.

(4) The much higher heat of atomization, melting point, and boiling point of beryllium show the strength of the metallic bonding and help explain why the electrode potential is not higher. Certainly the hydration energy of Be^{++} is high and would contribute to a higher potential.

Indeed, the oxides of this group illustrate a well-known trend of the major groups toward increased basicity with increasing atomic number. Beryllium atoms, being very small, compact, and relatively electronegative, do not give up their electrons to oxygen as easily, and the oxide formed contains oxygen that is not as negative. It is correspondingly less basic, and as previously mentioned beryllium oxide and hydroxide are amphoteric. When an oxide is amphoteric, it is both acidic and basic, but cannot be strongly either one, for the two properties, in their extremes, are mutually incompatible. Magnesium oxide and hydroxide are compounds of magnesium atoms which are larger,

less electronegative, and therefore permit more polar bonds to oxygen, with oxygen more negative than in the beryllium compounds. Greater basicity results. Although magnesium oxide is still not strongly basic, it is enough more basic than the beryllium compound to have lost any capacity to be acidic. It would therefore be characterized as weakly basic rather than amphoteric. Magnesium hydroxide is very insoluble in water ($K_{sp} = 6 \times 10^{-12}$), but can be used as an aqueous weak base if mixed with water to form a suspension or slurry. Such a preparation is "milk of magnesia." Calcium atoms are still larger and less electronegative, and form a more polar oxide and hydroxide which can be classed as fairly strongly basic. The importance of calcium hydroxide as a base has already been discussed in Chapter 22. Strontium hydroxide is somewhat more soluble and somewhat more basic, and barium hydroxide is the most soluble and the strongest base of the group (except, probably, radium hydroxide).

We noted a tendency for elements which lose electrons most easily to give them to oxygen molecules instead of causing the molecules to split into atoms in the process of oxidation. Thus sodium burns in air forming largely the peroxide Na_2O_2, and the heavier alkali metals readily form superoxides, MO_2. To a lesser degree this is observed in the alkaline earth metal chemistry, with barium showing the greatest tendency to form the peroxide BaO_2. Other peroxides exist in the group but are relatively less important. Barium peroxide can be used to make solutions of hydrogen peroxide. Addition to dilute sulfuric acid causes precipitation of the very insoluble barium sulfate, leaving the hydrogen peroxide in solution:

$$H_2SO_4 + BaO_2 \rightarrow BaSO_4 + H_2O_2$$

Because of the low electronegativity of the alkaline earth metals, they tend to form highly polar bonds and compounds which are commonly very stable. In Chapter 12 was noted the trend in stability of carbonates, from unstable beryllium carbonate to very stable barium carbonate. This trend is consistent with the increasing basic properties of the oxides and the increasing size and therefore diminished polarizing ability of the cations, all of which are dipositive. Similar trends are to be observed for other oxyanion salts of the metals of this group.

Many of the salts of these elements are very soluble in water. In part this is an effect of coordination of water about the cations, which decreases with increasing cation size. Beryllium ions have only a coordination number of four, but hold four water molecules quite tightly around them, at the corners of a regular tetrahedron:

$$Be^{++} + 4H_2O \rightleftharpoons [Be(H_2O)_4]^{++}$$

The cations of the remaining elements of this group show a coordination number more commonly of 6.

Beryllium compounds have relatively little practical application. Early use in phosphor coatings inside fluorescent lamp tubes has been largely discontinued because of the hazard of beryllium poisoning incurred if anyone was cut by a broken tube. Light metals in general, including beryllium, are of potential interest because of their relatively high heats of combustion per unit of weight. Light metal compounds are therefore under study as fuels.

Magnesium oxide is important as a weak base and as an ingredient of structural plaster and furnace linings. Calcium hydroxide has been described in Chapter 22 as an important industrial and agricultural base. Calcium phosphate in various soluble forms (calcium hydrogen phosphates) is of tremendous importance in agriculture, since phosphorus like potassium and nitrogen is one of the most important elements for plant growth. Calcium sulfate, anhydrous, and the hemihydrate ("plaster of Paris") $(CaSO_4)_2 \cdot H_2O$ are both hydrated to gypsum, $CaSO_4 \cdot 2H_2O$, which forms in strong hard crystals. These materials are therefore useful in hard plaster for construction. Calcium silicates and aluminates are essential ingredients of Portland cement. This exceedingly useful material is made by heating together a "calcareous" (lime-containing, such as limestone itself, $CaCO_3$) material and an "argillaceous" (clay-like, composed in part of aluminum silicates) material, until incipient fusion. The partly fused lumps are then cooled and ground to a fine powder. What is commonly called "cement" is actually "concrete," an aggregate made by adding water to a mixture of Portland cement, sand, and crushed stone or gravel. The "setting" of concrete is a complex process, involving most immediately hydration, followed very slowly by various interactions among the solid components. Calcium chloride has some application in speeding the setting of concrete, as well as the more familiar uses of melting ice on highways, keeping down dust, and dehumidifying. The last two depend on the hygroscopic (water-attracting) nature of the calcium chloride, which absorbs water vapor from the atmosphere around it.

Strontium compounds have relatively little use, except as flame coloring agents for pyrotechnics and signal flares, which often contain strontium nitrate to impart a brilliant crimson color. Barium compounds have similar use, to give green flames. In addition, barium hydroxide has some application as a base, barium sulfate as a white pigment for paints, barium soaps for lubricating greases, and barium oxide and carbonate in ceramics and in the production of optical glass.

Since these elements, especially calcium, strontium, and barium, are,

next to the alkali metals, the strongest reducing agents of all the metals, the production of the metals from their compounds is not easily accomplished by chemical means but is usually done by electrolysis of the fused salts. The production of magnesium is described in Chapter 21.

GROUP IIB

Some properties of these elements are given in Table 30. Electronically, these differ from the IIA elements by the filling of the underlying *d* orbitals, and the corresponding increase of nuclear charge by 10. The difference in properties between the zinc, cadmium, and mercury group and the alkaline earth metals is associated with the contraction and increasing compactness of the electronic spheres, and consequently the increasing electronegativity, that accompanies this filling of *d* orbitals.

Table 30 Some Properties of Group IIB Elements

	Zn	Cd	Hg
atomic number	30	48	80
electronic structure	2-8-18-2	2-8-18-18-2	2-8-18-32-18-2
atomic weight	65.37	112.40	200.59
atomic volume, ml/mole	9.2	13.1	14.1
metallic radius, Å	1.38	1.41	1.44
density, g/ml	7.14	8.64	13.50
melting point, °C	419.5	320.9	−38.9
heat of fusion, kcal/mole	1.77	1.46	0.56
boiling point, °C	908	765	356.6
covalent radius, Å	1.31	1.48	1.49
heat of atomization, kcal/g-atom	31.19	26.75	14.65
electronegativity	1.86	1.73	1.92
ionization energy, first, kcal/mole	216	207	241
electrode potential, volts	0.763	0.403	−0.85

Notes: (1) The high ionization energy of mercury, its negative electrode potential, its low melting point and boiling point, and low heat of fusion and heat of atomization are all consistent with the observation of the "inert pair" of *s* electrons.

(2) The large density increase from Cd to Hg reflects the filling in of 4*f* electrons, with corresponding nuclear change, following Ba and La.



Zn 28 + 2
(2-8-18-2)



Cd 46 + 2
(2-8-18-
18-2)



Hg 78 + 2
(2-8-18-
32-18-2)

Figure 121.

As a result, zinc is much more dense than calcium, but it has weaker metallic bonding because its valence electrons are more tightly held. This leads to a lower heat of atomization, lower melting point, higher volatility, and lower boiling point. Similarly, cadmium is much more dense than strontium, but has weaker metallic bonding, with results like those just mentioned for zinc.

Mercury is still farther removed from barium, because besides the filling of underlying *d* orbitals the 4*f* orbitals have also been filled, making the atomic number of mercury, and thus its nuclear charge, 24 higher than that of barium, instead of merely 10. The contraction which accompanies this filling of the *f* orbitals, added to that of filling the *d* orbitals, makes mercury much denser than barium and much more electronegative. In addition, the "inert pair effect" is shown in mercury, making its metallic bonding even weaker than would otherwise be expected. Mercury therefore melts much lower than barium, and is much more volatile.

Zinc is superficially oxidized in the atmosphere, and thereafter very resistant to corrosion. It is used extensively as a coating material to protect iron against rust. Iron so coated is called "galvanized" iron. Zinc is alloyed with copper to form brass, and is an ingredient of many other useful alloys. Cadmium is much less available, but finds similar use as a plating material to protect iron from rust. It is also used in low-melting alloys. Mercury is invaluable in its application in scientific instruments, such as thermometers and manometers. It also has some use for extracting silver and gold from rocks, for it dissolves most metals, but not iron, forming "amalgams." Rings and bracelets worn in the laboratory have an uncanny ability to find specks of mercury and thereby become amalgamated. No specks of mercury should be tolerated outside of closed containers, however, for its vapor, although very slight, is very poisonous.

As indicated, zinc, cadmium, and mercury differ greatly from the alkaline earth metals in their resistance to atmospheric corrosion. In finely divided form, zinc and cadmium do combine with oxygen quite easily, although unlike the alkaline earth metals they do not unite directly with nitrogen. Mercury is slowly oxidized when warmed in air. Zinc and cadmium oxides are thermally stable, but heating mercury oxide, HgO, is a well-known laboratory method of preparing pure oxygen. This is a reflection of the "inert pair effect." Since the only valence electrons a mercury atom has are the "inert pair," it does not

form very strong bonds with other atoms, including oxygen, that try to remove them.

The increase in electronegativity from the IIA to the IIB elements makes the oxides of the latter much less polar and correspondingly less basic. Whereas the alkaline earth oxides are strongly basic, zinc oxide is amphoteric, cadmium oxide is weakly basic and shows acidic properties only under extreme conditions such as fusion with potassium hydroxide, and mercuric oxide is very weakly basic but shows no acidity. The difference between the oxides of zinc and cadmium in part reflects the lower electronegativity of the latter and therefore the greater polarity of its oxide. Both zinc and cadmium form hydroxides when solutions of their ions are made alkaline, but the hydroxide of mercury seems to be unstable and only the oxide is precipitated under similar conditions.

Table 31 Comparison of Calcium and Zinc

	Ca	Zn
atomic number	20	30
electronic structure	2-8-8-2	2-8-18-2
atomic weight	40.08	65.37
metallic structure	hexagonal	hexagonal (distorted)
metallic radius, Å	1.97	1.38
covalent radius, Å	1.74	1.31
ionic radius, Å, M^{++}	0.99	0.74
ionization energy, first, kcal/mole	141	216
average of first two:	207	315
electronegativity	1.06	1.86
density, g/ml	1.55	7.14
melting point, °C	850	419.5
heat of fusion, kcal/mole	2.1	1.77
boiling point, °C	1492	908
heat of vaporization, kcal/mole	35.8	27.6
atomic volume, ml/mole	25.9	9.2
heat of atomization, kcal/g-atom	46	31.2
electrical conductance	0.29	0.17

Notes: Observe that increase of the nuclear charge by 10, accompanying the filling of the 3*d* orbitals, results in much more compact atoms (smaller covalent and ionic radii, higher density) with more tightly held electrons (higher ionization energy, higher electronegativity, lower conductance) and correspondingly weaker metallic bonding (lower melting point, heat of fusion, boiling point, heat of vaporization, and heat of atomization).

The sulfides of the IIB metals are all very insoluble, in contrast to those of calcium, strontium, and barium which are all soluble. This is doubtless related to the lower polar character of the bonding in the IIB sulfides. Instead of forming somewhat ionic crystals, as do the NaCl-structured alkaline earth sulfides, the IIB sulfides are of the "giant molecule" type, and might be termed "coordination polymers." For example, in zinc sulfide each zinc atom is joined equally to four sulfur atoms at the corners of a regular tetrahedron, and each sulfur atom is joined equally to four zinc atoms similarly located. Since each zinc atom originally had but two outermost electrons and six vacancies, and each sulfur atom had originally but two outermost vacancies and six electrons, it seems clear that sulfur is acting as donor to the zinc in the crystal. As implied by the equal positions, however, the bonds appear identical.

Salt-like hydrides are readily formed by calcium, strontium, and barium, as indicated in Chapter 13. Similar hydrides of zinc and cadmium have been prepared by special methods, but they are much less polar and less stable. Mercury hydride seems not to be stable above $-100°$.

The IIB elements form compounds also with the halogens and with other electronegative atoms and groups. In general these are quite stable, but they are less stable than the corresponding IIA compounds. For example, zinc is more electronegative than calcium, and it forms dipositive ions that are smaller and much more compact than those of calcium, and in addition do not have the inert-shell structure of calcium ions. Zinc atoms therefore give up electrons to a carbonate group less completely, and the resulting zinc ions exert a stronger deforming

Table 32 Calcium Chloride and Zinc Chloride: Comparison of Properties

	$CaCl_2$	$ZnCl_2$
melting point, °C	782(P)	318
heat of fusion, kcal/mole	6.78	5.5
boiling point, °C	—	730
density, g/ml	2.2	2.9
charge on chlorine	−0.40	−0.18
heat of formation, kcal/equiv.	−95.0	−49.7

Note: These compounds illustrate the general differences in chemistry of Ca and Zn, or IIA and IIB. Observe that the $ZnCl_2$ is lower melting, less polar, and forms with less heat evolved, suggesting lower stability.

(polarizing) influence on the carbonate group. The decomposition pressure of carbon dioxide over zinc carbonate reaches one atmosphere at 350°, but not until 900° over calcium carbonate.

IIB ions are correspondingly better electron acceptors than IIA ions, and these elements form many, and more stable, coordination complexes. In part, this is a cause of the amphoteric nature of zinc hydroxide, which readily coordinates additional hydroxide ions to form the soluble "zincate" complex $[Zn(OH)_4]^=$.

Compounds of the IIB elements, being generally less polar than those of the IIA elements, tend to be lower melting and more volatile, as well as less stable.

Mercury has a peculiarity, not shown by zinc and cadmium, of exhibiting a stable oxidation state of one as well as two. However, it forms two bonds per atom in the +1 state, one bond being to another mercury atom. The so-called "mercurous" ion is Hg_2^{2+} rather than Hg^+. Mercurous salts are about as well known as the mercuric. Hg_2Cl_2 is the compound known as "calomel."

Several compounds of zinc have industrial importance. Zinc oxide, as previously mentioned, conducts heat very well, and is compounded with rubber for heavy duty tires to help prevent deterioration of the rubber through overheating. Zinc sulfate solution mixed with barium sulfide solution precipitates all the ions, forming zinc sulfide and barium sulfate, both white, used as the pigment called "lithopone." Impure zinc sulfide is caused to emit light when struck by electrons, and thus finds application in television screens and similar devices. Cadmium compounds are useful in pigments, ranging from clear pale yellow to bright red. Mercury compounds have some application in medicine, but are not extensively used. Both cadmium and mercury and their compounds are toxic.

The IIB elements are reactive enough that they are not found native, except occasionally for some mercury, but because of the lower polarity and stability of their bonds they are relatively easily liberated from their compounds. Isolation of zinc is described in Chapter 21. Cadmium can be obtained similarly, and mercury, which occurs most commonly as the sulfide, is easily liberated by burning off the sulfur.

GROUP IIIA

Some properties of these elements are listed in Table 33. Boron follows the trend from lithium through beryllium in having smaller atoms, more compact and more electronegative. It might be metallic,

Table 33 Some Properties of Group IIIA Elements

	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
electronic structure	2-3	2-8-3	2-8-18-3	2-8-18-18-3	2-8-18-32-18-3
or, 3 electrons beyond:	He	Ne	Zn^{++}	Cd^{++}	Hg^{++}
atomic weight	10.811	26.982	69.72	114.82	204.37
atomic volume, ml/mole	4.3	10.0	11.8	15.7	17.3
density, g/ml	2.34	2.70	5.9	7.31	11.83
melting point, °C	2027	660	29.8	156.2	303.6
heat of fusion, kcal/mole	5.3	2.55	1.34	0.78	1.02
boiling point, °C	3927	2447	2237	2047	1470
heat of vaporization, kcal/mole	128.8	70.2	61.2	54.1	38.7
covalent radius, Å	0.82	1.18	1.26	1.44	1.48
ionic radius, calc., Å	0.20	0.50	0.62	0.81	0.95
heat of atomization, kcal/g-atom	141	77.5	65.0	58.2	43
electronegativity	1.88	1.39	2.10	1.88	1.96
ionization energy, kcal/mole: first,	190.3	137.4	137.7	132.8	140.2
sum of first three:	1636	1222	1279	1164	1293
fourth:	5947	2751	1474	1222	1165
electrode potential, volts		1.66	0.53	0.342	0.336 (Tl^{+})

by virtue of possessing more external vacancies than electrons, but in fact it is not. In this respect it is exceptional, since all other elements of this type are metals. Neither is boron typically nonmetallic, for the bonding in elemental boron appears not to be conventional covalent but rather intermediate in nature between localized and nonlocalized. Aluminum, with similar electronic structure, has, however, an underlying shell of 8 electrons instead of 2 like boron. These seem to shield the valence electrons from the nucleus well enough that the ionization energy is lower and the electronegativity is lower, and aluminum is then a metal. It conducts electricity better than any other metal except the "coinage metals," copper, silver, and gold, but chemically, as we shall see presently, its behavior is not considered characteristic of the most active metals.

The significance of discussing IIB elements immediately after IIA elements becomes apparent when we consider the next heavier member of the IIIA group, gallium. Although aluminum differs from boron in the number of electrons in the underlying shell, both bear the same relationship to the nearest inert element. Stripped of its valence electrons,

boron has an electronic configuration resembling that of helium, and in the same way aluminum resembles neon. But if gallium is stripped of its three outermost electrons, the resulting cation, Ga^{+++}, is not electronically similar to an inert element. Instead, it has 18 electrons in the outermost shell. The gallium ion is thus isoelectronic (having the same number of electrons) with the zinc ion. Going down Group IIIA, then, we do not find the same kind of regularity of electronic configurations that is shown by the elements of IA and IIA. Here, from Period 3 (Al) to Period 4 (Ga), there is a fundamental change from inert-shell to 18-shell type of element. This change was brought about by the insertion of the transition elements with the filling of the *d* orbitals. It could not have occurred in an earlier period, e.g. between magnesium and aluminum, because no *d* orbitals are available for filling in the $n = 2$ shell. As we observed in contrasting IIA and IIB elements, such filling is accompanied by contraction of the electronic cloud and increasing electronegativity. We cannot therefore expect as smooth a trend, if indeed any trend is observable, going down Group IIIA as in going down IA or IIA.

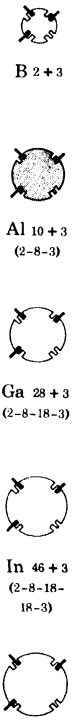


Figure 122.

Why is gallium placed beneath aluminum? The answer is that the periodic table is only an arbitrary representation for the purpose of systematizing as much chemistry as possible, and if we could do better by placing gallium somewhere else we would. But it happens that the most important consideration, although not the only one, is the nature of the bonding orbitals and the number of valence electrons in them. Certain similarities are bound to be shown by different atoms if they are alike in outermost electronic configuration, and especially if the underlying configurations are stable enough to remain uninvolved in the bonding. Since boron and aluminum and gallium—and here we may as well add the rest of the group, indium and thallium—all have three outermost electrons above closed underlying shells (whether 8 or 18), and these are in *s* and *p* orbitals, these elements tend to become bonded in the same way. Their compounds must therefore bear certain important resemblances. The trends are not perfect in any periodic group, but even here they are close enough to make the grouping much more useful than no grouping at all.

Indeed, we must never lose sight of the indisputable fact that each chemical element is a chemical individual, and cannot be expected to be or to behave *exactly* like any other element under any possible con-

ditions. We are simply lucky that there is enough similarity in electronic configurations to give us a basis for organization. Otherwise, chemistry would be a much more difficult science to learn and understand.

Gallium seems to differ in its metallic bonding. Although the heat of atomization of the elements in this group follows a consistent downward trend with increasing atomic weight and size, gallium melts very little above room temperature. This is 390° below the melting point of zinc, and 630° below the melting point of aluminum. The volume occupied by one mole of gallium atoms is greater than that of aluminum or zinc, although the metallic radius of gallium is less than that of aluminum. This suggests that the atoms cannot be as closely packed in gallium, weakening the crystal to allow for its low melting point. On the other hand, gallium boils nearly as high as aluminum, and much higher than zinc, which indicates that interatomic forces persist in the liquid over a wide temperature range. Indium and thallium, although melting higher than gallium, are similarly relatively low melting and soft metals. Although less electronegative than gallium, they are much more so than aluminum.

Boron is extremely difficult to isolate in pure form, and has relatively little practical application in the elemental form. It is used sometimes as a degasifier and deoxidizer in metallurgy, and small concentrations help in the heat treatment of steel. It can be used as a hardening agent for metals, by forming metal borides at their surface. Aluminum is of course one of our most valuable metals for construction, combining good strength with very low density. Indium has some use in alloys, but gallium and thallium are relatively unused.

Both boron and aluminum, having relatively small atoms of relatively low electronegativity, combine very strongly with oxygen. The oxides of the 18-shell elements of this group are not nearly as stable. All have the type formula E_2O_3. Remember that the oxide of beryllium, just preceding boron, is amphoteric. In keeping with boron's higher electronegativity and greater atomic compactness, its oxide is no longer basic, but very weakly acidic. It unites with water to form "boric acid," $B(OH)_3$ (often written H_3BO_3). Being an acidic oxide, boron oxide can be fused with basic oxides, forming metal borates. These are giant molecule type structures of widely variable composition. The simple salts of boric acid, prepared by neutralization in aqueous medium, are most commonly "metaborates." An "ortho" acid is one in which the maximum number of hydroxide groups is present, as in $B(OH)_3$. Removal of water from such a formula gives the formula of the "meta" acid, here HBO_2. The salts of metaboric acid, then, would have formulas such as MBO_2. Boric acid easily polymerizes by loss of water

among different molecules, one of the most familiar products being "tetraboric acid," $H_2B_4O_7$. This may be considered to be derived from four molecules of boric acid, by the removal of five molecules of water. The sodium salt of this acid, hydrated, is known as "borax."

Aluminum oxide forms an amphoteric hydroxide, as might be expected from the fact that the bonds to oxygen are more polar than in boric acid. Gallium hydroxide is also amphoteric but, in keeping with the higher electronegativity of gallium, the bonds are less polar and the hydroxide is less basic and more acidic than aluminum hydroxide. Indium hydroxide has more polar bonds than there are in gallium hydroxide, since indium is less electronegative. With larger atoms than boron, which is equal in electronegativity, it is amphoteric but more basic than acidic. Thallium hydroxide is very weakly basic, but seems to show no acidic properties. Boric acid is only sparingly soluble in cold water, but the metal hydroxides of this group are very insoluble, and precipitate out of alkaline solution unless it is so basic as to redissolve them as hydroxide complexes. For example, soluble carbonates and sulfides furnish sufficient hydroxide ion, through hydrolysis, to precipitate aluminum hydroxide. For this reason, aluminum sulfide cannot exist in the presence of water. Aluminum carbonate apparently cannot exist at all, presumably because of the strong polarizing power of the small, highly charged aluminum ion Al^{3+}.

The inert pair effect is indicated in this group by the existence of lower oxides, possibly of gallium and certainly of indium, In_2O, and thallium, Tl_2O. The latter is much more stable than Tl_2O_3, which easily loses oxygen. In water, Tl_2O forms TlOH, a soluble and moderately strong base. With only one oxygen instead of three attracting the electrons of the thallium atom, higher polarity can be achieved, which accounts for the much greater basicity of TlOH compared to $Tl(OH)_3$. When any one element forms more than one hydroxide, the lowest hydroxide is always the most basic or the most weakly acidic, for similar reasons.

With hydrogen boron forms not only diborane, as discussed in Chapter 11, but also several other compounds, of which B_5H_9 and $B_{10}H_{14}$ are the most important. All these show the peculiarities of bonding that characterize elemental boron itself. Aluminum forms a polymeric hydride, AlH_3, and the 18-shell elements also combine with hydrogen but the stability of the compounds is much less, decreasing down the group.

Compounds of the halogens with boron and aluminum have been discussed in Chapter 13. The 18-shell elements of this group form halides that in a general way resemble those of aluminum.

A diagonal similarity between aluminum and beryllium should be

noted. One step to the right of beryllium increases electronegativity, but one step down decreases it. The result is that the two elements are much alike in the nature of their compounds.

Boron oxide and borates have application as components of cleansing powders, to remove oxides from metal surfaces through formation of low-melting borates, and in the manufacture of Pyrex glass, which is made by fusing boron oxide with silica and certain metal oxides. They are also used in water softening, in the leather industry, in imparting fire-retardant properties to textiles, and in ceramics and fertilizer. Both the carbide and nitride can be made in extremely hard condition rivalling that of diamond, and they are valuable as abrasives. The "diamond form" of boron nitride is especially useful at higher temperatures, resisting oxidation when diamond itself would burn away. Note the interesting relation between boron-nitrogen compounds and carbon compounds—an "average" of boron and nitrogen would be carbon. Boron trifluoride, and to a lesser extent the trichloride, are important industrially as catalysts for a variety of reactions, chiefly in organic chemistry. Hydrides of boron, as already mentioned, are of great interest as possible high energy fuels, because of the high heat of combustion of boron and hydrogen, per pound.

Aluminum compounds are important in dyeing, in waterproofing textiles, and in ceramics, as well as in water treatment. Activated alumina, Al_2O_3, is an excellent sorbent for water vapor and other substances. One of the most important of all industrial catalysts, having a wide variety of applications, is anhydrous aluminum chloride, Al_2Cl_6. The three 18-shell elements of this group do not form compounds useful in large-scale practical applications. In part, this is due to the relatively rare occurrence of the elements.

GROUP IVA

Some properties of these elements are given in Table 34. In these elements, the halfway mark in filling the outermost shell to an octet is reached. As pointed out in Chapter 23, this brings to carbon the property shared only with hydrogen of having all its external orbitals fully occupied when all possible covalent bonds are formed. Each of the other elements of this group has outer *d* orbitals which can be used in at least some of its chemistry. As previously discussed, carbon has two major forms, graphite and diamond, the former depending on the capacity of carbon atoms to use *s* and *p* orbitals in multiple bonding. None of the heavier elements of this group appear capable of using

these orbitals for multiple bonding, although they may on occasion use the outer *d* orbitals in a somewhat similar way. The *d* orbitals are used, however, mainly only when the atoms bear appreciable positive charge as the result of electron withdrawal by more electronegative elements. In the elemental condition, multiple bonding appears to make no contribution to the state of aggregation of silicon, germanium, tin, or lead.

Although carbon appears to be strictly covalent, silicon, which has the diamond structure and hence seems to be held together by covalent bonding, does in some respects appear intermediate between typical metal and typical nonmetal, and therefore can be classified as "metalloid." It is, indeed, less electronegative than some metals, and in this respect resembles boron. A diagonal relationship between boron and silicon is similar to that pointed out for beryllium and aluminum, for similar reasons.

With germanium, the 18-shell type of element begins in this group. As previously discussed, there is consequently little justification for expecting that germanium, tin, and lead will continue exactly the trends begun by carbon and silicon. Indeed, with the greater compactness brought about with the filling of the 3*d* orbitals, germanium is more electronegative than silicon, and in some respects bears a greater resemblance to carbon than to silicon. In some ways, although germanium atoms are larger than those of silicon, they appear to be a little less metallic. Germanium is usually classified as a metal and silicon as nonmetal, but it is perhaps more accurate to classify both as metalloid and note the greater electronegativity of the germanium. Tin exists in both a metallic and nonmetallic form. The latter, called "gray tin," is a powder stable below 13.2°. The former, called "white tin," reverts to the non-metallic structure at low temperatures, but very slowly. This phenomenon, when it destroyed the organ pipes in cathedrals of Europe during cold winters, was thought to be a disease, and called "tin pest." Lead has only the metallic form. Both lead and tin are not typical metals either structurally or chemically. If their metallic structure requires more vacancies than electrons in the outer shell, these must be provided by the *d* orbitals. Both metals are among the highest in electronegativity, higher than both boron and silicon.

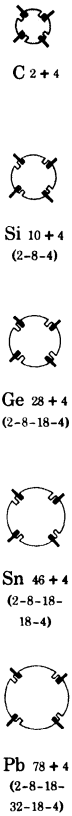


Figure 123.

Diamond dust is very valuable for grinding and polishing operations, and graphite mixed with clay serves as writing material in pencils

Table 34 Some Properties of Group IVA Elements

	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
electronic structure	2-4	2-8-4	2-8-18-4	2-8-18-18-4	2-8-18-32-18-4
or, 4 electrons beyond:	He	Ne	Zn^{++}	Cd^{++}	Hg^{++}
atomic weight	12.011	28.086	72.59	118.69	207.19
atomic volume, ml/mole	5.3	11.7	13.5	16.2	18.2
density, g/ml	3.5(d) 2.0(g)	2.33	5.35	7.28	11.34
boiling point, °C	3850(s)	2680	2830	2687	1751
heat of vaporization, kcal/mole	170	(105)	79.9	69.4	42.9
melting point, °C		1423	937	232	327
heat of fusion, kcal/mole		11.7	7.6	1.72	1.14
covalent radius, Å	0.77	1.11	1.22	1.41	1.47
heat of atomization, kcal/mole	171.7	105	90.0	72	46.8
electronegativity	2.47	1.74	2.31	2.02	2.01
ionization energy, first, kcal/mole	258.1	186.2	186.4	168.2	170.1

("pencil lead"). Large quantities of "amorphous" (noncrystalline) carbon, possibly very imperfect forms of graphite, are prepared by decomposition of hydrocarbons or by their incomplete combustion. These have extensive use as "carbon black" or "lamp black," compounded with rubber in the making of tires, and as pigments. "Active carbon" can be prepared, having a surface area of about 50,000 square centimeters per gram. Such material has high sorptive capacity, and is used in gas masks and in the purification of sugar and other chemicals. It also has high catalytic activity.

Silicon is used as an alloying material—evidence of its metallic nature—for example, imparting high acid resistance to iron. Pure silicon has its greatest application in making transistors and other electrical devices. Germanium is especially important for these purposes. The element is first purified to an extremely high degree. Then traces of a IIIA element are introduced into some of it and traces of a VA element into another portion of it. Incorporated in the diamond-like structure of germanium, a few IIIA atoms provide vacancies instead of the fourth electron, which increases the conductivity greatly because these "holes" permit electrons to move through the crystal. Likewise, the conductivity is increased by a trace of VA atoms, which have an extra electron beyond the lattice requirement, and these electrons

can also move through the crystal. A junction between the two types of germanium permits current to flow in one direction more readily than in the other, and thus serves to transform alternating current into direct current. A transistor consists of a combination of such junctions, capable of amplifying electrical signals as does a radio tube. (Much interest is similarly being shown in compounds of Group IIIA with VA elements, such as GaAs, and in some IIA-VIA combinations, such as MgTe, all of which appear to have such "semi-conductor" properties.)

Tin is widely used as a plating material, especially for iron, which it protects from rusting by covering it up (see also page 436). Tin and lead alloys are useful as solder. Lead was used for water pipes before its toxic nature became recognized. The element and its compounds are now known to be cumulative poisons causing many varieties of unpleasant symptoms. Lead has numerous applications where a soft, dense metal is needed, and in alloys. A major use is in storage batteries.

Carbon occurs naturally in all living matter, in coal, natural gas, petroleum, oil shale, and in carbonates, chiefly limestone, as well as in the carbon dioxide of the air. Silicon is the second most abundant of all the elements, exceeded only by oxygen. It makes up about one-fourth of the earth's crust, in combination with oxygen, as sand, and in combination with both oxygen and oxides of metals, called silicates. Elementary silicon can be isolated from its oxide by heating sand with coke at high temperatures in the presence of chlorine. This is a standard method for converting a stable oxide to a chloride, and has already been mentioned as used for the production of anhydrous aluminum chloride:

$$SiO_2 + 2Cl_2 + 2C \rightarrow 2CO + SiCl_4$$

The chloride may then be reduced to silicon by an active metal, such as sodium. Germanium is very scarce, occurring as traces with other elements, mainly with zinc ores. Its oxide is much more easily reduced, by simply heating with carbon. Tin is not very abundant, but occurs in a few high concentrations of SnO_2 ("cassiterite"), which is easily reduced to the metal by heating with carbon. Some comes from South America, especially Bolivia, and some from the Malay peninsula and the southwest Pacific islands. Lead occurs also, not very abundantly, in deposits of the sulfide and in various other minerals, from which the metal is easily recovered by reduction with carbon after conversion to the oxide.

Compounds of carbon and silicon with oxygen, hydrogen, and the halogens have already been mentioned in Chapters 11, 12, and 13. The

monomeric nature of gaseous CO_2, contrasted to the polymeric nature of solid SiO_2, reflect the lower electronegativity and reduced ability of silicon to form ordinary double bonds. In addition, multiple bonding of silicon through use of its *d* orbitals distinguishes it from carbon, which cannot use such orbitals. Consistent with the greater polarity of its bonds to oxygen, silicon dioxide is more weakly acidic than carbon dioxide, and its salts, the silicates, are, when soluble, even more extensively hydrolyzed than the carbonates. The silicates most commonly, however, are highly polymeric and thus insoluble in water. Germanium dioxide has less polar bonds than silicon dioxide, and one might expect greater acidity. This is realized—germanium dioxide is very slightly soluble in water giving solutions that are indeed more acidic than silicic acid, although less so than carbonic acid—but germanium dioxide also shows basic properties not shown by silicon dioxide. One may speculate that the reduced bond polarity is offset by the larger size of the germanium atom, permitting easier separation of hydroxide ions, but the true explanation of this amphoterism is uncertain. It is a general observation, however, that basicity appears to develop in the oxides of larger atoms, even those which are also weakly acidic, and it is exhibited also by the dioxides of tin and lead, which are likewise amphoteric.

As a consequence of this basicity, the tetrachlorides of germanium and tin can be isolated from aqueous solution if it is strongly acidified with HCl to minimize hydrolysis. In contrast, silicon tetrachloride is completely and irreversibly hydrolyzed, for once the oxygen becomes attached to the silicon it never ionizes away again.

In this group, too, the inert pair effect becomes noticeable down the group. Silicon seldom if ever shows a valence of two, but germanium does to some extent, tin does about as easily as it shows tetravalence, and lead compounds when polar are generally unstable in the (IV) state and much more stable in the (II) state. Tin(II) oxide is well known, but when heated in the air it readily is further oxidized to the (IV) oxide, SnO_2. PbO_2, on the other hand, is unstable, is a strong oxidizing agent, and readily loses oxygen to become PbO. Tin(II) compounds in general are good reducing agents. Lead(II) compounds are not.

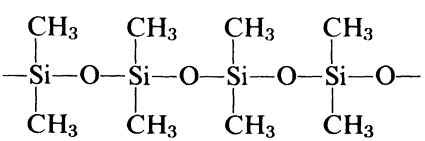
As mentioned in Chapter 12, silane, SiH_4, differs notably from methane in being spontaneously inflammable and completely hydrolyzable. If the trend were continued down the group, germanium hydrides would be very reactive. In fact, however, GeH_4 is not spontaneously inflammable and not hydrolyzed, and in this respect resembles methane more than it does SiH_4. Bonds between hydrogen and larger atoms are weaker, however, and although a few higher germanium

hydrides analogous to ethane, propane, butane, and pentane, and perhaps higher, are known, they are not very stable. SnH_4, stannane, decomposes slowly at 25°, and plumbane, PbH_4, is so unstable as to be almost unknown.

The (IV) chlorides of these elements are all known volatile liquids. In keeping with the inert pair effect, however, $PbCl_4$ is very unstable, and readily loses chlorine to become $PbCl_2$, a salt-like solid.

Organic compounds of carbon have already been discussed in Chapter 24. Inorganic compounds of carbon having wide utility are the carbonates, calcium carbonate being valuable in construction as limestone and marble and sodium carbonate as an extremely important material in industrial chemistry. The cyanides, especially NaCN, are also very useful, as are many other miscellaneous carbon compounds. When sand and coke are heated together in an electric furnace, to a very high temperature, the compound "silicon carbide," SiC, is formed. This is commonly known as "carborundum." It is an extremely hard, abrasive substance, finding wide application in grinding and polishing.

Silicon compounds that occur in nature are especially important in construction materials. The use of silica in glass has already been mentioned. Sand and lime together make mortar for bricks. The bricks themselves are made of clay, a mixture of complex aluminum silicates. These are heated until first moisture and other volatile components are evaporated, then easily oxidizable materials are oxidized, and finally the lowest melting silicate components just begin to melt. They are then very slowly cooled. The fused silicates harden as a glass which holds the unfused particles together, giving the clay brick strength and durability. Porcelain and other ceramic materials are similarly prepared. Portland cement was mentioned earlier in this chapter. In addition to these naturally occurring silicates, similar substances have been produced artificially and a wide range of compounds of silicon have been synthesized. Notable among these are the "silicones," polymeric materials that can take the form of fluids, temperature-resistant plastics, and synthetic rubbers, depending on the composition and treatment. These have usually two organic groups on each silicon atom, the silicon atoms then being bridged to other silicon atoms by oxygen. A "dimethylsilicone" has a structure represented by:



In the liquid forms, these compounds increase less in viscosity for a given amount of cooling than any other known fluids.

Germanium compounds have little practical application. Tin compounds are used in weighting silk and for miscellaneous minor purposes. Lead compounds of greatest interest include pigments, such as the basic lead carbonate called "white lead," $Pb_3(OH)_2(CO_3)_2$, and tetramethyl and tetraethyl lead, the organometallic compounds $(CH_3)_4Pb$ and $(C_2H_5)_4Pb$, which are the best known antiknock agents. "Leaded gasoline" is gasoline to which a few milliliters of "ethyl fluid" or "methyl fluid" have been added. The fluid contains the lead compound, together with ethylene dibromide, $C_2H_4Br_2$, and perhaps a dye to help identify it. These lead compounds are extremely poisonous, more so even than lead ordinarily is, but they are very effective in promoting smooth combustion of gasoline in the internal combustion engine. The burning should occur at a controlled rate to permit maximum effective power from the expanding hot gases pushing on the piston in the cylinder. If the burning is irregular, subject to accelerating suddenly at an explosive rate, the force is applied to the piston far more rapidly and briefly than the engine can respond to efficiently. The result is "knocking" and overheating, with poor utilization of available energy. The lead compounds can be made by action of the appropriate alkyl chloride on a sodium-lead alloy:

$$Na—Pb + C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 4NaCl$$

The purpose of the ethylene bromide is to help keep the lead residues from accumulating inside the cylinders. Lead bromide is somewhat volatile and can be blown out the exhaust.

GROUP VA

Some properties of these elements are listed in Table 35. The atoms of all these elements have five outermost electrons, which means pairing in one orbital, leaving only three vacancies for covalence. The "inert pair effect" has not quite the same meaning here that it had in the preceding groups, for in them it meant a tendency not to make full use of the *s* and *p* orbitals, whereas here it means a tendency not to expand to the outer *d* orbitals. These *d* orbitals appear to become more available with increasing principle quantum number, yet the tendency toward pentavalence decreases toward bismuth. All these elements can form compounds in which their atoms form three covalent bonds. The (V) state of nitrogen is of course a formal one, in that there are not

enough orbitals for expansion of the number of bonds to nitrogen beyond four. Phosphorus, arsenic, antimony, and bismuth can all form five bonds through utilization of an outer *d* orbital to which one of the paired electrons can be promoted. The tendency is greatest for phosphorus, least for bismuth, and apparently somewhat greater for antimony than for arsenic, although this is uncertain.

The downward trend is toward greater metallic nature, but even bismuth is not a very typical or active metal. Even phosphorus has a form, "black phosphorus," made under very high pressure, that bears some resemblance to a metal in its appearance and in being able to conduct a current somewhat, and arsenic has both metallic and nonmetallic forms. Antimony is metallic, or metalloid, but rather brittle and hard rather than malleable.

The chief use of elemental nitrogen is in the form of liquid nitrogen. Nitrogen boils ($-196°$) below oxygen ($-183°$) and thus can be distilled away from liquid air. Liquid nitrogen is a very useful refrigerant, especially in the scientific laboratory. Hydrogen, carbon monoxide, and methane, as well as the inert gases fluorine, oxygen, and nitrogen, are the only common materials exerting an appreciable vapor tension at this temperature, $-196°$, at which liquid nitrogen maintains itself in an environment of room temperature by constantly evaporating. All others can be frozen out in a trap immersed in liquid nitrogen. Because of the high stability of the N_2 molecule, nitrogen is quite inert and is often used as an inert atmosphere to prevent oxidation by air.

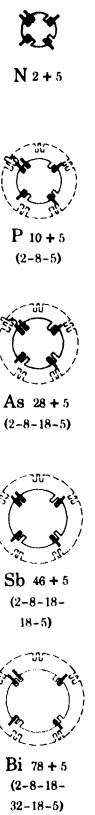


Figure 124.

Phosphorus has some application in incendiary bullets and bombs, and in the red form on the striking surface of safety match containers. Arsenic has some use as an alloying agent, for example, improving the sphericity of molten lead by increasing its surface tension, and for this reason being incorporated into lead shot. Antimony is useful in alloys, of which one is "babbitt metal" used for bearings, in which hard crystals of antimony imbedded in the softer other metal serve to bear the brunt of the load. The lead of storage batteries contains antimony to improve its physical properties. Bismuth and antimony both find some application in alloys of low melting point. They are especially useful for type metal, giving sharp adherence to the mold because, instead of contracting as do most metals on solidification, their alloys expand a little. The major use of bismuth as a metal is in easily fusible alloys,

Table 35 Some Properties of Group VA Elements

	N	P	As	Sb	Bi
atomic number	7	15	33	52	83
electronic structure	2-5	2-8-5	2-8-18-5	2-8-18-18-5	2-8-18-32-18-5
or, 5 electrons beyond:	He	Ne	Zn^{++}	Cd^{++}	Hg^{++}
atomic weight	14.007	30.974	74.922	121.75	208.980
atomic volume, ml/mole	17.3	17.0(wh)	13.1	18.2	21.3
density, g/ml	0.96	1.82(wh)	5.72	6.69	9.80
melting point, °C	−210.1	44.1(wh) 597(red)	817(P)	630.5	271.3
heat of fusion, kcal/mole	0.086	0.15	6.62	4.74	2.6
boiling point, °C	−196	280(wh) 431(s)(red)	613(s)	1637	1559
heat of vaporization, kcal/mole	0.67	2.97(wh) 7.2(s)(red)	34.5(s)	16.2	36.2
covalent radius, Å	0.75	1.06	1.19	1.38	1.46
heat of atomization, kcal/g-atom	112	79.8	69.4	62.7	47.5
electronegativity	2.93	2.16	2.53	2.19	2.06
ionization energy, first, kcal/g-atom	336	254	231	199	185

for automatic sprinkler systems and various applications of fusible plugs.

Nitrogen occurs not only in the atmosphere, of which it constitutes about 80 per cent, but also in deposits of nitrates. These can occur only in the nearly complete absence of rainfall, since nitrates are as a class very soluble. It is present in valuable concentrations in the excrement of birds and bats (guano), of which commercially useful accumulations have been found on desert islands and in caves. It occurs in coal, from which it is obtained as ammonia, and as the liquid compounds, aniline $C_6H_5NH_2$, and pyridine, C_5H_5N—the latter a benzene-like ring with one nitrogen atom taking the place of one of the CH groups. These compounds are among the pyrolysis products in the heating of coal to make coke. Pure nitrogen can be prepared in the laboratory by heating ammonium nitrite, NH_4NO_2 (or, more conveniently, its equivalent as a mixture of sodium nitrite and ammonium chloride):

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Phosphorus is present in all living matter. It is most commonly found in large deposits of "phosphate rock," which is chiefly calcium

phosphate, $Ca_3(PO_4)_2$, but frequently contains some calcium fluoride. In the high temperatures of an electric furnace calcium phosphate, coke, and sand interact, the silica in effect displacing the more volatile phosphorus(V) oxide from its calcium salt, leaving calcium silicate. The phosphorus oxide is reduced by the carbon, forming carbon monoxide and phosphorus vapor, which is condensed to white phosphorus.

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 \rightarrow 6CaSiO_3 + 10CO + P_4$$

Arsenic occurs in nature in various minerals such as FeAsS. It is relatively easily obtained by reduction of the oxide with carbon. Antimony is not very abundant, occurring mostly as the sulfide, from which the metal is obtained by heating with scrap iron, which combines with the sulfur. Bismuth occurs native in certain rocks. It can be recovered simply by heating the rock, because the metal melts and runs out. It also occurs as the sulfide and the oxide, but none of these sources is abundant. Most bismuth is obtained as a byproduct from lead ores, and in the anode sludge from the electrolytic purification of copper.

As the outermost shell becomes more nearly filled, the differences between inert-shell and 18-shell elements within a group diminish. The electronegativity difference between silicon and germanium is not as great as between aluminum and gallium, and to the right sulfur and selenium appear nearly alike in this property. The question arises, then, whether the change from the 8-shell type in phosphorus to the 18-shell type in arsenic produces an increase in electronegativity. The electronegativity values given in Table 35 alternate, phosphorus being lower than nitrogen, arsenic higher than phosphorus, antimony lower than arsenic and about the same as phosphorus, and bismuth lower than antimony. Other electronegativity determinations appear to indicate that arsenic is slightly less electronegative than phosphorus, rather than more. Unfortunately, there seems to be too little evidence for proof. However, we do know that nitrogen forms a sulfide, N_4S_4, and arsenic forms As_4S_4, but neither phosphorus nor antimony form such sulfides. We know that phosphorus and antimony, but not arsenic, form pentachlorides. We know that nitrogen(V) and arsenic(V), but not phosphorus(V), are strongly oxidizing. We know that the trimethyl compounds of nitrogen and arsenic are not spontaneously inflammable, but those of phosphorus and antimony are. These and a number of other properties, such as heats of formation and bond energies where available, suggest alternations that could be explained in terms of the alternations in electronegativity given in the table. However, the problem is complicated by other factors such as size differences and the

inert pair effect, and we can only say that the known facts are not inconsistent with the alternating values as tabulated.

The oxides of nitrogen and phosphorus were discussed in Chapter 13. Their molecular differences make it difficult to compare them profitably. However, we can observe that the much higher electronegativity of nitrogen than phosphorus makes the nitrogen-to-oxygen bonds much less polar, and correspondingly less stable thermally. Furthermore, the nitrogen oxides are generally strong oxidizing agents, whereas those of phosphorus, even P(V), are scarcely oxidizing at all. The nitrogen oxides are also expected to be more acidic, and although HNO_3 is certainly a stronger acid than HPO_3 (metaphosphoric acid, derived from orthophosphoric acid, H_3PO_4, by removal of one molecule of water), phosphorous acid, H_2HPO_3, is stronger than nitrous acid, HNO_2. It is difficult to know the significance of such comparisons, however, in view of the structural differences. HPO_3, for example, is polymeric instead of monomolecular like HNO_3, and H_2HPO_3 is anomalously strong, evidently somehow related to the attachment of a nonacidic hydrogen directly to the phosphorus.

Arsenic acid, H_3AsO_4, might be expected to be stronger than phosphoric acid if the bonds to oxygen are less polar, as they would be if arsenic is more electronegative than phosphorus. Actually, the first ionization is somewhat weaker than that of phosphoric, but the second two ionizations are considerably stronger, as predicted.

Antimony and bismuth also form oxides in both the (III) and (V) states, but the inert pair effect enters into the picture especially with bismuth, making its (V) oxide quite unstable and a powerful oxidizing agent.

All these elements form analogs of ammonia, but phosphine, PH_3, arsine, AsH_3, stibine, SbH_3, and bismuthine, BiH_3 are all much less polar than ammonia, and unassociated by protonic bridging. They are therefore gases, much more volatile than the lighter ammonia. Consistent with the weaker bonding of hydrogen to large atoms, they are increasingly unstable down the group, and on account of its instability BiH_3 is hardly known. Similarly, they are much poorer electron donors than ammonia, and form far fewer coordination compounds. They are all extremely toxic, even in traces, and must be guarded against. For example, they are likely to contaminate hydrogen formed by the action of aqueous acids on impure metals containing traces of these elements, especially arsenic. The action of dilute sulfuric acid on iron or zinc, in a laboratory hydrogen generator, may convert traces of arsenic present in the metal to arsine, which would be evolved with the hydrogen.

This is an example of the general hydrolytic reaction of a binary compound. The oxygen of the hydroxyl group goes to the less electronegative element, the metal, and the hydrogen goes to the more electronegative element, the arsenic:

$$M—As + H_2O \rightarrow M—OH + AsH_3$$

The halides of all these elements, some of which have already been discussed in Chapter 14, are all hydrolyzed by water, those of antimony and bismuth ordinarily only partially, with the formation of oxyhalides such as BiOCl. Being fairly high in electronegativity, these elements can unite with active metals as well as with nonmetals, becoming negatively charged in the metal compounds. The resulting nitrides, phosphides, arsenides, and antimonides are known for many of the metals.

In compounds, nitrogen is exceedingly important as ammonia and nitrates, as well as in other nitrogen compounds used in fertilizers, such as urea, $(NH_2)_2CO$, and guanidine, $(NH_2)_2CNH$. It is an essential part of many explosives also. Frequently these are combinations, within the same molecule, of easily combustible carbon and hydrogen, with oxygen joined to nitrogen, from which it cannot acquire high charge. In effect, a reducing agent and an oxidizing agent are bound together in the same molecule, giving as intimate a mixture as could be imagined. Among the factors resulting in high evolution of energy when the explosive decomposes are the great strength of the N_2 molecule which forms from the nitrogen and the heat of combustion of hydrogen and carbon by the oxygen. All the products are gaseous, and when a solid is changed suddenly within a confined space to a very hot gas, things are bound to happen. Nitrogen compounds also have many applications in drugs, dyes, plastics, and other products.

The phosphates are the most important of phosphorus compounds, especially for their application as plant food. A fertilizer labelled, for example, "5–10–5" is thus indicated to contain 5 per cent nitrogen, 10 per cent soluble phosphorus calculated as the (V) oxide, and 5 per cent potassium as the oxide. Phosphate rock is extremely insoluble and hence not available for plant food. However, introduction of hydrogen in place of part of the calcium imparts water solubility, just as it does in bicarbonates, bisulfates, and similar compounds. Phosphate fertilizers are made by treating phosphate rock either with sulfuric acid, which introduces inert calcium sulfate to the mixture, or with phosphoric acid, which gives a more highly concentrated source of phosphate ion. Phosphorus sulfides are used in the heads of strike-anywhere matches.

Arsenic compounds are notorious for their toxicity. Many accidental as well as purposeful poisonings have resulted from the presence of arsenic where it was unsuspected. An entire family was made ill when they moved back into a riverbank home which had recently been flooded. The illness was traced to the decomposition of arsenic-containing ingredients of the wallpaper, caused by moisture and bacteria, liberating gaseous arsenic compounds. In England, a mysterious mass poisoning of beer drinkers was investigated, and it was discovered that a trace of arsenic was present in the sulfuric acid which had been used in the production of glucose to be used in making the beer. With such potential, it is not surprising that the major uses of arsenic take advantage of its toxicity. Calcium and lead arsenates, $Ca_3(AsO_4)_2$ and $Pb_3(AsO_4)_2$, are valuable insecticides, and certain other arsenic compounds make up the deadly "Lewisite" and "mustard gas" used in warfare. Arsenous oxide, As_4O_6, has some application in glass, serving to remove most of the color due to iron or manganese. Sodium arsenate, Na_3AsO_4, has some use in printing inks, and medicinal applications of hundreds or thousands of arsenic compounds have been investigated, but not always without tragic results. Perhaps the most successful has been the organic arsenic compound known as "606," or "salvarsan," the first effective drug for treatment of syphilis prior to the discovery of the antibiotics.

Antimony compounds have numerous practical applications. The oxide, Sb_4O_6, is used to flameproof textiles such as canvas, as a white pigment in paints and lacquers, in ceramic enamels, and in glass and pottery. The sulfide, Sb_2S_3, is used in camouflaging paints, ammunition primers, and safety matches. The (V) sulfide is used in some rubber in place of carbon black for vulcanizing; it imparts the familiar red color. The chlorides have some application in the coloring of metals, and as catalysts for chlorination and other reactions. Bismuth compounds have more limited use. They have been applied in ceramics, cosmetics, medicinal compounds, and pigments.

GROUP VIA

Some properties of these elements are listed in Table 36. With now six electrons in the outermost shell of each atom, and only two vacancies, metallic properties are only approached toward the bottom of the group. Selenium and tellurium have some metallic qualities but are metalloid at most, rather than metallic, although tellurium is usually classed as a nonmetal. Oxygen is so highly electronegative that it would not use

outer *d* orbitals even if it had them, but the other elements in this group, especially in combination with oxygen or fluorine, are able to promote electrons to outer *d* orbitals, thus expanding their valence from 2 to 4 or 6.

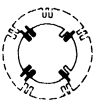
Oxygen has applications in artificial atmospheres, as in hospitals and diving operations, in welding, and in the steel industry, where large quantities are used to oxidize impurities in the iron. The present consumption in the steel industry exceeds 12,000 tons per day. Another 8,000 tons per day are used in other parts of the chemical industry, and enormous quantities are used in the rocket propulsion systems under development. Among other chemical applications are the production of acetylene from other hydrocarbons, and the production of olefin oxides and related compounds, as well as in the production of synthesis gas for ammonia.

Sulfur is used in the vulcanization of rubber and as an insect repellent dust. Selenium is photosensitive, its electrical conductivity increasing remarkably in the light. It is therefore very useful for photoelectric cells, which allow current to flow only when they are activated by light. It also has the quality of imparting a red color to glass. This is not only useful in making red glass, but it also helps to make cheap glass more nearly colorless. The common impurity of iron gives ordinary glass a greenish tint. Addition of a little red neutralizes this, saving the cost of purifying the raw materials from which the glass is made. Tellurium has some application in semiconductors, but otherwise has little practical use.


O 2+6


S 10+6
(2-8-6)


Se 28+6
(2-8-18-6)


Te 46+6
(2-8-18-
18-6)


Po 78+6
(2-8-18-
32-18-6)

Figure 125.

The chemistry of oxygen has been discussed in some detail in Chapter 12. It is much more electronegative than any of the other elements in its family, and can therefore form oxides with them in which the bonds are somewhat polar, although of course not highly so. Sulfur, sulfur dioxide, and sulfur trioxide have already been discussed. Selenium forms analogous oxides, SeO_2 and SeO_3, and analogous acids, H_2SeO_3 and H_2SeO_4. The oxides differ from those of sulfur in being more highly associated, polymerization through single bonding being favored over multiple bonding in single molecules. They differ also in the stability of the oxidation states. SeO_2 is a much more active oxidizing agent than SO_2, being readily reduced to elemental selenium. SeO_3 is only made by the agency of a strong oxidizer, and itself readily oxidizes

Table 36 Some Properties of Group VIA Elements

	O	S	Se	Te
atomic number	8	16	34	52
electronic structure	2-6	2-8-6	2-8-18-6	2-8-18-18-6
or, 6 electrons beyond:	He	Ne	Zn^{++}	Cd^{++}
atomic weight	15.999	32.064	78.96	127.60
atomic volume, ml/mole	14.0	15.5	16.5	20.4
density, g/ml	1.27	2.06	4.82	6.25
melting point, °C	−218.9	119.0	220	450
heat of fusion, kcal/mole	0.053	0.34	1.25	4.28
boiling point, °C	−183	440.6	688	1390
heat of vaporization, kcal/mole	0.81	2.3	6.29	12.1
covalent radius, Å	0.73	1.02	1.16	1.35
heat of atomization, kcal/g-atom	59.2	56.9	49.4	46.5
electronegativity	3.46	2.66	2.76	2.34
ionization energy, first, kcal/g-atom	314	239	225	208

other substances to become reduced. Selenious acid, unlike sulfurous acid, is stable enough to be isolated. The solution is about as acidic as sulfurous acid, and similarly selenic acid is about as strong as sulfuric acid. Both the selenium acids, however, are much stronger oxidizing agents than the sulfur acids. Since sulfur and selenium appear to be quite close in their electronegativities, we must find some other basis for explaining these differences. The only one obviously available is the larger size of the selenium atom, together with the fact that oxygen would not be expected to form as stable bonds to larger atoms, if polarity were to be the same. However, we have already noted that germanium dioxide is not as stable as silicon dioxide, and that arsenic(V) oxide and arsenic acid, H_3AsO_4, are much more strongly oxidizing than the corresponding phosphorus compounds. To the right of sulfur and selenium in the periodic table are chlorine and bromine. Although oxides of chlorine are not very stable, they are much more so than oxides of bromine, even though their bonds would be expected to be less polar. There is thus evidence that the transition from 8-shell to 18-shell element may bring about differences in the nature of the bonding to oxygen that cannot be interpreted solely on the basis of electronegativities, and may depend on electronic structure as well as on atomic radius.

Tellurium, on the other hand, is much less electronegative than sulfur and selenium, and its bonds to oxygen are much more polar. TeO_2 is a solid, only slightly soluble in water, and amphoteric therein. Strong oxidizing agents can oxidize it to telluric acid, $Te(OH)_6$, but this is not formally analogous to sulfuric and selenic acids. It is very soluble in water, but a very weak acid, as one would predict from the number of hydrogens, which help to give the oxygen a higher negative charge than otherwise.

The hydrogen compounds, water and hydrogen sulfide, have already been described. Hydrogen selenide, H_2Se, and hydrogen telluride, H_2Te, are also known. In keeping with the larger size of the anion, going down the group, the electron donating ability of the anion to a proton diminishes and therefore the acidity of the solutions of these gases increases, H_2Te forming the strongest acid, although it is still very weak. In keeping with the increasing size, also, the bonds to hydrogen are thermally less stable, and these gases decompose to the elements easily. They are likewise easily oxidized by moist air to water and the free element, selenium or tellurium.

Salts of these hydrogen acids are known for most of the metals, and at least formally analogous to the oxides, there are sulfides, selenides, and tellurides. Various halides are known, all relatively nonpolar, volatile, and not highly stable as a class. They include hexafluorides of selenium and tellurium, which are nearly but not quite as inert chemically as SF_6, because the six fluorines do not protect the larger selenium or tellurium atoms as well.

Compounds of oxygen of industrial importance are of course very familiar. Sulfuric acid is undoubtedly the most important single sulfur compound. Other sulfur compounds of significance include sodium thiosulfate, $Na_2S_2O_3$, used in photography because of its solvent action on silver halides:

$$Ag^+ + 2S_2O_3^= \rightarrow Ag(S_2O_3)_2^{\equiv}$$

as well as "sulfa drugs," sulfonates used as detergents, and many others. Compounds of selenium and of tellurium have relatively little practical application, in part because these elements are so scarce.

GROUP VIIA

Some properties of these elements, the halogens, are given in Table 9, page 278. They have already been discussed in some detail in Chapter 14. Except for their compounds with oxygen, mentioned in Chap-



F 2 + 7



Cl 10 + 7
(2-8-7)



Br 28 + 7
(2-8-18-7)



I 46 + 7
(2-8-18-
18-7)



At 78 + 7
(2-8-18-
32-18-7)

Figure 126.

ter 12, most of the important compounds of the halogens find them in their -1 oxidation state, as halides. These compounds have already been discussed in connection with the other elements. Fluorine, being most electronegative of all the elements, would never use outer *d* orbitals even if it had them, but the other halogens in combination with fluorine or oxygen can acquire positive oxidation states in which the *d* orbitals would appear to be involved.

Fluorine occurs chiefly as fluorspar, CaF_2, which in contrast to $CaCl_2$ is very insoluble. It also occurs in minerals associated with phosphate rock. It is present in the mineral cryolite, Na_3AlF_6, which was mentioned in Chapter 21 as being the electrolytic medium for production of aluminum. Fluorine can only be freed from its compounds by electrolysis, ordinarily of a fused KF-HF mixture. Chlorine has its greatest source in sodium chloride, from which it is formed by electrolysis of either the fused salt or aqueous solution. Chloride ion can also be oxidized by strong chemical agents. Bromine is very thinly distributed, and the chief commercial source is the sea, in which it occurs in a concentration of about 65 parts per million. To recover it, batches of seawater are first acidified, to minimize the following reaction of all the halogens but fluorine with water:

$$X_2 + 2H_2O \rightarrow HOX + H_3O^+ + X^-$$

Chlorine is then passed into the water, where it oxidizes the bromide ions to free bromine. Air is next bubbled through to sweep out the bromine, which is collected in one of several chemical solutions which absorb bromine and from which the bromine can easily be recovered later. By this means, approximately one pound of bromine can be isolated from about 8 tons of seawater.

Iodine is much less abundant than bromine, and in seawater it is present in concentration too low for practical recovery by chemists—but not by seaweed. Kelp, for example, absorbs iodine from the sea and concentrates it within the plant. Men harvest the kelp, dry and burn it, and isolate iodine from the ash. Some iodate, $NaIO_3$, is found crystallized with the $NaNO_3$ in Chile saltpeter, and can be reduced to elementary iodine by action of bisulfite:

$$5HSO_3^- + 2IO_3^- \rightarrow I_2 + 5SO_4^= + 3H^+ + H_2O$$

From salt wells containing iodide ion, free iodine can be obtained by the action of chlorine.

Free fluorine has no practical uses except as a reagent to form fluorine compounds but, being a powerful oxidizing agent, it has potential in rocket propulsion. Free chlorine was applied as the first weapon in gas warfare. It is used in the purification of water to kill microorganisms. Bromine has no uses save as a brominating agent; iodine has application mainly in solution in alcohol, as the antiseptic "tincture of iodine."

Compounds of fluorine have become of increasing importance in recent years. A vast new field of chemistry has been opened up by the discovery that many organic compounds have analogs in which all the hydrogen attached to carbon is replaced by fluorine. "Fluorocarbons" and their derivatives ("perfluoro-compounds") are being investigated very actively. Despite their much higher molecular weight, fluorocarbons are often as volatile or more so as the corresponding hydrocarbons. This can be explained as the consequence of inter-fluorine repulsions. The high polymer "teflon" is an extremely stable and chemically unreactive product of "perfluoroethylene," $CF_2{=}CF_2$. Hydrogen fluoride is important as a catalyst in the petroleum industry, especially in "alkylation," a process of combining isoparaffin gases with olefin gases to make high quality liquid gasoline. The "freon" used in refrigeration and as a propellant in aerosols is difluorodichloromethane, CF_2Cl_2. This compound is odorless and nontoxic. Small traces of sodium fluoride in drinking water have been shown to be effective toward preventing tooth decay, becoming part of the mineral content of the enamel and hardening it.

Chlorine compounds are widely used. Aluminum chloride is one of the most important catalysts for organic reactions. Carbon tetrachloride and other chlorinated hydrocarbons are very valuable solvents. "Chlorox" is widely used as a laundry bleach. This is a solution of sodium hypochlorite, NaOCl, formed by electrolysis of a stirred sodium chloride solution. Hydrogen is evolved at the cathode, but the chlorine evolved at the anode is thoroughly mixed with the hydroxide ions left in solution, reacting to form chloride ion and hypochlorite ion:

$$Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O$$

The reaction is conducted in the cold, because when heated, solutions of hypohalite disproportionate to higher and lower oxidation states, forming from hypochlorite mainly chlorate, ClO_3^-, and chloride ion:

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

Chlorates, perchlorates, and perchloric acid, $HClO_4$, the most stable of the chlorine-oxygen acids, are useful oxidizing agents. Perchloric acid is the strongest of the common acids, and even in the monohydrate it is largely in the form of hydronium perchlorate, $[H_3O^+][ClO_4^-]$. The low negative charge on the oxygen in the perchlorate ion prevents effective electron donating action toward a proton, so that a proton is easily removed from a perchlorate ion (as $HClO_4$) by a molecule of water.

The greater part of the bromine isolated from the sea is converted to ethylene dibromide, previously discussed as an ingredient of ethyl fluid, the antiknock agent for gasoline. This compound is also useful as a soil fumigant. Methyl bromide, CH_3Br, is also used as a fumigant. Although it is toxic, it is nonflammable, and has some application as a fire extinguisher in locations far enough removed from personnel. Silver bromide is important in photography, being sensitive to light and converted by its agency to free silver on a film or photographic plate. Iodine compounds must be present in the diet to prevent goiter, and some sodium iodide is introduced into table salt, which is then called "iodized salt." Bromine and iodine compounds have great importance as intermediates in organic synthesis but few direct practical applications. Hydrogen bromide and hydrogen iodide are gases very similar to hydrogen chloride, and form even stronger acids in solution. This is related to the diminishing ability of an anion as its size increases to coordinate a proton. Thus iodide ion is a weak base toward a proton, which makes hydriodic acid very strong.

SUMMARY OF THE PERIODICITY OF THE MAJOR GROUP ELEMENTS

We can perhaps best summarize the trends observed in the preceding survey of inert-shell and 18-shell elements by listing some general principles.

(1) The first period of 8 elements differs from subsequent period elements in having but two electrons in the underlying shell instead of 8 or 18. This permits smaller atoms, stronger bonds, and closer interaction as needed for multiple bonding.

(2) Within Groups IA and IIA, the elements are as electronically similar as the inert elements of Group O. Consequently, reasonably smooth, or at least consistent, trends in properties from top to bottom are to be expected and are observed.

(3) From Group IIIA to the halogens, the electronic configurations within each group encounter a fundamental change in going from

8-shell type in Period 3 to 18-shell type in Period 4. This change has significance in that the 18-shell elements have more compact electronic clouds and higher electronegativity than would otherwise be expected in the group. These effects appear to diminish as the number of outermost electrons is increased, and to disappear in the halogens. It results in alternations rather than steady sequences of properties, going down Groups IIIA, IVA, and VA especially.

(4) Despite the changes from 8-shell to 18-shell element, the trend is fairly constant toward increasing metallic character down a group.

(5) The general trend down a group is toward larger atoms and lower ionization energies, forming compounds of diminished stability.

(6) Within a major group the valence tends to be constant, as determined by the number of outer shell electrons and vacancies. However, the *s* electrons tend to become less available for bonding, the higher their principal quantum number, and this leads to valences two less than maximum for the heaviest members of the groups.

(7) The cations of the elements within a group increase in size with increasing atomic number, and this corresponds to diminished polarizing power and diminished electron-acceptor power.

(8) Cations of 18-shell elements, however, tend to have greater polarizing power and to form more stable coordination complexes than cations of inert-shell elements.

(9) Anions of the same group have diminished ability to donate electrons to a proton with increasing size and atomic number. The hydrogen compounds therefore tend to increase in acidity.

(10) Except where certain transitions from 8-shell to 18-shell element are involved, the trend in electronegativity is downward within a group. This corresponds to a rough downward trend, usually not very extreme, toward diminished acidity and/or increased basicity of the oxides.

(11) Across the periods the trends are more reliably consistent. Fundamentally, they result from increased number of outermost electrons, reduced number of outermost vacancies, usually increased ionization energy and always increased average ionization energies for removal of all valence electrons, always diminished atomic radius, always increased nuclear charge, and always increased compactness and electronegativity.

(12) Compounds of the elements with the more highly electronegative nonmetals, including oxygen, sulfur, and the halogens, follow trends from left to right across a period of: (*a*) decreasing bond polarity, (*b*) decreasing lattice energy, (*c*) decreasing thermal stability, (*d*) decreasing melting point, (*e*) increasing volatility, (*f*) decreasing electron donor power, (*g*) increasing electron acceptor power, (*h*) decreasing reducing

power, (*i*) increasing oxidizing power. These trends hold generally but not without exception.

(13) Across a period, more confidently than down a group, one can predict the properties of an element from a knowledge of the properties of its closest neighbors. Similar predictions can be made within a group provided possible changes in fundamental electronic configuration are taken into account.

(14) Especially between periods 2 and 3 diagonal relationships are observable, because a trend one step to the right is reversed by one step downward.

(15) Hydrogen can more properly be placed near the center of the periodic table of the major groups, above and perhaps slightly to the left of IVA. Hydrogen is intermediate in electronegativity, and can become partially negative or partially positive in its combination with other elements. The binary compounds of hydrogen therefore show the following trends from left to right across the periodic table of major group elements: (*a*) from highly negative hydrogen through neutral to moderately positive hydrogen, (*b*) from highly condensed, ionic crystalline salts of negative hydrogen, through hydridic bridged aggregates containing less negative hydrogen, to molecular, volatile compounds containing neutral and positive hydrogen, with increasing tendency toward protonic bridging in the compounds of period 2 elements, (*c*) from strongly electron-donating through neutral to electron-accepting hydrogen compounds, (*d*) from reducing agents to oxidizing agents, (*e*) from basic through neutral to acidic substances.

SPECIAL HELP

Test Your Memory

1. What are the chief distinguishing characteristics of the alkali metals?
2. What are some important compounds of these metals and their uses?
3. Name some alkaline earth compounds and their uses.
4. What is "borax"?
5. Of what use is elementary boron?
6. Name some useful compounds of boron.
7. List some important uses of elementary carbon and elements of its group.

8. What are some practical uses of silicates?
9. What is meant by "leaded" gasoline?
10. Write the equation for the production of white phosphorus from phosphate rock.
11. What are some practical applications of elementary arsenic, antimony, and bismuth?
12. What are the chief uses of the oxygen group elements and their compounds?
13. How is bromine obtained from the sea?
14. What are "fluorocarbons"?

Test Your Understanding

1. How would you expect the alkali metal hydrides to compare in stability, and why?
2. Why should barium hydroxide be a stronger base than beryllium hydroxide?
3. What qualities do BF_3 and $AlCl_3$ have that make them so useful as catalysts?
4. Why should the heat of combustion be higher for boron than for carbon?
5. How might boron oxide function in removing oxide coatings from metal surfaces?
6. "Mortar" before the development of Portland cement consisted usually of sand, slaked lime, and water. Suggest how this might "set" on standing.
7. Considering the acidic nature of silica and some silicates, suggest why glass bottles containing alkaline solutions are frequently fitted with rubber instead of glass stoppers in the laboratory.
8. A general method of preparing binary hydrogen compounds that do not react with water is by action of aqueous acid on a binary compound. This forms the hydroxide of the less electronegative element and the hydrogen compound of the more electronegative element, in keeping with the principle of combining to form the most polar bond possible. Consider the possible hazards of dissolving in acids impure metals containing traces of arsenic.
9. Why is not the iodine present in the sea removed with the bromine?

26

Survey of the Transition Elements

THE AVAILABILITY of underlying *d* electrons for bonding gives the transition elements certain qualities which, although not yet completely understood, are generally agreed to set these elements apart as a distinct type of element. Some of the fundamental and distinguishing differences are summarized as follows:

(1) They do not appear to form stable bonds to hydrogen or to carbon, whereas other types of elements do. Instead of forming the stoichiometric binary compounds of hydrogen characteristic of the inert-shell and 18-shell elements, the transition metals absorb hydrogen more or less indefinitely, the amount dependent on conditions and limited by the crystal structure or other factors. The hydrogen in some of these metals approaches a conventional stoichiometric relationship but never quite reaches it. The hydrogen appears to be held more as an alloy, interstitially, rather than by bonds to particular metal atoms. In some cases the hydrogen so held is extremely reactive, in other cases extraordinarily inert. With the exception of platinum and, to a much

lesser extent, gold, these elements do not form stable organometallic compounds, at least not of the types and having properties of those formed by the other elements.

(2) The transition metals, characteristically although not uniquely, tend to show a variety of positive oxidation states for each element. In the transition metal groups, the lower states appear to be more stable, the higher states less stable, for the first element of the group. For the remaining two members, the higher oxidation states are the more stable, the lower states sometimes not even being observed, and the highest state no longer being unstable as for the first element. This tendency is somewhat the reverse of that observed in the major group elements, where the increase in "inert pair" effect down the group leads to decreased stability of the highest oxidation states.

As would be predicted, the same element tends toward less basicity, higher acidity, with increasing positive oxidation state.

(3) Transition metal compounds, both in solution and out, tend to be highly colored, suggesting that the energy levels in the *d* orbitals are in most cases sufficiently close together to allow light of specific wavelengths in the visible spectrum to be absorbed by transition of electrons. Color is not, of course, confined to transition metal compounds, but it is quite, although not without exception, characteristic of them. Different oxidation states generally show different colors, as might be expected.

(4) Transition metal ions, although again not unique in this respect, characteristically have a great tendency to form coordination complexes. Thousands of such complex compounds are known. Certain characteristics of these complexes, such as magnetic properties and colors or absorption spectra in general, can be interpreted by consideration of the nature of the *d* orbitals involved, in which respect complexes of transition metals differ from the complexes of the other elements.

(5) As metals, the transition elements tend to have very strong metallic bonding, which gives them valuable mechanical properties as well as corrosion resistance, making them as a group superior to nontransition metals for construction purposes.

The general shapes, or boundary surfaces, of *s*, *p*, and *d* orbitals were shown in Figure 7 on page 49. The *d* orbitals are much more difficult to depict all together, but not too difficult to describe separately. Instead of consisting of two lobes extending in opposite directions from the nucleus, as do the *p* orbitals, the *d* orbitals more nearly resemble two *p* orbitals together, forming a square cross with four lobes extending from the nucleus toward the four corners of the square. These lobes are more ellipsoidal than spherical. Now let us imagine that we

have five such crosses and wish to fit them together symmetrically so that they have all five intersections at the nucleus of an atom. Visualize the usual orthogonal coordinates, consisting of X, Y, and Z axes with the atomic nucleus at their origin. We can place one d orbital in the X-Y plane, so that its lobes extend halfway between the axes, as shown in Figure 7(a). Call this the d_{xy} orbital. Another d orbital can be placed similarly in the X-Z plane, and a third in the Y-Z plane. Call these the d_{xz} and d_{yz} orbitals. The six projections of the three axes are still free and unfilled by orbitals. You can see that we could place one more d orbital with its lobes extending along any two of the axes. Let us place it along the X and Y axis and call it the $d_{x^2-y^2}$ axis. If we try to place the fifth orbital with the others, we find the only position left available to be along the Z axis. This has room for only two lobes. The other two would lie in the X-Y plane which is already fully occupied, both along the X and Y axes and between them. However, a hybrid can be formed by averaging two such positions, which leads to a fifth d orbital extending mainly along the Z axis, but which includes a small doughnut-shaped ring perpendicular to it at the nucleus. This is called the d_{z^2} orbital, and is depicted in Figure 7(b).

When the five d orbitals are so placed together, perfect external spherical symmetry results. If we were to represent the individual lobes of the five orbitals as circles on the surface of the atomic sphere, we would find 18 such circles, four from each of the first four orbitals and two from the last. These would be distributed as three orthogonal rings of 8 circles each around the sphere. The second ring would share two of the circles of the first ring at the two points of intersection, and the third ring would share four of the circles of the first two rings at the four points of intersection. The total number of rings (lobes) would thus be $8 + 6 + 4 = 18$.

The five d orbitals in the isolated atom are exactly equivalent in energy. Electrons tend to spread out as they are added in the building up of the transition element atoms, one to each d orbital. No pairing occurs until necessary—in other words until the sixth electron, which has no place to go other than into an orbital that is already occupied. As has already been noted (Chapter 2), the condition of 5 d orbitals exactly half full, or 5 d orbitals exactly full, is sufficiently stable that when the condition is closely approached, an electron can drop back from the outer s orbital to complete it. This occurs in chromium, which instead of having 4 d electrons and 2 outer s, has 5 d electrons and 1 outer s, and in copper which instead of having 9 d electrons and 2 outer s has 10 d electrons and 1 outer s.

Ligand Field Theory

Although the five *d* orbitals are exactly equivalent in the isolated atom or ion, they do not necessarily remain so in the electrical field of an approaching electron donor, or ligand. Such a ligand tends to repel electrons from certain of the *d* orbitals (the ones closer to it) more than it does the electrons of other *d* orbitals. In other words, it makes the energy levels unequal. If the field of the ligand is strongly repelling enough, it may cause *d* electrons which are initially unpaired to find it more stable to be *paired* in a different orbital than to remain *unpaired* where they are. If they do become paired on this account, they leave their original orbital vacant to accept an electron pair from the ligand. If the ligand field is not strong enough to force this pairing, and the electrons remain unpaired, the ligand must use some other vacant orbital, such as an *outer d* orbital, in order to become coordinated to the transition metal ion. These are some of the fundamental ideas behind what is called the "ligand field theory," by which a number of interesting and otherwise puzzling aspects of the coordination chemistry of transition elements can be explained. For example, the absorption of light, responsible for the colors of many of these compounds, appears to depend on the induced differences in *d* orbital energy levels, allowing transitions of electrons from one such level to another to absorb certain frequencies of light. A more complete description of this theory is beyond the scope of this book, but will be encountered in advanced chemistry courses.



Sc 18 + 3
(2-8-9-2)

GROUP IIIB

These elements, scandium, yttrium, and lanthanum, include the rare earth elements, in which the 4*f* electrons are being added, leaving the valence shell nearly constant. They are quite rare and have relatively little practical application, as yet. Some of their properties are given in Table 37. Like all transition elements, these elements are all metals, being quite reactive in this state. They form oxides of type formula M_2O_3, which are weakly basic but much more so than the corresponding oxides of Group IIIA. Some are basic enough to absorb carbon dioxide from the air.



Y 36 + 3
(2-8-18-9-2)



La 54 + 3
(2-8-18-
18-9-2)

Figure 127.

Table 37 Some Properties of Group IIIB Elements

	Sc	Y	La
atomic number	21	39	57
electronic structure	2-8-9-2	2-8-18-9-2	2-8-18-18-9-2
or, 3 electrons beyond:	Ar	Kr	Xe
atomic weight	44.956	88.905	138.91
atomic volume, ml/mole	18.0	16.2	22.6
metallic radius, Å	1.44	1.62	1.69
density, g/ml	3.04	4.34	6.18
melting point, °C	1423	(1500)	920
heat of fusion, kcal/mole	3.85	4.1	2.7
boiling point, °C	2480	(3230)	3370
ionization energy, first, kcal/mole	154	150	129
electrode potential, volts ($M \rightarrow M^{3+}$)	2.08	2.37	2.52
heat of atomization, 25°, kcal/g-atom	82	102	99.6
oxidation states	3	3	3

Table 38 Some Properties of Group IVB Elements

	Ti	Zr	Hf
atomic number	22	40	72
electronic structure	2-8-10-2	2-8-18-10-2	2-8-18-32-10-2
atomic weight	47.90	91.22	178.49
atomic volume, ml/mole	10.6	14.3	(14.3)
metallic radius, Å	1.32	1.45	1.44
density, g/ml	4.49	6.52	13.31
melting point, °C	1677	1852	2222
heat of fusion, kcal/mole	3.7	4.0	5.2
boiling point, °C	3280	4380	5280
ionization energy, first, kcal/mole	158	160	127
heat of atomization, 25°, kcal/g-atom	112.6	146	168
oxidation states	4,3,2	4	4
oxidation potential, volts ($M \rightarrow M^{4+}$)	1.63(Ti^{++})	1.53	1.70

GROUP IVB



Ti 18 + 4
(2-8-10-2)



Zr 36 + 4
(2-8-18-
10-2)



Hf 68 + 4
(2-8-18-
32-10-2)

Figure 128.

Some properties of these elements are given in Table 38. Their atoms, like those of IIIB, appear to be less compact than those of the corresponding major group elements and more metallic. Electronegativity values for these, as well as the other transition elements, appear to be known only very approximately, but seem to fall in the range from 1.2 to 1.7 for all transition metals.

Titanium is widely distributed in the soil and rocks, but in concentrations too small to make these a commercial source. Deposits of the oxide and related minerals are found in certain areas, including Florida and India. The oxide, TiO_2, may be converted to chloride with carbon and chlorine and then reduced with magnesium. Zirconium and hafnium are found mainly as the dioxides, the hafnium practically always associated with the zirconium, about one part of hafnium to fifty parts of zirconium. Hafnium compounds bear so remarkable a resemblance to the corresponding zirconium compounds that the metals are very difficult to obtain pure, uncontaminated by the other. Conversion to the tetraiodide and thermal decomposition of the iodide produces the free metals.

Although relatively low in density (4.5), titanium is extremely strong and tough, and resistant to corrosion even at high temperatures. It thus has importance as a structural metal which will undoubtedly increase as it becomes more readily and cheaply available. Zirconium has application in nuclear reactors.

Perhaps the most important compound of titanium is the dioxide, which when pure is very white and suitable as a nondarkening pigment. Titanium tetrachloride is a colorless liquid used in making smoke screens. Zirconium and hafnium dioxides are good high temperature insulating materials.

GROUP VB

Vanadium, niobium, and tantalum have properties as listed in Table 39. As is characteristic of transition metals, the first member of the group shows lower oxidation states, but the others tend to show chiefly



V 18 + 5
(2-8-11-2)



Nb 36 + 5
(2-8-18-
12-1)



Ta 68 + 5
(2-8-18-
32-11-2)

Figure 129.

the highest. Thus vanadium has compounds in which its oxidation state is +2, +3, +4, and +5, but the chief state of the other two metals in their compounds is +5.

Vanadium occurs in combination with sulfur, V_2S_5, and in certain other minerals containing lead or uranium. Niobium and tantalum are very rare, being found chiefly together in the form of oxides that are extremely difficult to reduce.

The chief use of vanadium as a metal is in alloys with iron. It removes harmful oxygen and nitrogen from steel, and, when alloyed with it, imparts greater strength, elasticity, and toughness. Niobium is relatively little used, but resembles tantalum in extreme corrosion resistance. Tantalum is so resistant to chemical attack, especially by acids, that despite its scarcity it finds valuable application in equipment for chemical manufacturing.

Probably the most important compound of vanadium is the pentoxide, V_2O_5, a red solid valuable as a catalyst in oxidation, as in the contact process for sulfuric acid. Tantalum carbide is used in tools for high speed—and thus high temperature—machining of metals.

Table 39. Some Properties of Group VB Elements

	V	Nb	Ta
atomic number	23	41	73
electronic structure	2-8-11-2	2-8-18-11-2	2-8-18-32-11-2
atomic weight	50.942	92.906	180.948
atomic volume, ml/mole	8.5	10.8	10.9
metallic radius, Å	1.22	1.45	1.44
density, g/ml	5.98	8.58	16.69
melting point, °C	1917	2487	2997
heat of fusion, kcal/mole	4.2	6.4	7.5
boiling point, °C	3380	4930	5400
ionization energy, first, kcal/mole	156	156	138
heat of atomization, 25°, kcal/g-atom	122.8	177.5	186.8
oxidation states	5,4,3,2	5,3	5

Table 40 Some Properties of Group VIB Elements

	Cr	Mo	W
atomic number	24	42	74
electronic structure	2-8-13-1	2-8-18-13-1	2-8-18-32-12-2
atomic weight	51.996	95.94	183.85
atomic volume, ml/mole	7.3	9.4	9.5
metallic radius, Å	1.17	1.29	1.30
density, g/ml	7.2	10.2	19.1
melting point, °C	1900	2610	3380
heat of fusion, kcal/mole	3.3	6.6	8.4
boiling point, °C	2642	4830	5530
ionization energy, first, kcal/mole	156	166	184
heat of atomization, 25°, kcal/g-atom	80.5	155.5	201.6
oxidation states	3,6,2	6,2,3,5,4	6,2,3,4,5
electrode potential, volts ($M \rightarrow M^{3+}$)	0.74	0.2	

GROUP VIB

Some properties of these metals are listed in Table 40. Again we find the tendency for the lightest metal of the group to form the lower oxidation states, the highest states being most stable for the other members. Chromium shows +2, +3, and +6 states; molybdenum +3, +4, and +6; tungsten mainly +6.

Chromium occurs principally as "chromite," $FeCr_2O_4$. This can be reduced directly to an iron-chromium alloy, or the chromium can be separated chemically and then isolated. Molybdenum occurs mainly as "molybdenite," MoS_2. This can be converted to MoO_3 by heating in air; the oxide is then reduced at high temperature by hydrogen. Tungsten is found in "tungstates," metal salts of tungstic acid, H_2WO_4. The acid is precipitated when the salts are acidified, and dehydrated to the trioxide by heating. This can be reduced to the metal by hydrogen. Both molybdenum and tungsten have very high melting points, with the result that reduction gives the metal in the form



Cr 18 + 6
(2-8-13-1)



Mo 36 + 6
(2-8-18-
13-1)



W 68 + 6
(2-8-18-
32-12-2)

Figure 130.

of a fine powder instead of a metallic mass. It is sintered together by heat and pressure.

Chromium as a plating metal for steel is well known. In addition, it is used as an alloying metal for steel, giving it a resistance to corrosion that has led to the term "stainless steel" when it is used in proportions from 10 to 25 per cent of the steel. Most molybdenum metal is used in steel manufacture as an alloying agent, giving fine grain and great toughness to the steel. Tungsten has uses as a filament in incandescent lamps and as an alloying agent for making "tungsten steels," useful for high-speed cutting because they retain toughness even at high temperatures.

Among the useful compounds of chromium are the "chromates," salts of "chromic acid," H_2CrO_4, and the "dichromates," salts of "dichromic acid," $H_2Cr_2O_7$. Dichromates are orange, and chromates yellow. Their interrelationship is observed when a solution of chromate is acidified:

$$2CrO_4^{=} + 2H_3O^{+} \rightleftharpoons Cr_2O_7^{=} + 2H_2O$$

Solutions of dichromates (i.e., acid solutions of chromates) are good oxidizing agents. "Cleaning solution" in the laboratory, useful for removing traces of grease from glassware, consists of a mixture of concentrated sulfuric acid with sodium or potassium dichromate (*never* permanganate!) from which red CrO_3 slowly settles out. Chromium(III) oxide, Cr_2O_3, is a green pigment called "chrome green." The chief uses of molybdenum and tungsten lie in the metals rather than their compounds. In keeping with the greater stability of the highest state in these elements, molybdates and tungstates are not oxidizing agents, in contrast to the chromates.

GROUP VIIB

Some properties of manganese, technetium, and rhenium are listed in Table 41. Manganese occurs mainly as MnO_2, Mn_2O_3, or Mn_3O_4, from which the metal can be obtained by reduction with powdered aluminum. More commonly it is obtained as an alloy of iron, by reducing a mixture of iron and manganese oxides with carbon monoxide. Technetium is unknown in nature, being unstable in the nucleus, but it has been synthesized by bombarding molybdenum with neutrons. Rhenium is extremely rare, being found only as traces in certain minerals.

Manganese as the metal is used mainly in steel manufacture. It

Table 41 Some Properties of Group VIIB Elements

	Mn	Tc	Re
atomic number	25	43	75
electronic structure	2-8-13-2	2-8-18-14-1	2-8-18-32-13-2
atomic weight	54.938	(99)	186.2
atomic volume, ml/mole	7.6		8.6
metallic radius, Å	1.17		1.28
density, g/ml	7.21	11.5	20.9
melting point, °C	1244	2127	3180
heat of fusion, kcal/mole	3.5	5.5	7.9
boiling point, °C	2041		5630
ionization energy, first, kcal/mole	171		182
heat of atomization, 25°, kcal/g-atom	66.7	155	185.7
oxidation states	2,7,4,6,3	7	7,6,4,2,−1

forms compounds with oxygen and sulfur, in the molten steel, which are exceedingly insoluble, and thus serves to remove these impurities from the steel. As an alloying agent, relatively large amounts, of the order of 10 per cent or more, make the steel very tough and hard. Rhenium has some activity as a hydrogenation catalyst.

Manganese dioxide is used in dry cells, as discussed in Chapter 20. In the +7 oxidation state, manganese forms the unstable, explosive Mn_2O_7, and the salts of the hydrate of this oxide, especially $KMnO_4$, "potassium permanganate," a purple-brown solid having powerful oxidizing action. In acidic solution the manganese is reduced to the +2 state, but in alkaline solution to the +4 state (MnO_2). In contrast, rhenium is easily oxidized by heating in air to the oxide, Re_2O_7, which is stable and not an oxidizing agent. Its aqueous solutions are also nonoxidizing.



Mn 18 + 7
(2-8-13-2)



Tc 36 + 7
(2-8-18-
13-2)



Re 68 + 7
(2-8-18-
32-13-2)

Figure 131.

GROUP VIIIB-A

Some properties of the elements of VIIIB are listed in Table 42.

Iron is the fourth most abundant of the elements, and widely distributed over the earth's surface. Its ores are mainly Fe_2O_3 and Fe_3O_4,



Fe 18 + 8
(2-8-14-2)



Ru 36 + 8
(2-8-18-
15-1)



Os 68 + 8
(2-8-18-
32-14-2)

Figure 132.

which can be reduced as described in Chapter 21. Ruthenium occurs in nature as an alloy with osmium and iridium, from which it can be separated by a rather complex chemical process. Osmium is similarly obtained, but more easily isolated because of the volatility of its very poisonous tetraoxide, OsO_4. This compound distills off readily when the solution is acidified, and can be reduced easily to the metal.

The uses of iron and steel have been discussed in some detail in Chapter 21. Ruthenium has very little application except as a hardening agent in iridium or platinum, for fountain pen tips and similar uses. Osmium has similar application.

Compounds of these metals have little practical application, except from some of iron, especially some complex cyanides which form Prussian blue and Turnbull's blue pigments. Iron is of course the important center of the complex blood haemoglobin which carries oxygen to the tissues.

GROUP VIIIB-B

Cobalt occurs much less commonly than iron, chiefly in minerals containing arsenic. The ores must be roasted, dissolved in sulfuric acid, and the hydroxide precipitated by adding sodium carbonate. The oxide can be reduced by hydrogen. Rhodium is a very rare element occurring native, alloyed with platinum. Iridium occurs with osmium, and is separated chemically and then isolated.



Co 18 + 9
(2-8-15-2)



Rh 36 + 9
(2-8-18-
16-1)



Ir 68 + 9
(2-8-18-
32-17)

Figure 133.

Cobalt is important mainly in alloys. With chromium it forms an alloy, "cochrome," that resists corrosion at high temperatures and can be used in electrical heating. Cobalt itself is ferromagnetic, and is an important constituent of "Alnico" alloys extensively used for permanent magnets, these consisting of cobalt, nickel, aluminum, and copper. Other cobalt alloys are useful in high-speed cutting tools and in surgical instruments. Rhodium is used as a plating material in jewelry, and it imparts desirable properties in platinum used for scientific apparatus, especially for high temperature use. Iridium is used mainly as a hardening agent for platinum.

Table 42 Some Properties of Group VIIIB-a Elements

	Fe	Ru	Os
atomic number	26	44	76
electronic structure	2-8-14-2	2-8-18-15-1	2-8-18-32-14-2
atomic weight	55.847	101.07	190.2
atomic volume, ml/mole	7.10	8.27	8.38
metallic radius, Å	1.17	1.24	1.26
density, g/ml	7.86	12.30	22.7
melting point, °C	1539	2427	2727
heat of fusion, kcal/mole	3.67	6.1	7.0
boiling point, °C	2887	3727	4230
ionization energy, first, kcal/mole	182	173	201
heat of atomization, 25°, kcal/g-atom	99.8	144	160
oxidation states	3,2	3,4,6,8,2	4,2,3,6,8
oxidation potential, volts	$0.440(Fe^{2+})$ $-0.771(Fe^{2+} \rightarrow Fe^{3+})$		

Table 43 Some Properties of Group VIIIB-b Elements

	Co	Rh	Ir
atomic number	27	45	77
electronic structure	2-8-15-2	2-8-18-16-1	2-8-18-32-17
atomic weight	58.933	102.905	192.2
atomic volume, ml/mole	6.67	8.29	8.53
metallic radius, Å	1.16	1.25	1.26
density, g/ml	8.83	12.42	22.65
melting point, °C	1495	1966	2454
heat of fusion, kcal/mole	3.64	5.2	6.3
boiling point, °C	2877	3727	4130
ionization energy, first, kcal/mole	181	178	212
heat of atomization, 25°, kcal/g-atom	101.6	133	150
oxidation states	2,3	3,2,4	4,3,6,2
electrode potential, volts	0.277(++)	−0.8(+++)	

Compounds of these elements have little practical importance, but thousands of them, especially coordination compounds of cobalt, are of great theoretical interest.

GROUP VIIIB-C

Nickel occurs chiefly in mixed sulfides together with iron. Carbon monoxide reacts with nickel forming a volatile compound at 80° called "nickel carbonyl," $Ni(CO)_4$. The Mond process for purifying nickel consists of forming this compound at 80°, separating it from the impurities through its volatility, and decomposing it, to liberate the nickel again, by heating it to 200°. Palladium occurs in alloys with other VIII metals, from which it can be separated by dissolving the alloy and precipitating with cyanide. $Pd(CN)_2$ decomposes when ignited, leaving metallic palladium. Platinum is separated from naturally occurring alloys by dissolution in aqua regia and precipitation as $(NH_4)_2PtCl_6$, which can be decomposed thermally to give the metal.

Nickel is similar to cobalt but more resistant to oxidation. Most of it is used in alloy steels where it imparts corrosion resistance and in-

Table 44 Some Properties of Group VIIIB-c Elements

	Ni	Pd	Pt
atomic number	28	46	78
electronic structure	2-8-16-2	2-8-18-18	2-8-18-32-17-1
atomic weight	58.71	106.4	195.09
atomic volume, ml/mole	6.59	8.87	9.10
metallic radius, Å	1.15	1.28	1.29
density, g/ml	8.90	12.0	21.5
melting point, °C	1455	1550	1769
heat of fusion, kcal/mole	4.21	4.0	4.7
boiling point, °C	2840	3127	3827
ionization energy, first, kcal/mole	176	192	207
heat of atomization, 25°, kcal/g-atom	101.3	94	134.8
oxidation states	2,3	2,4	4,2,6
electrode potential, volts ($M \rightarrow M^{2+}$)	0.250	−0.987	

creased strength. Some is used in plating steel to prevent rust. Nickel is also used in coinage, the so-called "nickel" five-cent piece consisting of about 90 per cent copper and 10 per cent nickel. Nickel is important as an industrial catalyst, especially for the hydrogenation of olefinic double bonds, as in the hardening of natural fats. Palladium is used in jewelry and for making optical mirrors. Platinum is extremely useful in scientific work for its chemical inertness under many conditions where other materials are attacked. It is also valuable as a catalyst for the oxidation of ammonia in nitric acid manufacture, to some extent in the contact process for sulfuric acid, and in various processes in the petroleum industry.

The compounds of these metals have little practical importance. Thousands of complex compounds, especially of platinum, are known for this group.



Ni 18 + 10
(2-8-16-2)



Pd 36 + 10
(2-8-18-18)



Pt 68 + 10
(2-8-18-
32-17-1)

Figure 134.

GROUP IB

Copper, silver, and gold form a transition from transition to 18-shell elements, thus having properties not typical of either class. They appear to be closer to typical transition elements than to those of 18-shell type. The electronic configurations, given in Table 45, suggest that these are 18-shell elements, but in fact they appear to make use of some of the "closed shell" of 18 electrons underlying the outermost shell of one electron. Copper shows oxidation states of +1, +2, and +3; silver shows +1 and +2, and gold +1 and +3, the latter being the more common.

The occurrence and isolation of these metals has been described in detail in Chapter 21. The metals are commonly called the "coinage metals" because of their use in making coins. Silver and gold especially have been used for centuries as media of exchange, and copper coins of considerable antiquity have also been found. The most important use of these metals, however, arises from their peculiar electronic configurations, which appear to impart to their outer electrons a greater ease of mobility than is even very closely approached in any other metal, aluminum coming closest. This electron mobility makes these metals



Cu 18 + 11
(2-8-18-1)



Ag 36 + 11
(2-8-18-
18-1)



Au 68 + 11
(2-8-18-
32-18-1)

Figure 135.

Table 45 Some Properties of Group IB Elements

	Cu	Ag	Au
atomic number	29	47	79
electronic structure	2-8-18-1	2-8-18-18-1	2-8-18-32-18-1
atomic weight	63.54	107.870	196.967
atomic volume, ml/mole	7.1	10.3	10.2
metallic radius, Å	1.17	1.34	1.34
density, g/ml	8.92	10.50	19.3
melting point, °C	1083	960.5	1063
heat of fusion, kcal/mole	3.11	2.70	3.03
boiling point, °C	2582	2177	2707
heat of vaporization, kcal/mole	72.8	61.0	77.5
ionization energy, first, kcal/mole	178	175	213
electrode potential, volts ($M \rightarrow M^+$)	−0.521	−0.799	−1.68
heat of atomization, 25°, kcal/g-atom	81.1	68.4	84.7
oxidation states	2,1	1,2	3,1

extraordinarily superior in the conduction of heat and electricity. Copper, being cheapest, finds greatest application, in vessels to be heated and especially in wires and other devices that must conduct electricity. It is also a valuable ingredient in alloys such as brass and bronze. Silver and gold are too expensive for wide application, but are sufficiently corrosion resistant to be extensively used in plating, where beauty and utility are to be combined. Gold is especially familiar in jewelry, alloyed with copper or silver. Pure gold is "24 carat." For example, "14 carat" gold is an alloy composed of 14 parts gold and 10 parts another metal, usually copper. Colloidal gold imparts a beautiful ruby red to glass, and is used in stained glass windows.

Copper compounds have some application in the control of fungi and of certain marine vegetation, to which traces of copper are poisonous. Copper sulfate is most commonly used for these purposes. Silver salts, especially the bromide, are of course of great importance in photography.

CONCLUSION

The practical applications of the elements and their compounds depend as much on man's ingenuity as on the properties of these substances.

It is quite possible that the relative importance indicated in the preceding discussion will change continually as new information is found and new discoveries are made. At the present time, the nonmetals appear most useful in the form of compounds. Nontransition metals appear to be useful in both free and combined states, but the least reactive are more useful in the free state, the most reactive in the combined states. With but relatively few exceptions, the transition metals are by far more important in the metallic state than in their compounds. Their chemistry, aside from their combinations with the principal nonmetals, and aside from the science of isolating the metals from their naturally occurring compounds, consists almost entirely of the chemistry of their complex or coordination compounds. Most of these that have been studied to date are combinations of a wide variety of ligands with the transition metal cations in aqueous solutions. Current research activity in this area is intense, and constitutes a substantial part of the total research in the field of inorganic chemistry.

SPECIAL HELP

Test Your Memory

1. What are the distinguishing characteristics of transition elements?
2. List some important practical uses of each transition metal.
3. Why are the IB elements not typically 18-shell elements?
4. What are some uses of IIB metals and their compounds?

Test Your Understanding

1. What if anything should strength of metallic bonding contribute to corrosion resistance?
2. On what basis would one predict lower basicity and higher acidity for oxides of a metal in higher oxidation states?
3. What might be predicted, and why, concerning the existence of such salts of the transition metals, in high oxidation states, as carbonates, sulfates, nitrates, and so on?
4. How might a soluble compound be made from a transition metal oxide, with the help of sodium hydroxide?
5. Chromium(VI) oxide is much lower melting than either of the cor-

responding molybdenum or tungsten oxides. What does this suggest about these oxides, and why?

6. What does the magnetic quality of certain alloys tell us about the nature of magnetism?

7. It has been pointed out that tin, when defective as a plating metal, speeds the corrosion of iron. What would you predict about the similar behavior of zinc on galvanized iron, and why?

27

Nuclear Reactions

EXCEPT FOR PHENOMENA such as reaction rates, which are affected by the mass of reacting particles, the chemical properties of an atom are influenced by the nucleus only by virtue of its positive charge. An explanation of chemical bonding in terms of the extranuclear structure of atoms has therefore been considered adequate. Reactions involving this structure have been observed never to result in the destruction or creation of atoms. Consequently, no matter what chemical combinations may be formed, the amount and identity of each element remains unchanged.

RADIOACTIVITY

In striking contrast to such chemical reactions, processes called "natural radioactivity" have been observed to proceed spontaneously in certain substances, leading to changes in the *identity* of the elements. Such changes, called "transmutation," were sought for centuries by alchemists

seeking to transform baser metals into gold, but in vain, because the only means at their disposal were chemical, involving only the electronic cloud about the atom. No change in the identity of an element could possibly occur without the necessary change in the charge of the nucleus. Natural radioactivity therefore must involve changes in nuclear charge.

The term "radioactivity" means "active in radiating, or giving forth rays." Natural radioactivity was first discovered when undeveloped photographic plate was left in the same drawer with a sample of the mineral called "pitchblende," which contains uranium. Although no light could have reached the plate, it was found to be streaked as though by light. The only possible source of radiation present appeared to be the pitchblende. An investigation showed that the sample was indeed radiating, spontaneously and invisibly, some kind of radiation capable of penetrating to the emulsion on the plate. This discovery, by Becquerel in 1896, led to exceedingly laborious and thorough studies by him and many others, especially the Curies, which disclosed the element radium to be one in an elaborate series of radioactive transformations beginning with uranium and ending with a non-radioactive isotope of lead. In some of these processes, helium was apparently being formed. Since these changes were essentially changes in atomic number, or nuclear charge, and since they appeared to be independent of the environmental conditions, they evidently must originate as the result of some inherent instability of the nuclei of the atoms involved.

The radiation given forth by these radioactive transformations was found to be of three types, called "alpha," "beta," and "gamma." Alpha radiation was found to consist of positively charged particles, in fact, helium ions, He^{++}, ejected with considerable force from a heavy nucleus. As soon as these could encounter stray electrons they became helium atoms, and thus the formation of this element was accounted for. Beta radiation was found to be oppositely charged, and hence negative—actually, electrons thrown out of the nucleus with high velocity. Concurrent with these radiations were observed gamma rays, which were simply high frequency X-rays, electromagnetic radiations at the short wavelength end of the spectrum of light.

The only naturally occurring radioactive elements were found to be those having an atomic number equal to or higher than 86. Element 86 is the inert "radon," so called because it is radioactive and a product of the radioactive disintegration of radium. To a much slighter degree, some activity was observed also for potassium, but the remaining elements seemed completely stable. The significance of the discovery of radioactivity was therefore greatly expanded when it was found later by Fermi that normally stable nuclei could be made unstable by bombard-

ment with nuclear particles. Thus, radioactive isotopes of most of the other elements can be made. Since through their spontaneous radiation, these atoms change in atomic number, and therefore in the identity of the element, this was the old dream of the alchemist brought to realization over a much wider area. This is not a practical way of producing the elements, unless in very special instances, but it provides, as we shall see, an extremely useful tool in the study of fundamental chemistry.

RADIOCHEMISTRY

The availability of radioactive isotopes of most of the chemical elements has made possible investigations never before possible, capable of discovering information that might be revealed in no other way. An important branch of chemistry, concerned with chemical reactions as is ordinary chemistry and not primarily with nuclear reactions as is "nuclear chemistry," has developed to make use of these radioactive isotopes. This branch is termed "radiochemistry."

Detection of Radioactivity

When energetic radiation, such as alpha, beta, or gamma radiation, passes through a gas, it knocks electrons loose from the gas molecules, leaving a pathway of gaseous ions behind it. When a gas such as air contains a slight excess or is supersaturated with a condensable vapor such as water (a condition that can easily be brought about, for example, by suddenly allowing air that is saturated with water vapor to expand, cooling it slightly so that it is supersaturated at the lower temperature), the ions in the air can serve effectively as nuclei for condensation. The pathway of ions left by the radiation can thus become a pathway of water droplets, which under proper lighting conditions can be made visible and photographable. The famous Wilson cloud chamber is such a device. With its help, much has been learned about radioactivity, because the passage of individual charged particles, such as alpha particles, can be observed.

Ions produced in the air by such radiation not only can serve as nuclei for the condensation of vapors, however. They also increase the conductivity of the air. If the air was between two charged plates, with essentially no current passing through it, and a single particle emitted from a nuclear disintegration should travel through the space between

the plates, suddenly increasing the conductivity of the air, a surge of electricity could then pass from one plate to the other. Detection of such a surge is easy, and therefore detection of the single nuclear disintegration. One of the best known of such devices is the Geiger counter, which counts and announces, in one way or another—commonly by an audible click—each ray from a radioactive source that happens to stray into the space between the charged plates.

Tracer Techniques

Unless billions of atoms or ions of the same kind are present, chemical methods even in their highest refinement cannot detect them. In contrast, the sensitivity of radiation counters is phenomenal, for concentrations of radioactive elements far too small to be discovered by ordinary chemical means can be both detected and quantitatively measured by the use of the counters. It is not even necessary that the element be separated from other elements before its amount can be determined, for as long as the element in question is radioactive and the others are not, its presence can be unambiguously known.

For example, it has long been known that corn requires phosphorus in the soil in order to grow, and that corn takes up that phosphorus in the process of growing. How could one possibly discover, by ordinary chemical means, how rapidly the corn assimilates the phosphorus and in what parts of the corn this element becomes most concentrated? At best, this would be an extremely laborious undertaking. But, if radioactive phosphorus is available, one can introduce a little of this to the ordinary nonradioactive phosphate in the fertilizer, stir the fertilizer in the soil, and begin checking the corn stalks and leaves and tassels and ears with a radiation counter. Radioactivity of an isotope in no way alters its chemistry before it decays, so the radioactive phosphorus will become distributed at exactly the same rate and in the same places as the nonradioactive phosphorus. The difference is that its presence can be easily detected without subjecting the cornstalk to the destructive processes of chemical analysis.

A familiar similar application in the human body is the use of radioactive iodine in studies of the thyroid gland. Iodine is known to become concentrated in this gland. Intake of a little radioactive iodine will make its distribution through the body, and its concentration in the thyroid gland, easy to follow by the external placement of a radiation counter—much easier on the patient than removal of the gland for analysis.

Much light has been, and in the future will be, shed on the mechanisms of chemical reactions in general by the use of these "tracer" techniques. A chemist often wishes to know not merely the identity of the products of a chemical reaction but also how they are formed. Which particular atoms were involved? Do hydrogen atoms from this compound interchange freely with hydrogen atoms from this other compound? Problems such as these often could not be solved by any other known method, but tracer techniques give a means of solving them.

The chief other way of tagging atoms, not making them radioactive, is by using isotopes and following them by measurements of mass. Many studies of hydrogen compounds, for example, have made use of deuterium, the isotope of hydrogen having mass 2, to distinguish it from ordinary hydrogen of mass 1. A mass spectrometer measures the difference. However, radioactive tracers are usually more easily available than pure isotopes differing only in mass, and they can be followed more easily in most experimental conditions.

TYPES OF NUCLEAR CHANGE

As a consequence of countless investigations in this area, we now know that quite a variety of nuclear transformations are possible. The search for the reasons for such transformations is still going on, but thus far certain consistencies have been observed. We have already considered the facts that neutrons are unstable when isolated but stable when associated with protons, and that protons cannot coexist in a stable nucleus without the presence of at least as many neutrons. Some association between protons and neutrons in the nucleus that stabilizes neutrons and much more than compensates for the electrostatic repulsions among protons is thus indicated. Theories of the nuclear structure that would explain or at least describe this association are not yet finally established, but some very interesting facts have been observed. A nuclear structure roughly analogous to the electronic structures, of successive energy levels of the nucleons has been proposed to help account for properties. The facts that appear most significant, although not yet explained, are the following: (1) The neutron/proton ratio for the stable isotopes of all the elements is 1 for the lighter elements, and increases with increasing atomic number. (2) A band of isotopic weights for each number of protons occurs which represents the stable nuclei. Numbers of neutrons per atom above and below that band appear to impart instability, and hence radioactivity. (3) Especially stable nuclei are those in which the number of protons, or the number

of neutrons, or preferably the number of each, equals what is called, for lack of understanding, a "magic number": 2, 8, 20, 50, 82, or 126.

An isotope that does not come within the stability limitations indicated above, can change spontaneously in one of various ways, such as the following:

(*a*) If the nucleus has too high a neutron-proton ratio, it may eject a neutron. This usually happens too rapidly to be observed, and is relatively uncommon.

(*b*) If the neutron-proton ratio is too high, the more common action is the emission of a beta particle, for this leaves behind a proton which was not originally present, thus reducing the neutron-proton ratio and increasing the atomic number by one. For example, the isotope of sodium having a mass of 24 instead of the usual 23 ejects a beta particle to form magnesium, having a mass 24, since the electron mass is negligible. Thus radioactive sodium changes to stable magnesium.

(*c*) If the neutron-proton ratio is too low, one way for the atom to become more stable is by absorption of an electron from the innermost (*K*) shell, which converts a proton of the nucleus to a neutron, thus decreasing the atomic number by one. An outer electron must fall into the *K*-shell vacancy thus created, its loss in energy by this transition being radiated as *X* radiation. For example, argon of mass 37 undergoes this change to become chlorine, with atomic number one less (17) and mass 37.

(*d*) Emission of a positron may also compensate for a neutron-proton ratio that is initially too low, by leaving behind a neutron that was initially not present except as a proton. The positron, being a positive electron, has no mass that is significant here, and the result is again a decrease in the atomic number by one.

(*e*) If the nucleus is unstable just by containing too many nucleons, it is likely to emit alpha particles as a means of ridding itself of two protons and two neutrons at one time. By this method, for example, radium, of atomic number 88 and mass 226, is converted to radon of atomic number 86 and mass 222.

Any of these particle ejections is followed by a readjustment of the nucleus toward greater stability, energy being lost by gamma radiation.

RELATIVE RADIOACTIVITY AND HALF-LIFE

Although we find it convenient to classify the atomic nuclei as either "stable" or "radioactive," many degrees of radioactivity are observed. Some isotopes give forth intense radiation and change rapidly. Others

give far less frequent or energetic radiation and change extremely slowly. The rate of "radioactive decay" is found to follow a statistical or probability curve, such that a certain period of time corresponds to the decay or transformation of one-half the atoms present at the beginning of the time period. Whether the radioactive element is "free" or combined, hot or cold, it decomposes inexorably at the same rate, and nothing appears able to speed or slow its pace. Assigned to each radioactive isotope is a definite, fixed period of time, therefore, called the "half-life" of the isotope. It refers to statistically large numbers of atoms, billions or trillions of them, and denotes the length of the period at the end of which half will be left unchanged. At the end of a second period of equal length, half of those remaining will still be unchanged. In a general way, the intensity of the radiation is related to the half-life, in that long half-life and low intensity, or short half-life and high intensity, appear to go together. Examples of different radioactive isotopes and their half-lives are given in Table 46.

In Chapter 3, when the instability of the isolated neutron was discussed, it was suggested that the type of decay represented by the existence of a constant half-life may be the result of random changes in the orientation or structure of the neutron among numerous forms, some of which are stable and some of which are unstable and immediately disintegrate. Since the changes are entirely at random, the half-life will depend on the ratio of stable to unstable forms or configurations, but there is in no case any way of predicting when a given

Table 46 Some Representative Radioactive Isotopes and Their Half-Lives

ATOMIC NO.	ELEMENT	NO. NEUTRONS	HALF-LIFE
1	H	2	12.4 years
4	Be	3	54 days
	Be	6	2.7×10^6 years
6	C	8	5,568 years
9	F	9	1.87 hours
11	Na	11	3 years
13	Al	15	2.4 months
14	Si	17	2.62 hours
15	P	15	2.2 months
16	S	19	88 days
17	Cl	17	33 months
	Cl	19	4×10^5 years
20	Ca	25	152 days

individual neutron will explode. It might be now, or a thousand years from now. Perhaps a similar description of radioactive disintegration in general would have some validity, but we do not know.

TRANSURANIUM ELEMENTS

We have seen that artificial radioactivity can be caused by bombarding a stable nucleus with some nuclear particle, such as a proton or a neutron or an alpha particle, and also that emission of a beta particle causes an *increase* in atomic number by leaving a proton where originally was a neutron. When uranium, which has the highest atomic number of all naturally occurring elements, is bombarded by neutrons under proper conditions, the U^{238} nucleus absorbs one neutron, becoming the isotope U^{239}. This is much less stable than the U^{238}, and quickly emits a beta particle. The resulting atom is no longer uranium, but a new element of atomic number 93, which has been named "neptunium." This isotope of neptunium is also unstable, decomposing by beta emission to produce element number 94, which has been named "plutonium." By analogous means, elements up to atomic number 103 have been produced artificially, one of the most interesting and startling results of modern science. All these elements are unstable, and although still higher atomic numbers may be prepared, high stability of any of them is not expected. Chemically, these elements appear to be closely analogous to the rare earth elements, and can be explained electronically on the reasonable assumption that they represent the filling of the 5*f* orbitals.

BINDING ENERGY AND NUCLEAR ENERGY

The famous laws of conservation of mass and of energy, which for years were believed to be absolute in the universe, were recognized to require some modification when Einstein deduced an equivalence between mass and energy. This equivalence is expressed mathematically:

$$E = mc^2$$

E is the energy in ergs (1 erg $= 2.39 \times 10^{-8}$ cal), m is the mass in grams, and c is the speed of light, 3.00×10^{10} cm/sec. If one gram of matter is converted completely to energy, $E = 9.00 \times 10^{20} \times 2.39 \times 10^{-8} = 2.15 \times 10^{13}$ calories. The heat of vaporization of water per mole is 9.72 kcal or 9.72×10^3 calories. $2.15 \times 10^{13}/9.72 \times 10^3 = 2.21 \times 10^9$

moles of water, which is 4.38×10^4 tons. In other words, the energy produced by complete conversion of one gram of matter would be enough to convert 43,800 tons of liquid water to steam.

Viewed another way, the burning of one ton of coal, assuming it to be pure carbon, liberates 7.14×10^9 calories of heat. $2.15 \times 10^{13} / 7.14 \times 10^9 = 3 \times 10^3$. The conversion of one gram of matter to energy would produce as much energy as the burning of 3,000 tons of coal.

Any way you look at it matter is seen to be a fantastic source of energy, if some practical way of bringing about the conversion could be discovered. Naturally, the word "practical" implies maintaining control, for obviously any uncontrolled conversion of matter to energy could be disastrous.

A clue to the possibilities of converting matter to energy comes from the atomic weights of the elements, when these are compared with the sums of the masses of the individual nucleons believed to make up their atomic nuclei. For the sum of the masses of the protons and neutrons of an atom, in atomic weight units, always is greater than the mass of the atom. For example, the helium nucleus contains two protons and two neutrons. The masses of these particles are 1.00866 for the neutron and 1.00732 for the proton. The helium nucleus would add up to 4.03196 atomic weight units. For oxygen, the mass of 8 neutrons would be 8.06928, and the mass of 8 protons, 8.05856, adding to give the sum 16.12784. Yet the atomic weight of helium is only 4.002, indicating a deficiency of 0.030 atu, and for oxygen, the deficiency is about 0.128 atu.

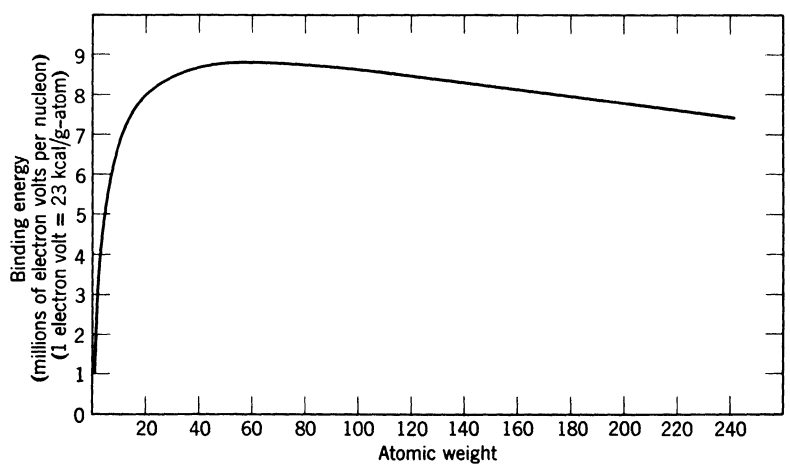


Figure 136. Binding energy per nucleus compared with atomic weight.

These "deficiencies," or mass differences, are believed to represent the energy released when the nucleus was formed, and thus give a measure of the stability of the nucleus. Indeed, the energy of binding of the nucleons together in the nucleus may be calculated by converting the mass difference to energy. Then, to compare the situation in different nuclei, one may divide this total binding energy by the number of nucleons, to find the average binding energy per nucleon.

This has been done for many of the elements and leads to a curve like that shown in Figure 136. Notice that in the neighborhood of iron, atomic number 26, the nucleus appears to have highest stability, and that elements of very low atomic number are much less stable and those of higher atomic number somewhat less stable also. In principle, the conversion of lighter elements to heavier, up to the region of iron, should be productive of energy, as should the conversion of heavier elements to lighter ones, down to the region of iron.

Fission

In 1939, experimental evidence was first obtained suggesting that a reaction unlike ordinary radioactivity had occurred. An atom of unstable nucleus, instead of decaying by ejection of a small particle, split into two approximately equal particles. Here was recognized the possibility of producing an unusually large amount of energy by a nuclear reaction, since the two nuclei ultimately formed would be much more stable than the original nucleus which produced them. The world was soon thrown into the agonies of war, and under the extreme urgency of the situation a full-scale, all-out investigation of the production of nuclear energy by atomic disintegration was launched. This led to the development of the first atomic bomb, which was successfully exploded in 1945, with repercussions that may never end, unless with the destruction of life on earth.

The disintegration of an unstable nucleus into approximately equal parts instead of by ejection of a more fundamental particle is called "fission." Certain of the transuranium isotopes undergo fission spontaneously, others under circumstances relatively easily created, and still others only under extreme conditions. Uranium of mass 238 is not easily fissionable, but its isotope of mass 235 is. When neutrons of appropriate velocity strike the nuclei of U^{235} atoms, they may stick, raising the mass to 236 and creating an extremely unstable nucleus which then at once undergoes fission, producing the smaller nuclei and also a

number of neutrons. Each of these neutrons can strike another U^{235} atom, causing further fission, and liberation of still more neutrons. The process, through this sort of "chain reaction," rapidly builds up to explosive speed and dimensions.

Explosion occurs, that is, if the mass of U^{235} isotope is large enough to permit such a rate of reaction to build up. If the mass is smaller, more neutrons escape or are slowed to harmless velocity than are liberated, and the reaction cannot be self-sustaining. The minimum mass required for a nuclear explosion to occur is called the "critical mass." When two aggregates of fissionable material, each somewhat smaller than the critical mass but together in excess of that mass, are kept apart with a neutron-impervious shield between them, even a stray neutron coming accidentally from outside cannot cause an explosion. When the two masses are placed together as one, and neutrons are deliberately released in their vicinity, explosion is certain. The terrible destruction wrought by such an explosion, even with seemingly relatively small quantities of fissionable material, has made the thought of future warfare more terrifying than ever before.

If instead of thrusting two masses of fissionable material together one keeps removable neutron barriers, such as rods of cadmium, in among a "pile" of such material, the fission reaction can be controlled, and thus produce useful instead of destructive energy. Nuclear reactors are devices of various design based on this principle. Potentially such devices can liberate mankind from much of his most arduous labor.

The fission reaction is never simple, and a mixture of products is produced, most of which are highly radioactive. Some of these, in fact most of them, have relatively short half-lives, not exceeding a day or two, and thus they become rapidly less dangerous with time. A few of the products, notably strontium isotope of mass 90, have long half-lives and remain dangerously radioactive for years. The hazard of "atomic fallout," which is dust formed in an atomic bomb explosion and distributed widely throughout the earth's atmosphere by the blast and the prevailing winds, lies principally in the isotopes that remain radioactive. Especially dangerous are those which, like strontium, may be absorbed by living matter—plants, cows, and ultimately people—and retained therein. Strontium 90, like ordinary strontium, can, like calcium, become deposited in the bones. Ordinary strontium is harmless in traces, but radioactive strontium 90, or any radioactive element, emits radiation which is harmful to living cells and may cause terrible illness and death.

One of the major problems in the production of nuclear energy on a

practical scale is to keep the dangerous materials formed as fission products from ever harming anyone. The problem of disposal of radioactive wastes is very difficult.

Fusion

Reactions involving the coalescence of light nuclei to make heavier ones, although believed to be the source of energy in the sun and stars, require extremely high temperatures, in the range of millions of degrees, for initiation. Such temperatures are not normally even remotely within reach on earth, but fission reactions do produce them. It has been found possible, however, to bring about nuclear "fusion," as this process of nuclear synthesis is called, through the agency of nuclear fission. An explosion of a fissionable material can produce the energy to promote a synthesis, or fusion reaction, which itself is a tremendously energetic process. This is a basis of the thermonuclear device known as the "hydrogen bomb," more appropriately termed the "hell bomb." Details of such devices are not yet public knowledge. The supply of fusionable material, hydrogen, is from a practical viewpoint unlimited, and thus the quantity of energy that can be produced by such an explosion apparently has no theoretical limit. If fusion can be worked out on a practical scale for the carefully controlled production of useful energy for peacetime purposes, man can achieve thereby material heights, and the means of achieving spiritual heights never before imagined. This presupposes the complete abandonment of warfare, except for warfare on fear, hunger, and want, on ignorance and intolerance, on human selfishness and greed.

SPECIAL HELP

Test Your Memory

1. Distinguish among alpha, beta, and gamma radiation.
2. How does emission of each of these particles affect the atomic number of the atom which emitted them?
3. What property of radiation permits detection of single particles?
4. What is a "radioactive tracer"?
5. What is meant by "magic number"?
6. Name four types of spontaneous nuclear transformation.

7. What is meant by "half-life"?
8. What is Einstein's equation relating mass to energy?
9. What is nuclear fission?
10. What is nuclear fusion?

Answers to Some of the Test Your Math Problems

Chapter 3. (2) 18% B^{10}, 82% B^{11}; (6) 8.87 g.
Chapter 6. (3) 4,000 atm; (5) 19.3 lit; (7) 690 g; (9) 4.6×10^{-6} g.
Chapter 8. (2*a*) 2.04 moles; (2*c*) 0.58 mole; (2*e*) 0.70 mole; (4) 3.15 tons; (6*a*) MnO_2 59.5 g, Cl_2 48.6 g, $MnCl_2$ 86.3 g, H_2O 24.7 g; (6*c*) HCl 205.9 g, MnO_2 122.5 g, $MnCl_2$ 177.5 g, H_2O 50.8 g; (7*c*) Ca 17.1%, H 1.7%, P 26.5%, O 54.7%; (8*a*) $K_2Cr_2O_7$; (9) C_4H_{10}; (11) 0.212 ton; (13) 0.56 ton.
Chapter 9. (1) 88.6 g S; (3) 7.68 lit CO; (5) 160 g Fe_2O_3.
Chapter 10. (2) 4, 4, 4, −2, 6, 4, 6, 6.
Chapter 12. (1) 3.65 g $KClO_3$; (3) 4 moles H_2O; (5) 800 g; (7) 0.714 g Na.
Chapter 13. (2) 1279 lit H_2; (4) 1072 lit H_2; (6) 4.78 g NH_4Cl.
Chapter 14. (1*a*) 800 ml H_2 remaining; (2*b*) 108 g C; (4) 1414 g; (5*b*) 2.37 tons.
Chapter 15. (3) 18.8.
Chapter 16. (1) 100 g C_2H_5OH; (3) 8.37; (5) 0.007; (7) 4.26 g Cl^-; (9) 480 g NaOH; (11) 74 ml; (13) 10^{-15} mole/lit; (14) 10^{-18}.
Chapter 17. (1) 1.06°C; (3) 0.25 molal; (5) 638.
Chapter 18. (1) 5.4; (3) 9.5×10^{-4}; (5) 5.6×10^{-10}.
Chapter 19. (1) $1.6 \times 10^{-8}M$; (3) 2 g.
Chapter 21. (2) 318 lb; (4) 431 days.

Answers to Test Your Understanding

CHAPTER 3

1. The center of negative charge which is shaped like a spherical shell will be at the hollow center, just as the center of gravity of a hollow rubber ball is at the hollow center.

2. It does. But it changes only those properties affected by mass, such as density, rate of motion when possessed of a specified quantity of kinetic energy, and rate of joining other atoms. Such changes are always minor, compared to the differences between atoms of different atomic number. The similarities among isotopes of the same element are always much more significant than the differences.

3. Owing to the repulsions between negative charges, two electrons are not as stable in the same orbital as in two separate orbitals.

4. The 4*s* orbital is only more stable than 3*d* until the nuclear charge reaches 21. Then a 3*d* orbital becomes more stable. The 3*d* orbitals gradually become more and more stable as the nuclear charge increases.

5. Apparently a special extra stability is associated with a set of half-filled orbitals, or a set of filled orbitals. If Cr had 2 outermost 4*s* electrons, it would have four half-filled 3*d* orbitals, and one empty. Evidently the extra stability of having 5 half-filled *d* orbitals is enough to cause one of the 4*s* electrons to move to the fifth 3*d* orbital. Similarly, a set of filled *d* orbitals is created by moving one 4*s* electron back to 3*d* in copper.

CHAPTER 4

1. In helium atoms, the two electrons complete the shell, leaving no vacancies to accommodate electrons from outside and therefore no possibility of bonding. In beryllium atoms, three empty orbitals are available, permitting relatively easy accommodation of electrons from outside. Furthermore, they make it possible for the filled orbital electrons to become unpaired without large energy requirement, through promotion of one electron to one of the vacant orbitals. This creates simultaneously the requisites for forming two covalent bonds. In the helium atom, an electron would have to be promoted to the next higher principal quantum level, which would require an impractically large amount of energy.

2. Two aspects must be considered. First, although an atom is electrically neutral at distances of many diameters from it, closer approach shows the effects of a given point in space outside an electron cloud being unable to be equidistant from all parts of the cloud at once. Second, the electron cloud is deformable (polarizable) and dissymmetries not originally present may be induced by the approach of another charge cloud. The result of repulsions among like charges and attractions among unlike charges is therefore certain to distort the atoms so that like charges are farther apart and unlike charges closer together, leading to a net attraction.

3. When the number of vacancies does not exceed the number of electrons, no vacancies can then remain after all possible ordinary covalent bonds have been formed. There is consequently no alternative to the bonding electron pairs remaining localized between a given pair of atoms.

4. The same forces that lead to one bond lead to all possible bonds, because the attractions between nucleus and electrons of other atoms persist as long as an outer vacancy remains available. The outer vacancy is the site where the nucleus is not well shielded by the other electrons.

CHAPTER 5

1. Heat content, or enthalpy, determines whether a given substance, at a certain temperature, will be solid, liquid, or gas. The potential for interattractive forces remains constant. The essential difference between one physical state and another is therefore heat content, which is always highest for gas, next for liquid, and lowest for solid. Since cooling is the extraction of heat and thus the reduction of enthalpy, it can never bring about the changes mentioned in the question.

2. Thermal expansion. These forces decrease with increasing distance.

3. By being of different mass. The larger mass contains more heat. More energy was needed to raise it from 0°K to the temperature under consideration. *Temperature* is the same because it is a measure of the *average* vigor of motion of the molecules. *Heats* are different because heat is energy and varies in quantity depending on the number of molecules in the sample.

4. By keeping the environment of the container at the desired temperature, so that no more heat can be lost than gained.

5. Reduce the pressure. Sulfur would then have a lower boiling point.

6. Low melting point implies only very weak van der Waals forces—hence, small molecules, composed of atoms having relatively few electrons.

7. The state of aggregation must be extensive and stable—either strong metallic bonds or covalent bonds holding many atoms together in units. Otherwise, the element would be vaporized at the high temperature.

8. The vapor tension is the vapor pressure at equilibrium with the liquid. This is the maximum vapor pressure unless there is supersaturation, which may occur momentarily when a saturated vapor is suddenly cooled, before condensation has time to occur. But any lower vapor pressure might occur, in the absence of liquid phase, or before equilibrium could be reached.

9. In general, the higher the boiling point of a gas the more readily it tends to become sorbed on a solid of high surface activity. Evidently, the same factors that contribute to the fact that the gas does have a high boiling point, indicating relatively significant intermolecular association, are also involved in sorption. Nitrogen and oxygen molecules, which do not attract each other strongly at all, are not strongly sorbed by the charcoal, but the chlorine is so readily

sorbed that charcoal can be used in gas masks to afford protection against toxic quantities of chlorine in the atmosphere. When the temperature is reduced to where oxygen and nitrogen are near their boiling points, they too are sorbed by charcoal, indeed so thoroughly that the residual pressure in a confined space may be reduced to quite a low value.

CHAPTER 6

1. Each gas would exert a pressure proportional to the concentration of its own molecules, and independent of all other gases present. The total pressure would be the sum of the separate "partial pressures." This is Dalton's law of partial pressures.

2. The molecules do get in each other's way, shortening their mean free path, but the average positions of the individual oxygen molecules are the same throughout the container, whether the nitrogen molecules are present or not. There are therefore as many oxygen molecules near the surface as before, and they can strike it just as frequently.

3. Gravity holds the gases near the earth, although the atmosphere does thin out rapidly with increasing altitude.

4. The heavier molecules do tend to be drawn closer to the earth, despite their thermal motion. However, this effect is too slight within a container of ordinary laboratory size to be significant. If gravity were increased, as by centrifuging, the effect would become more noticeable.

5. Partly because mercury has a very low vapor tension (about 2×10^{-3} mm) at ordinary temperatures, and the correction would be smaller than the accuracy of reading the mercury level. At higher temperatures, the vapor tension of mercury does become significantly high. However, if both surfaces of the mercury are at the same temperature, the vapor tension effect on readable pressure is cancelled. If only one surface is involved, as when a volatile substance is introduced into the closed end (the Torricellian vacuum), then the vapor tension of mercury must certainly be taken into account.

6. Pressures must be corrected to correspond to mercury at 0°C.

7. Molecules of different gases must react in a ratio of small whole numbers in order to form compounds of definite proportions of the elements. If the reacting gas volumes also react in a ratio of small whole numbers, then equal gas volumes must contain equal numbers

of molecules. Conversely, equal numbers of gas molecules, under the same conditions of pressure and temperature, occupy equal volumes.

8. One mole of any gas occupies 22.4 liters. The density of any gas is the weight per liter. Hence, D = molecular weight in grams/22.4; or $D = 1/22.4$ times the molecular weight $= k$ (a proportionality constant) times W (the molecular weight).

CHAPTER 7

1. Because the outer-shell structure determines the bonding within the element, and hence the physical properties resulting from the state of aggregation, and also because the bonding with other elements, and therefore the chemical properties are also determined by this structure. Elements of similar outer electronic structure must therefore have similar properties.

2. Because transition elements also use underlying *d* electrons and orbitals in bonding, which major group elements do not.

3. Hydrogen atoms have but one vacancy and thus no tendency toward the metallic state. The IA atoms all have seven outermost vacancies to participate in the bonding.

4. The Group VIIA elements have three pairs of outer electrons per atom, not present in hydrogen atoms.

5. Because all atomic numbers correspond to elements already discovered.

CHAPTER 8

1. Na_2O, because the convention is to give the symbol of the metal first. NH_3, because the formula given can be divided by 2 and is therefore not in its simplest form. The reversal of the order is not sensible, just customary, and the custom is long established. $MgCl_2$ is all right as it stands. Al_2O_3 should be the last, since as given it is not reduced to its lowest or simplest form.

2. (*a*) KF (not FK because K is the metal, F the nonmetal), (*b*) TiO_2, not O_2Ti for the reason given in (*a*), (*c*) $BeCl_2 \cdot 4H_2O$. If we knew that the water molecules surround the beryllium atom, which they do, then we might better write $Be(H_2O)_4Cl_2$.

3. When the substances are gaseous, the true molecular formula can rather easily be determined and should always be used. These gases,

like nitrogen and fluorine also, are diatomic in the free state and should be written Cl_2, H_2, O_2, N_2, and F_2. This is important. Writing them simply as the symbol without the subscript implies that these are lone atoms, not combined in diatomic molecules. All these elements may exist as lone atoms, under special conditions, but they are in this form very much more reactive chemically than the diatomic molecules. Under ordinary conditions, the atoms always combine to form the diatomic molecules.

4. Often the solid elements consist of atoms joined together throughout a fragment, containing trillions of atoms. P_4 and S_8 are molecular but, to be consistent, these too are written simply as P and S. The only exception is iodine, which is written as diatomic, I_2, which it has been shown to be in crystal, liquid, and vapor. Similarly, if compounds are not molecular, the empirical (simplest) formula is always used. But when the molecular formula of a compound is known, it is always used.

5. Because no atom can either be created or destroyed in a chemical reaction, and the equation must be consistent with this principle.

CHAPTER 9

1. We must assume that since each hydrogen can utilize only one of the bonding orbitals of a carbon atom, the remaining three bonds must be from carbon to carbon. The molecular structure must there be H—C≡C—H. The possibility that both hydrogens are attached to one carbon is excluded, because this would leave at least two bonding positions of the second carbon unutilized, and the group would combine further to use full bonding capacity: $H_2C{=}C{=}C{=}CH_2$.

2. The simplest use of the bonding ability of sulfur atoms would result in SF_2, since each sulfur atom has initially six outermost electrons, and only two vacancies, and can thus form only two covalent bonds. But the outer *d* orbitals are available, and promotion of one of an outer pair on sulfur to one of these *d* orbitals gives the sulfur the capacity to form two additional bonds. One of the second outer pair can similarly be promoted to another outer *d* orbital for another two bonds. But there is no way in which bonding capacity can be increased by only one at a time—hence no SF_3 or SF_5.

3. Ionization energy is the energy required for *complete* removal of an electron from an atom. Electron affinity is the energy released when an atom gains an electron completely. Electronegativity, on

the other hand, measures the relative attraction for *shared* electrons, which are neither completely gained nor completely lost. Furthermore, the number of electrons shared by an atom may be as many as 8 or more, whereas the ionization energy and electron affinity refer to a single electron.

4. It suggests that more than one pair of electrons is involved, at least partially, in the bonding. A polar bond is expected to be somewhat shorter than a nonpolar bond, and if the bond is shorter than calculated taking into account the polarity, multiplicity is indicated.

5. Linearity tells us that all valence electrons on the central atom are involved in the two bonds which it forms. These may be single or multiple, or some combination, but will nevertheless tend to be far apart from one another as they can. Any outer electrons not involved in the bonding would force the two bonds out of linearity.

6. If no outer unpaired electrons were present, the three bonds would be directed toward the corners of a triangle, in plane with the central atom. Therefore, the pyramidal structure tells us that a pair of electrons uninvolved in the bonding must be present, pushing the bonds out of planarity.

7. Each atom of a IVA element has four outermost electrons and can form four single covalent bonds. Each atom of a VIA element has six outermost electrons but therefore only two vacancies, and can form but two single bonds. Since VIA elements are more electronegative than IVA elements, the bonds between atoms of the two would be expected to be somewhat polar, the IVA atom bearing partial positive charge and the VIA atom bearing partial negative charge. It is more probable that bonds will exist between atoms of opposite charge than of like charge, which suggests that atoms of IVA will be joined if possible to atoms of VIA, and vice versa. A "giant molecule" type of structure seems to be the only reasonable possibility under the stated conditions, with two atoms of VIA to each atom of IVA in the formula. Each IVA atom would then be joined to four VIA atoms, the other bond of each of which would be to another IVA atom, making a three-dimensional network. The arrangement about the IVA atom would be tetrahedral, and the bond angle at the VIA atom would be expected also to be close to tetrahedral, or 109°.

8. Cadmium is in Group IIB, and its 48 electrons are arranged in the structure 2—8—18—18—2. Tellurium is in Group VIA, and its 52 electrons are arranged in the structure 2—8—18—18—6. Evidently each element can form but two covalent bonds. The bonding of cadmium is limited by the number of outermost electrons, and that

of tellurium by the number of outermost vacancies. The formula should therefore be 1 : 1 or CdTe. The bonding orbitals of cadmium extend in opposite directions and can hardly be expected to participate in the same bond. Furthermore, neither cadmium nor tellurium would be expected to form double bonds using only *s* and *p* orbitals. Therefore single molecules of formula CdTe could not be formed. If then each cadmium atom must be joined to two tellurium atoms, a chain of alternate cadmium and tellurium atoms is suggested. We might then decide upon a chain structure for the compound. However, we have not yet considered the fact that the electronegativity of tellurium is greater than that of cadmium, in keeping with its greater number of outermost electrons, making the bonds polar with cadmium positive and tellurium negative in their partial charges. Furthermore, if an atom of cadmium forms only two single covalent bonds, two outermost vacancies are left uninvolved in the bonding. If each atom of tellurium forms only two single covalent bonds, two outermost electron pairs are left uninvolved in the bonding. As has been noted earlier, the tendency is for chemical combination to continue to occur until all outermost electrons and vacancies are used. We may therefore expect each tellurium to donate a pair of electrons to each of two other cadmium atoms, and each cadmium atom to accept a pair of electrons from each of two other tellurium atoms. This would give a network in three dimensions, with each cadmium atom surrounded tetrahedrally by four tellurium atoms, and each tellurium atom surrounded tetrahedrally by four cadmium atoms. This structure has been verified by experiment.

9. The formation of such chains implies that each atom can form but two bonds. This means that electronically the structure must have either two outermost electrons or two outermost vacancies. But if it had two outermost electrons, then the atoms would condense together in a metallic lattice, in order to make fuller use of the available vacant orbitals. Consequently, the structure with six outermost electrons and only two vacancies is favored for the chain formation. Such a structure is observed, for example, in sulfur, whose eight-atom rings break up on heating and join together in long chains. "Plastic sulfur" is a form of sulfur resulting when melted sulfur containing such chains is suddenly cooled, too rapidly to reform the S_8 rings.

10. In CHF_3, because here three fluorine atoms are attracting electrons away from the carbon atom, making it more electronegative and causing it to take a greater share of the electrons bonding it to the hydrogen atom. In CH_4, the carbon only takes slightly more than half share of the bonding electrons.

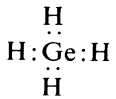
11. In CH_3Cl, because here is only one chlorine atom drawing electrons from the less electronegative carbon and hydrogen atoms. In carbon tetrachloride, four chlorine atoms are competing for the electrons of one carbon atom, and no one chlorine atom can become very negative.

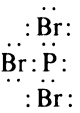
12. To answer this question, you must know the formulas of the radicals and their charge as ions. If you have not yet memorized them, better do so now. (*a*) $NaHSO_3$, (*b*) $In_2(SO_4)_3$, (*c*) Li_2CO_3, (*d*) $(NH_4)_3PO_4$, (*e*) $Zn(HSO_4)_2$, (*f*) $Mg(HCO_3)_2$, (*g*) $Al(NO_3)_3$.

13. From the periodic table or from the individual electronic structures of the component atoms, you can reason out these formulas. (*a*) CdS, (*b*) MgO, (*c*) here you must assume the maximum oxidation state possible for chromium, a transition element capable of several valences. You can determine this state either as the periodic group number, VIB, or by subtracting the atomic number of the next lower inert element from the atomic number of chromium to find out how many electrons in excess of the inert structure are in an atom of chromium. The atomic number of chromium is 24 and that of the next lower inert element, argon, is 18, the difference being 6, the same as the group number; hence the formula would be CrO_3, (*d*) following a similar procedure for hafnium, HfF_4, (*e*) Rb_3P, (*f*) HgS, (*g*) Al_2Se_3, (*h*) Li_3As, (*i*) Ca_3P_2, (*j*) Ba_3N_2, (*k*) $TiBr_4$, (*l*) V_2O_5 (again determined as for chromium and hafnium). In case you are worried about the fact that nonmetals like phosphorus and sulfur and arsenic can also show oxidation states that are positive, they cannot exhibit such states in combination with elements less electronegative than they, but must always become negative. Their bonding capacity is then indicated by the number of outermost vacancies, since their atoms have more electrons than vacancies in the outer shell. This number can be determined by subtracting the atomic number from that of the next higher inert element. For example, arsenic has atomic number 33, and the next higher inert element is krypton, 36. The difference, 3, represents the number of vacancies in the outer shell of the arsenic atom, and thus the maximum negative oxidation state it can have. Arsenic can also have positive oxidation states, notably $+3$ and $+5$, but these only in combination with elements more electronegative, such as fluorine and oxygen.

14. (*a*) A hydrogen atom can form but one bond. A germanium atom has an atomic number of 32, compared to the inert element krypton, 36. This tells us that 4 vacancies occur in the outermost shell of germanium, signifying the presence of 4 electrons. Also, germanium is Group IVA, and has the electronic structure represented

by 2—8—18—4. We would therefore predict the formula, GeH_4, and represent it electronically in two dimensions as:



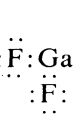


(*b*)

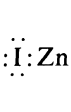
(*c*) Here the question arises whether sodium and tellurium are sufficiently different in electronegativity for the bonds to be ionic. If they are, which is probably not quite true, we would represent the ions separately: $[Na^+]_2$  . If the bonds are considered polar covalent, however, the compound would be represented as 



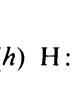
(*d*)  (*e*) Here there is little doubt that the bonding is essentially ionic: Cs^+ 



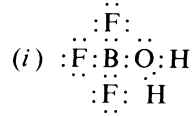
(*f*)



(*g*)



(*h*)



(*i*)

CHAPTER 10

1. It is +3 in each, because oxidation number is defined to indicate only the number of electrons and direction of their transfer in the bonding, with no provision for distinguishing different extent of transfer. The partial positive charge on boron is undoubtedly higher in BF_3 than in BI_3, and in neither is it anywhere near to +3.

2. Again, only by definition. With three extra electrons on the second ion, the cobalt undoubtedly is in effect less positive, but the oxidation number is +3 in each.

3. Only if it changes in both directions (which sometimes happens). Always whatever is oxidized must reduce something else, or some of itself.

CHAPTER 11

1. The great majority of the component particles of the crystal are on the interior, and therefore in exactly equivalent positions. Conse-

quently, the forces of attraction that hold them together are broken down at the same level of kinetic activity.

2. Impurities upset the symmetry of the crystal lattice, preventing as stable an arrangement of component particles and therefore making them more susceptible to thermal breakdown. They also tend to make the crystal melt over a wider temperature range, since in their presence certain portions of the crystal are held together more strongly than other portions, instead of the attractive forces being uniform.

3. This is usually a result of large molecules among which the total van der Waals attractions are considerable. Before enough kinetic energy can be supplied to loosen the molecules from one another as individual units, certain portions of the molecules may become so violently agitated thermally that they break loose. The compound therefore breaks into fragments before it becomes liquid, or before it vaporizes.

4. Both nitrogen and oxygen are more electronegative than hydrogen, making the hydrogen partially positive in both ammonia and water. Both nitrogen and oxygen have extra electron pairs not involved in the bonding, which make the molecules of ammonia and water geometrically unsymmetrical. The combination of dissymmetry and bond polarity makes a molecule as a whole polar, both ammonia and water molecules having appreciable dipole moments. They might attract one another by a dipole-dipole attraction, the negative oxygen end of the water molecule attracting the positive hydrogen end of the ammonia molecule and the negative nitrogen end of the ammonia molecule attracting the positive hydrogen end of the water molecule. Also, both molecules have the requisites for protonic bridging: A small, negatively charged atom having unshared electron pairs and positively charged hydrogen. Water and ammonia molecules can therefore become attached by protonic bridges.

5. The presence of either unoccupied outer orbitals or unshared electron pairs can give combined atoms potential additional combining power. The tendency is for combination to continue until maximum use of such outer orbitals and electrons occurs. If a molecule has only outermost electron pairs, it cannot join with a like molecule although it may attract another different kind of molecule having outermost vacancies.

6. The element these compounds have in common is sulfur, whose atoms have six outermost electrons and therefore only two vacancies. All the other elements mentioned except chlorine are less electronegative than sulfur. In combination with sulfur, they will therefore become partially positive, leaving sulfur partially negative. By form-

ing two covalent bonds, as permitted by the vacancies, and by becoming partially negative, sulfur acquires the oxidation state of -2, a number which could also have been reached by subtracting 8 from the group number (6) or by subtracting the atomic number of the next higher inert element, argon, 18, from the atomic number 16 of sulfur. There is no question here of expanding the valence octet of sulfur, because this only happens when sulfur is oxidized, not when it is the oxidizing agent.

With potassium, which has one electron more than the inert element argon, 18, sulfur must combine to give a compound of formula K_2S. Since sulfur is much more electronegative than potassium, the bonds must be highly polar. Individual molecules of K_2S would contain potassium atoms of relatively high positive charge and three outer vacant orbitals apiece, together with sulfur atom of relatively high negative charge and two outermost pairs of electrons not used in the bonding. Whenever such a situation exists we know that further combination occurs, to make fuller use of the outer electrons and vacancies and to bring the positive and negative charges into a more symmetrical arrangement. Consequently, we can predict that K_2S will form an aggregation of highly condensed ions in a crystalline form of high stability. Relatively high melting point and low volatility can thus be predicted. Actually, K_2S is a crystalline solid melting at 840°.

Magnesium atoms have two outermost electrons, and would therefore combine 1 : 1 with sulfur, forming a compound of formula MgS. Again, sulfur is much more electronegative than magnesium, and the bonds must be highly polar. Individual molecules, if they were possible, would have two outer orbitals unused on the magnesium atom and two outer electron pairs unused on the sulfur atom. A highly condensed crystalline solid would therefore be predicted, having high thermal stability, high melting point, and low volatility. Magnesium sulfide is a crystalline solid melting above 2,000°.

Carbon we know has the capacity to form four single covalent bonds per atom, but it can also form double bonds. Since sulfur can form two bonds per atom, there is no difficulty about predicting the formula of the compound, CS_2. However, although we have evidence that sulfur is less able than oxygen to form double bonds of the type formed by carbon and nitrogen, we do not know whether in combination with carbon it would form double or single bonds. We can predict that if it forms single bonds to carbon, then each carbon will become attached tetrahedrally to four sulfur atoms, and each sulfur atom to two carbon atoms, and thus a three-dimensional

"giant molecule" structure will be created. On the other hand, if sulfur can form double bonds to carbon the carbon can acquire two sulfur atoms, and CS_2 will be not only the empirical but also the molecular formula. The giant molecule structure would be expected to be stable and solid, with a high melting point because liquefaction could not occur without actually breaking stable covalent bonds. The molecular CS_2, however, should be very volatile, since the molecules are relatively small and present to one another nothing but outer unshared electron pairs on the sulfurs. Actually, carbon disulfide is molecular, melting at $-112°$ and boiling at 46°.

Since hydrogen atoms can form but one single covalent bond, the formula of their compound with sulfur must be H_2S. The bond angle must be something near to tetrahedral, making the molecule unsymmetrical. Since sulfur is only a little more electronegative than hydrogen the bonds cannot be very polar, and the molecule has a smaller dipole moment. The hydrogen atoms cannot be very positive, and with the sulfur so much larger, protonic bridging would not be expected. We would therefore predict relatively low melting and boiling points for hydrogen sulfide. Actually, it has the predicted molecular structure, and melts at $-86°$, boiling at about $-60°$.

Arsenic and sulfur are not too different in electronegativity, and must form nearly nonpolar bonds. Since both these elements have more electrons than vacancies in their outer shells, no outermost vacancies can possibly occur when they have joined together. But arsenic atoms have three outer vacancies to two for sulfur, and the formula we can predict is As_2S_3. The simplest way in which two arsenic atoms could be joined to three sulfur atoms would appear to be by each sulfur bridging the two arsenics. We do not know enough to predict whether this would be the structure or whether something more complex should be expected. We might, for example, imagine a three-dimensional network, with chains of alternate arsenic and sulfur atoms held together by sulfur bridges between arsenic atoms. All we can really say with confidence about the physical properties, therefore, is that if relatively small molecules are formed, they cannot attract one another with other than van der Waals forces and should cause the compound to be low melting and relatively volatile. Actually, the compound of empirical formula As_2S_3 has the molecular formula As_4S_6, and melts at about 300°.

Arsenic and chlorine both form more than one compound with sulfur. The only compound between sulfur and chlorine that we could predict directly, however, would be the dichloride SCl_2, since chlorine can form but one bond. This we would expect to be molec-

ular, since no intermolecular attractions of substantial strength are to be expected, and the molecule would be bent, having a bond angle about 109°. The compound should be relatively low melting and volatile. Actually, SCl_2 exists, boiling at about 59°.

7. In order to produce a steady flow of vapor into the atmosphere from a heated liquid, it is only necessary for the vapor pressure of the liquid very slightly to exceed the atmospheric pressure. When the combination of water vapor pressure and other compound vapor pressure equals one atmosphere, the two liquids will distill together, and at temperatures below either of their boiling points. In practice, steam is passed into the heated liquid and, bubbling through it, carries with it vapor of the liquid. The mixed vapors are condensed and the immiscible liquids separated by their difference in density. This procedure, called "steam distillation," is a useful one in the laboratory, permitting separation of liquid compounds that might decompose if heated to their own boiling points.

8. Assuming that the atmospheric pressure remains unchanged, a rise in boiling point means that the liquid being distilled is a mixture, and that the more volatile portion has distilled away first, leaving higher boiling material in the distilling flask. In an efficient fractional distillation the temperature will remain essentially constant as long as a certain compound is distilling. When this compound has been separated, the temperature will rise to the boiling point of the next most volatile component. A curve of boiling temperature versus time will therefore show plateaus corresponding to the boiling points of the individual pure components.

9. No, because the zinc would be quite positive and the chlorine quite negative. In addition the zinc atom would have two outermost orbitals vacant in the individual molecule, and the chlorine atoms would have three unshared pairs of outermost electrons each. According to the observation that chemical combination tends to continue until all outer vacancies are utilized, we would expect zinc chloride molecules to condense to aggregates of indefinitely large extent, thus making fuller use of the orbitals of the zinc and also giving the most stable possible arrangement of negative chlorine and positive zinc atom charges.

10. The gaseous state is characterized by independent molecules, whose interattractions are thoroughly overcome by their kinetic energy. The attractions in the giant molecule are covalent bonds, and could not be broken to permit vaporization without destruction of the molecule.

11. Judging by the inertness of atomic number 18, element 15 must lack 3 electrons for an outer octet and therefore must have 5 outer electrons. With only 3 vacancies, it can form only 3 covalent bonds. Two of its outer electrons are paired. When 3 bonds are formed, together with the unshared pair, there are 4 electron pairs tending to separate as far as possible, which means to the corners of a regular tetrahedron. The three covalent bonds will therefore form a low pyramid, with bond angles about 109°.

Element 53 (B), judging from the inertness of element 54, lacks but one electron of a complete octet, and must therefore have 7 outer electrons but only one vacancy. It can form only one bond per atom. The predicted formula of the compound is therefore AB_3. The structure is pyramidal. The molecule would be like a tetrahedron with the fourth position occupied by a pair of electrons.

12. In general, elements of atomic number slightly less than that of an inert element are relatively high in electronegativity, because the tendency is for electronegativity to increase with the filling in of the outer shell. The more nearly filled this shell, while vacancies still occur, the more electronegative the element is likely to be. Hence B would appear likely to be more electronegative than A, the bonds therefore being somewhat polar, with A partially positive and B partially negative.

13. The molecular exterior would have only electron pairs, and no vacancies (unless outer *d* orbitals). Therefore no strong intermolecular association would be predicted. Van der Waals forces plus some molecular polarity should be appreciable attractive influences, however, and the compound might well be an easily volatile, relatively low melting solid, or a liquid.

In fact, the compound is PI_3, a red solid melting at 61°, and having a pyramidal structure as predicted.

14. BF_3 itself is a planar molecule, because all three valence electrons of the boron atom are fully occupied with the bonding to the three fluorine atoms. When an ammonia molecule, with an unshared pair of electrons on the negatively charged nitrogen atom, comes near to the boron, the fourth orbital of the boron can accept the electron pair from the nitrogen, forming a coordinate covalent bond. By so doing, however, the boron increases its number of electron pairs from three to four. The fourth forces the original three out of the planar configuration into a tetrahedral one, in which all four bonds are now as far separated as possible.

15. A nitrogen atom has five outermost electrons and only three

vacancies, which limit its bonding capacity to three covalent bonds. These could not be directed toward the corners of a triangle if the unshared pair of electrons were present on the nitrogen, because the structure would then be tetrahedral with the electron pair at one corner. Evidently the electron pair of the nitrogen atom is somehow involved in the bonding. Since each silicon atom is joined to nitrogen and also to three hydrogen atoms, the tetravalence of which it is capable seems to be complete. Then how could the electron pair of the nitrogen be involved? Remember that outer *d* orbitals on silicon can on occasion be employed for bonding. Here it is believed that the electron pair of the nitrogen partially occupies an outer *d* orbital of each of the three silicon atoms, producing bonding that is described as "resonance." With all nitrogen electrons involved in three bonds, the planar configuration now makes sense.

CHAPTER 12

1. The negative charge of the oxygen must be removed.

2. In principle, less energy should be required to separate oxygen from its compound with an active nonmetal, because the nonmetal would be nearer to oxygen in electronegativity, causing the bonds to be less polar and correspondingly less stable. Bonds of oxygen to active metals are highly polar and very stable and difficult to break.

3. At ordinary temperatures, both oxygen and nitrogen are well above their critical temperatures. These are the temperatures above which no amount of pressure can cause liquefaction. Until the air is cooled below these critical temperatures, it cannot be liquefied.

4. In general, any atom that initially has a very high attraction for electrons will tend to hold them tightly when it gains them and not give them up to some other atom. In contrast, an atom that initially attracts electrons relatively weakly will, when it acquires them, become a good reducing agent because it cannot hold the electrons tightly. Oxygen has too high an attraction for electrons to give them up easily once they are gained. However, it can share with other atoms, when it becomes highly negative, by acting as donor in coordination.

5. Tl_2O is much more basic. In it only one oxygen is attracting electrons from two atoms of thallium, whereas in Tl_2O_3 the oxygen is competing with two other oxygen atoms. Consequently, the oxygen can acquire more negative charge in Tl_2O, which gives it more basic

properties. TlOH, which is formed when Tl_2O reacts with water, is quite a strong base, whereas Tl_2O_3 is only very weakly basic.

6. Tin, in Group IVA, has four valence electrons and would therefore be expected to combine with two oxygen atoms, giving a compound of formula SnO_2. This, since it cannot contain double bonds, must be a giant molecule structure with four oxygens tetrahedrally located around each tin atom and two tin atoms connected by each oxygen. Melting would require breaking of at least some of these bonds and therefore require a high temperature. In fact, tin does form SnO_2, a white solid that melts at about 1930°.

Zinc, in Group IIB, has two valence electrons per atom and should unite with oxygen in a 1:1 ratio, forming an oxide of formula ZnO. This would not remain molecular even if it could exist so initially, which is doubtful, because it would leave uninvolved two vacant orbitals on the zinc and two unshared electron pairs on the oxygen. Furthermore, the electronegativity of zinc being much less than that of oxygen, the bonds would be highly polar. For both reasons, condensation to a highly polymeric solid would be expected. This would be quite nonvolatile and high melting, since breaking of strong bonds would be necessary to disrupt the crystal. In fact, zinc does form the oxide ZnO, a giant molecule type of structure in which each zinc atom is surrounded tetrahedrally by four oxygen atoms and each oxygen by four zincs. The oxide melts at 2248°.

Indium atoms have three outermost electrons, and should therefore combine with oxygen in a two to three ratio, giving an oxide of formula In_2O_3. This, by virtue of high bond polarity as well as the fourth orbital of indium, should form highly condensed aggregates, relatively nonvolatile and high melting. Actually, indium does form In_2O_3, a solid for which the melting point does not appear to be known.

Selenium might be expected to combine with oxygen 1:1, since it has an electronic structure similar to that of oxygen. However, oxidation can serve to promote electrons out of unshared pairs in *s* or *p* orbitals to outer *d* orbitals, thus increasing the capacity to form covalent bonds. If one such promotion were to occur with selenium it would form SeO_2, and if two such promotions were to occur selenium would form SeO_3. Both these compounds are known, but not SeO. Since selenium is itself fairly high in electronegativity, these compounds would not be expected to have very polar bonds, and should be somewhat low melting and volatile. SeO_2 sublimes without melting at 315°, and SeO_3 melts at 118°.

From its atomic number of 22, just 4 greater than the inert argon,

titanium would be expected to have a maximum positive oxidation state of +4. It could therefore combine with oxygen to form TiO_2. This, since the bonds would be very polar and since titanium would have vacant outer orbitals otherwise, would be expected to condense to a crystalline solid of low volatility and high melting point. In fact, titanium does form the white pigment TiO_2, which melts at 1800°.

Tungsten, with two outermost electrons and four underlying *d* electrons beyond closed shells, can form a maximum of six bonds, and with oxygen it would be expected to form WO_3. This would probably be polymeric and relatively high melting. Actually, WO_3 does form and melts at 1473°.

7. In H_2O_2, each oxygen atom is bound to one hydrogen and the other oxygen. Since the oxygen atoms cannot remove charge from one another, each oxygen can acquire only as much negative charge as can be gained from one hydrogen, whereas in water, the oxygen has two hydrogen atoms from which to attract electrons. Consequently, the oxygen in water has a higher negative charge and therefore lower electronegativity and less oxidizing power than the oxygen in H_2O_2.

8. The right hand neighbor oxide will be an oxide of an element in a higher oxidation state. The right hand element will also be more electronegative. For both reasons, that of higher electronegativity and greater competition among oxygen atoms for the electrons, the right hand oxide will have less polar bonds, with lower partial negative charge on oxygen. This will make the right hand neighbor a stronger oxidizing agent and more strongly acidic. It will have lower bond energy and therefore be less stable thermally. Physically, it will tend to be less associated, more volatile, lower melting. If the two elements are nearer the left hand side of the periodic table, the right hand oxide will be less basic rather than more acidic, and a poorer electron donor rather than a stronger oxidizing agent.

9. The greater volatility of the oxide of (1) suggests that (1) is more electronegative and is oxidized to a higher state than (2), and therefore must be located to the right of (2) in the period. Its atoms must be smaller than those of (2) since size diminishes with the filling of the outer shell, going from left to right across the periodic table.

10. An element that is relatively volatile must be located at the right hand side of the periodic table because it must have more electrons than vacancies in its outermost shell, in order not to be metallic or otherwise highly condensed. Its electronegativity must be fairly high. Its oxide is therefore likely to be relatively acidic, since this is

characteristic of oxides in which oxygen has not succeeded in acquiring very high negative charge. An acidic oxide would certainly react with the strong base, sodium hydroxide, to form a sodium salt of a complex oxyanion, such as a sulfate, nitrate, chlorate, or similar compound.

11. A volatile element, as mentioned above, must occur on the right hand side of the periodic table, by virtue of its electronic configuration which must include more electrons than vacancies in the outermost shell. Consequently, it must be relatively high in electronegativity, making its bonds to oxygen low in polarity. Its oxide would therefore be expected to be volatile.

12. To have a high melting point, an element must either be metallic or have its atoms united in a giant molecule structure. It is probably either a transition metal or an element that associates in giant molecule structure, such as carbon and silicon. In order for an oxide to have a relatively low melting point, it must present an exterior of electron pairs that prevents intermolecular association any stronger than van der Waals interaction. An element of high melting point therefore might form an oxide of low melting point if the oxygen atoms were double-bonded to the element in a symmetrical way blocking from external approach any orbital vacancies that might still remain. Examples of such oxides that actually exist are CO_2 (m. p. $-56.6°$), CrO_3 (m. p. 183°), OsO_4 (m. p. 56°).

CHAPTER 13

1. The strongly basic solution must contain a hydroxide of an alkali or alkaline earth metal, for only these have this property. The original hydrogen compound must therefore have been a hydride of an element of IA or IIA. In general, the reaction of water with a binary compound involves the hydrogen becoming attached to the more electronegative element of the binary compound and the hydroxyl group becoming attached to the less electronegative element, thereby forming the most polar bond possible. In a metallic hydride, the more electronegative element to which the hydrogen of water becomes attached is the hydrogen, and the less electronegative element to which the hydroxyl becomes attached is the metal. The most polar bond possible in such combination is the metal to oxygen bond.

2. The liberation of hydrogen tells us that one of the original compounds must have been a compound containing negative hydrogen,

and the other must have contained positive hydrogen. Consequently, the other element in the first must have been less electronegative than hydrogen, and the other element in the second must have been more electronegative. A bond between the other element of the first compound and oxygen would therefore be much more polar than a bond between the corresponding element of the second compound and oxygen. Oxygen would have a higher negative charge in the first compound, making it basic. Oxygen would have a much lower negative charge in the second compound, making it acidic. A basic oxide would react with an acidic oxide forming a salt of the first metal with the oxyanion containing the second "other element." For example, the first compound could have been sodium hydride and the second hydrogen chloride. Sodium oxide is basic, but oxides of chlorine are acidic. If the chlorine oxide is Cl_2O_7, then Na_2O would react with it forming $2NaClO_4$.

3. Increasing partial negative charge increases the reducing ability of any element. However, the more strongly an atom attracts electrons initially, the less readily it will release them (act as a reducing agent) when it has succeeded in acquiring them. Oxygen is initially too high in electronegativity to be able to release electrons easily even when it has become quite negative. Hydrogen is intermediate in electronegativity, and what is acquired with less greed can be given up more gracefully. Not as much energy was released when hydrogen became negative, and not as much energy is required to make it less negative again.

4. Production of hydrogen by reaction of two binary hydrogen compounds tells us that one of the compounds contained partially negative hydrogen and the other partially positive hydrogen. The other element in the first case must be less electronegative than hydrogen, and the other element in the second case more electronegative than hydrogen. The first is evidently a metal, the second a nonmetal. Except in the relatively few elements where giant molecule aggregation occurs, and especially in the elements more electronegative than hydrogen, smaller molecules occur having relatively high volatility. Element A must be a nonmetal, B a metal. In the salt formed by A and B, B must bear the positive charge and A the negative charge.

5. The fact that each element has at least one outer electron pair per atom proves that they must be members of Groups V or VI, for they cannot be of Group VIIA or they would have three outer electron pairs per atom. Since they must have different numbers of valence

electrons, one must be in VA and the other in VIA. The volatility of the compound X and the nonreactivity of the two hydrogen compounds with one another merely reinforce our conclusion.

6. The only binary hydrogen compounds that are strongly acidic are the hydrogen halides. Since the halogens are relatively high in electronegativity, their bonds with oxygen cannot be very polar, and their oxides also will present an exterior containing no unoccupied orbitals. Little intermolecular attraction is predicted, and we can therefore expect the oxide to be low melting and volatile. The relative weakness of nonpolar or slightly polar bonds between unlike elements suggests that the oxide will not have very high thermal stability. The fact that neither the halogen nor the oxygen can acquire much negative charge in the oxide suggests that the compound will be a strong oxidizing agent, and also acidic.

7. According to the Pauli principle, hydrogen with but one orbital can accommodate no more than two electrons and can form but one covalent bond. By forming a bridge between two molecules, hydrogen appears to be divalent. However, in ordinary protonic bridging the hydrogen atom remains relatively close to the rest of the molecule of which it is originally a part, and is considerably farther away from the pair of electrons on another molecule which attracts it. The force of attraction is therefore regarded as essentially electrostatic and not considered to involve use of the hydrogen orbital. Thus no violation of the Pauli principle appears.

There does exist in the "bifluoride" ion, FHF^-, a situation not so readily explained. Here the proton sits midway between two fluoride ions and clearly is attached to one fluorine atom just as strongly as to the other—by bonding three or four times stronger than ordinary protonic bridging. A possible rationalization of this bonding is to describe it as covalent bonding of hydrogen to two fluorine atoms at once, using a total of four electrons, and one orbital from each fluorine overlapping or coalescing with the hydrogen orbital. Calculation of the charge distribution resulting from electronegativity differences between fluorine and hydrogen shows that on the average the fluorines take so much of the bonding electrons to themselves that the hydrogen is left at any one time with only a little more than one electron. Since it can hold two, this need not be described as a violation of the Pauli principle. However, much remains to be learned about bonding.

8. A hydrogen compound that is readily hydrolyzed must contain

negative hydrogen. Therefore the other element must be less electronegative than hydrogen. Its oxide would be quite polar, with the oxygen highly negative and therefore basic. A basic oxide will react readily with an acid, forming a salt. For example, magnesium oxide will react with hydrochloric acid, forming magnesium chloride and water.

9. If the hydrogen compound of an element is acidic, the element must be more electronegative than hydrogen, and therefore a nonmetal. Its oxide would be acidic, because of the low negative charge on oxygen, and would not be expected to react with another nonmetal oxide which would also be acidic. Reaction would occur only if one of the oxides happened to be able to oxidize the other. For example, N_2O_5 or Cl_2O_7 would oxidize SO_2 to SO_3, becoming themselves reduced in the process. But there would be no salt formation.

10. Preparation of a water solution implies that hydrolysis does not occur, and that therefore the hydrogen in the compound is not negative. Elements in which the atoms are closely packed, however, are metals, and in combination with them hydrogen would be negative. We must conclude that such a water solution could not be prepared.

11. The vaporization of ammonia is restricted by the presence of protonic bridging among the molecules, which must be broken before single molecules can escape into the vapor phase. Protonic bridging cannot occur in hydrogen sulfide because, although the hydrogens are just as positive, the sulfur is a much poorer electron donor to a proton. Even the electrostatic attraction of an electron pair for a proton is not as effective when the electron pair is spread out on a large atom. Protonic bridging requires the negative atom to be small, apparently because otherwise the electron pair is not concentrated enough for substantial attraction for the proton. This restricts protonic bridging mostly to compounds of nitrogen, oxygen, and fluorine.

12. The unreactivity with water, electron acceptors, or electron donors suggests that this hydrogen compound is of an element whose bonding capacity is completely utilized in combining with the hydrogen. No unshared outer electron pairs or unoccupied orbitals occur. This at once restricts the element to Group IVA. The lack of reactivity with water tells us that the hydrogen is not negative, and probably not very positive, and therefore must be nearly equal in electronegativity to the other element. The other element must be carbon or germanium, and the compound CH_4 or GeH_4.

CHAPTER 14

1. An element having more than 6 closest neighbors in the free state must be a metal. It will therefore certainly have a lower electronegativity, probably much lower, than that of chlorine. The bond to chlorine will therefore be very polar, the metal becoming partially positive and the chlorine partially negative.

2. Since fluorine is most electronegative, and the halogens diminish in this property in the order chlorine, bromine, and iodine, the most polar bonds to other elements (excepting oxygen, chiefly) must be expected to be those formed by fluorine. The combination of higher polarity and smaller size of fluorine will make these bonds strongest, which means that more heat will be evolved when they form. The heats of formation of chlorides will correspondingly be expected to be greater than those of bromides, which in turn will be greater than those of iodides.

3. An oxide that is acidic contains oxygen of relatively low negative charge. The other element must therefore be of fairly high electronegativity. Its chloride will therefore have bonds of low polarity, imparting little intermolecular attraction. The chloride should consequently be relatively low melting and volatile.

4. Six bonds around a central atom will be distributed, when they are as far apart as possible, toward the corners of a regular octahedron. Such a distribution will be very symmetrical, and it would nearly or completely shield the central atom from outside approach. The compound should therefore be molecular, with relatively low van der Waals attractions, because the molecules can come in contact with one another only through their exteriors of negative fluorine atoms with their outermost electron pairs. High volatility would be predicted. In actuality, the following hexafluorides and their boiling points are known: SF_6 (sublimes at $-64°$), SeF_6 (sublimes at $-47°$), TeF_6 ($-39°$), ReF_6 (48°), OsF_6 (47°), and IrF_6 (53°).

5. The properties given for the bromide suggest that it is highly polar and therefore must be the bromide of an active metal with low electronegativity. It would thus be less electronegative than hydrogen, and would form a hydride in which the hydrogen would be partially negative. Such compounds will react with compounds of positive hydrogen, such as hydrogen chloride, liberating hydrogen. By so doing they form the most polar bond possible, between the

metal and the chlorine, and permit the negative and positive hydrogen to unite.

6. If we were comparing a fluoride with a similar chloride, we would predict the chloride to be more volatile because it would be less polar and be more weakly held together. If we were comparing several fluorides, or several of the same halides of a given element, we would predict greater volatility the more halogen atoms competing for the electrons of the central atom, because no one atom could succeed as well as with less competition. Higher halides would tend to be more volatile than lower halides because of the lesser polarity of the bonds. Here we are comparing a lower fluoride with a higher chloride, and there is little question what the prediction should be: greater volatility for the chloride on two counts. It would be more volatile than the fluoride in the first place, and in addition there are three chlorines but only two fluorines.

7. The volatility of the chloride suggests either that it contains a relatively large number of chlorine atoms per central atom, or it is the chloride of a highly electronegative element. In either case, the bonds would not be very polar, and the chlorine would be potentially active as a chlorinating agent if this chloride could find another element which would provide higher negative charge to the chlorine. An element having fewer outer electrons than vacancies is metallic. It is therefore probably much less electronegative than the other element of the chloride, and would be chlorinated by that chloride under favorable conditions.

8. The displacement of the other halogen by chlorine proves that the chlorine forms a stronger, more polar bond with the other element than the other halogen did. Chlorine must therefore be more electronegative than the other halogen, which limits the latter to being either bromine or iodine. Both bromine and iodine have more electrons per molecule than chlorine, and correspondingly higher van der Waals interactions. They therefore melt higher than chlorine.

9. Halides in general are very susceptible to hydrolysis unless the other element is quite basic. The products of hydrolysis are hydrogen halide and the hydroxy compound of the other element. Only if the other element forms a completely ionized hydroxide will no hydrolysis occur. We can say with confidence that if the bromide does not react with water, the element must be a metal which loses electrons easily, and hence a metal whose atoms have very few outer electrons per atom.

CHAPTER 15

1. (*a*) The equation is $2NaNO_3 \rightleftharpoons 2NaNO_2 + O_2$. Both sodium nitrate and sodium nitrite are solids, and their concentration, like that of any solid, cannot be changed. Therefore the equilibrium constant is simply

$$K = [O_2], \text{ or } K = p_{O_2}$$

(*b*) Since this is a thermal decomposition, the forward reaction is endothermic. Increasing temperature speeds all reactions but favors the endothermic. A new equilibrium would be reached at a higher temperature in which the pressure of O_2 would be higher. The system changes in the direction of absorbing the stress, as predictable by the principle of LeChatelier, here apparently trying to keep the temperature from being raised by increasing the concentration of molecules (O_2) having higher potential energy.

(*c*) Adding sodium nitrite would have no effect on the oxygen pressure, because even though this would initially give more surface for the oxygen to join it would then create more nitrate to give off oxygen. The amount of a solid in an equilibrium mixture can be changed, but not the concentration.

(*d*) Increasing pressure would shift the equilibrium to the left, until the pressure of O_2 was the same as it was before an attempt to increase it was made. The pressure could be increased by decreasing the volume of the system. This would increase the concentration of O_2 molecules, and therefore increase their rate of rejoining the solid, without increasing the rate of liberation. Momentarily, therefore, the equilibrium would be upset until the pressure was reduced to its initial value. According to Le Chatelier's principle, any attempt to increase pressure will cause the system to try to avoid that increase by decreasing the number of gas molecules. This is in effect what happens here.

(*e*) Removing some of the nitrate will have no effect on the equilibrium pressure. It will, of course, reduce the surface from which oxygen can escape, but at the same time it will reduce the surface which the oxygen can rejoin by exactly the same amount. The pressure of oxygen over the surface therefore remains unchanged.

2. Activation energy is needed. This is supplied electrically. Once the reaction is started, it furnishes its own activation energy and continues rapidly until completed. Activation energy is needed because

the ingredients already represent combinations of atoms. These combinations must be disrupted before new combinations can form. Activation energy makes this disruption possible.

3. When a reaction proceeds by a chain mechanism, a whole series of reactions is brought about by the introduction of just enough activation energy to excite one molecule. If this chain can be "nipped in the bud," the reaction can be checked before it has become very extensive, and it must await the chance of new activation before it can start again. An inhibitor can be something which, although present only in small concentrations, nevertheless gets in the way of a chain reaction, stopping it by forming products which do not continue the chain. One molecule of inhibitor, although it may not happen to intercept a chain reaction until hundreds of molecules have already reacted, may then, by sacrificing itself through reaction with a free radical, prevent the chain from continuing through reaction of many thousands of additional molecules of the substance being protected.

4. (*a*) The equation is $2CO_2 \rightleftharpoons 2CO + O_2$
Since these are all gases, the equilibrium constant expression would include all of their concentrations:

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

(*b*) Increasing the pressure will favor the reaction that yields fewer molecules. The equation shows two molecules on the left and three on the right. This tells us that increasing the pressure on the system will speed the reverse reaction more than it will speed the forward reaction. A new equilibrium will therefore be reached at which the concentrations of products are proportionally less than before.

(*c*) Decreasing the temperature, since the forward reaction is endothermic, will favor the reverse reaction by slowing it less than it slows the forward reaction. A smaller equilibrium constant will result at the lower temperature. This will correspond to a relatively larger concentration of carbon dioxide.

(*d*) If some CO_2 were removed from the system at equilibrium, the forward reaction would be slowed without momentarily changing the speed of the reverse reaction. The relative quantities of products would therefore diminish, for they would not be formed as rapidly as they react, until more CO_2 is formed and equilibrium is reached again.

CHAPTER 16

1. Only mole fraction gives directly the relative numbers of molecules of solvent and solute. Even this does not represent as directly as possible what we would often like to know about a solution—the number of solvent molecules per molecule of solute. To obtain this, which we might term "the solvent number," we would divide the mole fraction of solvent by the mole fraction of solute. Such a number would be very useful for comparing solubilities of different compounds in the same solvent, and in different solvents.

2. It tells us that the attraction between oil molecules and water molecules cannot be as great as the attraction among oil molecules and/or the attraction among water molecules. Otherwise they would mix.

3. If other salts of the same acids are insoluble, the solubility of alkali metal salts cannot be attributed to the hydration of the anions. If other cations are more strongly hydrated than alkali metal ions, this too cannot explain the solubility of the alkali metal salts. Only one cause seems to remain—the nature of the crystal lattice. The lattice energy of the alkali metal salts appears to be lower, probably largely because of the relatively large size of alkali metal ions compared to other metal ions and because of their low charge compared to other metal ions. Also, the high polarity of the bonds makes it easier for the atoms to be separated as ions than would be true of any other metals. The alkali metal salts are most ionic of all, because the alkali metal atoms are lowest in electronegativity. We cannot really explain fully the relative solubilities of substances.

4. The solubility of nitrates suggests that the nitrate crystal lattice is relatively easily separated into ions, and that the nitrate ion must be hydrated with considerable energy. The latter could involve protonic bridging to water. Incidentally, many metal nitrates are highly hydrated in the crystal. The presence of coordinated water makes interattractions among the ions weaker by keeping them farther apart, and thus contributes to the ease of separation of the ions in the solvent.

5. Although there are some exceptions, most familiar of which is NaCl (whose solubility changes relatively slightly with temperature), increasing the temperature usually increases the solubility, often to a surprisingly great extent. A complete explanation is not available, but we can at least speculate that increased thermal agitation of the

component particles of the crystal results in expansion, and thereby diminishes the interparticle attraction, making it easier for solvent molecules to effect a complete separation by dissolution. Also, with increased kinetic energy of the dissolved particles, the possibility of their joining the crystal when they strike its surface would presumably be diminished. Thus equilibrium would be reached at a higher concentration of dissolved solute. Le Chatelier's principle would help us predict increased solubility at higher temperature if the dissolution process is endothermic.

Furthermore, a solution is a more disordered state than the system of separate solute and solvent, and therefore has higher entropy. The entropy term, $T\Delta S$, is higher with higher temperature, and increased solubility is favored by the increase in entropy.

6. This is certainly not an easy question to answer, but at least we can think about it in terms of the expected effects of temperature. One effect should be diminished solvation of the solute particles. Increased thermal energy should tend to cause decomposition of solvates, a given ion or molecule being more weakly solvated at higher temperatures. This would tend to slow the process of dissolution, so that equilibrium would be reached at a lower solute concentration. Comparing this to the answer to the preceding question, you will see that several opposing factors may be involved, and we may not be able easily to predict which will predominate. If the dissolution is exothermic, reduced solubility at higher temperature would be predicted by Le Chatelier's principle.

7. Carbon and hydrogen are so similar in electronegativity that the bonds in hydrocarbons are nearly nonpolar. Intermolecular interactions are thus mainly restricted to van der Waals attractions, which between segments of hydrocarbons of similar size should be nearly alike no matter what the total molecular size or structure. Consequently, there should be no difficulty about changing the environment of a molecule from one kind of neighborhood to another, as long as all neighborhoods have the similarity of being hydrocarbon. Energy required to separate like molecules is regained by the energy of association of unlike molecules.

8. Dissolution of sodium chloride in liquid ammonia requires the separation of sodium and chloride ions by dispersing them through the ammonia, and the separation of ammonia molecules which are held together through protonic bridging. The energy needed for these purposes is made available if ammonia molecules and sodium and chloride ions attract one another sufficiently strongly. Since am-

monia, like water, consists of polar molecules, these can become attached to the ions by an ion-dipole electrostatic attraction. This might be enough to cause some sodium chloride to dissolve in liquid ammonia. In fact, it does.

9. This is a hydrocarbon, with essentially nonpolar bonds and therefore only weak van der Waals forces of intermolecular attraction. Therefore it should be easy for water molecules to penetrate between the hydrocarbon molecules. However, before such penetration could occur the water molecules would need to break loose from the other water molecules to which they are attached by protonic bridging. This would require energy, as would also be required for hydrocarbon molecules to push aside protonic bridging and penetrate among the water molecules. No apparent source of attraction between water molecules and hydrocarbon molecules exists sufficient to compensate for the energy of overcoming the water-water attractions. Therefore the two liquids would be predicted to be practically immiscible.

10. A cation has a net positive charge and also vacant exterior orbitals. By virtue of the charge alone, it can attract the negative end of the water dipole, the oxygen end, which can be held to the cation by electrostatic forces. Depending on the amount of nuclear attraction exerted at the vacant orbitals of the cation, specific coordinate covalent bonds may be formed by donation of electron pairs on the negative oxygen of the water molecules to the vacant orbitals of the cation. To summarize the extremes, the attraction between a water molecule and a cation might be an ion-dipole attraction or a coordinate covalent bond.

CHAPTER 17

1. The boiling-point elevation depends on the concentration of solute particles. If the molecular weight is less than indicated by the empirical formula, then there must be a higher concentration of particles than expected, such that a smaller amount would have the same effect. In other words, then, the compound must be dissociated to some extent, to smaller units than molecules, in the solution.

2. This tells us that the actual molecular weight of the compound, as it exists in solution, is an integral multiple of the empirical formula weight, and thus that either simple molecules are associated in pairs, trios, or the like in the solvent, or else the simplest molecules are actually multiples of that indicated by the empirical formula. Not

uncommonly, different degrees of association among molecules are observed in different solvents. Then the determination of freezing point does not tell us anything but what the particular degree of association is in that particular solvent, at the particular concentration used.

3. Electrical conductance through a solution of an electrolyte depends on the migration of ions through the solution, as well as on their discharge at the electrodes. This migration will depend on the mobility of the ions. The mobility will depend on how much solvent they must drag with them as they move, on how much the effect of other ions may be, on the viscosity of the solvent, the size of the ions, and other factors. Consequently, different solutes will have ions that under similar conditions migrate at different rates. The conductance of the different solutions will be different.

4. In the first place, a dissolved solute represents a degree of dispersion that rather closely resembles the gaseous state, in that the component particles are separate and independent of one another. In this situation they are especially vulnerable to chemical attack, and chemical reactions can occur nearly as rapidly in solution as they can in gases—especially if in the gases there are gaseous diluents that are inert, to correspond to the solvent molecules which dilute the solute.

Second, the equilibrium processes are quite analogous, the solute leaving and reentering the solution phase much as the vapor leaves and reenters the gas phase. Increasing the concentration of the dispersed phase molecules or particles has the similar effect in each of speeding the return to the condensed phase, and removal of dispersed phase is in both situations compensated for by continued transfer from the condensed to the dispersed phase.

5. Evidently this hydrate was unstable enough to exert an appreciable pressure of water vapor at room temperature. When the partial pressure of water vapor in the atmosphere of the room happened to drop below the dissociation pressure of the hydrate, the salt became anhydrous. When during the next few days, the humidity rose and the partial pressure of water vapor exceeded that of the hydrate, the salt took up water again and became hydrated.

6. This would mean only one-third as many particles are present as calculated for the expected number of molecules. Evidently this solute goes into solution under the conditions of measurement as a trimer.

7. This would call for distillation of the solvent at a greatly reduced pressure, thus reducing the boiling point enough to avoid thermal decomposition of the solute.

CHAPTER 18

1. The action of sodium with water produces hydrogen and sodium hydroxide, a strong base. As the reaction proceeds, the concentration of hydroxide ion increases. This cannot increase without simultaneous decrease of the hydronium ion concentration, which initially was only 10^{-7} mole per liter, or one ion in 550 million water molecules. If sodium reacted only with hydronium ion, the reaction would rapidly slow as the concentration and therefore availability of hydronium ion changed from very small to exceedingly slight. This is especially true since the hydroxide ions would be formed at the surface of the sodium and more rapidly than they could diffuse throughout the solution, so that their local concentration would almost immediately become very high. There is no question about whether hydronium ions, if present in substantial concentration, would react with sodium. Of course they would, and more actively than water molecules.

2. When a proton transfers from one water molecule to another, it leaves behind an electron. If this becomes distributed, as seems reasonable, between the remaining hydrogen and oxygen in accordance with their relative electronegativities, it gives hydrogen a partial negative charge, in contrast to its positive charge in water, and the oxygen becomes much more negative than it is in water. From the water to which the proton becomes attached, the high positive charge attracts electrons, causing the charge distribution over the oxygen and the other two hydrogens to adjust. All three hydrogens should thus become more positive than they were in water, and the oxygen should become less negative. Unquestionably neither the hydrogen nor the oxygen in hydronium ion or in hydroxide ion are in a condition comparable to their condition in the water molecule. Nevertheless, the convention of oxidation number places upon hydrogen the same $+1$ and on oxygen the same -2 whether they are in hydroxide ion, water molecule, or hydronium ion. Furthermore, if removal of electrons is oxidation and acquisition of electrons is reduction, the hydrogen and oxygen in hydroxide ion have both been reduced from their condition in the water molecule, and oxidized in hydronium ion. But we do not call this oxidation or reduction, because of the convention of defining such a process as involving a change in oxidation number. The combination of a hydronium ion with a hydroxide ion to form two molecules of water is clearly very similar to what is conventionally called an oxidation-reduction reaction, but because the formal oxidation numbers do not change it is not customary to refer

to this aqueous acid-base neutralization as oxidation-reduction. This is a serious deficiency in the artificial concept of oxidation-reduction.

3. The only chemical reaction that occurs in these neutralization reactions is the combination of hydronium and hydroxide ions to form water. This reaction is independent of the nature of the base cation or the acid anion as long as the base and acid are completely ionized. Consequently, the heat of neutralization must be equal for all such reactions.

4. A Brönsted acid is a proton donor, and a Brönsted base is a proton acceptor. In water, the proton donor is the hydronium ion, and the proton acceptor is the hydroxide ion. In the Lewis system, the acceptor is the acid and the donor is the base. In aqueous neutralization, the proton is the acceptor and the hydroxide ion the donor; hence, the proton is the acid and the hydroxide ion the base.

5. The fact that the oxygen in a complex anion is highly negative tells us that it will be an effective electron donor, more so than the oxygen in water, and that therefore the anion can be expected to remove protons from water (or hydronium ion) to a limited extent, leaving a surplus of hydroxide ions. Atoms which are relatively large in diameter in their respective periods must begin these periods, since size decreases from left to right across a period. The elements that begin the periods are the most active metals, having lowest ionization energies and, as cations, having least attraction for electrons. These cations will therefore not remove hydroxide from water molecules. In other words, the anion will hydrolyze and the cation will not. Consequently the solution of the salt will be alkaline, with a pH greater than 7.

6. The anion hydrolysis would involve acquiring protons, leaving a surplus of hydroxide ions and therefore tending to make the solution basic. The failure of the solution to be basic thus indicates that the cation must also hydrolyze, uniting with hydroxide ions and leaving a surplus of hydronium ions. The extent of the two hydrolyses must be equal, resulting in a neutral solution.

7. Only the alkali metals and calcium, strontium, and barium form hydroxides that are strong bases. All other metal hydroxides are weak bases. Therefore most metal chlorides are salts of the strong acid, HCl, and the weak base, metal hydroxide. Such salts are expected to hydrolyze, the metal ions removing hydroxide ions from the water, leaving a surplus of hydronium ions to make the pH less than 7. Viewed a little differently, most metal ions, by possession of both positive charge and vacant outer orbitals, are attracters of electrons and

electron acceptors. In water, water molecules act as donors through their negative oxygen atoms with two unshared pairs of outermost electrons, and become coordinated to the metal ions. The water that is coordinated has electrons partially withdrawn from it by the metal, leaving the oxygen less negative and the hydrogens more positive than they are in water alone. The hydrated cation can therefore lose protons to the surrounding water, making it slightly acidic. By either view, the pH of the metal chloride solution is somewhat less than 7.

8. Lithium hydroxide is a strong base, and lithium ion therefore has no tendency to remove hydroxide ions from water. The anions of triprotic, and most diprotic, acids bear a negative charge of -3 or -2, which makes them good electron donors to a proton. To some extent, then, they remove protons from water, leaving a surplus of hydroxide ions. Stated a little differently, although the first ionization constant of a polyprotic acid may be large, the constants for the second and third ionizations are progressively very much smaller, by a factor of about 1/100,000 per ionization. A lithium salt of a triprotic or diprotic acid is therefore only partly the salt of a strong acid, but partly also the salt of a weak acid, and hydrolysis is expected to produce alkalinity. Therefore, the pH would be greater than 7.

9. A solution of high pH is much to be preferred, in order to keep most of the hydrogen cyanide in the form of water and cyanide ion. The equilibrium is:

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

In an alkaline solution, the reaction is forced to the right by the removal of hydronium ion through reaction with hydroxide ion. Indeed, we might write the reaction:

$$HCN + OH^- \rightleftharpoons H_2O + CN^-$$

From a neutral or acidic solution, HCN molecules would escape with the rest of the gas stream.

10. Within a period, atomic radius diminishes from left to right. Therefore the question of which has the smaller atoms is equivalent to the question of which element is to the right in the period. It must be that element which is more electronegative, since electronegativity increases from left to right. In a complex oxide the more electronegative element will be part of the anion, since its oxide must be the more acidic one. Element 1 is therefore the one with smaller atoms.

11. An element with low ionization energy is one which is an active metal, since atoms with fewest outer electrons lose an electron most easily. An active metal not only loses electrons easily but also is very low in electronegativity. An element that is low in electronegativity will form a very polar bond with oxygen, in which the oxygen becomes very negative leaving the other element very positive. Any compound in which oxygen is very negative is basic, and will react vigorously with strong acids to form stable salts and water.

12. An element that is relatively volatile in the free state must be one whose atoms have more outer electrons than vacancies, and therefore a nonmetal relatively high in electronegativity. An oxide of such an element cannot have highly polar bonds, and the oxygen cannot have acquired very high partial negative charge in this oxide. Such an oxide is always acidic rather than basic. Its oxygen is not sufficiently negative to act as electron donor to a proton, but its other element is sufficiently positive to attract to a vacant orbital a pair of electrons from a more negative oxygen such as occurs in a base.

13. An element which in the free state shows closest packing of atoms must be a metal, and consequently relatively low in electronegativity. Its oxide will therefore have highly polar bonds with the oxygen quite negative and therefore basic. An element which in combination with chlorine is a good chlorinating agent must be one so electronegative that it has not permitted the combined chlorine to acquire a very high negative charge, or it would not be a chlorinating agent. This element must therefore be a nonmetal, and its oxide acidic. When a basic oxide unites with an acidic oxide, the element of the acidic oxide always must accept the electrons of the more negative oxygen in the basic oxide, thus becoming part of the anion.

14. Bromides are only very stable when the bromine has become highly negative. This can happen only when the other element is very low in electronegativity. Such an element naturally forms an oxide of high polarity, which is therefore strongly basic.

CHAPTER 19

1. In most cases, the lattice energy of a salt formed by complex ions must be lower than that of a salt formed by simple ions, since in the latter the electrostatic forces have the opportunity for much closer interaction. The solvent therefore finds it easier to overcome the lattice energy of a complex salt. It is also possible that a complex

ion may be more thoroughly and more energetically hydrated than a simple ion, which would also contribute to the solubility. Formation of a complex does not always increase solubility, however, for there are many insoluble complexes. Many complexing agents can serve as precipitating, rather than solubilizing, agents.

2. Lead chloride is not wholly insoluble, and precipitation with the stoichiometric amount of chloride ion leaves some lead ions and some chloride ions in solution. Equilibrium between undissolved and dissolved lead chloride is established. Addition of more chloride ion speeds the precipitation, or recrystallization, reaction without changing the rate of dissolution. But the additional chloride ion could precipitate lead chloride only by taking the lead ion with it, out of solution. A new equilibrium is reached, in which the rate of recrystallizing is kept the same as the rate of dissolution because to compensate for the surplus of chloride ions the lead ions are less concentrated than before. Measured by the dissolved lead concentration, the lead chloride is less soluble in the chloride solution than it is in pure water.

3. This fact suggests at once that with excess chloride ion present silver must form a complex chloride which is more soluble. The dissolution of AgCl can be represented by the equation:

$$AgCl + Cl^- \rightleftharpoons AgCl_2^-$$

4. Remember that the actual concentrations determine the exact behavior of ions only in a solution so dilute that the different ions do not significantly interfere with one another. As the solution becomes more concentrated, regardless of the kinds of ions, they must on the average be closer together and, being charged, must influence one another. We therefore find it necessary to correct for these effects by multiplying the actual concentrations by an "activity coefficient" that gives the true "activity" of the ion. In a more concentrated solution, the activity of an ion is less than would be expected from the concentration, because of the drag of other ions. We find it approximately correct, in dilute solutions, to use concentrations in equilibrium constant expressions, such as that for solubility product. Strictly, however, activities should be used. Precipitation does not occur until the solubility product using activities is exceeded. If the activities are appreciably smaller than the concentrations, the solubility of the compound is greater than otherwise expected. When it is desired to precipitate an ion quantitatively so that the compound can be determined by weighing, a small excess of precipitating agent is

desirable to make the compound more insoluble, but a large excess is to be avoided because it may make the compound more soluble even when it does not form complexes with it. (Another and even better reason to avoid excessive amounts of precipitant is to avoid occlusion of this substance as an impurity in the solid that precipitates. Such occlusion of ions that are normally soluble often presents a serious problem in quantitative analysis.)

5. The change from a metastable to a stable condition should always involve the release of energy. Crystallization of the excess solute from a supersaturated solution should therefore be exothermic.

6. Neutral molecules, such as those of sugar, can rejoin the solid from solution individually and independently. Ions, however, could not rejoin a crystal entirely independently or they would build up a high charge on the crystal if one kind joined faster than the opposite kind. Therefore the crystallization of an ionic compound from a solution of ions must depend on the concentrations of both the cation and the anion.

7. As suggested in the preceding answer, to preserve the essential neutrality of the crystal two silver ions must join it simultaneously with one sulfide ion. The rate of crystallization is proportional to the concentration of silver one ion, squared, times the sulfide ion concentration.

CHAPTER 20

1. The anode would probably be oxidized, becoming part of the melt, and then migrating as the cation to the cathode where it would be discharged to form the metal again.

2. A bromide would presumably give a strongly acidic solution only through hydrolysis, which would produce hydrobromic acid. It must therefore be the bromide of an element not very low in electronegativity. The bonds in the bromide would then not be highly polar, and it is doubtful whether the molten bromide would conduct electricity well.

3. Easy conduction of electricity tells us that the melted fluoride must be ionic. The other element must therefore be an active metal, having a low ionization energy.

4. Evidently this coulometer permits the measurement of the number of electrons passing through a circuit by weighing the silver deposited by these electrons from the silver nitrate solution. Therefore one would have to connect this cell in series in the electrical circuit so that the weighable electrode is the cathode on which the silver will be deposited. One gram-atomic weight of silver would be deposited for every 96,500 coulombs (one faraday).

5. If neutral water molecules can indeed be decomposed at an electrode, forming ions in the process, then it would seem possible that other neutral molecules, such as molecules of halides, might also be electrolytically decomposed, giving the impression of ions already present where there might be none. Low conductivity would suggest undissociated molecules in the melt, but high conductivity would not necessarily prove that the melt contained ions before electrolysis.

6. The highest positive value represents greatest reducing ability. The order is Ag, Cu, Pb, Mn, Na, Ca, Li.

7. These elements are so readily oxidized by water that they would react to completion without connecting the outside circuit.

8. A potential difference exists between two different metals, and placing them together in contact causes electrons to flow from one to the other. Corrosion is oxidation. It involves formation of positive ions, or their liberation from the metallic lattice. This liberation can occur more readily the less it is inhibited by surplus negative charge remaining on the metal. If some less easily corroded metal is in contact, electrons can flow to this and thus permit ions of the more easily corroded metal to leave more easily. Oxidizing agents can then remove the excess electrons from the less easily corroded metal without corroding it. Corrosion of the more active metal is thus accelerated by the junction of the two metals, but the less active metal is protected against corrosion. Thus, in the case of magnesium protecting an iron pipeline, the iron is kept slightly negative by electrons from the magnesium. Any oxidizing agents approaching the iron can remove these electrons without attacking the iron itself. The magnesium is corroded, and gradually changes completely into compounds and must be replaced. While it is present, it protects the iron.

9. The process from which energy is to be derived involves removal of electrons by oxygen from the hydrocarbons. If this energy is to be useful as an electric current, the electrons must flow externally from the hydrocarbons to the oxygen.

CHAPTER 21

1. Characteristic metallic properties arise in the electronic structures of the atoms, which have more outer vacancies than electrons. No possible combination of atoms not having these features would appear able to duplicate such properties. If it is molecular structure that determines properties, we can sometimes produce similar properties in similar structures, using different atoms. But if it is atomic structure that determines the properties, not much can be done to influence them.

2. If the mixture is heated under conditions permitting the escape of sulfur dioxide, and the oxide of the metal is not too stable, such a reaction may occur. For example, copper can be obtained by heating a mixture of the sulfide and oxide: $Cu_2S + 2CuO \rightarrow 3Cu + SO_2$.

3. Metals described here must be the least electronegative of the elements, and therefore must form the most ionic of halides. It would be very difficult to persuade a halogen atom, especially a fluorine or chlorine atom, to release a metal atom which supplies it so well with an electron. Electrolytic reduction therefore seems the most likely means of isolating the metal.

4. Lack of polarity of the metal hydride suggests a relatively high electronegativity of the metal, which means that its bonds to sulfur would not be very polar, and hence perhaps not very strong. Such a metal might be liberated by heating its sulfide with some more active metal that would combine with the sulfur. Alternatively, it could be roasted to convert the sulfide to oxide, and the oxide could be reduced with carbon or hydrogen. The oxide should not be too difficult to reduce, in view of the other properties of the metal.

5. Complex salts tend to be more stable the more completely the anion can control the electrons and the lower the polarizing power of the cation. Cations have lower polarizing power the lower the radius and the smaller the positive charge.

The high stability of the carbonate suggests that the metal ion is not highly polarizing, and may therefore be relatively large and low in charge. This would presumably be a very active metal, to lose its electron(s) so completely to the carbonate ion. Such metals are difficult to reduce chemically, because no other chemical reagent will give up electrons to them, or displace them from their combination with nonmetal(s). The best way to isolate this metal might be to destroy the carbonate by dissolving it in hydrochloric acid, and electrolyze the fused chloride.

6. Mercury can be used as a solvent to extract such metals as gold and silver. Then it can be distilled away, leaving behind the extracted metal.

CHAPTER 22

1. The stability of a complex anion such as sulfate depends on the extent to which it has been able to acquire electrons from the cationic portion of the compound and hold them in undistorted array. The proton with its very small size is much more effective as a polarizing agent than a much larger sodium ion could be. Furthermore, hydrogen is much more electronegative than sodium and therefore would not give up its electron to sulfate so completely. Both these differences would combine to make sulfuric acid much less stable thermally than sodium sulfate.

2. Down the group stability would probably increase, because the larger cations would have less polarizing action on the nitrate ion. Furthermore, the larger atoms are likely to be less electronegative, which would mean that they would give up electrons more completely to the nitrate ion. This also would contribute to nitrate stability.

3. Formation of a very stable carbonate implies a large cation of a metal of low electronegativity. The iodide of such a metal would therefore be quite polar, forming ionic crystals relatively high in melting point and low in volatility. The binary hydrogen compound would be a hydride with a rather high negative charge on hydrogen, making it reducing and easily hydrolyzed.

4. A pH higher than 7 would be desired, because the anion could preserve its identity in a basic solution. In a neutral or acidic solution, it would acquire a proton or two, and the free acid thus formed would be much less stable than the anion, owing to deformation by the protons.

5. The temperature of 900° is that at which the decomposition pressure of CO_2, at equilibrium with CaO and $CaCO_3$, equals one atmosphere. Decomposition begins at a considerably lower temperature, and at such a temperature could be caused to continue to completion simply by removing the carbon dioxide as it is formed, preventing equilibrium from being attained.

6. Calcium hydroxide is a source of soluble hydroxide ions. Hydroxide ion is a stronger base, a stronger electron donor to a proton, than is the ammonia molecule. An ammonium salt is an ammonia molecule that has already taken on a proton, plus whatever anion is

associated with it. This does not prevent a competition for that proton, however, when hydroxide ion is encountered. The hydroxide wins, and ammonia is liberated: $NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$. If the reaction occurs near the surface, the ammonia may escape as a gas and be blown away.

7. A direct reaction would be useful if it could be caused to occur. But how could it be done? It could not occur in water, because the only combination of opposite ions that is insoluble is calcium carbonate. NaCl, $CaCl_2$, and Na_2CO_3 are all soluble. In the absence of water, suppose at least partial reaction would occur if NaCl and $CaCO_3$ were heated together. How would you separate the products? But here is an example in which heats of formation (better yet, free energies of formation) of all reactants and products would tell us whether the problem would be worth investigating. The standard heat of formation is the difference in heat content between the elements in their usual state at 25° and the compound at 25°. The standard free energy is similar. The difference between the sum of the heats of formation of the reactants and the sum of the heats of formation of the products is the heat of reaction. (Free energies similar). For the reactants here, the heats of formation (and free energies of formation) are: 2NaCl, −195.6 (−196.4); $CaCO_3$, −288.5 (−269.6). For the products, they are: $CaCl_2$, −190.0 (−179.3); Na_2CO_3, −270.3 (−250.4). The sums are, reactants: −484.1 (−460.3); products: −460.3 (−429.7). The heat of reaction is thus −460.3 − −484.1 = 23.8 kcal *absorbed.* The free energy of reaction is −429.7 − −466.0 = 36.3 kcal *absorbed.* The endothermic nature of the proposed reaction suggests that it would certainly not be very likely to proceed spontaneously. The positive free energy change tells us definitely that the reaction will not occur spontaneously. In other words, if the reaction occurs under reversible conditions it will form calcium carbonate and sodium chloride, not sodium carbonate and calcium chloride.

8. The reaction is $Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$. The $CaCO_3$ is insoluble and of little use as a base, leaving only two moles of hydroxide ion, available in the products. In the reactants, the equivalent of four moles is present, for the sodium carbonate could neutralize two moles of hydronium ion.

CHAPTER 23

1. The object is to take a lot of heat to the sulfur bed. Water in the liquid state can supply a greater quantity of heat within a small space.

2. Both processes depend on bringing about a gas reaction which is exothermic and therefore favored by lower temperatures, yet does not occur at temperatures where yields would be good because of lack of activation. Both surmount the difficulty by using a catalyst to reduce the requirement of activation energy to bring about the desired reaction.

3. The problem is to explain why the bisulfate ion is not so weak an acid that sulfate ion would hydrolyze appreciably, which it does not. The partial charge on oxygen in the sulfate ion suggests that it should be a good electron donor to a proton, and therefore that HSO_4^- ion should be a weaker acid than it seems to be. The most apparent clue is that the sulfate ion is much more symmetrical. Acquisition of a proton would require it to lose much of this symmetry, a process probably requiring absorption of energy. This may be a reason for the sulfate ion in general being a poorer electron donor than we might otherwise expect.

Furthermore, the multiplicity of the S-O bonds concentrates oxygen electrons in the bonds, thus allowing oxygen lone pairs to spread out where they cannot so readily coordinate protons. This causes the sulfate ion to be a less effective donor than suggested by the charge on oxygen.

4. HNO_3 is actually $HONO_2$, just as other oxygen acids have their acidic hydrogen attached to oxygen rather than to the central atom. If HNO_3 were to lose a hydroxide ion to a proton from H_2SO_4, the products would be H_2O, NO_2^+, and HSO_4^-. The H_2O would at once react with H_2SO_4, presumably forming H_3O^+ and HSO_4^-. The reason for discussing these possibilities is that in nitrating mixtures which contain concentrated HNO_3 and concentrated H_2SO_4, it is believed that the nitronium ion, NO_2^+, plays an important role.

CHAPTER 24

1. Unless there is some special attribute of the functional group that will influence intermolecular attractions more in the smaller molecules, the melting point and volatility should change regularly along the series, the melting point rising and volatility diminishing. More effective van der Waals forces occur the larger the molecule and greater the number of electrons.

2. Identical sets are *b*, *c*, and *d*; also *a* and *f*. All different isomers are *e*, *g*, and *h*. All shown are isomeric heptanes.

3. The carbon-carbon bond angles, normally 109°, must be cramped

to 60° in cyclopropane. This would make the bonds weaker either because the orbitals do not overlap as fully or because the electrons in the separate bonds are now closer to one another and the bonds repel one another.

4. We know that an olefinic double bond, between two carbon atoms, is not twice as strong as a single bond. Greater stability would be achieved, then, if the double bond could become two single bonds. This might happen either by adding some other chemical reagent to the two extra bonds or by joining two molecules together, changing the double bonds to single bonds in that manner.

5. Here the formula is $(CH_3)_2Mg$. Since magnesium is less electronegative than either carbon or hydrogen, the bonds from magnesium to carbon must be quite polar, with both the carbon and hydrogen negative and the magnesium positive. Here we must regard the alkyl group as being "functional," for it is the negative component in contrast to its usual role. With water, the hydroxide should go to the magnesium, because this would be the most polar bond that could be formed, and the hydrogen should go to the methyl groups, forming CH_4. These are indeed the major products.

6. A halogen atom is more electronegative than either carbon and hydrogen, but the latter are more electronegative by far than sodium. Therefore the most polar bond possible here would be between the sodium and the halogen. The halogen, in other words, would tend to leave its combination with the alkyl group to enter into a new combination which can furnish it with higher negative charge. This would leave the alkyl group as a free radical, with one bond more to be formed. Two such alkyl groups could join together, or one might give the other a hydrogen, becoming itself an alkene. Both types of reaction have been observed. Sodium chloride is the product whose formation dominates the reaction.

7. A sodium alcoholate is the product of displacement of hydroxyl hydrogen from an alcohol by sodium. Reaction with an alkyl halide would form sodium halide, the most stable possible combination available, leaving an alkoxy or alcohol group, and the alkyl group from the alkyl halide. These can get together to form an ether, the halide alkyl group taking the place of the original hydroxy hydrogen on the alcohol. This is indeed a method of preparing ethers.

8. Again a kind of methathetical reaction, or double decomposition, would produce sodium chloride, and the other product would be "benzene hydroxide," which is C_6H_5OH and called "phenol." A trivial name is "carbolic acid."

9. In the order given, -4, -2, 0, $+2$, $+4$.

10. Substituting fluorine for hydrogen would, because of the very high electronegativity of fluorine, withdraw electronic charge from the other atoms. Carbon would therefore become more positive, hydrogen more positive, and oxygen less negative. This would be true also of the anion, which, with less negative oxygen, would be a poorer electron donor to a proton. This is equivalent to saying that the acid would be stronger. Indeed, when three fluorine atoms are substituted in acetic acid, it becomes a very strong acid, although acetic acid itself is quite weak.

11. HNO_2 is much weaker as an acid than HNO_3. CH_3CH_2OH, ethyl alcohol, although only very slightly acidic, is much less so than acetic acid. In both pairs of compounds, the more oxygens present the stronger the acidity. In competition, oxygen cannot become as negative as it can alone.

12. From an alcohol and monocarboxylic acid, removal of water produces an ester. A glycol simply has two alcohol groups, and with an acid of two groups should by splitting of water produce long chain molecules having intermittent ester groups. This could be called a "polyester." Such compounds are known and very useful.

13. Carbonic acid, which is too unstable to be isolated and is supposed to exist only in water solution, would have the structure $OC(OH)_2$. It readily loses H_2O and forms OCO (CO_2).

CHAPTER 25

1. In general, bonds are weaker between larger atoms and between atoms more different in size. On this basis, one would expect the alkali metal hydrides to decrease in stability down the group. They do.

2. Two reasons can be cited. One is the lower electronegativity of barium than beryllium, which makes the bond to oxygen more polar and therefore the hydroxide more ionic. The other is the larger size of the barium ion, permitting easier separation of the hydroxide ions, since electrostatic attractions diminish with increasing distance.

3. Without a knowledge of exactly how these catalysts function, we cannot answer the question positively. However, we can note that a catalyst makes molecules more reactive. This could be done by forcing them out of their normal symmetry. Both BF_3 and $AlCl_3$ have one empty orbital on the central atom that can serve as electron

acceptor. These molecules may then become attached to any other molecules having external electron pairs, which includes most other molecules, in at least a weak attachment that should upset the electrical symmetry and make the other substance more vulnerable to chemical attack.

4. Boron is less electronegative than carbon, and therefore forms more polar bonds with oxygen. More polar bonds, other factors being similar, are more stable and their formation produces more heat. The boron-oxygen bond energy is undoubtedly greater than the carbon-oxygen bond energy, but this difference might be obscured if we were really considering the burning of elementary boron and carbon instead of their compounds. The reason is that to burn the elements, we must, in effect, first atomize them. The heat of atomization of carbon is greater than the heat of atomization of boron, 172 to 141, and this alone would give an advantage to the burning of boron even if the bond energies were equal, because energy required for the atomization is not available to be released by the overall combustion process. In other words, the carbon-oxygen bond energy might be (although it is not) equal to or somewhat higher than the boron-oxygen bond energy, but we would not know this from the heat of combustion of the elements because the carbon is harder to atomize.

5. Metal oxides such as would be on corroded metal surfaces are basic. Boron oxide is acidic, and can combine with the metal oxides, forming fusible metal borates.

6. What you might now know offhand is that slaked lime, calcium hydroxide, forms a crystalline hydrate, and this is probably the first reaction in the setting of the mortar. We also know that silica in the rocks or bricks is acidic and can be reactive with alkali, forming calcium silicates which would help bind the mortar to the stones or bricks. Finally, the air contains carbon dioxide, which reacts with the calcium hydroxide forming crystalline calcium carbonate, a form of limestone, as the mortar stands long exposed to the atmosphere. Once the mortar near its surface has been changed to carbonate, further reaction of carbon dioxide depends on the success of this gas in penetrating the dense solid toward the interior. Studies of masonry walls several feet thick, in cathedral ruins centuries old, have shown that even after hundreds of years the carbonate formation had only penetrated a foot or two, the interior still being mainly calcium hydroxide, plus silicates from slow reaction with the sand.

7. Alkaline solutions attack the glass, and glass stoppers in the

bottles tend very easily to become "frozen" in place. Rubber resists the reaction of the alkali and makes a much superior closure for this purpose.

8. The arsenic might well be present as metal arsenide, a binary compound susceptible to attack by water or acids. The proton would go to the more electronegative element, which here would be the arsenic, forming arsine, AsH_3, a very deadly gas. This is a real hazard to workmen using sulfuric acid, for example, to remove rust from scrap iron, if the iron or the acid contain arsenic even in traces. One would certainly be wise to avoid inhaling hydrogen formed by a typical treatment of zinc or iron with acid, for fear of arsenic being present as an impurity in the metal and forming arsine in the evolved hydrogen.

9. No doubt any iodide ion is oxidized by the chlorine along with the bromide ion. However, the next step, blowing the bromine out of the water, works because bromine is volatile, but the iodine would not be volatile under these conditions and therefore would remain in the seawater.

CHAPTER 26

1. If metal atoms are held together in the metallic crystal extremely tightly, they cannot easily be separated in the process of oxidizing them. The metal may therefore tend to resist corrosion when it is in the massive state, although perhaps if finely powdered it would be easily oxidized.

2. On the basis of the partial charge on oxygen, which must be less negative, the more oxygen atoms are competing for the electrons of a metal atom. Metal oxides may be strongly acidic if the metal is in a sufficiently high positive oxidation state. Examples are CrO_3, the anhydride of chromic acid and Mn_2O_7, the anhydride of permanganic acid.

3. Knowing that these oxyanions become less stable when they are less able to acquire electrons completely and when they are deformed by highly polarizing cations, of small size and high charge, we can predict that in their higher oxidation states the transition metals will not form salts of these oxyanions at all. This is correct. There are very few such salts in which the oxidation state of the metal is as high as $+4$, and the most stable such salts are of metals in the $+1$ or $+2$ states.

4. If the transition metal oxide is amphoteric or acidic, it can be caused to react with sodium hydroxide just as any acidic oxide would, forming a complex oxyanion containing the transition metal, combined with the sodium ion as a salt. Sodium salts in general are soluble in water.

5. This seems to suggest that CrO_3 is molecular, with relatively weak intermolecular attractions, but MoO_3 and WO_3 must be of a polymeric, giant molecule structure. This further suggests that oxygen is able to form double bonds to the chromium, but molybdenum and tungsten more stably form single bonds to oxygen. Melting would require only the overcoming of van der Waals forces in the CrO_3 but probably the actual breaking of covalent bonds in MoO_3 and WO_3.

6. If, as they do, certain alloys containing several elements are able to be more magnetic even than pure iron, magnetism evidently cannot be explained solely on the basis of atomic structure.

7. Zinc protects the iron, its electrode potential showing it to be a better reducing agent than iron.

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