DOCUMENT RESUME

ED 477 258 SE 067 619

AUTHOR	Huheey, James
TITLE	Diversity and Periodicity: An Inorganic Chemistry Module.
ISBN	ISBN-06-561121-7
PUB DATE	1978-00-00
NOTE	116p.; Produced by the Chemistry Association of Maryland. For Teacher's Guide, see SE 067 620. For other modules in series, see SE 067 618-630.
PUB TYPE	Books (010) -- Guides - Classroom - Learner (051)
EDRS PRICE	EDRS Price MF01/PC05 Plus Postage.
DESCRIPTORS	*Chemical Nomenclature; *Chemistry; Curriculum Design; Instructional Materials; Interdisciplinary Approach; Science Instruction; Secondary Education

ABSTRACT

This book is one in a series of Interdisciplinary Approaches to Chemistry (IAC) designed to help students discover that chemistry is a lively science and actively used to pursue solutions to the important problems of today. It is expected for students to see how chemistry takes place continuously all around and to readily understand the daily problems facing them and their environment. Contents include: (1) "Periodicity: A Chemical Calendar"; (2) "Structural Chemistry of Metals and Their Compounds"; (3) "Inorganic Molecules"; (4) "Acids and Bases"; (5) "Chemistry of the Transition Elements"; and (6) "Bioinorganic Chemistry". (KHR)

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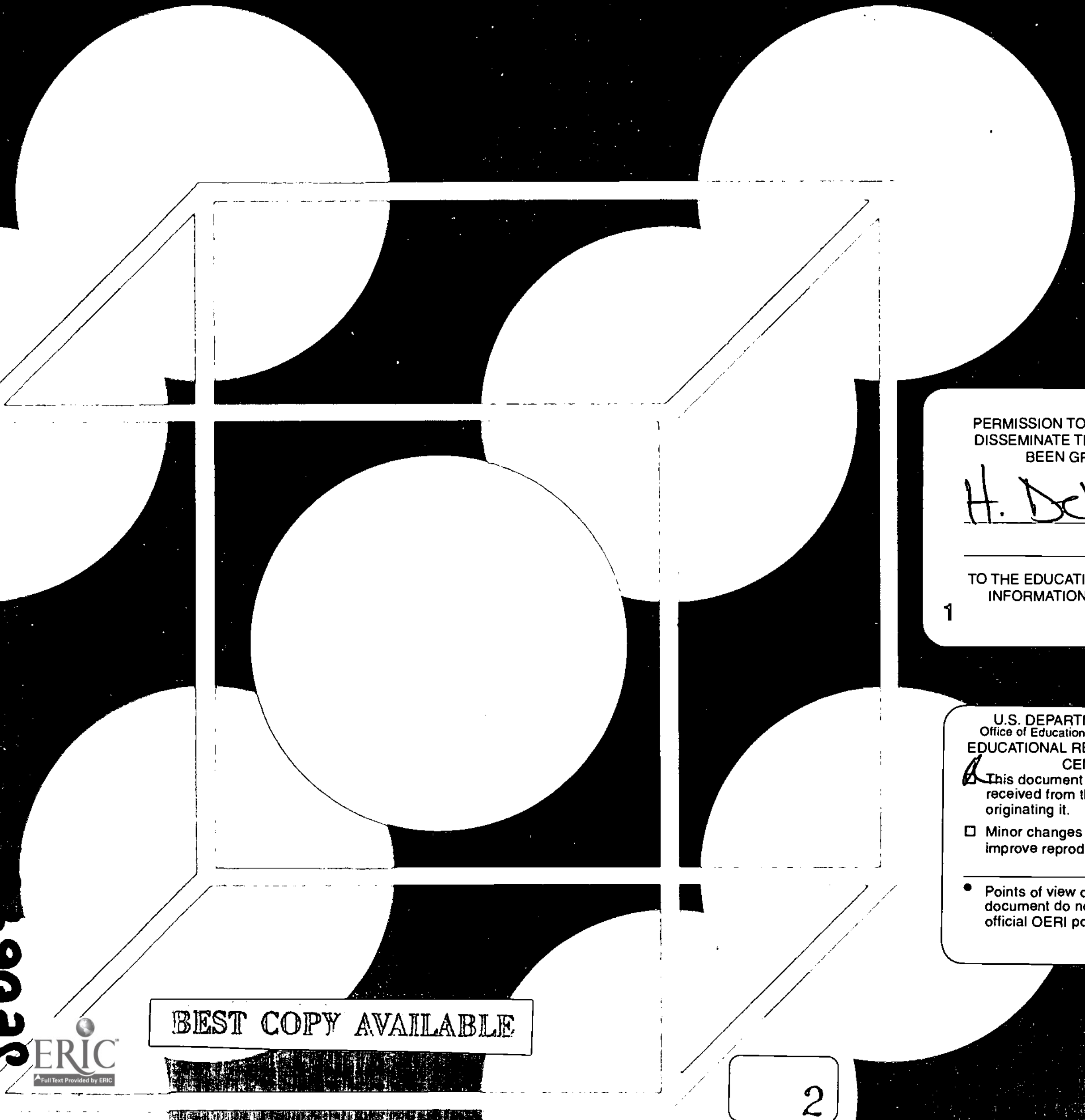
DIVERSITY AND PERIODICITY

AN INORGANIC CHEMISTRY MODULE



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James Huheey

1817
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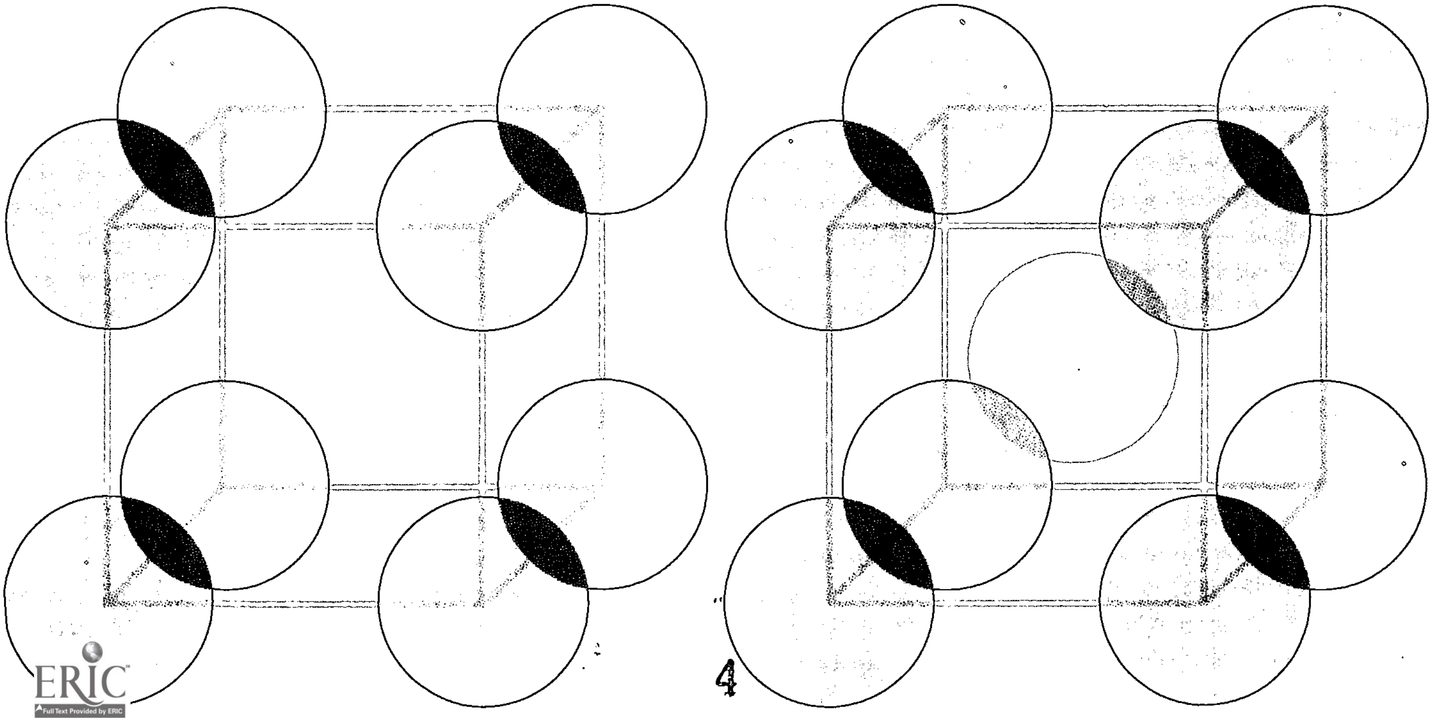
New York Hagerstown San Francisco London



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Printed in the United States of America.

STANDARD BOOK NUMBER 06-561121-7

89012MU0987654321

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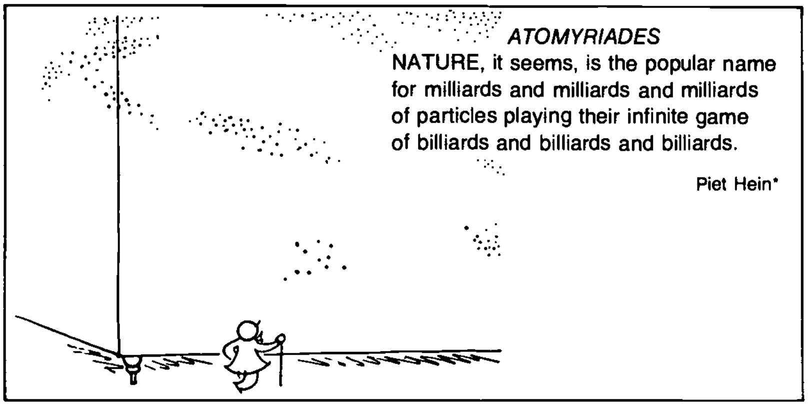
DIVERSITY AND PERIODICITY:
AN INORGANIC CHEMISTRY MODULE

JAMES HUHEEY

When not driving his red and white truck up and down the mountains of western North Carolina in search of "the perfect salamander," ratchet-jawing with the 18-wheelers out on "that ol' boulevard" with his CB, or pounding a typewriter to keep his editor happy, Jim Huheey finds time to do some of the other things inorganic chemists do: research on electronegativity and related topics, lecture preparations, faculty meetings, Sunday afternoon football games, etc., etc. Ever since he joined the University of Maryland from the University of Illinois via Worcester Polytech, Jim Huheey has been a major contributor to the mainstream of the department life. Characterizing himself (in a friendly needle to the organic chemists) as a chemist of *the other* 106 elements, his work in the past has been geared mostly to the college and university levels. Lately he has extended his range to encompass high school as well.

Capping his many achievements, in 1971 he received the Young Chemistry Teachers' Award sponsored by the District of Columbia division of the American Institute of Chemists; and in 1972 his publishers brought out his second book, a college text titled *Inorganic Chemistry: Principles of Structure and Reactivity.*



ATOMYRIADES

NATURE, it seems, is the popular name
for milliards and milliards and milliards
of particles playing their infinite game
of billiards and billiards and billiards.

Piet Hein*

© 1966 by Piet Hein

PREFACE

Welcome to IAC Chemistry. Enjoy this year as you explore this important area of science. Chemistry is to be enjoyed, cultivated, comprehended. It is part of our culture, of our everyday lives.

Polymers, paints, pharmaceuticals, people, and pollution all have something in common—a chemical base. IAC Chemistry is relevant, interdisciplinary, student centered, and filled with important concepts and processes.

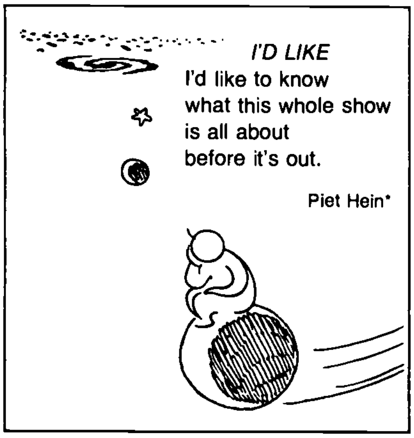
IAC will help you discover that chemistry is a lively science and being actively used to pursue solutions to the important problems of today. You will see how chemistry is taking place continuously all around. You will more readily understand the daily problems facing you and your environment.

Students throughout this country and in a number of other countries as well have let us know that they like and learn from the IAC modules. Classroom teachers have suggested changes to make them even better.

Since the IAC authors believe that student involvement in chemistry is very important, there are many activities that allow you to develop and apply chemistry concepts directly. We have tried to make the modules flexible, easy to read, and enjoyable, discussing everyday problems and adding a bit of humor that may help you remember some of the more important ideas. The Time Machines are intended to give you a sense of when the more important discoveries in chemistry happened in relation to other events.

Wonder—inquire—investigate. Think through all that you find here. But most of all—enjoy chemistry as you learn about the atoms, molecules, elements, and compounds that make up your universe. IAC is written for your learning pleasure.

Marjorie Gardner
Director
Interdisciplinary Approaches to Chemistry



I'D LIKE

I'd like to know
what this whole show
is all about
before it's out.

Piet Hein*

© 1966 by Piet Hein

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*Piet Hein is a Scandinavian poet who often served as a "mental Ping-Pong partner" for the famous chemist Niels Bohr.

CONTENTS

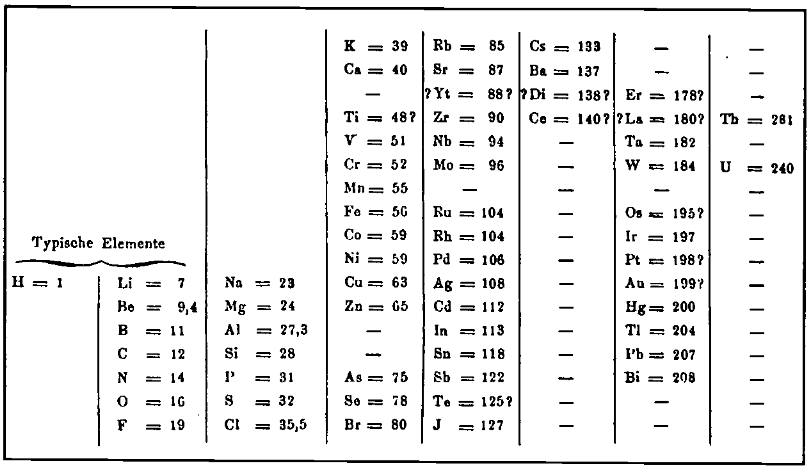
APPENDIX

Introducing Inorganic Chemistry

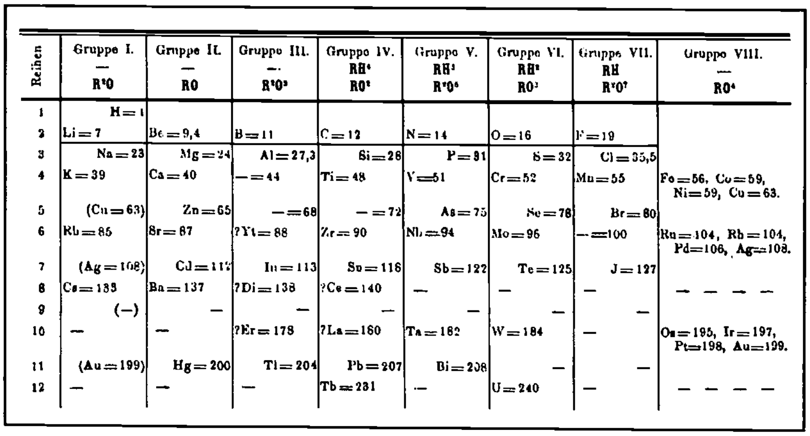
What is inorganic chemistry? A recent college textbook has defined it as "any phase of chemistry of interest to an inorganic chemist." But what exactly *is* of interest to an inorganic chemist? Well, to begin with—the one hundred and six known elements.

This stamp, issued in 1934, commemorated the centennial of the birth of Dmitri Mendeleev who discovered that a natural order exists among the elements. He arranged the elements according to atomic weight and then pointed out that elements grouped together behave in the same way. Using this first riodic table, Mendeleev predicted elements not yet discovered and explained their properties with accuracy.

Inorganic chemistry, we might say, is a study of the relationships—that is, the differences and similarities—of these elements. Since no two elements are exactly alike, the attempt to find a pattern among the properties of the one hundred and six elements is a challenging pursuit. And the study of inorganic chemistry is an endeavor that offers many rewarding surprises and discoveries to the persistent investigator.



			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	?Yt = 88?	?Di = 138?	Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	?La = 180?	Tb = 281
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
Typische Elemente			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	—	Au = 199?	—
	Be = 9,4	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
	B = 11	Al = 27,3	—	In = 113	—	Tl = 204	—
	C = 12	Si = 28	—	Sn = 118	—	Pb = 207	—
	N = 14	P = 31	As = 75	Sb = 122	—	Bi = 208	—
	O = 16	S = 32	Se = 78	Te = 125?	—	—	—
	F = 19	Cl = 35,5	Br = 80	J = 127	—	—	—



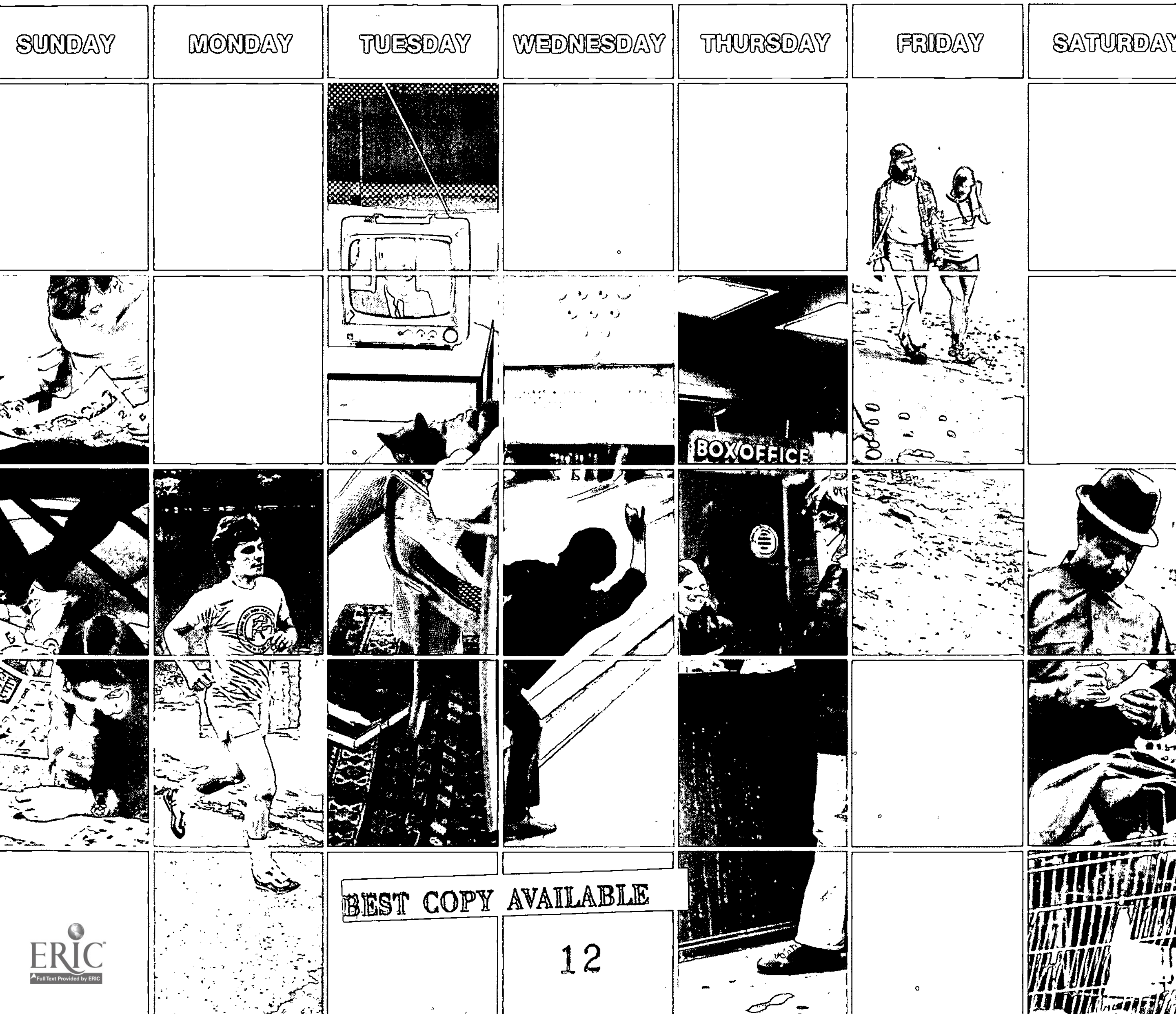
Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rb=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=116	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Tb=231	—	U=240	—	— — — —

Mendeleev's vertical periodic table was published in 1869 (*top*). His horizontal version was published in 1871 (*bottom*). Can you determine any new predictions in the later table?

All the elements differ from one another. But, in some ways, the one hundred and six elements also show certain resemblances to one another. One of the most successful endeavors of inorganic chemistry has been to use the knowledge of the chemistry of one element to predict the properties of another. If chemistry is a successful science, it should be able to provide a unifying description of the elements rather than having one hundred and six separate and unrelated descriptions, one for each element.

Periodicity: A Chemical Calendar

Elements have periodic properties. A periodic property of an element is one that varies in cycles. A *cycle* may be looked upon as a recurrent sequence of events or conditions. A familiar example is the cycle of activities that we experience each week. Certain aspects of our lives are predictable—many of our day-to-day activities fall into a weekly cycle.



Saturday is the day for most college football games, but professional football is played on Sunday. At one time, Monday was set aside as the traditional day for doing the family laundry. This was before the day of automatic washers and dryers. Almost everyone likes to take a break in the middle of the week. A family may reserve Wednesday evening for a movie, bowling, or a game of cards. In some industries, Friday is payday. On Saturday the lawn gets mowed. This, then, is a common weekly cycle—laundry, bowling, payday, mowing the lawn.

In addition to having certain activities for certain individual days, it is common to classify these days as the "weekdays," Monday through Friday, which are typically work and school days, and the "weekend," Saturday and Sunday, which are devoted to recreational and religious activities. In many ways Friday is intermediate. Although it is a work and school day, Friday evening often resembles part of the weekend.

I-1 Chemical Cycles

Why get involved in a discussion of weekly activities? Because it provides an excellent analogy to the way in which certain properties of the elements tend to recur at fixed intervals. Instead of a cycle of seven, the basic cycle in the periodicity of the elements is *eight*. Chemists arrange the elements according to their atomic number. This arrangement is known as *The Periodic Table of the Elements*. The table is sometimes referred to as the *periodic chart*.

Just as it is possible to divide the days of the week into weekdays and weekends, the chemist divides his elements into two groups, *metals* and *nonmetals*. Each group has particular properties, just as weekdays differ from weekends. From the standpoint of your weekly activities, one Saturday is much like another Saturday. Similarly, all the elements occurring in a single column of the periodic chart have similar properties. These elements form a single *family* of elements.

The elements within a family have similarities. Still, they are not identical, any more than two succeeding Saturdays are exactly the same. In the fall and winter Wednesday night perhaps is reserved for bowling and Sunday for pro football. During the summer Wednesday might be set aside for night games and Sunday for doubleheaders (if you are a baseball fan!).

In the same way you may watch your favorite TV show every Tuesday, but that doesn't mean that the same shows are repeated week after week (until the reruns start!).

Our analogy points to another resemblance between the cycles of the weeks and the cycles of the elements. Suppose a friend asks you to play tennis ten days from now. The calendar says the date will be a Saturday. Although there is no school on a Saturday, you do have your regular activities on that day. So you reply, "Sorry, but I'll be tied up on the eighteenth. You *know* I always spend Saturdays studying chemistry!" Knowing your cycle, you made a prediction. You did not have to wait until the eighteenth to find out it was going to be a Saturday. This last thought seems a little ridiculous, but its very absurdity shows how important a calendar is in thinking about weekly cycles.

An inorganic chemist can also make predictions. He bases his predictions about the elements on a chemical periodicity, just as you based your prediction about a Saturday on the weekly periodicity. The chemist does not have to wait until element 107 is discovered (if it ever is!) before he can make some definite plans about what he might be able to do with it. In fact, by predicting properties ahead of time, he simplifies his effort to discover element 107—or any other.

Neil Bartlett used periodic trends to predict that xenon would form compounds. He was right!

I	II	III	IV	V	VI	VII	VIII
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4	10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12	27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulfur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84	(210) **At** Astatine 85	(222) **Rn** Radon 86
(223) **Fr** Francium 87	226.0 **Ra** Radium 88						

TIME MACHINE

1960	John F. Kennedy is elected 35th president of the United States.
1961	Roger Maris breaks Babe Ruth's record by hitting 61 home runs.
1962	**Neil Bartlett synthesizes the first compounds of xenon, considered impossible by some.**
1963	Beatles record their first hit, "She Loves Me."
1963	Valentina Tereshkova (USSR) is first woman in space.
1964	Cassius Clay, later known as Muhammad Ali, becomes world heavyweight boxing champion.
1965	Ralph Nader publishes *Unsafe at any Speed*, first of his consumer information studies.
1966	*Man of La Mancha*, a musical, opens in New York.

I-2 Ultraman vs. Flintstones

The chemist finds it convenient to classify elements into two categories, *metals* and *nonmetals*. You are already familiar with some common metals: iron in automobiles and nails; aluminum

METALS				NONMETALS					
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4			10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
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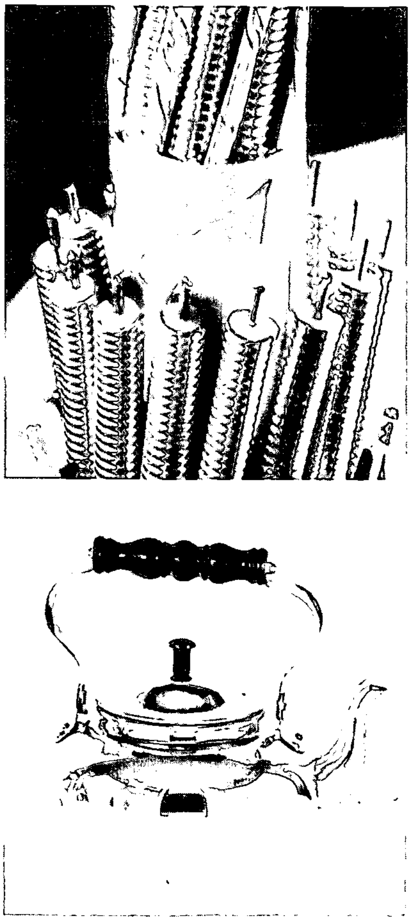
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84				

Three properties of metals are illustrated here. Can you determine what they are?



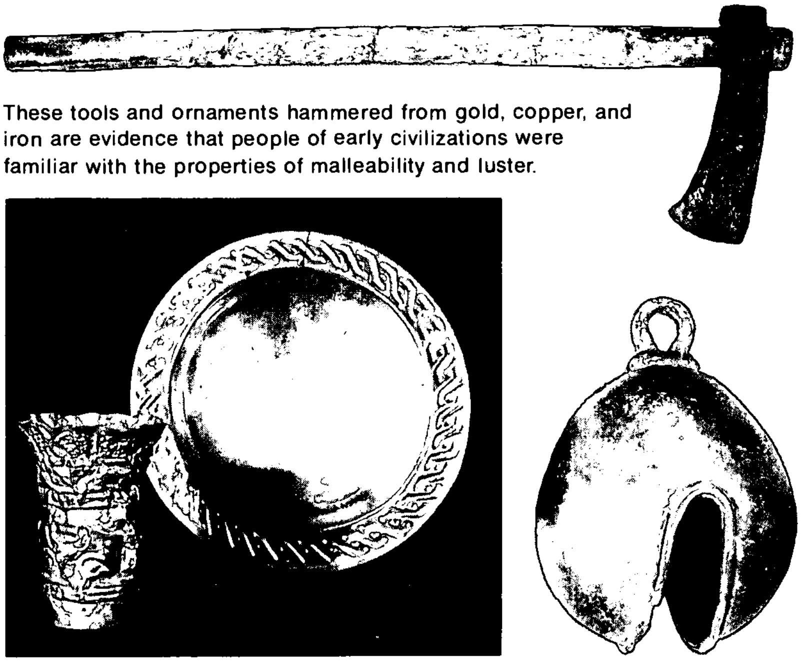
in kitchen foil and pans; nickel, copper, and silver in coins. These metals have several properties in common. For example, they all conduct an electric current. Copper and aluminum are used in electrical wiring. Pots and pans used for cooking are made of iron, copper, and aluminum. Metals are good *conductors* of heat.

Luster is also a common property of metals. Having luster, metals tend to reflect light. Have you ever polished a penny and made it glisten? Have you ever polished silver? Metals have a typical metallic appearance. Metals such as silver and aluminum reflect a white, silvery light. Copper and gold have reddish and yellowish hues. A metal, of course, may react with another element and become covered with a coating that hides its luster. For example, silver becomes tarnished and iron rusts.

Very early in the development of civilization, people learned that metals could be used for everyday tasks. Even before they learned enough chemistry to separate metals from their compounds (smelting), they found lumps of gold, copper, and silver. At first these were probably saved because of their shiny appearance. Then someone discovered that these metals could be hammered into different shapes either for tools or for decorations.

This was probably how the properties of malleability (the ability to be hammered into sheets) and ductility (the ability to be drawn into wires) were discovered. These properties made it possible to fashion crude tools from copper by pounding it with stones. Metals remain in wide use because of these properties.

Nonmetals differ in their properties from metals. Nonmetals are poor conductors of heat and electricity. A nonmetal is likely



These tools and ornaments hammered from gold, copper, and iron are evidence that people of early civilizations were familiar with the properties of malleability and luster.

A Native American craftsman (*above*) skillfully shapes copper and silver into beautiful, prized pieces of jewelry. The artisan must be familiar with the properties of certain metals to be able to use them to their best advantage.

to be brittle; it cannot be hammered into sheets or drawn into a wire. It is neither malleable nor ductile. In contrast with common metals such as iron, copper, and aluminum, pure nonmetals are less familiar in everyday use. True, the atmosphere you breathe is composed almost entirely of the nonmetals nitrogen and oxygen, but since you do not "see" the atmosphere, you are likely to overlook this fact.

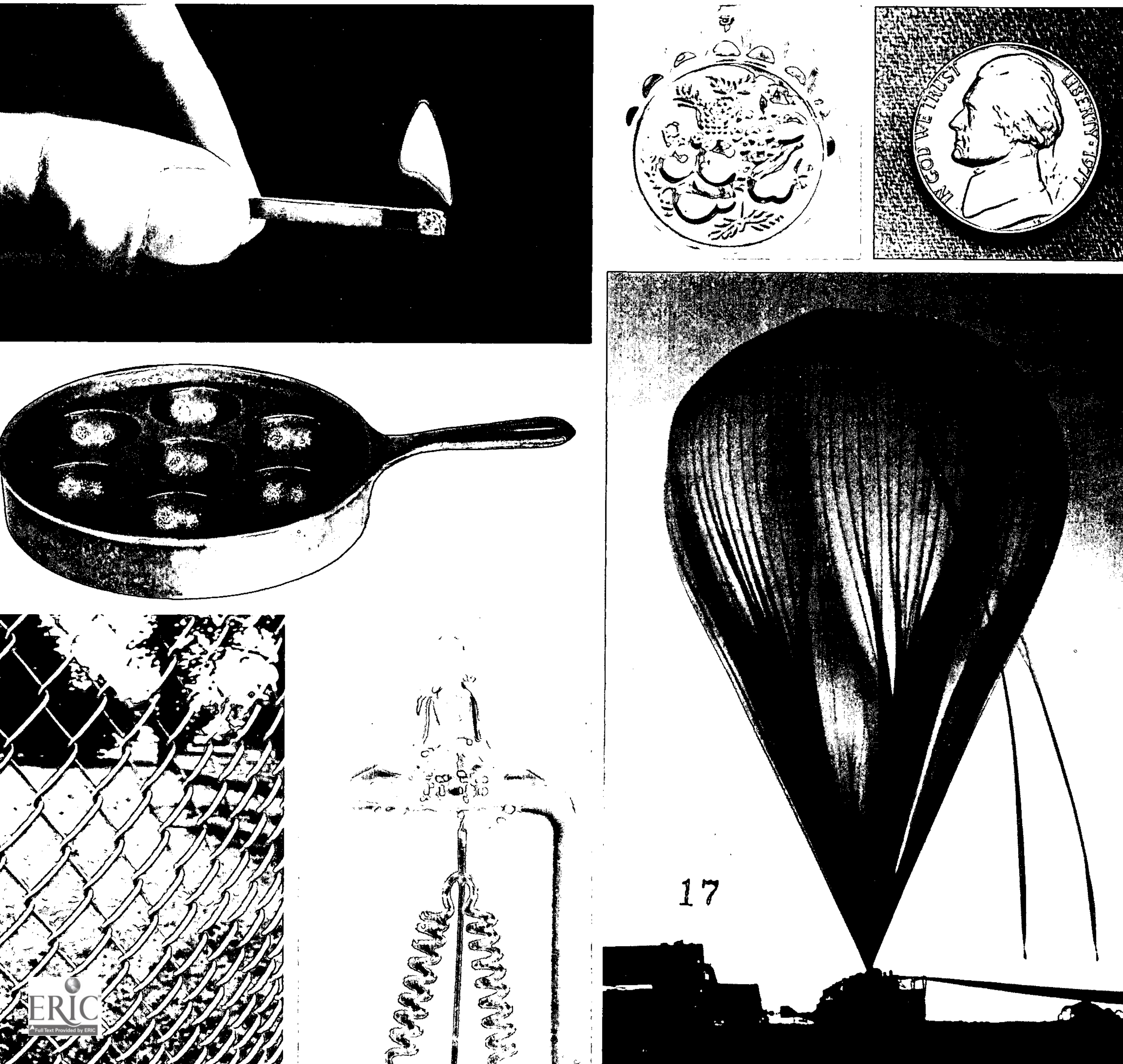
A common nonmetal is carbon, which is found in several forms. Diamond is one form of pure carbon. A diamond is the hardest natural substance known, and it is used industrially as an abrasive. Another form of carbon is graphite, which is mixed with a binder to form the "lead" in pencils. A pencil lead writes smoothly because of the graphite, not because of the binder. Graphite is used in some lubricants. Rather impure and amorphous forms of carbon are found in coke, soot, lampblack, and charcoal.

Other examples of nonmetals that are encountered in everyday life are neon, the gas that glows in neon lights; iodine, found as a solution in many medicine cabinets; and sulfur, found as a yellow powder in gardening mixtures. Another nonmetal is phosphorus, which is used in manufacturing matches and detergents.

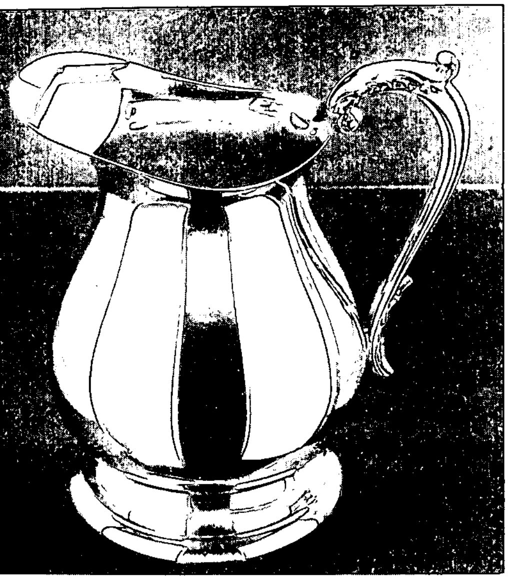
One difference between metals and nonmetals is immediately apparent. Metals tend to look much like one another. In contrast, nonmetals exhibit a wide array of appearances; some are solids (sulfur and carbon), many are gases (nitrogen, oxygen, neon), and one is a liquid (bromine). Nonmetals have no characteristic color or luster. Sulfur is yellow, iodine is purple, nitrogen and oxygen are colorless.

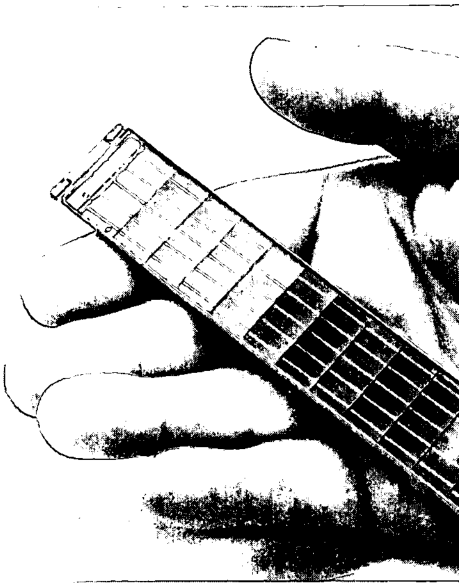
Nonmetals, as we have noted, are poor conductors of heat and do not conduct electricity. We could use nonmetals as insulators to retard the flow of electricity and as insulation to prevent the flow of heat. However, there are compounds that are much better for these purposes than pure nonmetallic elements. Among such compounds are glass and asbestos. Rubber is also an excellent insulator. It is used as an insulator in electrical wiring. You no doubt have seen it used in extension cords and on cords for electric lamps and other appliances.

At least sixteen natural elements are illustrated here. Try to determine the names and uses of each. Which are metals? metalloids? nonmetals? Try to place each of these elements in the periodic table.

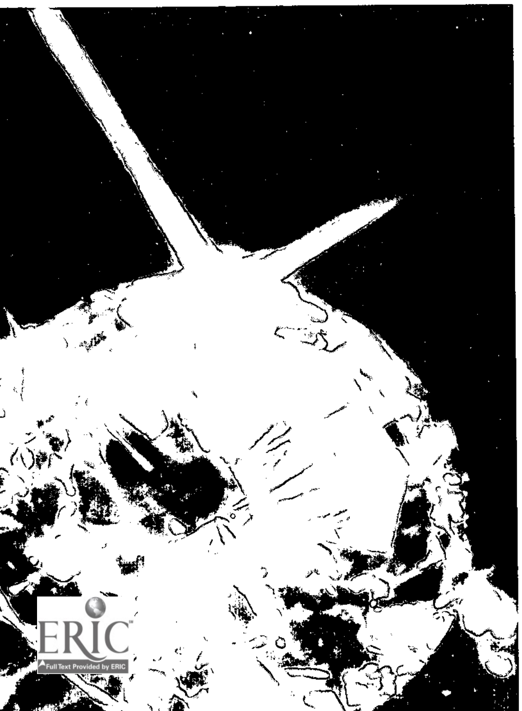


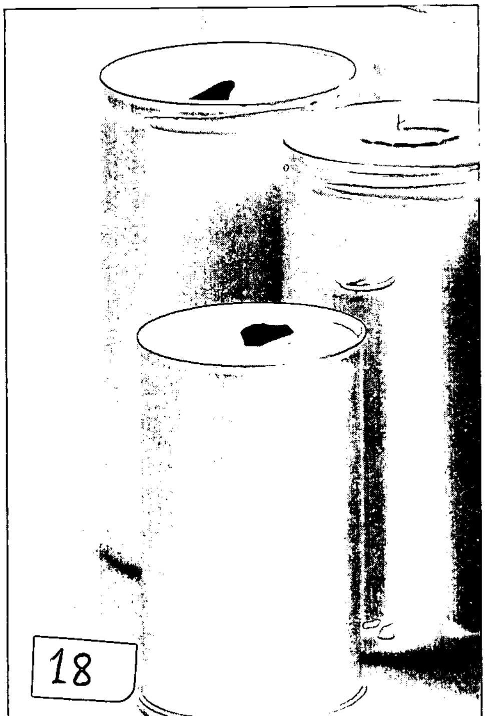
There are a few exceptions to the general rule that pure nonmetals are nonconductors. These elements are sometimes called *metalloids* (meaning "metallike"), but in most of their properties they resemble nonmetals. Carbon is an example. One form of carbon—diamond—has properties that you would expect of a nonmetal. But another form of carbon—graphite—conducts electricity. Carbon is a nonmetal which (in one form) has a *single* metallic property. Do you remember the weekday-weekend analogy discussed earlier? Carbon is a "Friday-night" element!





Solar cells (*top right*) use elements on the border between metals and nonmetals. They offer the hope of inexpensive, pollution-free energy for the future.

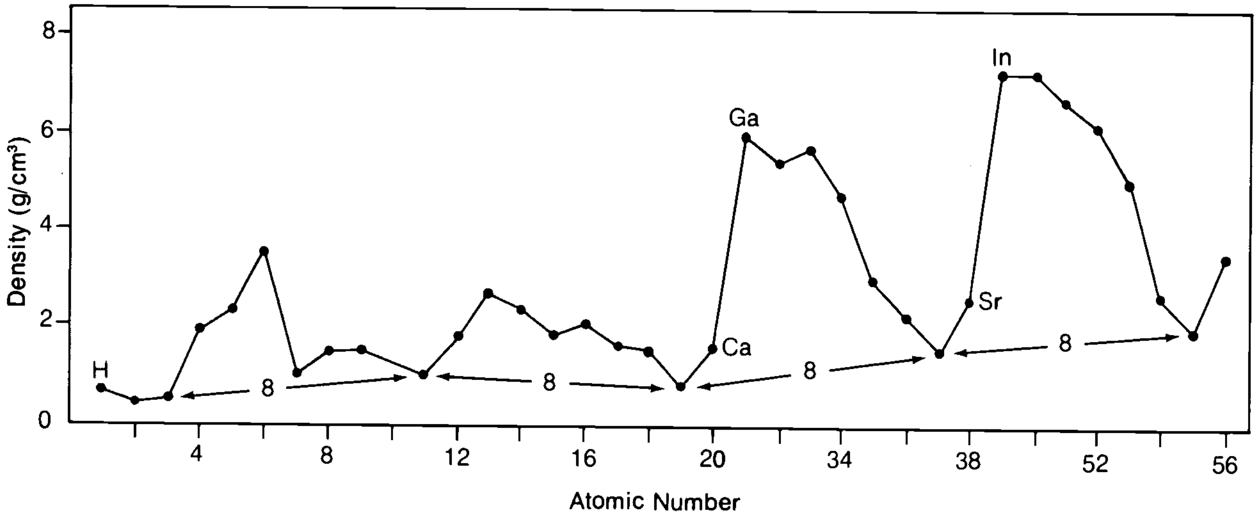




SUBSTANCE	DENSITY (g/cm³)
water	1.0
bromine	1.7
iron	7.9
lead	11.3
oxygen	0.0014
carbon dioxide	0.0020

I-3 Periodic Properties

A fundamental property of any sample of matter is its *density*—its mass per unit volume. The density of a given element depends upon whether it is a solid, a liquid, or a gas. Solids are usually denser than liquids, and both are about one thousand times more dense than gases. When comparing densities, therefore, we must compare solids with solids, liquids with liquids, and gases with gases. The following graph compares the densities of some representative elements in their solid forms. The elements are listed in the order of their atomic numbers. Note that there is a cyclic nature to the graph, much like the daily rise and fall in temperature.

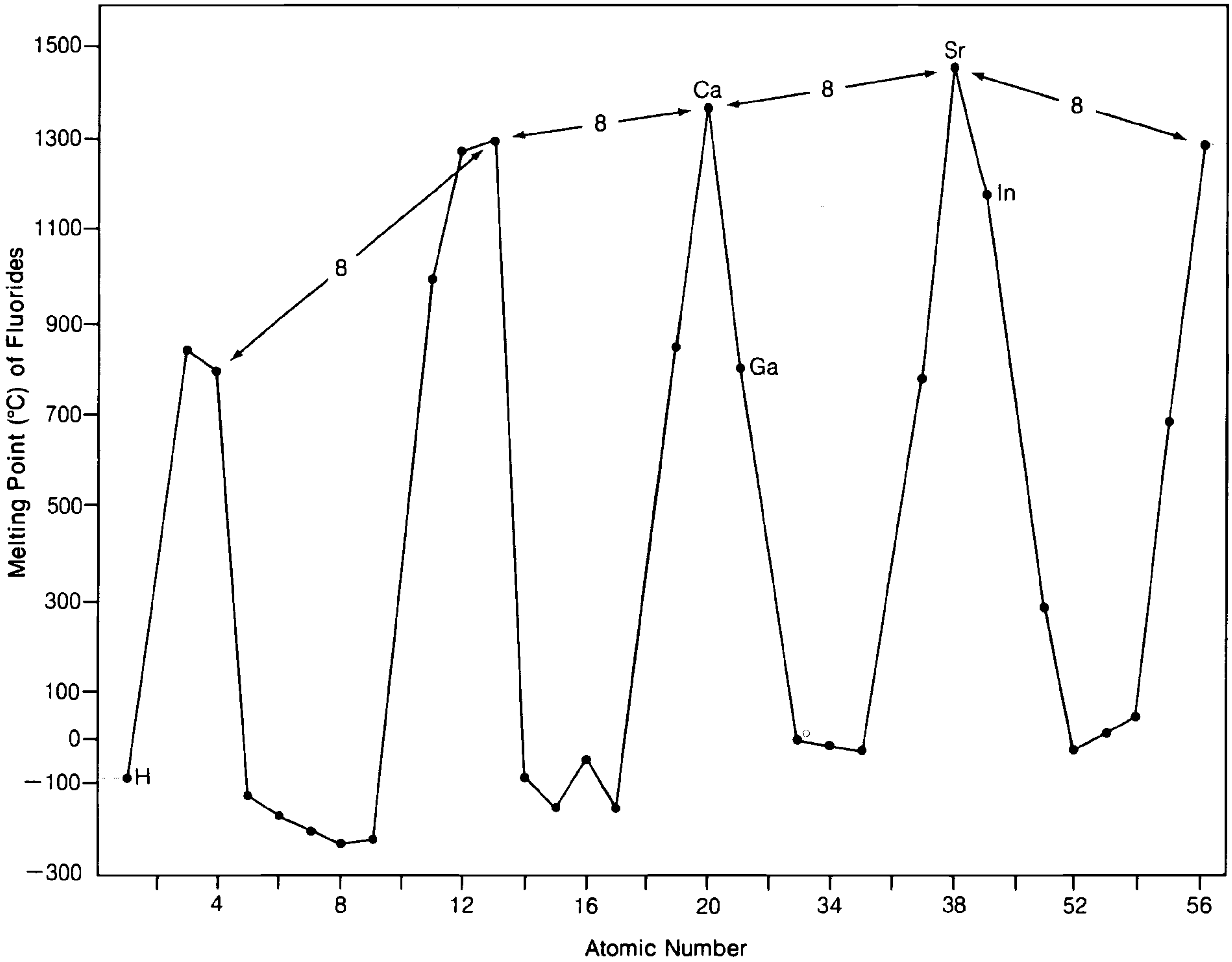


Another distinguishing property of an element or compound is its melting point. Fluorine forms compounds with more elements (over one hundred!) than does any other single element. The melting points of the fluorides of the representative elements are shown in the following graph. Although almost all of these compounds have fairly low melting points, there are two or three elements in each series that have melting points several hundred degrees above the rest. These occur in cycles of about eight elements, just as the cycles of minimum density do.

Note that the cycles in the melting-point graph do not correspond with the density cycles. The maxima and minima (high points and low points) occur at different places along the series of elements in the two graphs. The important fact is not *where* the maxima and minima occur. Rather, the fact to be noted here is that in *both* graphs the periodicity operates on *a cycle of eight*.

We now should note one further example of the periodicity of chemical properties. It is one of fundamental importance in determining other chemical properties. If Dmitri Mendeleev had known about this additional periodic property when he devised the first periodic chart over one hundred years ago, his task in preparing the periodic chart would have been greatly simplified.

This further example of the periodicity of chemical properties—which Mendeleev knew nothing about—involves a kind of chemical reaction that can occur when one atom loses one or more electrons and a second atom gains one or more electrons. Such a reaction is possible only if one of the atoms has a small attraction for its electrons and the second atom has a strong attraction for electrons. This second atom has an attraction not only for its own electrons but for the electrons of other atoms as well.



The measure of the attraction that an atom has for its own electrons is the *ionization energy*. This is the energy needed to remove an electron from an atom. The atom from which the electron is removed becomes a positive ion, or *cation*. The atom that gains an electron becomes a negative ion, or *anion*.

IONIZATION ENERGIES
(Relative to Hydrogen)

$H \longrightarrow H^+ + e^-$ $I = 1.00$
$Na \longrightarrow Na^+ + e^-$ $I = 0.38$
$K \longrightarrow K^+ + e^-$ $I = 0.32$
$F \longrightarrow F^+ + e^-$ $I = 1.34$
$Cl \longrightarrow Cl^+ + e^-$ $I = 0.96$

Of the elements included in the table at the left, only sodium and potassium have low enough ionization energies to permit the formation of ionic compounds containing sodium (Na^+) and potassium (K^+) ions. Hydrogen, fluorine, and chlorine must either accept electrons from another element or share electrons. It costs too much energy to form cations from hydrogen, fluorine, and chlorine.

You can see that whether an element has a high or a low ionization energy at least partially determines how it will behave chemically. In view of their interest in chemical behavior, chemists pay special attention to the ionization energy of the different elements. In the following miniexperiment you will decide exactly how ionization energy varies from element to element.

---

miniexperiment

I-4 Periodicity

The ionization energies of the representative elements (relative to that of hydrogen, $I_H = 1.00$) are given in the accompanying table. Plot on a graph the first ionization energy for each element against its atomic number, Z. Plot the atomic numbers consecutively as they are listed. For example, plot element 2 after 1, element 18 after 17, and element 31 after 20.

List the elements on the horizontal axis and the ionization energies on the vertical axis. Connect all the points consecutively with straight lines.

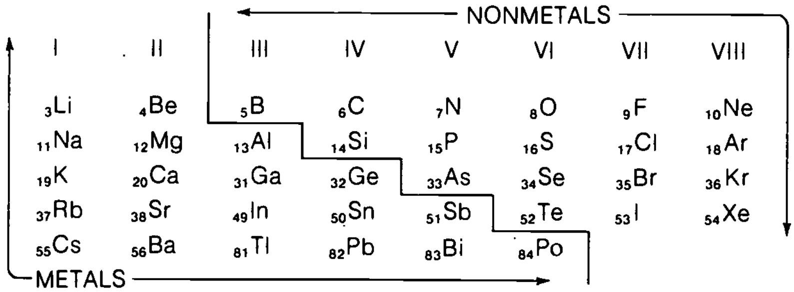
RELATIVE IONIZATION ENERGIES

Z	Element	I	Z	Element	I
1	H	1.00	19	K	0.32
2	He	1.84	20	Ca	0.45
3	Li	0.40	31	Ga	0.44
4	Be	0.70	32	Ge	0.58
5	B	0.62	33	As	0.72
6	C	0.84	34	Se	0.71
7	N	1.08	35	Br	0.88
8	O	1.00	36	Kr	1.03
9	F	1.34	37	Rb	0.33
10	Ne	1.58	38	Sr	0.42
11	Na	0.38	49	In	0.42
12	Mg	0.56	50	Sn	0.54
13	Al	0.44	51	Sb	0.64
14	Si	0.60	52	Te	0.66
15	P	0.80	53	I	0.77
16	S	0.76	54	Xe	0.89
17	Cl	0.96	55	Cs	0.29
18	Ar	1.16	56	Ba	0.38

With a pair of scissors cut the graph vertically into pieces after elements 2, 10, 18, 36, and 54. Then rearrange the pieces and paste them one below the other.

Do you observe any repetitive pattern? Can you suggest a logical arrangement of the elements based on your observations? How are hydrogen and helium somewhat unusual? These two elements are discussed separately in section *I-6*.

When we attempt to distinguish the chemical families on the basis of the *metal-versus-nonmetal* distinction, we find that families I and II are composed only of metals and that families VI, VII, and VIII are composed exclusively of nonmetals. Families III, IV, V, and VI contain both metals and nonmetals. If we attempt to classify each individual element as either a metal or a nonmetal, we obtain the following separation:



I	II	III	IV	V	VI	VII	VIII
${}_{3}$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	${}_{31}$Ga	${}_{32}$Ge	${}_{33}$As	${}_{34}$Se	${}_{35}$Br	${}_{36}$Kr
${}_{37}$Rb	${}_{38}$Sr	${}_{49}$In	${}_{50}$Sn	${}_{51}$Sb	${}_{52}$Te	${}_{53}$I	${}_{54}$Xe
${}_{55}$Cs	${}_{56}$Ba	${}_{81}$Tl	${}_{82}$Pb	${}_{83}$Bi	${}_{84}$Po		

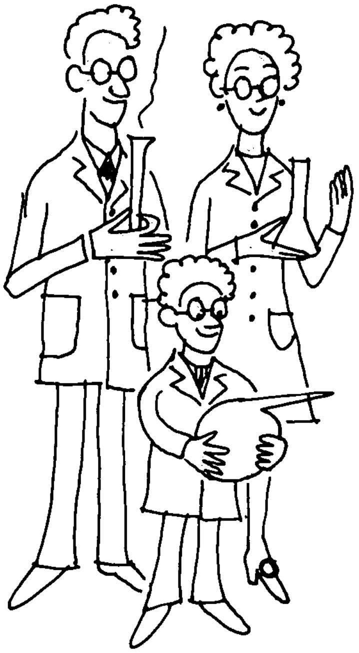
Although this division into metals and nonmetals is convenient, it must be emphasized that along the "stair-step" border between the two groups the elements are in some ways intermediate. Carbon (in the form of graphite) conducts electricity like a metal but is best classified as a nonmetal. The elements boron, silicon, arsenic, and tellurium all show some metallic properties but are best classified as nonmetals. Intermediate cases such as these pose problems in classification and prevent us from making nice "pigeonhole" schemes in arranging the elements.

The desire to fit elements (or chemical compounds or, for that matter, people) into neat little compartments arises in the human mind. But this notion may not reflect the true picture of the universe around us. Nature is often complex. If we can devise a simple picture to represent it, fine. But if we find intermediate elements that show properties of both metals and nonmetals we should not be surprised.

Chemists, as we have noted, have arranged the one hundred and six elements into the chart known as *The Periodic Table of the Elements*. In devising their table chemists grouped the elements according to their chemical properties and in a logical sequence based on the atomic numbers. The table places the elements in horizontal rows called *periods* and in vertical rows known as *families*. You can see how the chart is set up by referring to the periodic table in section *I-7* or at the end of this module.

TIME MACHINE

1971	U.S. table-tennis team visits mainland China, opening new era in foreign relations.
1972	*Grease*, a musical comedy recalling the fifties, begins long run on Broadway.
1973	**Ernst Otto Fischer and Geoffrey Wilkinson, inorganic chemists, win Nobel Prize for study of unusual "sandwich" compounds.**
1974	Skylab 3 astronauts complete world's longest space flight: 84 days, 1 hour, 17 minutes.
1975	Cincinnati Reds, for the first time, win two World Series in a row (1974–1975).
1976	**William Lipscomb wins Nobel Prize for work on boron and hydrogen.**
1977	James Earl Carter becomes 39th president of the U.S.



A CHEMICAL FAMILY

TIME MACHINE

1865	The American Civil War ends at Appomattox Courthouse.
1866	Fyodor Mikhailovich Dostoevsky writes *Crime and Punishment.*
1867	**Alfred Nobel patents dynamite.**
1867	United States purchases Alaska from Russia.
1868	Louisa May Alcott writes *Little Women.*
1869	**Dmitri Mendeleev publishes his first periodic table.**
1870	Jules Verne writes *Twenty Thousand Leagues Under the Sea.*
1871	Four square miles of Chicago are razed by fire—attributed in myth to Mrs. O'Leary's cow kicking over a lantern.

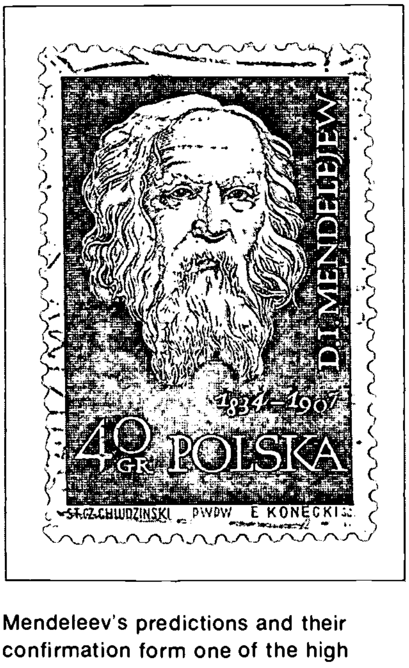
I-5 Chemistry's Crystal Ball

Dmitri Mendeleev devised the periodic table on which the present chart is based. Although earlier workers had suggested periodic relationships among the elements, it was Mendeleev who perfected the periodic table and used it to predict the properties of undiscovered elements.

The table that Mendeleev devised is based on the periodic properties of the elements. He was the first chemist to treat the periodicity of the elements as a fundamental law of nature rather than as an oddity. When Mendeleev conceived the periodic chart, several of the elements that we know today had not yet been discovered. Mendeleev had sufficient faith in his ideas not only to predict that these elements would be discovered but even to predict their properties.

Among the elements that were unknown to Mendeleev in the 1860s were numbers 31 and 32. Mendeleev called these undiscovered elements *ekaaluminum* and *ekasilicon*. (*Eka* means one or one more, that is, the next elements after aluminum or silicon in family III or IV.) Mendeleev observed the properties of the other known elements in families III and IV, as well as the properties of the elements to the right and left of the spaces that the undiscovered elements would occupy in the table. He then predicted several of the properties of the undiscovered elements.

Mendeleev predicted properties such as density, atomic weight, and melting point. He based his predictions on the periodicity of the elements. Periodicity, remember, places elements having similar properties in the same families. Sure enough, element 31 was discovered in 1875. This element was given the name gallium. Then in 1886 element 32, now known as germanium, was discovered. Gallium and germanium have properties that are much like those that Mendeleev had predicted. Mendeleev was still living when gallium and germanium were discovered. He thus lived to see his faith in the periodicity of the elements justified.



Mendeleev's predictions and their confirmation form one of the high points of early chemistry. The postage stamp on the right lists Mendeleev's prediction of the atomic weight of gallium (68) with that established later (69).

MENDELEEV'S PREDICTIONS OF ELEMENTS 31 AND 32

Element 31, "Ekaaluminum"	**Element 31, Gallium**
Predicted by Mendeleev 1871	Discovered by Boisbaudran 1875
Atomic mass about 68	Atomic mass 69.7
Density of metal 5.9 g/cm^3	Density of metal 5.94 g/cm^3
Low melting point	Melting point 29.8°C
Should dissolve slowly in acids and alkalies	Dissolves slowly in acids and alkalies
Should form an oxide of formula M_2O_3 with a density of 5.5 g/cm^3	The formula of the oxide is Ga_2O_3 with a density of 6.5 g/cm^3
The oxide should dissolve in acids to form salts of the type MX_3; M(OH) should dissolve in both acids and alkalies	The oxide dissolves in acid to form salts of formula GaX_3; $Ga(OH)_3$ dissolves in both acids and alkalies
Element 32, "Ekasilicon"	**Element 32, Germanium**
Predicted by Mendeleev 1871	Discovered by Winkler 1886
Atomic mass about 72	Atomic mass 72.6
The density of the metal should be 5.5 g/cm^3	Density of the metal is 5.47 g/cm^3
Should form a dioxide (MO_2) with a density of 4.7 g/cm^3	Forms a dioxide (GeO_2) with a density of 4.703 g/cm^3
Should form a tetrachloride (MCl_4) with a density of 1.9 g/cm^3 and a boiling point of less than 100°C	Forms a tetrachloride ($GeCl_4$) with a density of 1.887 g/cm^3 and a boiling point of 86°C

III	IV
10.8 **B** Boron 5	12.0 **C** Carbon 6
27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14
69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32
114.8 **In** Indium 49	118.7 **Sn** Tin 50
204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82

I-6 The Hydrogen and Helium Puzzle

What should be done with hydrogen and helium? Where do they belong in *The Periodic Table of the Elements*? This question has troubled chemists to some extent because these two elements do not fit as logically into a specific family as do the other elements. Helium has the highest ionization energy of any element. It therefore seems reasonable to place it with the elements of family VIII, even though there are not seven elements preceding it in the table.

Including helium, there are six elements in family VIII. These six elements are helium, neon, argon, krypton, xenon, and radon. Collectively, they are known as the *noble gases*. All the noble gases have high ionization energies. They do not react readily with other elements. Although helium is preceded only by hydrogen, it does differ from the next element in family VIII, neon, by a cycle of eight.

VIII
4.00 **He** Helium 2
20.2 **Ne** Neon 10
39.9 **Ar** Argon 18
83.8 **Kr** Krypton 36
131.3 **Xe** Xenon 54
(222) **Rn** Radon 86

Hydrogen—the first element, with atomic number 1—is particularly difficult to place in the periodic table. It has a fairly high ionization energy, although not so high as helium. Some of its other physical properties resemble those of the elements in family VII, just to the left of the noble gases. Placing it just above fluorine is a possibility, but we shall see later that hydrogen shares few chemical characteristics with the family VII elements, which are called *halogens*. Where, then, should we place hydrogen?

Hydrogen shares some chemical properties with the elements of family I. In view of this, some chemists have suggested that it could be considered to be the first member of family I and placed just above lithium. However, hydrogen obviously is not a metal, so placing it there is not quite satisfactory. The best compromise is to admit that hydrogen, the very first element, is in many ways unique. We can indicate this uniqueness and show hydrogen's relationship to both family I and family VII by placing it as follows:

$_{1}$H

I	II	III	IV	V	VI	VII	VIII
							$_{2}$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	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se	$_{35}$Br	$_{36}$Kr
$_{37}$Rb	$_{38}$Sr	$_{49}$In	$_{50}$Sn	$_{51}$Sb	$_{52}$Te	$_{53}$I	$_{54}$Xe
$_{55}$Cs	$_{56}$Ba	$_{81}$Tl	$_{82}$Pb	$_{83}$Bi	$_{84}$Po		

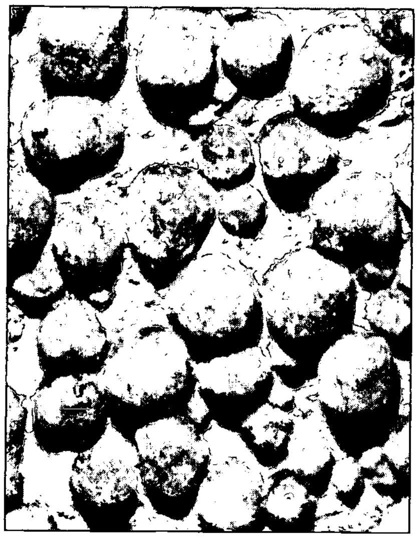
I-7 Keeping Up with the Trends

You may have noticed that the group of "representative metals" in the left-hand portion of the periodic table (see page 13) is not actually a "representative" sampling of the metals encountered in everyday life. Magnesium, aluminum, tin, and lead are familiar and useful metals, but the remaining elements shown in this portion of the table are almost unknown outside the chemistry laboratory. The names "sodium" and "calcium" may be familiar to you, but only as elements in compounds, not as the metals themselves.

The familiar metals used in coinage and in making jewelry are not included among the representative metals. Metals such as silver, gold, copper, nickel, and platinum appear elsewhere in the table. The familiar industrial metals—iron, chromium, vanadium, manganese, and zinc—are also not classified as representative metals.

Everyday metals such as those mentioned in the preceding paragraph are classed as *transition metals.* The name suggests that these metals show properties of an intermediate, or transitional, character. Such metals provide a transition between representative metals such as sodium, potassium, magnesium, and calcium and representative nonmetals such as nitrogen, oxygen, fluorine, and chlorine. Thus, the transition metals tend to be somewhat less malleable (and are therefore stronger and more useful as building materials) than the representative metals.

The transition metals are certainly less reactive than some of the representative metals. For example, iron rusts slowly when it is wet. In contrast, representative metals such as sodium and potassium react immediately and in some cases explosively with water—not exactly the type of material you want to leave out in the rain! The terms *representative* and *transition* are probably poor choices in view of what we now know about the metals, but they have been used so long that it seems useless to try to think of better words now.



Manganese nodules found at the bottom of the Pacific Ocean are a potential source of transition metals such as copper and nickel.

PERIODIC TABLE OF THE ELEMENTS

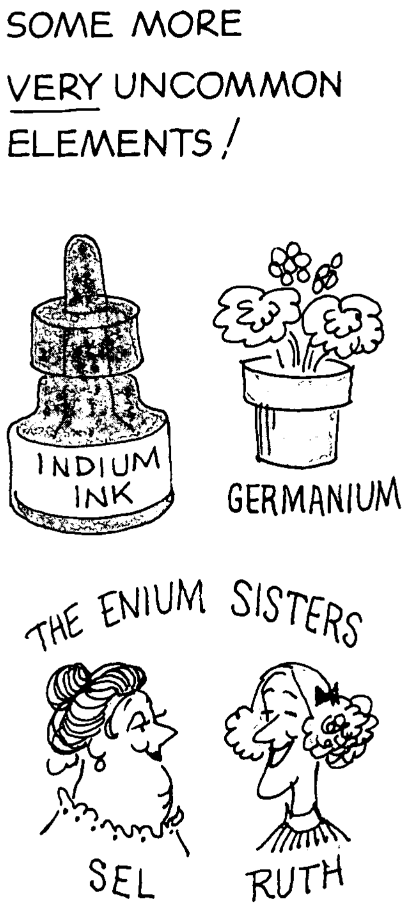
200.6 — atomic mass
Hg — symbol
Mercury — name
80 — atomic number

IA	IIA	IIIB	IVB	VB	VIB	VIIB	← VIIIB →			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 **H** Hydrogen 1																	4.00 **He** Helium 2
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4											10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12											27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulfur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybd'm 42	(97) **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	138.9 **La*** Lanthanum 57	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.8 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84	(210) **At** Astatine 85	(222) **Rn** Radon 86
(223) **Fr**† Francium 87	226.0 **Ra** Radium 88	(227) **Ac**** Actinium 89	‡ 104	‡ 105	‡ 106												

*	140.1 **Ce** Cerium 58	140.9 **Pr** Praseody'm 59	144.2 **Nd** Neodymium 60	(145) **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
**	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	(242) **Pu** Plutonium 94	(243) **Am** Americium 95	(245) **Cm** Curium 96	(245) **Bk** Berkelium 97	(251) **Cf** Californium 98	(254) **Es** Einsteinium 99	(254) **Fm** Fermium 100	(256) **Md** Mendel'm 101	(254) **No** Nobelium 102	(257) **Lr** Lawrencium 103

†The most stable known isotopes are shown in parentheses.

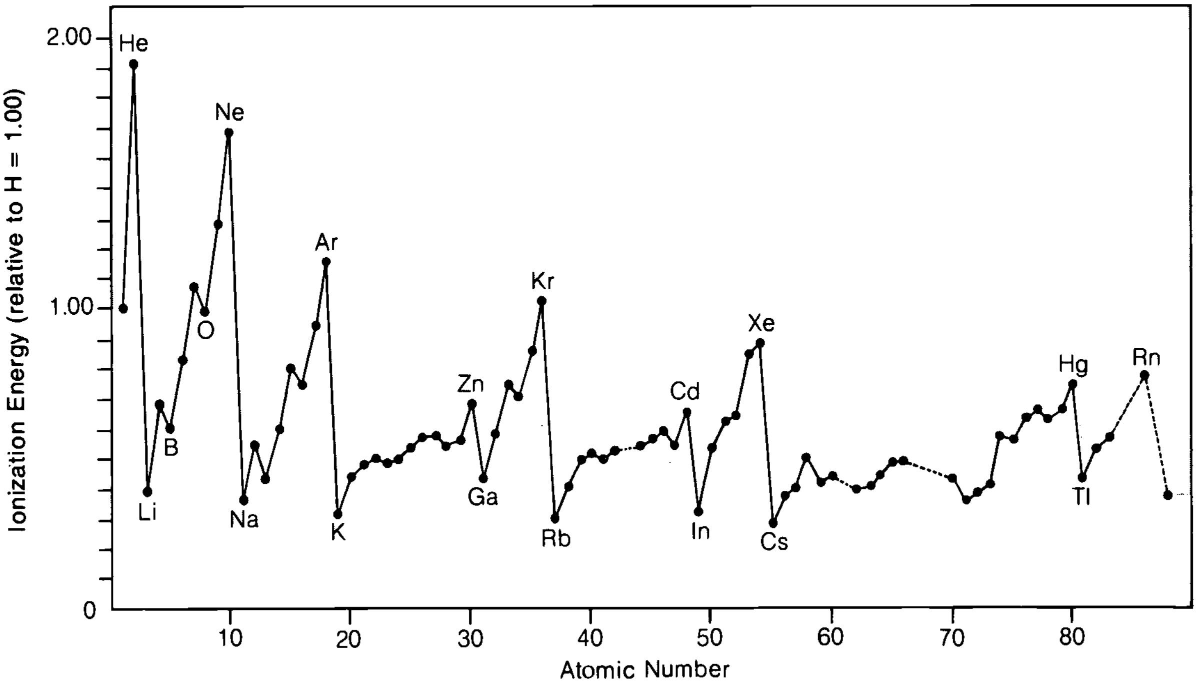
‡The discovery of elements 104, 105, and 106 has been claimed by both American and Soviet scientists. The Americans have suggested the name *rutherfordium* and *hahnium* for 104 and 105; the Soviets have suggested the names *kurchatovium* and *nielsbohrium* for these same elements. No name has yet been proposed for element 106.



We encounter the first transition metal, scandium, at position 21 in the periodic table. We find two series of ten elements each, 21 to 30 and 39 to 48. The chemistry of the transition metals will be discussed later, but for now we may note that the transition metals are placed in the periodic table between Groups I and II of representative metals and Groups III and VIII of representative metals and nonmetals. To distinguish the representative elements, the letter A is often added to the group number. For example, sodium is in family IA. The transition metals are marked with the letter B. Manganese belongs to family VIIB.

What effect will including the transition metals have on the periodic trends of the elements shown earlier in the figures and in the table of ionization energies? We based our earlier discussion of periodicity solely on the representative elements and on the observed cycles of eight. Will inclusion of transition metals destroy the periodicity shown in properties such as ionization energy? The answer is no, but if the transition metals are included, the cycles are no longer constant at eight elements. They increase in length toward the bottom of the table.

The following graph shows the periodicity of the ionization energy of all the elements, including the transition metals. The resulting graph is similar to that plotted in miniexperiment *I-4 Periodicity,* but the length of the cycles is now found to increase: 8, 8, 18, 18, 32. . . . There are good reasons for this increase in the length of the periodic series. These reasons are related to the atomic structure of the elements. More important for our present purposes, they are related to the inclusion of ten transition



elements between calcium (Ca) and gallium (Ga) and between strontium (Sr) and indium (In) and the inclusion of twenty-four transition elements after barium (Ba).

The next series of transition metals contains ten elements corresponding to those in the first two series, but it also contains fourteen more. Where do we put the added fourteen elements? We could expand the table again in order to get all twenty-four elements (numbers 57 to 80) on a single line. Although this might be the most logical arrangement, it results in a table that is thirty-two elements wide and exceedingly cumbersome. Instead, chemists have agreed to place those fourteen elements that make this series different from the earlier transition series in a separate place in the table, usually at the bottom. Sometimes an asterisk (*) is used to indicate the connection with element 57. A second series of this type, beginning with element 90, is also usually placed at the bottom of the table with double asterisks (**) to indicate the connection with element 89.

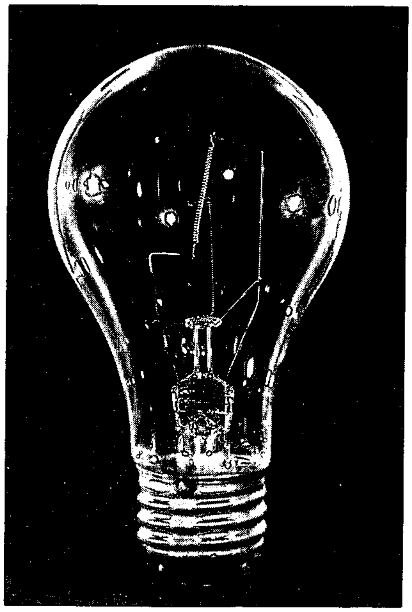
*	140.1 **Ce** Cerium 58	140.9 **Pr** Praseody'm 59	144.2 **Nd** Neodymium 60	(145) **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
**	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	(242) **Pu** Plutonium 94	(243) **Am** Americium 95	(245) **Cm** Curium 96	(245) **Bk** Berkelium 97	(251) **Cf** Californium 98	(254) **Es** Einsteinium 99	(254) **Fm** Fermium 100	(256) **Md** Mendel'm 101	(254) **No** Nobelium 102	(257) **Lr** Lawrencium 103

I-8 Family Relationships

The periodic relationships of the elements will be discussed in some detail in the following sections. A brief summary will be given here. As we have noted, some physical properties of the elements occur in periodic cycles. The chemical properties tend to follow the same cycles.

The tendency of an atom to lose electrons is the result of a low ionization energy. Elements in the first families on the left of the periodic table, especially Group IA, lose electrons most readily. In contrast, the elements on the far right of the chart, the noble gases, show almost no tendency to lose electrons. They also show no tendency to accept electrons. They are thus not very reactive. Only radon, xenon, and krypton react at all—and then only with the most active of elements. The term *noble gases* relates to this reluctance to react. (Early chemists equated "nobility" with a certain aloofness! Although modern chemists are much more democratic, the older term has stuck!)

Although fluorine is the most active element, the other elements of Group VIIA—chlorine, bromine, and iodine—are also very reactive. They have a strong affinity (attraction) for electrons, and they take them away from other elements when possible. This



Two natural elements are "working together" to provide light. Can you determine what they are and why these two elements really don't *work together*?

occurs frequently in the formation of ionic compounds ("salts"). The Group VIIA elements are referred to as *halogens* ("salt-formers"). In the following miniexperiment we will investigate the reactivity of some of these halogens.

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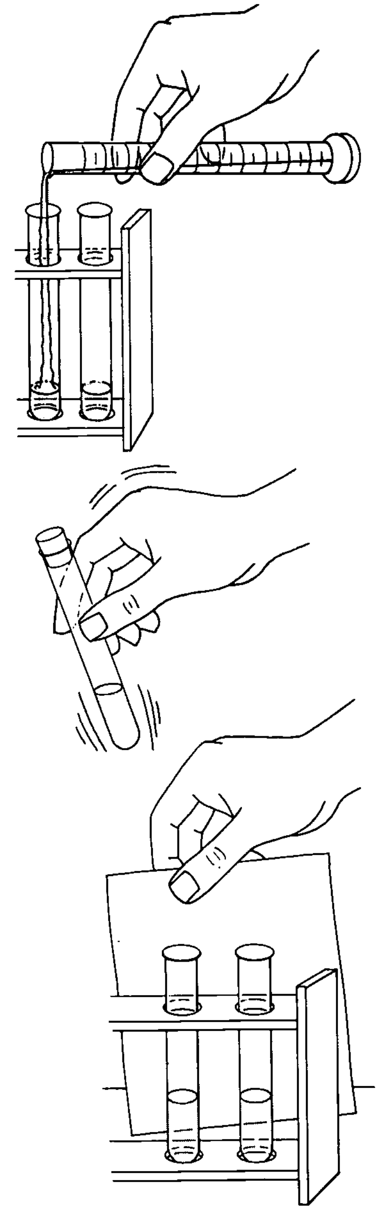
miniexperiment

I-9 All in the Family



Before you proceed with this experiment, be sure you review and discuss the *Safety* section in the *Appendix* at the end of this module.

Reactions with Chlorine: Take two test tubes and add 1 cm^3 TTE (trichlorotrifluoroethane) and 1 cm^3 chlorine water (a solution of chlorine in water) to each. Now add 1 cm^3 potassium bromide solution (KBr) to one tube and 1 cm^3 potassium iodide solution (KI) to the other. Do you observe any color changes? Stopper the tubes with corks and shake them. What happens? Record your results.

Reactions with Bromine: Take two test tubes and add 1 cm^3 TTE and 1 cm^3 bromine water to each. Now add 1 cm^3 potassium chloride solution (KCl) to one tube and 1 cm^3 potassium iodide solution (KI) to the other. Do you observe any color changes? Stopper the tubes with corks and shake them. What happens? Record your results.

Reactions with Iodine: Take two test tubes and add 1 cm^3 TTE and 1 cm^3 iodine solution to each. Now add 1 cm^3 potassium chloride solution (KCl) to one tube and 1 cm^3 potassium bromide solution (KBr) to the other. Do you observe any color changes? Stopper the tubes with corks and shake them? What happens? Record your results.

Controls: Take three test tubes and add 1 cm^3 TTE to each. To the first, add 1 cm^3 chlorine water, to the second 1 cm^3 bromine water, and to the third 1 cm^3 iodine solution. The TTE will tend to extract the chlorine, bromine, and iodine into it (the lower layer), and thus you will see the colors of these three elements and be able to tell when they are present or absent in your experiments.

On the basis of your observations, complete and balance the following equations. If you observed no reaction, write N. R.

$$KBr + Cl_2 \longrightarrow$$
$$KI + Cl_2 \longrightarrow$$
$$KCl + Br_2 \longrightarrow$$
$$KI + Br_2 \longrightarrow$$
$$KCl + I_2 \longrightarrow$$
$$KBr + I_2 \longrightarrow$$

Questions: Which of these three halogens (Cl_2, Br_2, I_2) is the most reactive? Which is the least reactive? Why do you suppose fluorine was not included in the miniexperiment? Where would it have ranked? Why?

I-10 Gainers and Losers

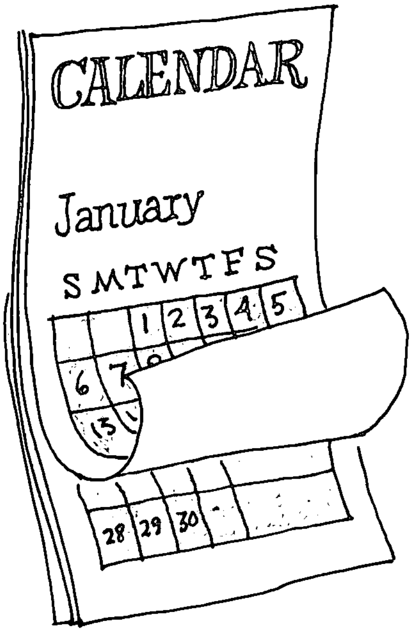
Now let's turn our attention back to all three families of elements mentioned previously: Group IA, Group VIIA, and Group VIIIA. We can compare these three families on the basis of their tendency to gain or lose electrons.

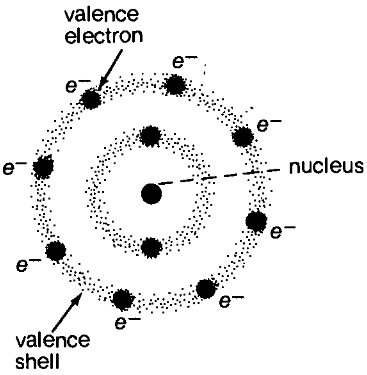
PROPERTY	GROUP VIIA	GROUP VIIIA	GROUP IA
Number of Electrons	**Octet Minus One**	**Perfect Octet**	**Octet Plus One**
Tendency to lose electrons	Little tendency to lose electrons; the ionization energy is high	Almost no tendency to lose electrons; the ionization energy is at maximum in this group	Lose electrons relatively easily to form cations such as Li^+, Na^+, K^+, etc.; low ionization energy
Tendency to accept electrons from another element	Great tendency to accept electrons; all of these elements accept electrons readily to form halide anions such as F^-, Cl^-, Br^-, and I^-	No tendency to accept electrons	No tendency to accept electrons
Chemical reactivity	Very great, especially toward metals which can donate an electron so that halide ions can form	Almost no chemical reactivity	Very great, especially towards nonmetals such as the halogens that are good electron acceptors

In looking over this table you may have wondered why Group IA was placed on the right instead of on the far left as in the periodic table. It was so placed to emphasize the relation to Group VIIIA. We have already seen that the noble gases show very little tendency to gain or lose electrons and form chemical compounds. The Group IA elements are very reactive, losing electrons readily. But they share one characteristic in common with the Group VIIIA elements: they have absolutely *no* tendency *to accept* electrons.

The group VIIA elements react readily by accepting electrons. However, they resemble the Group VIIIA elements in one respect: they have very little tendency *to lose* electrons. These similarities may not seem to be important, but they are the key to understanding bonding. That is why the Group VIIIA elements were placed in the middle of the table with the other groups on either side.

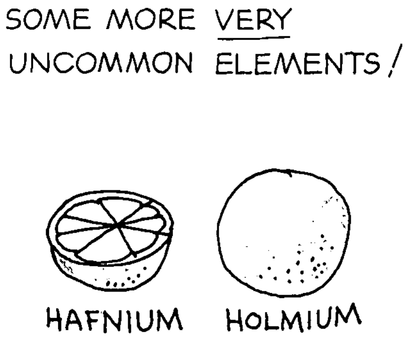
Why don't we arrange the periodic table in the same way? We could if we wanted to. The periodic table is a continuous listing of numbers. But, like the calendar, it must stop somewhere on the left and right. Custom has dictated that the calendar stop





with Saturday at the end of each week. Chemists have decided that the periodic table should end each period (horizontal row) with a noble gas element, Group VIIIA. This is because these elements have eight electrons in the outside shell, the largest number possible. The electrons in the outer shell of an atom are known as *valence electrons.* They are available for bonding with another atom.

The group number for each chemical family is the same as the number of electrons that the elements in the family have available for bonding. Thus, the elements of Group IA have one electron available for bonding—one valence electron. Those of Group VIIA have seven valence electrons. Having seven valence electrons, the elements in Group VII can either gain or share an electron with another element to complete the stable octet arrangement of eight electrons.



The elements of Group VIIIA have eight electrons potentially available for bonding, yet they are the most unreactive of all the elements. There appears to be some property associated with a total of eight electrons that discourages the gain or loss of electrons. The idea that eight valence electrons seems somehow to be the best arrangement for an atom is strengthened by our observation that atoms with seven valence electrons (Group VIIA) have a strong capacity to accept or share another electron, thus achieving a total of eight valence electrons.

Take a look at *The Periodic Table of the Elements.* Note the order in which the elements appear. Observe how a Group VIIIA element shows up at the end of each period. Neon, for example, is the last element in period 2. A new period then starts with sodium, a Group IA element. Having made this observation, you can see how the loss of an electron by a Group IA element helps to explain bonding. When a group IA element loses its one valence electron, it is left with eight electrons in the outer shell.

The alkali metals (Group IA) thus represent an arrangement of electrons similar to that of the preceding noble gas except that they each have one more electron. This electron is situated farther

FORMULAS OF FLUORIDES AND OXIDES OF SOME ELEMENTS

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	←VIIIB→	
	CsF	**BaF_2**	**LaF_3**	**HfF_4**	**TaF_5**	**WF_6**	**ReF_7**	OsF_7	IrF_6
Ratio F/M	**1**	**2**	**3**	**4**	**5**	**6**	**7**	7	6
	Cs_2O	**BaO**	**La_2O_3**	**HfO_2**	**Ta_2O_5**	**WO_3**	**Re_2O_7**	**OsO_4**	IrO_2
Ratio O/M	**½**	**1**	**1½**	**2**	**2½**	**3**	**3½**	**4**	2

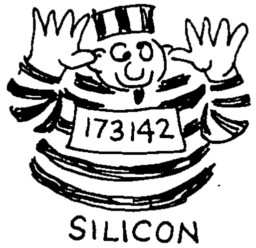
from the nucleus than the set of eight electrons (the noble gas electron pattern). It can readily be lost, and a positive ion, a cation, is formed. If this happens, the arrangement of electrons becomes exactly that of the preceding noble gas and the ion is quite stable.

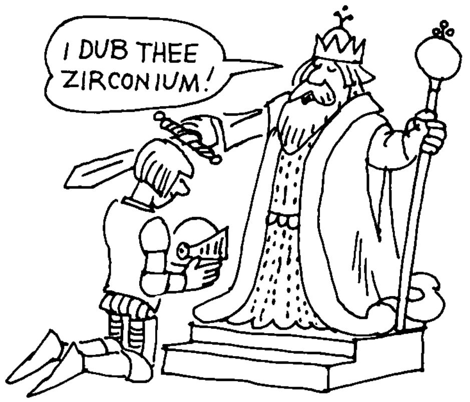
Since the reactivity and *valence* (combining ability) of an atom are determined largely by the number of valence electrons, it is not surprising that the chemical behavior of the element is reflected in the periodic chart. For example, in the table *Formulas of Fluorides and Oxides of Some Elements*, consider the formulas of fluorides which are formed with the elements cesium to radon.

We have seen that fluorine needs one electron to achieve the stability associated with eight valence electrons. The number of fluorine atoms that can combine with a single atom of another element depends upon the number of electrons in the second atom. Cesium has but a single valence electron. Hence, one atom of cesium can give its electron to one atom of fluorine to form cesium fluoride (Cs^+F^-). Barium has two electrons to donate, and so a single barium atom can satisfy the need of two fluorine atoms: barium fluoride ($Ba^{2+} + 2F^-$, or BaF_2).

We also obtain the formulas LaF_3, HfF_4, TaF_5, WF_6, ReF_7, HgF_2, TlF_3, PbF_4, BiF_5, PoF_6, and AtF_7. These conform to our expectations based on the group numbers of the elements involved. There are some deviations towards the end of the transition series. For example, OsF_7, IrF_6, and PtF_6 are the formulas found (rather than MF_8) based on the group number VIIIB. Perhaps it is difficult to obtain a valence of eight no matter what the group number is.

Oxygen belongs to Group VIA and can accept two electrons to complete a set of eight. Thus, a single barium atom can contribute these two electrons to form the compound barium oxide (BaO), but two cesium atoms are required to form cesium oxide (Cs_2O). The formulas of the oxides of the elements from cesium to radon are listed in the table above. With certain exceptions (IrO_2, PtO_2, and Au_2O_3) occurring at the end of the transition series, there is good agreement between these formulas and the group numbers of the elements.

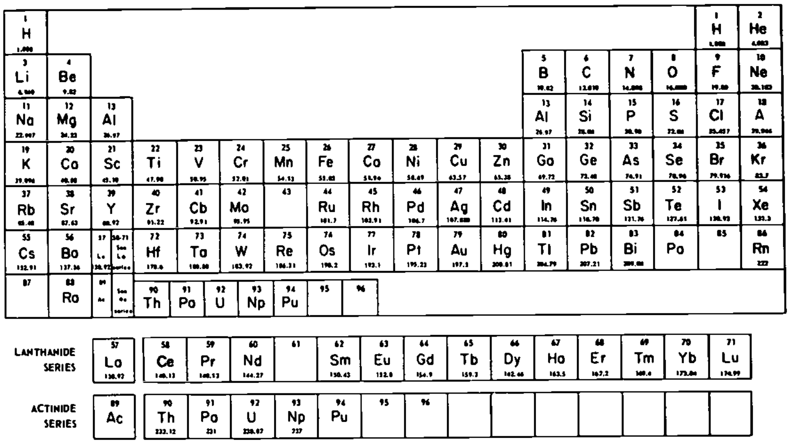




VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
PtF_6	AuF_3	**HgF_2**	**TlF_3**	**PbF_4**	**BiF_5**	**PoF_6**	**AtF_7,?***	?**
6	3	**2**	**3**	**4**	**5**	**6**	**7**	
PtO_2	Au_2O_3	**HgO**	**Tl_2O_3**	**PbO_2**	**Bi_2O_5**	**PoO_3**	**At_2O_7,?***	?**
2	1½	**1**	**1½**	**2**	**2½**	**3**	**3½**	

Some elements form more than one compound with fluorine (PbF_3 and PbF_4) or oxygen (Bi_2O_3 and Bi_2O_5). *Little is known of the chemistry of astatine (At). The compounds IF_7 and I_2O_7 are known. **Little is known of the chemistry of radon. The compounds XeF_6 and XeO_4 are known. Note that there are some exceptions to the regularity (shown in lighter type). The M in F/M and O/M gives the ratio of the *f*luorine to *m*etal or oxygen to *m*etal in the compounds.

A periodic table devised by Glenn T. Seaborg in 1945. This was the first time a periodic table was set up in a style similar to the one used today in most chemistry laboratories. Try to determine which elements were not yet discovered at this time.

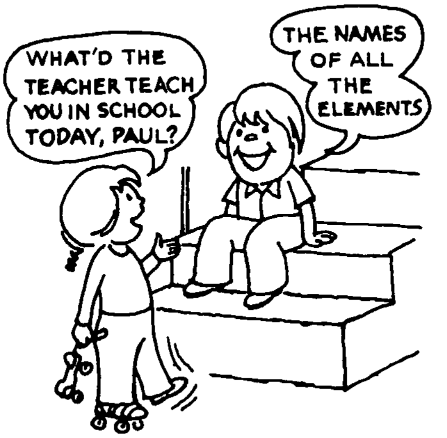


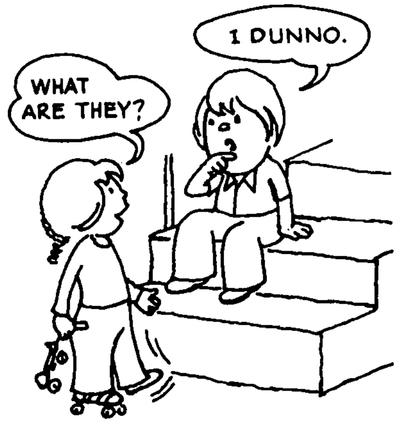
PERIODIC TABLE SHOWING HEAVY ELEMENTS AS MEMBERS OF AN ACTINIDE SERIES

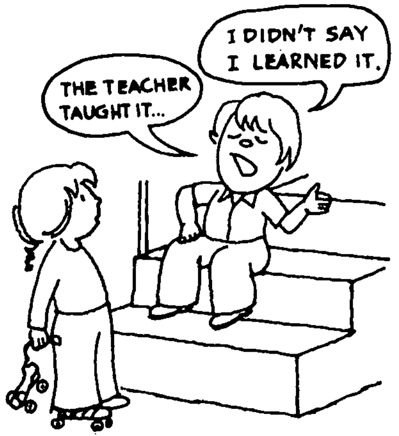
ARRANGEMENT BY GLENN T. SEABORG 1945

1 H																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										13 Al	14 Si	15 P	16 S	17 Cl	18 A
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Cb	42 Mo	43	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La 58-71 See La series	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85	86 Rn
87	88 Ra	89 Ac See Ac series	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96								

LANTHANIDE SERIES	57 La	58 Ce	59 Pr	60 Nd	61	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDE SERIES	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96							







As we stated at the beginning of this module, the *periodic law* is the unifying theme of inorganic chemistry. At a theoretical (or even philosophical) level, it is most satisfying to have such a unifying thread woven into the fabric of chemistry. It is such unification and predictive power that distinguish science from a mere collection of unrelated and poorly understood facts.

At the more practical level, the periodic table is a valuable tool for the chemist. Not only does it predict the properties of new and unknown elements, but on the simple level of day-to-day chemistry, it is indispensable. Without it, the chemist would need to memorize an untold number of facts about the elements. With the periodic table always at hand, a chemist or a student can readily check the similarity of palladium and platinum, the most likely valence of technetium, and a host of other facts that he needs in his work.

PROBLEMS

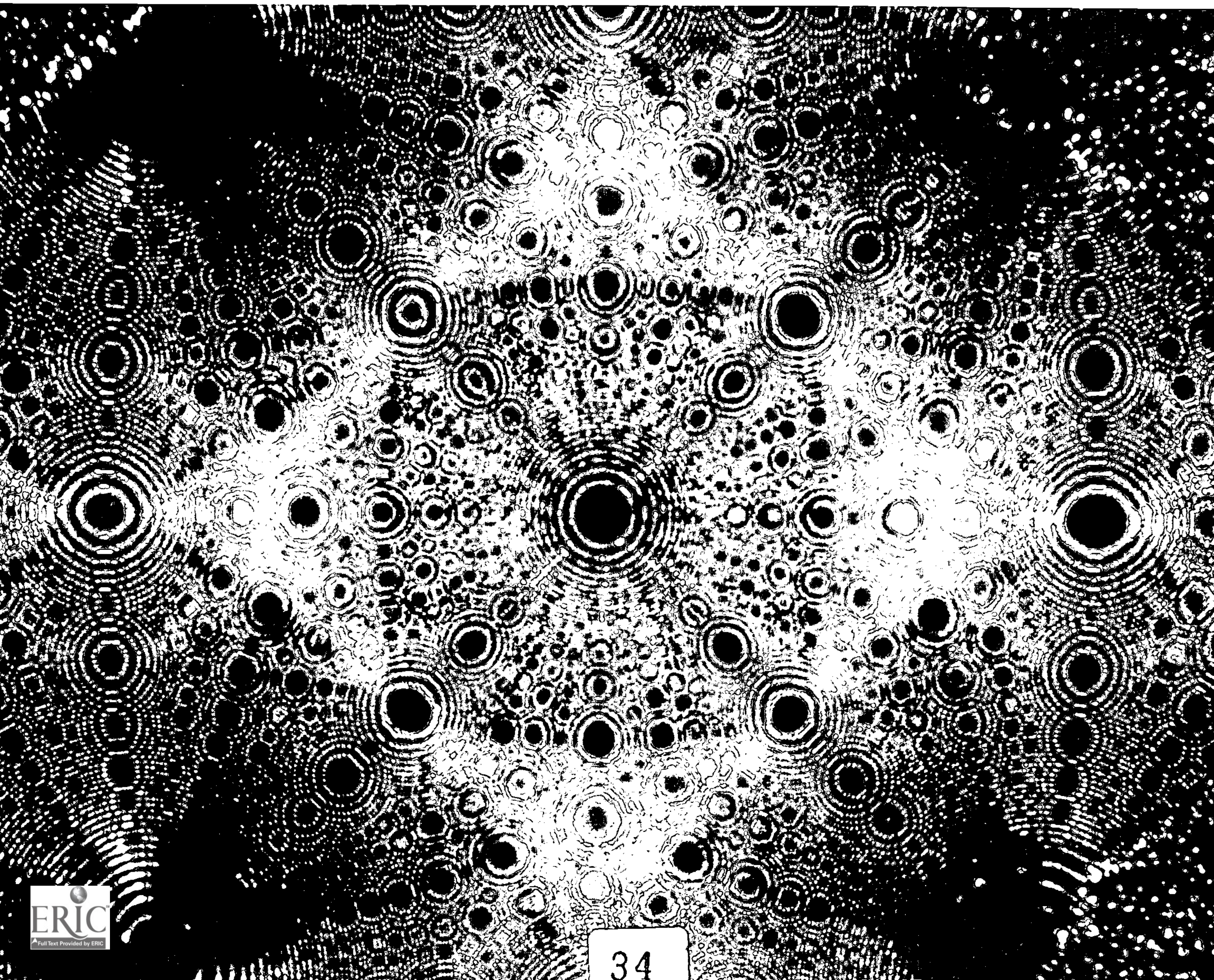
1. Using the periodic chart, group the following elements into families (for example, Cl, Br, and I are part of a family): Cl, Au, Ca, Ra, Cu, Br, Ag, I, Sr.
2. Do you know any properties that the members of these families share?
3. Which group of three elements will resemble each other: Al, Si, and P; or Al, Ga, and In? Why?
4. Using a periodic chart, classify each of the following elements as either a metal or a nonmetal: C, Cs, Mo, S, N, I, Ca, B, K, Fe, P, Ni, Ne.
5. Complete the following equations:

$$KBr + Cl_2 \longrightarrow$$
$$KI + Br_2 \longrightarrow$$
$$KCl + F_2 \longrightarrow$$

Structural Chemistry of Metals and Their Compounds

In our previous discussion of the elements and their periodic properties, we classified the elements into two very large groups: *metals* and *nonmetals*. Let's devote our attention a little more closely to the first group, the metals. There are many facts about them that we have already observed. They are good conductors of electricity and heat. They are shiny, malleable, and fairly hard.

By using the field-ion microscope, Dr. Edwin Mueller in 1951 was able to give the world its first look at the pattern of atoms. This is a crystal of platinum magnified over two million times. Each luminous spot represents an individual atom. The arrangement of the latticelike rings around the "atom" reflects the order and symmetry of crystalline atomic structure.



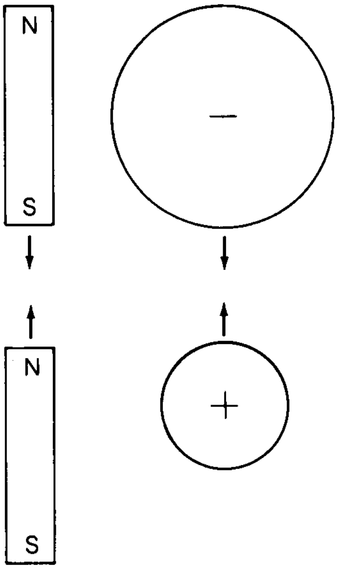
I-11 Why Are Metals "Metallic"?

Metals are good conductors. Metals are malleable. How do we explain these facts? We can attempt to answer this by relating the physical properties of metals to the ways the atoms are arranged and held together in the solid.

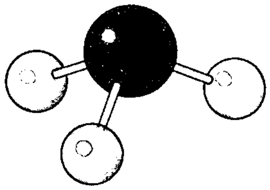
Bonds between atoms in metals differ considerably from the bonds found in salts and in simple molecules. Bonding in salts such as sodium chloride (NaCl, common salt) is ionic. Simple molecules such as water (H_2O) and ammonia (NH_3) display covalent bonding. We can characterize *ionic bonding* as an attraction of oppositely charged particles, in some ways resembling the attraction of one magnet for another magnet. Ball-and-stick models, on the other hand, provide a crude analogy for *covalent bonding,* the sharing of electrons.

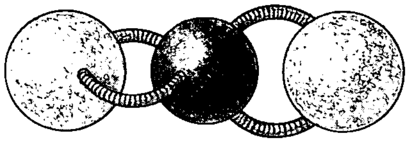
In contrast, the bonding in solid metals does not depend upon oppositely charged ions or upon fixed covalent bonds. Instead the entire structure of a metal is held together by strong attractions but not by fixed bonds. In many ways the structure of a metal is similar to a structure built of Ping-Pong balls stuck together by thick molasses. This explains why metals are malleable and can easily be hammered into sheets. It also explains why they are ductile—why they can be drawn into a wire. The metals are malleable and ductile because their atoms can be moved without breaking any bonds. Because the bonding in metals is different from both ionic and covalent bonding, we give it a new name, the *metallic bond.*

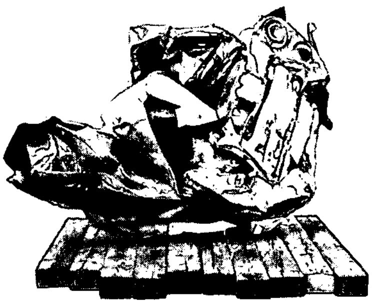
The electron clouds in a metal atom act like "molasses." They do not prevent the atoms from moving, but they continue to hold the atoms together when they are moved. In addition, the valence electrons can also move about, even if the atoms don't. The electrons are not tightly held by any given atom. Metals are good conductors of electricity because these electrons are free to move. Just as molasses can flow down through a pile of Ping-Pong balls, electrons can move back and forth in a metal.

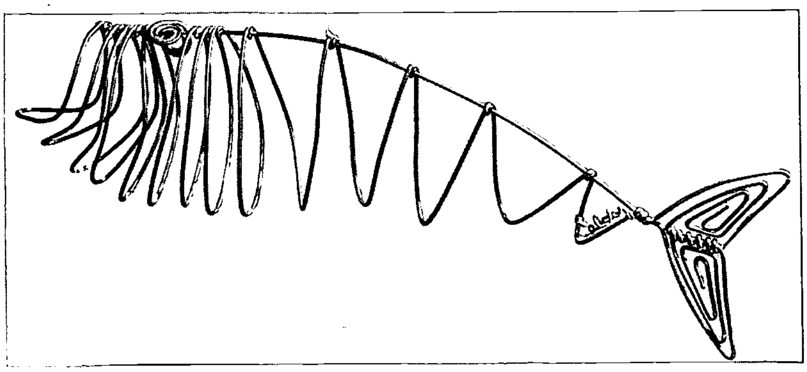


AMMONIA









The malleability and ductility of metals are again demonstrated in these two serious art-form sculptures, both on exhibit.

I-12 Who's Who?

miniexperiment

To get a better sense of what we mean by the various properties that distinguish metals from nonmetals, we can do a miniexperiment. Obtain pairs of solid elements from your teacher. Test some of their physical properties to classify them as metals or nonmetals. Then rank the metals by the degree of their metallic properties. Compare your results with those of other students.

I-13 How's Your Coordination?

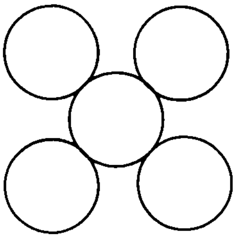
In discussing the structure of solids, it is convenient to describe the *coordination number* of any of the atoms involved. By this, we mean the number of other atoms each atom is in contact with. In the illustration of two-dimensional segments of crystals, note that in example A, the central atom finds itself touching four other atoms. It has a coordination number of four. Similarly, in example B, the coordination number is three because the central atom is touching only three other atoms.

The coordination number of an atom depends upon several factors, but a simple and important one is the relative size of the atoms in a solid. In example B, a coordination number of four for the central atom is impossible because of the large size of the atoms surrounding it. There is simply not enough room around the smaller central atom for more large atoms!

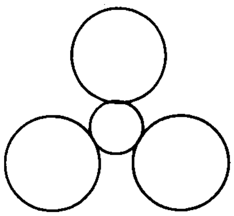
Another important concept is *efficiency of packing*, which is related to coordination number. For example, there are several ways to pack grapefruit in a crate, apples in a basket, or students at a rock concert. Some ways are more efficient than others. That is, it is possible to pack more items in a given amount of space in some instances than in others. In order for the arrangement to be at all efficient, it must be orderly; the items cannot be dumped in helter-skelter. Some sort of regular and repeating arrangement of atoms must be obtained to achieve the greatest efficiency of packing. This orderly arrangement of atoms is known as a *lattice*.

We can define the efficiency of a lattice as the volume of space actually occupied by atoms divided by the total volume of the solid. The space "wasted" between atoms will lower the efficiency.

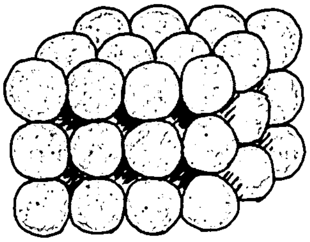
The greater the number of atoms that can be placed in a given volume, the greater are the forces between them. Such an arrangement is more stable than any other structure. Thus, there is a tendency for the most efficient lattices to be used.



A



B



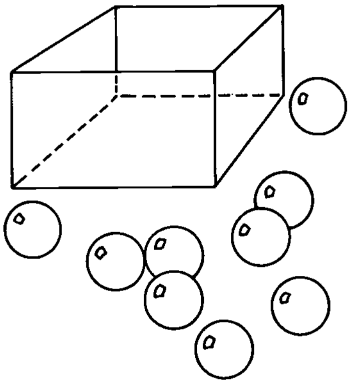
A LATTICE

MORE LATTICE

Let's try our hand at some crystal packing to see what kinds of arrangements, or lattices, provide the greatest efficiency.

EXPERIMENT

I-14 Becoming an Efficiency Expert



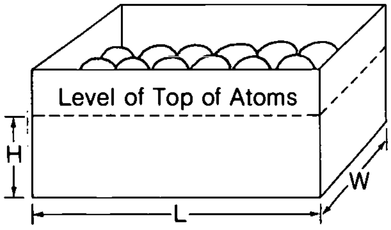
In this experiment you will use small Styrofoam balls to represent atoms and plastic boxes to hold them in place. Your objective is to find various ways in which neutral atoms can be arranged efficiently. In addition to providing the Styrofoam balls and the boxes, your teacher will give you some ideas concerning the arrangements. There are no "right" or "wrong" ways to arrange the balls. Instead, there are only "different" ways, some more efficient than others.

First, build one layer of atoms. Without distorting the Styrofoam balls, see how many different ways you can find in which the atoms can be arranged. For each arrangement, determine the coordination number and the efficiency.

Finding coordination numbers is simple. All you have to do is count the number of atoms surrounding a given atom. Pick an atom that is completely surrounded by other atoms (do not choose an atom that is along an edge) and count the number of other atoms that are touching it. (Later, when you are working with three-dimensional structures, it may be difficult to keep track of all the atoms. You may find it convenient to replace the central atom with one of another color. You then can see which atom is which.)

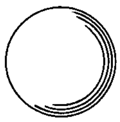
The coordination number can be found merely by counting atoms, but determining the efficiency requires a few simple calculations. Efficiency is the amount of space that is filled up with atoms compared with the total volume that the arrangement of atoms uses. The following five steps can be used as a guide to estimating the efficiency:

1. In the box, build a lattice of the type of structure you wish to examine.
2. Measure the amount of space your structure uses in the box. This will be the length of the box times the width of the box times the height to which the box is filled ($l \times w \times h$).



Volume of Box = L × W × H

sphere



$V = 1.33\pi r^3$

3. Determine the amount of space used by the balls. Count the number of balls in your structure and multiply by the volume of one ball. Below is a sample calculation to show the amount of space occupied by a structure made of 60 balls. Each ball has a diameter of 2.54 centimeters (cm).

   $0.5 \times \text{diameter} = \text{radius}$
   $0.5 \times 2.54\ \text{cm} = 1.27\ \text{cm}$
   $(\text{radius})^3 = (1.27\ \text{cm})^3 = 2.05\ \text{cm}^3$
   $\text{volume of a sphere} = 1.33\pi r^3$
   $\pi = 3.14$
   $\text{volume of each atom} = (1.33)\,(3.14)\,(2.05\ \text{cm}^3) = 8.56\ \text{cm}^3$
   $\text{volume of structure} = (60\ \text{atoms})\,(8.56\ \text{cm}^3/\text{atom}) = 514\ \text{cm}^3$

4. The efficiency is the ratio of the two numbers you determined in steps 2 and 3:

$$\text{efficiency} = \frac{\text{volume of atoms}}{\text{volume of lattice}}$$

Keep in mind that the "volume of lattice" refers to the volume of space in the box that is occupied by your structure. Measure to the top of the balls, not to the top of the box.

Find out how many different three-dimensional structures you can arrange. For each arrangement, determine the coordination number and the efficiency. Your instructor will help you to keep track of the different structures. After you have finished determining the efficiency and coordination number for each of the structures, examine your results. Since you don't yet have names for the various types of packing arrangements, identify each one by its coordination number.

Questions: Which coordination number has the greatest efficiency? Which coordination number has the lowest efficiency? Are there any coordination numbers that have more than one packing arrangement? If so, are all packing arrangements for a particular coordination number equally efficient?

I-15 Metallic Properties: Look Again

In the last experiment, you worked with many different structures. There were different ideas such as efficiency and coordination number to think about. Moreover, you were busy putting the structures together. You had a job to do, with much to think about. Now you may be asking yourself, "Why is anyone interested in the crystal lattices of metals? What difference does it make whether a metal has a coordination number of 6, or 8, or 12? Of what importance are coordination numbers or efficiencies to chemists?"

As it turns out, almost all the important physical properties of metals are related to the structure of the solid. The structure, of course, is related to the efficiency and coordination number. Such findings help us to explain the properties of a metal. For example, there are no known metals that crystallize in a simple cubic lattice (Figure 1). Can you guess why?

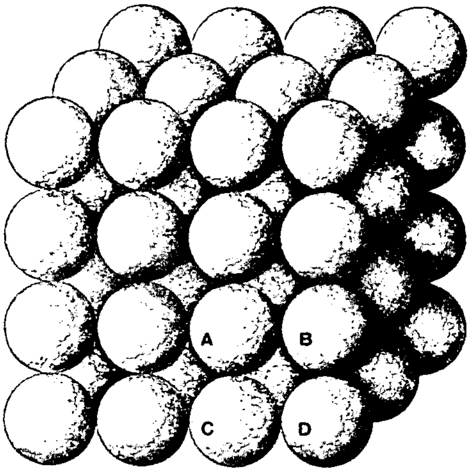


FIGURE 1 SIMPLE CUBIC LATTICE

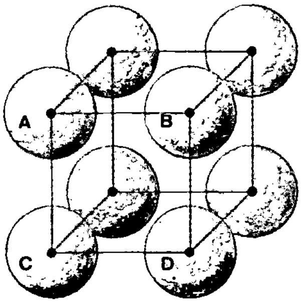


FIGURE 2 UNIT CELL

In this section you will review briefly the structures that you determined in your previous experiment. You will look at some drawings. (The boxes of balls are usually easier to "see" than a drawing, but it's easier to carry your book to study hall than to lug around a box of plastic balls!) The drawings represent the three-dimensional structures that you arranged with your "atoms," or plastic balls.

The simplest structure is called *simple cubic*. Figure 1 illustrates this lattice. The simple cubic arrangement seems to be a logical way to pack atoms, baseballs, grapefruit, or other objects. But no metal is known with this lattice. The simple cubic structure has the lowest coordination number, which is 6. With such a low number, the simple cubic is the least efficient. This, we can say, is the reason that no metal crystallizes in a simple cubic lattice.

Figures 1 and 2 show two ways of looking at the structure. Figure 1 simply shows a stack of balls. Figure 2 represents the unit cell. The *unit cell* is the smallest segment of the crystals that shows how the atoms are related to each other. If you made a hundred unit cells, you could stack them up to make the total crystal (not shown here).

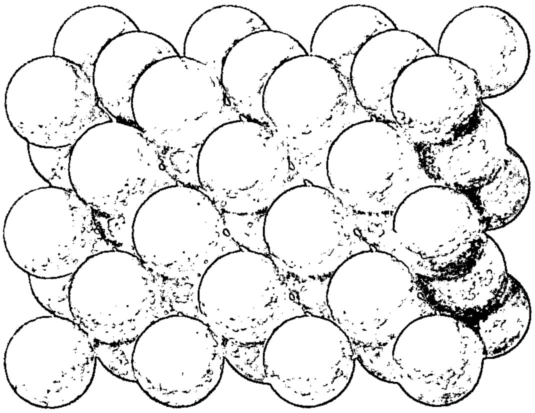


FIGURE 3 FACE-CENTERED CUBIC LATTICE

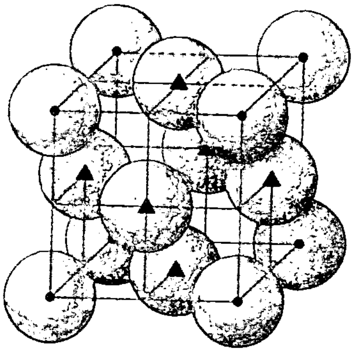


FIGURE 4 UNIT CELL

A second lattice is the *face-centered cubic* (Figure 3). This is so named because in the unit cell (Figure 4) there are eight loosely spaced atoms that form a cube, with six more lying on the *faces* of this cube. (Can you be sure that there are six?) The coordination number is twelve. (It is almost impossible to figure this out from the drawings. If you didn't get this answer, go back to the boxes and try again!) The efficiency is also high. This is a common lattice. Metals such as copper, silver, and gold crystallize with this structure.

As can be shown by a simple demonstration with a pyramid of balls (such as a stack of cannonballs), the face-centered cubic structure is the same as the structure called the *cubic closest-packed* (Figure 5). The two views are just two different ways of looking at the same structure. Having two different names for the same thing may seem confusing, but there is a reason for the two names. The names point out two different properties of the lattice. The name *face-centered cubic* describes the unit cell. The name *cubic closest-packed* emphasizes that the lattice is closest-packed. That is, the atoms are packed just as efficiently as possible. Note that in this structure there are three kinds of layers: A and B, then C and A again. The fourth layer is exactly like the first and directly over it.

The other closest-packed structure is the *hexagonal closest-packed* lattice (Figure 5). It also consists of closest-packed layers, but the layers alternate: A, B, A, B, etc. The relation of the layers in this structure is fairly easy to see from the "exploded view" (Figure 6). Because it is a closest-packed structure, the hexagonal closest-packed lattice has a high coordination number (12) and high efficiency. Metals such as titanium, zirconium, and molybdenum crystallize with this structure.

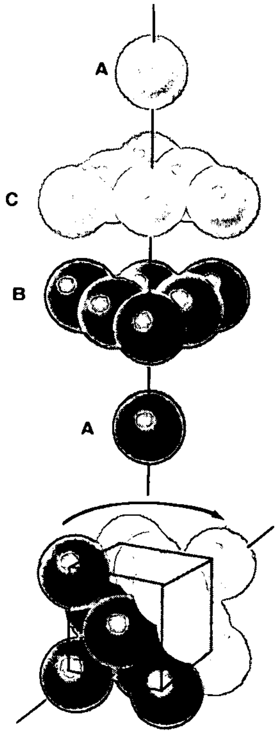


FIGURE 5
CUBIC CLOSEST-PACKED
STRUCTURE

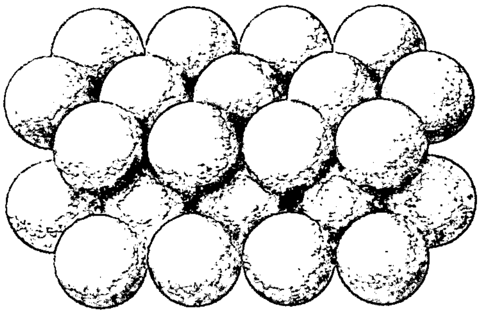


FIGURE 6 HEXAGONAL CLOSEST-PACKED LATTICE

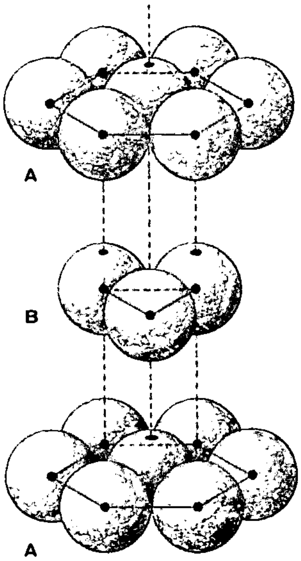


FIGURE 7
CLOSEST-PACKED LAYERS
(exploded view)

The last structure is the *body-centered cubic* lattice (Figure 8). It is so named because there is a single atom at the center of the "body" of the unit cell (Figure 9), with eight atoms forming a cube around it. From the unit cell it is fairly easy to see that the coordination number is eight. This is lower than in the closest-packed structures but higher than in the simple cubic. The efficiency is also intermediate. Some common metals that crystallize in this lattice are iron, chromium, and tungsten.

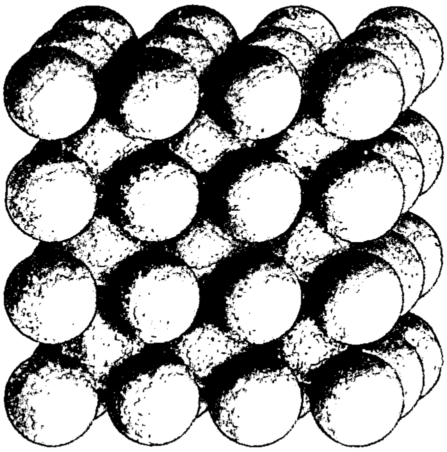


FIGURE 8 BODY-CENTERED CUBIC LATTICE

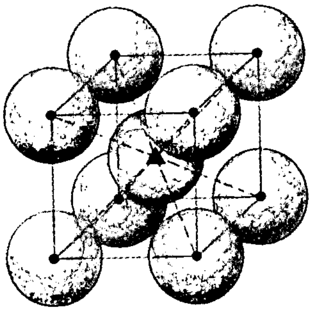
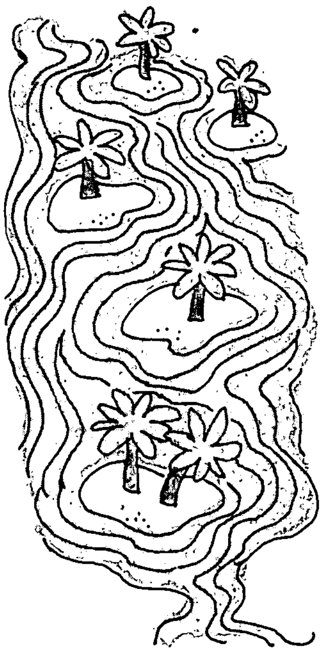


FIGURE 9 UNIT CELL

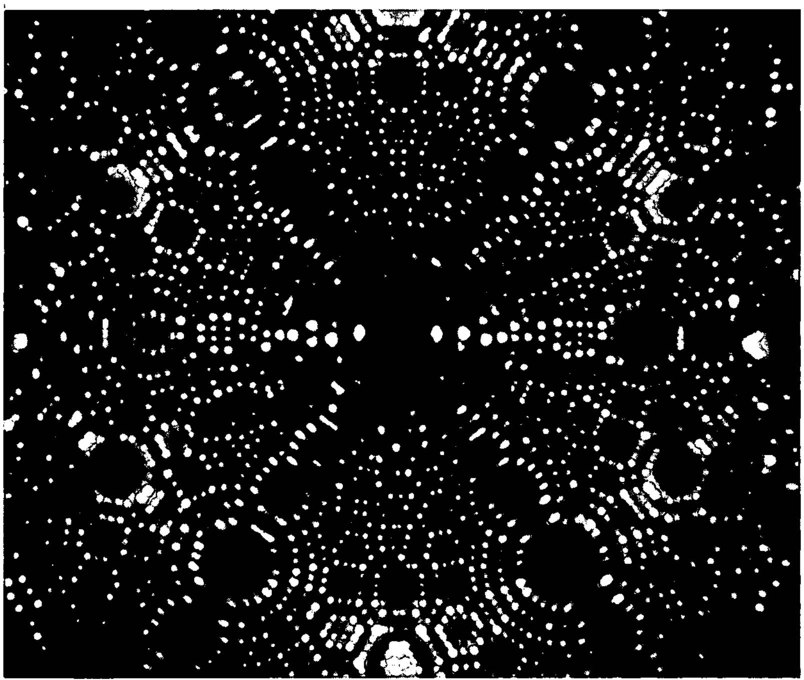
Now what about the properties of metals? How can these be related to structure? One of the most important physical properties of metals is the ability to carry an electric current. It was pointed out earlier that the bonding in metals does not consist of the attraction of positively charged and negatively charged ions or of covalent, "ball-and-stick" kind of bonding. Instead, the bonding resembles a sticky molasses. It holds the atoms together in the solid, but does not prevent the atoms from moving. The structure of solid metals has often been likened to atomic islands. Electrons are relatively free to flow back and forth, much as seawater can flow back and forth during tides. The flowing electrons make up an electric current, which is a flow of electrons in one direction.



A second important property of metals is their malleability and ductility. We have included malleability and ductility as a single property because both reflect the solid metal's ability to be worked into another shape mechanically. This property has two aspects: the relative ease of displacement of the atoms and the ability of the atoms to stick together after displacement.

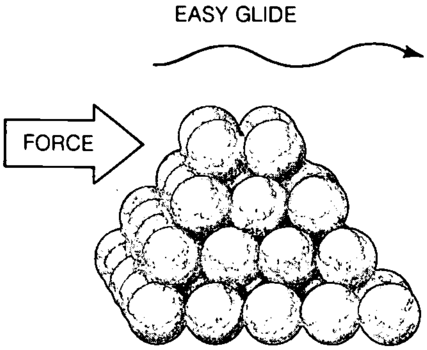
One factor that affects both of these aspects is the inherent strength of the bonding between the atoms—the thickness and stickiness of the "molasses." Although this is too complicated a theoretical problem to discuss simply, we can note that the hardness of metals—the tendency of the atoms to resist displacement—is related to the number of valence electrons in the atoms of the metals. The metals of Groups IA (Li, Na, K, Rb, Cs), Group IB (Cu, Ag, and Au), Group IIA (Be, Mg, Ca, Sr, Ba), and Group IIB (Zn, Cd, Hg) have few electrons and are soft, malleable metals. The hard metals that are useful in construction belong to Groups IVB through VIIIB. Among such metals are titanium, vanadium, chromium, molybdenum, nickel, and, of course, iron, the most important.

A tungsten crystal under the field-ion microscope showing the patterns of the atoms that make up the crystal (magnified over a million times).



TIME MACHINE

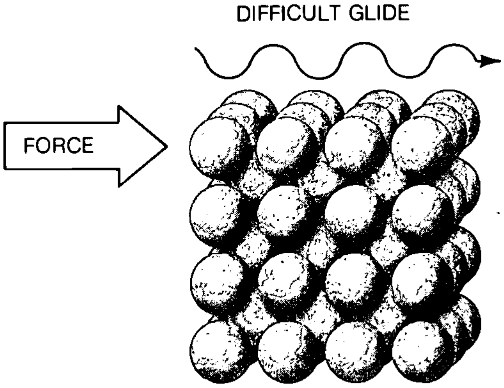
1825	Erie Canal is completed, linking Albany and Buffalo.
1826	Joseph Niepce, French chemist, invents first photographic process, later improved by Daguerre.
1827	John James Audubon publishes *Birds of North America*.
1828	**J. B. Neilson invents the blast furnace in Scotland for the production of steel.**
1828	**Friedrich Wöhler synthesizes the first "organic" compound, urea, from inorganic materials.**
1829	Louis Braille completes system of finger-reading for the blind.
1830	Peter Cooper's *Tom Thumb* locomotive hauls a load of 40 persons at 10 miles an hour over hilly Baltimore & Ohio Railroad route.



HEXAGONAL CLOSEST-PACKED STRUCTURE

A second factor affecting malleability is the geometry of packing. Metals tend to be soft if their atoms are arranged in layers and if one layer can slip past another easily. Look at the figure of a hexagonal closest-packed structure. Two of the layers have been "lifted" from the lattice to show how they could slide back and forth very easily. Imagine a hammer striking the crystal where the arrow is drawn. This layer of atoms and all above it could slide (the technical term is "glide") easily across the bottom layers. Such a metal would deform easily if hit with a hammer.

On the other hand, consider a body-centered cubic lattice. Again, imagine that a hammer strikes at the arrow. Notice that the atoms in this structure are also in layers but that the atoms in one layer do not touch each other. They touch the atoms in the next lower layer. These atoms in adjacent layers stick in between the atoms in the other layers. It's like pushing a wagon over a bumpy road—the top layer has to go up and down over the "bumps" of the atoms below. This makes it hard to push and tends to make the metal harder than it would otherwise be. Some of the hardest metals known—vanadium, chromium, tungsten, iron—have a body-centered cubic structure that resists deformation.



BODY-CENTERED CUBIC LATTICE

A 300-ton stamping press produces metal seat belt components. What properties of metals must the engineer and designer be concerned with in this operation?

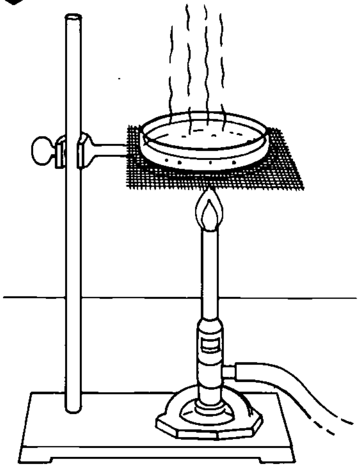
Go back and look at each figure in this section. Try to decide whether metals having the structures illustrated would deform easily or not. Are there layers that will slide easily? Single out a metal that you already know and decide for yourself whether it would be easy or difficult to deform the metal. Remember, there are two important things to consider. One is the structure of the metal. The second is the number of bonding electrons, the "thickness" of the "molasses." Both have a bearing on the malleability of a metal.

PROBLEM

Of the metals mentioned in this section, some are hard and some are soft. Can you explain which are hard and which are soft on the basis of their structures and the number of bonding electrons?

I-16 Growth Is the Name of the Game

miniexperiment



In the next section we will begin discussing the properties of compounds that form *ionic crystals*. That section will have more meaning for you if you have had a chance to grow some ionic crystals. Fortunately, some are extremely easy to grow if you follow directions carefully.

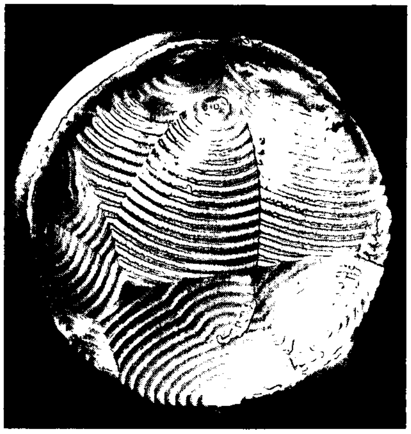
Materials: copper(II) sulfate, $CuSO_4 \cdot 5H_2O$
potassium aluminum sulfate ("alum"), $KAl(SO_4)_2 \cdot 12H_2O$
ammonium aluminum sulfate, $NH_4Al(SO_4)_2 \cdot 12H_2O$
potassium permanganate, $KMnO_4$

Take a *clean* Pyrex petri dish or petri dish cover (5–15 cm diameter). Fill about two-thirds full with a saturated solution of one of the salts listed under "Materials." Heat carefully to boiling with a Bunsen burner. Turn off the Bunsen burner and allow the solution to cool undisturbed.

If no crystals have formed by the end of the laboratory period, lay a paper tissue over the dish to keep out dust and allow the solution to remain overnight.

When enough crystals have grown, decant any excess solution from the petri dish and allow the crystals to dry. **Caution:** *Do not handle the crystals directly with your fingers; $KMnO_4$ is corrosive*. Also, the crystals tend to lose their beautiful luster when handled—but do examine their properties.

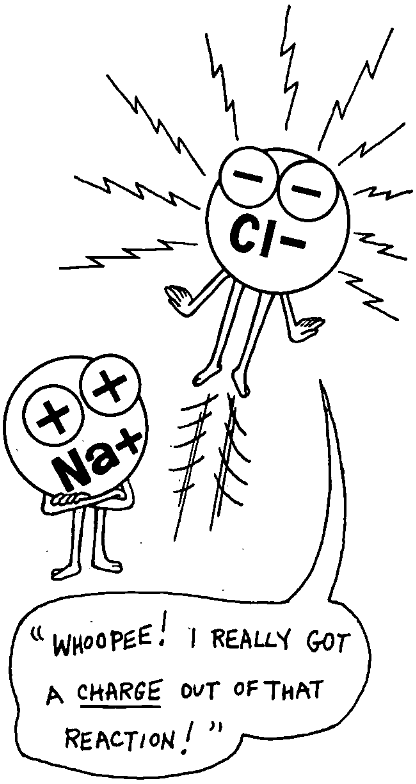
Questions: Note the color of your crystals. Do they have a regular shape? Are they brittle or are they malleable and ductile like a piece of metal?



Crystals of potassium acetate formed in a round-bottom flask.

I-17 Getting a Charge

We have seen that the properties of metals (malleability, ductility, conductivity) are related to the way the atoms are arranged in the metallic lattice. Solid ionic substances such as sodium chloride (NaCl), common table salt, also have characteristic properties closely related to their lattice structure.



The chemical reactivity of metals depends upon their releasing one or more electrons to form positive ions, or *cations*. These electrons are accepted by nonmetals to form negative ions, or *anions*. An example of this is the reaction of sodium (a metal) with chlorine (a nonmetal) to form sodium chloride:

$$2Na + Cl_2 \longrightarrow 2(Na^+Cl^-)$$

The resulting compound, sodium chloride (NaCl), is called an ionic compound because it is composed of ions.

The resulting ions, Na^+ and Cl^-, seek to establish a solid lattice that has the greatest stability. That is, the attractive forces between the oppositely charged ions will be as great as possible, while the repulsive forces between the ions of similar charge will be as small as possible. The purpose of the following miniexperiment is to determine some of the arrangements in which oppositely charged ions can exist to provide stable solid lattices for ionic compounds such as sodium chloride (NaCl). You will use magnets to simulate the behavior of oppositely charged particles.

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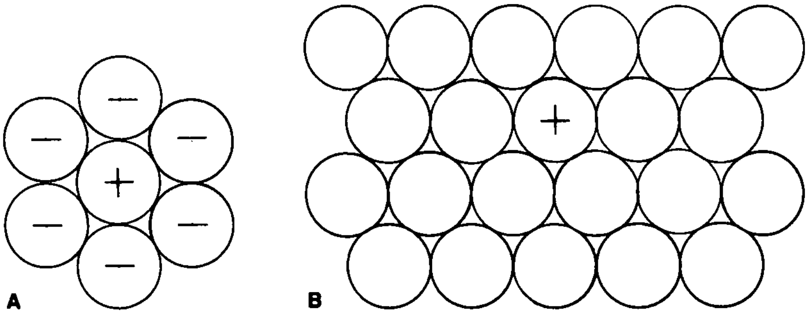
miniexperiment

I-18 Attracting Opposites

Here you will be observing two-dimensional arrays. You have seen that the most stable arrangements for packing metal atoms are those that have the maximum coordination number. You constructed lattices in experiment *I-14 Becoming an Efficiency Expert* by building up hexagonal layers that provide a coordination number of six within the layer plus additional coordination from above and below the layer.

Try to arrange a six-coordination ionic structure with magnets. Use a circular magnet to represent a cation or an anion. Now place six circular magnets around the center magnet. The six magnets should have polarities that are opposite the polarity of the center magnet. Your placement of the magnets should yield the arrangement as shown in Figure A.



From the results of your miniexperiment, what conclusion can you draw about the building of lattices based on oppositely charged ions in a lattice such as the one shown in Figure B?

Can you suggest a better arrangement?

Although the miniexperiment is simple, it gives you some idea of the requirements for an ionic lattice. (Remember, ions are not magnets. The magnets are just helpful replacements.) Even though the miniexperiment deals only with two-dimensional arrangements, you can imagine that in three dimensions the same principles will apply. An ion will try to attract several ions of the opposite charge, but ions of the same charge repel each other and cannot be too close to each other.

Because there are many different kinds of ions with different charges and different sizes, there are many kinds of ionic lattices. We are going to consider only two of the simplest and most common. Both lattices are based on a cubic arrangement of ions. First, we will see what structures are possible, and then we will try to explain some properties of ionic compounds in terms of their structures.

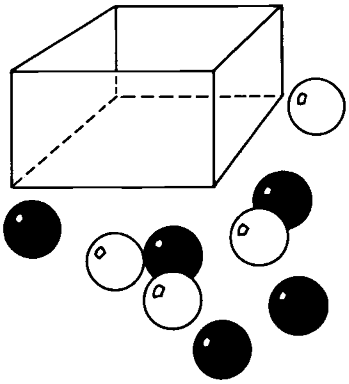
We will investigate a simple ionic lattice by doing an experiment. We will use Styrofoam balls to determine the structure of sodium chloride (NaCl). Balls of different colors will represent oppositely charged ions.

OPPOSITES ATTRACT

I-19 Packing Ions

EXPERIMENT

First, build a simple cubic lattice in the box to remind yourself of what it looks like. Then dump out all of the Styrofoam balls and, one layer at a time, build a structure that has the balls in the same position as in the simple cubic arrangement but in which half of the balls are white and half are colored. Can you build such a structure so that no two white balls touch each other? With no two colored balls touching? The colored balls represent sodium ions (which repel each other and should not touch each other). Pick a sodium ion in the structure and determine its coordination number. If your lattice resembles the simple cubic lattice in geometry and if no adjacent atoms are of the same color, you have built a sodium chloride lattice.



Problem: If possible, obtain models of both the sodium chloride (NaCl) lattice and the cesium chloride (CsCl) lattice and compare them with your structure. What is the coordination number of the CsCl lattice?

You have considered only two ionic lattices, those of cesium chloride (CsCl) and sodium chloride (NaCl). These two structures are illustrated in Figures 10, 11, and 12. There are several physical properties of ionic compounds that may be related to the arrangement of the ions in the lattice. The most obvious of these properties is the structure of the crystals.

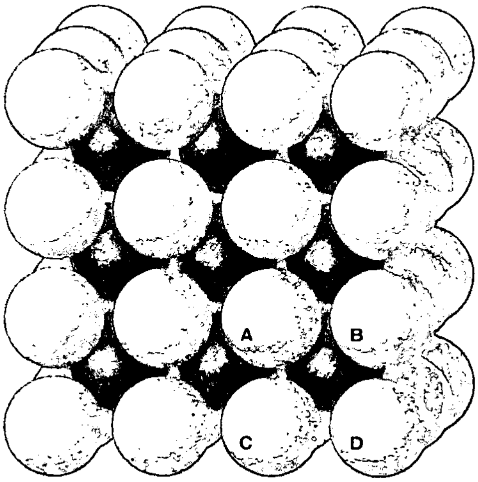


FIGURE 10 CsCl LATTICE

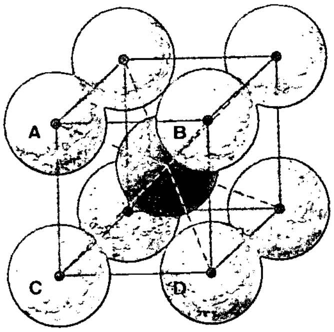


FIGURE 11 UNIT CELL

If you look at crystals of table salt (sodium chloride), you will find that, with the exception of those that have been crushed or damaged, they are small cubes. This results from the cubic structure of the ions. Not surprisingly, cesium chloride also crystallizes to form cubes.

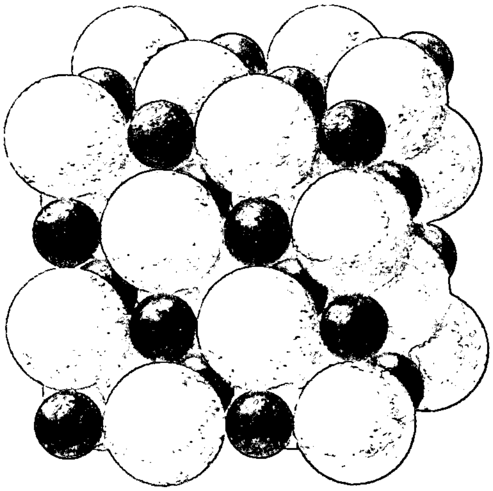
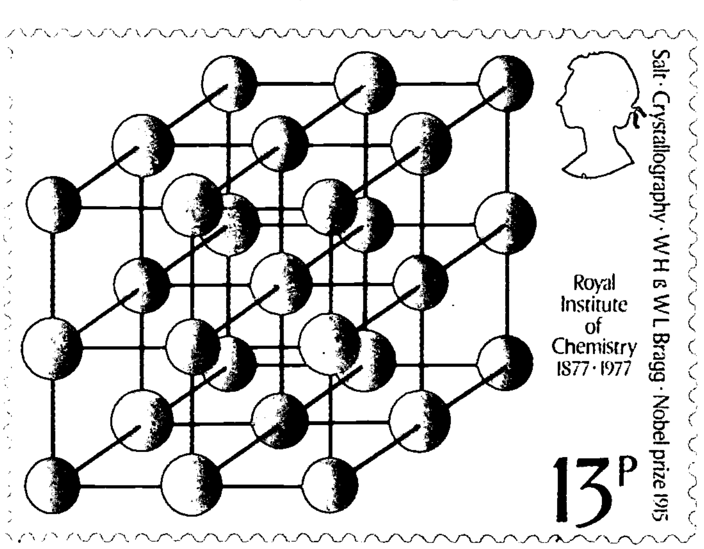


FIGURE 12 NaCl LATTICE



The father-and-son team of W.H. and W.L. Bragg perfected the crystallographic technique for determining the structure of crystals and won the Nobel Prize in 1915. In 1977 the British Post Office issued a series of stamps honoring British chemists including the Braggs. Can you identify the structure shown on the stamp?

Crystals of sodium chloride (NaCl) as photographed under the electron microscope, magnified 47 times.

In sodium chloride and cesium chloride, it is fairly simple to relate the shape of crystals to the arrangement of ions. More complicated compounds require sophisticated experimental apparatus and computers to enable us to determine the arrangement of ions or atoms.

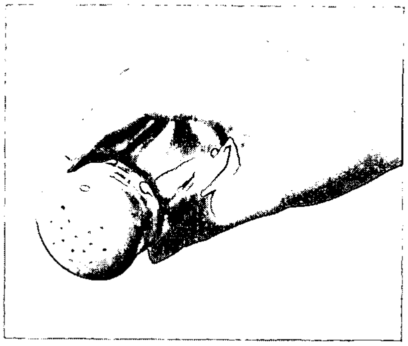
There are other properties of ionic crystals that are determined by the presence of ions; and before discussing these, you will have an opportunity to discover them for yourself in the following miniexperiment.

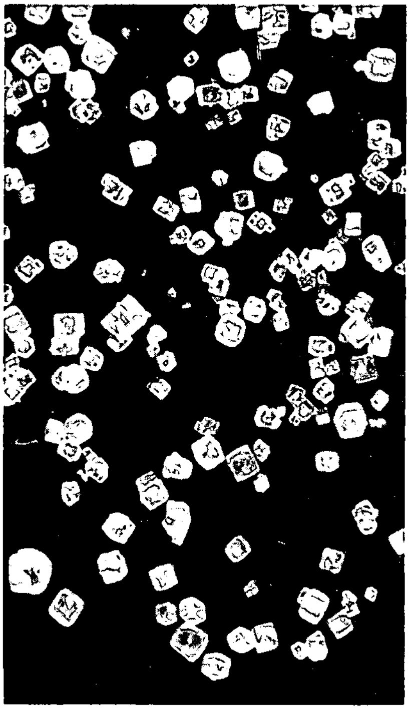
I-20 The Effects of Hanging Together

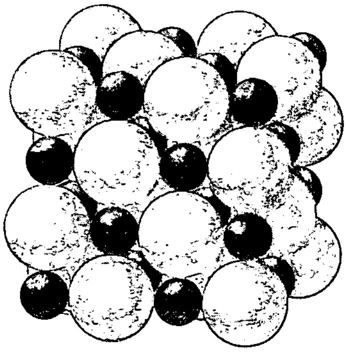
miniexperiment

Obtain samples of ionic compounds together with samples of the metals and nonmetals with which you have previously experimented. Compare properties such as color, malleability, ductility, density, and melting point. What properties do the ionic compounds have in common?

By doing the miniexperiment, you have observed that ionic compounds have some properties in common. In a few properties, they may resemble the pure metals or nonmetals. Yet in many ways they are different. How can the properties of ionic crystals be explained?





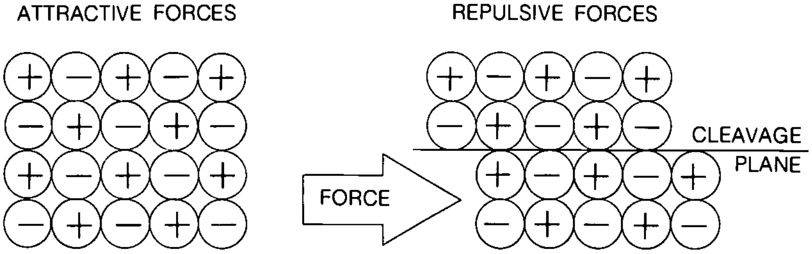


First, ionic compounds have high melting points and high boiling points. This is because there are strong attractive forces between the positive cations and the negative anions. In order to break up the lattice in the process of melting, it is necessary to supply energy in the form of heat to overcome these forces.

We might have expected ionic compounds to conduct electricity because of the presence of charged ions. When in the liquid state, ionic compounds do conduct electricity. Solid ionic compounds will not conduct electricity. Each ion is locked in its place in the lattice by all of the surrounding ions. It is not free to move. If the lattice is broken by melting, the ions become free to move. Molten ionic compounds are excellent conductors.

Another characteristic property of ionic compounds is their solubility or insolubility in various solvents. Ionic compounds are insoluble in many common solvents such as benzene, carbon tetrachloride, TTE, etc. This is because the very strong attractive forces between ions do not let the ions separate and dissolve in the solvent. Ionic compounds are soluble only in solvents that can overcome these forces. Water is such a solvent. Many ionic compounds such as sodium chloride (NaCl) and calcium bromide ($CaBr_2$) are soluble in water. Some ionic compounds such as calcium fluoride (CaF_2) have forces so strong that even water cannot overcome them, and they are insoluble in water. If an ionic compound *does* dissolve in water, its ions will be free to move and conduct an electrical current.

Finally, ionic compounds of metals differ in a fundamental way from their parent metallic elements. Metals themselves are malleable. Ionic compounds of metals are brittle. This is because the attractive forces can be turned into repulsive forces if the ions are displaced by merely the thickness of one ion. This can be shown in two dimensions in the figure that follows:

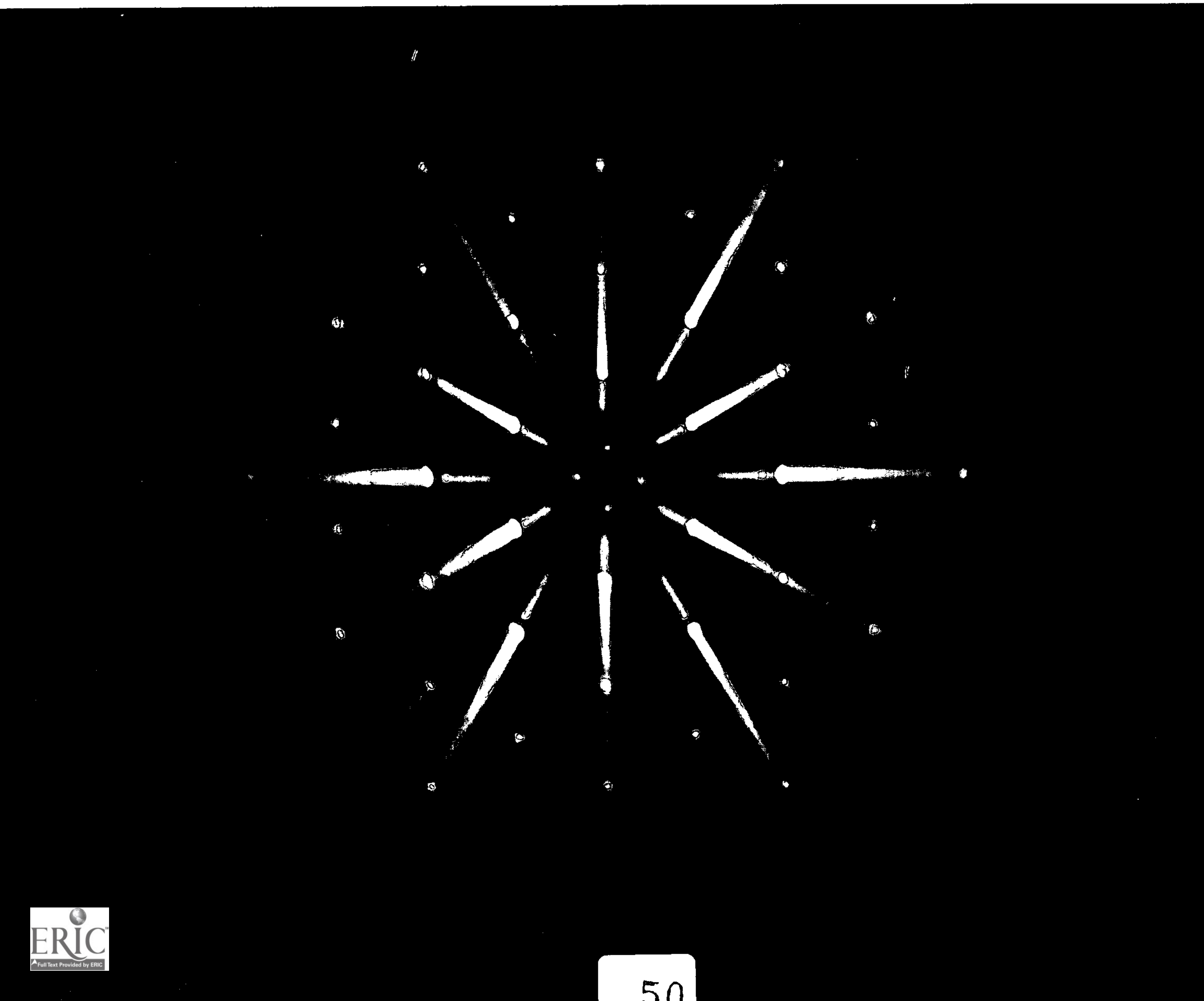


By displacing the ions one space to the right, the positive cations are no longer placed opposite negative anions. Instead, they are placed opposite other cations and are strongly repelled. The anions also find themselves opposite to and repelled by other anions. Thus, hitting an ionic crystal with sufficient force to displace the ions slightly will cause it to shatter as a result of the repulsive forces that are set in motion.

Inorganic Molecules

We have observed that compounds form between metals and nonmetals by the transfer of one or more electrons from the metal to the nonmetal. The resulting compounds are described as ionic because they contain charged atoms, or *ions*. When two nonmetals react, electron transfer cannot take place. This is because both elements would "like" to receive electrons, but neither is willing to let the other have any of its own electrons.

X rays passing through a single snowflake are diffracted; the resulting patterns reveal the atomic symmetry within the snowflake crystal.



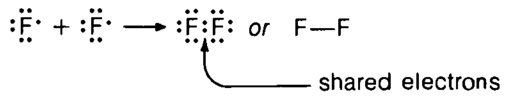
I-21 The Covalent Bond: Share or Else!

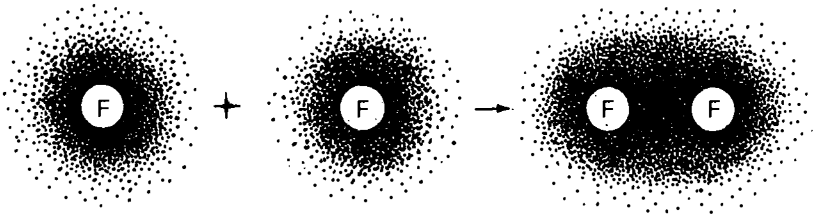
Suppose we have an instance in which two elements would "like" to gain electrons but neither is willing to let the other have any of its own electrons. In such a situation, the *octet rule* can be obeyed if the two atoms share their electrons. (An outer shell, remember, is filled when it contains eight, or an octet, of electrons.)

Consider what happens if two atoms of fluorine happen to collide. Each atom of fluorine has seven valence electrons and would like to have eight. This can be accomplished if each fluorine atom keeps six of its electrons to itself but shares the seventh electron with the other atom. Each contributes its seventh electron to form a pair of electrons (one electron from each atom). Such a shared pair of electrons is called a *covalent bond*. The covalent bond holds the two fluorine atoms to each other because neither atom is willing to let the other atom have both electrons. As a result, each atom holds the shared pair tightly, and thus holds the other atom as well:

It is easy to talk about atoms as if they were people: "A fluorine atom would *like* to accept an electron and become a fluoride ion." Obviously atoms are not people, and they do not have desires and wishes of their own. Although such usage is open to the charge of *anthropomorphism*—talking about inanimate objects, plants, and animals as if they were people—little harm is done as long as no one really believes that atoms are "alive."

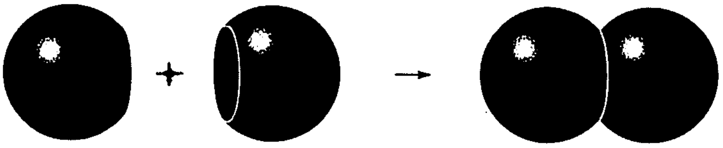
The alternative is to talk in a less direct style: "There is a strong *tendency* for a fluorine atom to gain an electron." Less vague and more proper from a scientific viewpoint is "It is *energetically favorable* for a fluorine atom to accept an electron and become a fluoride ion." If you take further courses in chemistry, you will learn the proper scientific phrasing. For now, the object is to convey the chemical principles in the clearest possible way.





Fluorine atoms

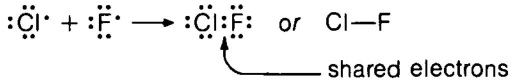
Fluorine molecule



Fluorine atoms
(models)

Fluorine molecule
(model)

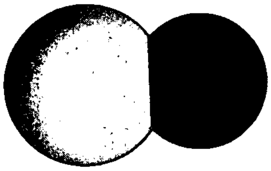
The resulting molecule of fluorine (F_2) contains a single shared pair of electrons—a covalent bond. The covalent bond in F_2 is of exactly the same kind as that found in many nonmetals. For example, all the halogens form diatomic molecules (that is, two atoms per molecule)—F_2, Cl_2, Br_2, I_2, and At_2. In addition, there are several compounds formed between two different halogen atoms such as ClF, BrCl, ICl, IBr, etc. For example, if a chlorine atom encounters a fluorine atom, the two combine to form a molecule of chlorine fluoride (ClF). Both the chlorine atom and the fluorine atom have seven valence electrons.



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}\cdot \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}: \quad \textit{or} \quad \mathrm{Cl—F}$$

shared electrons

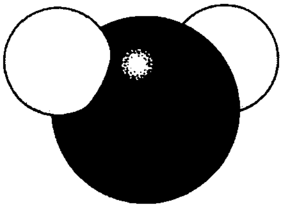
Neither the chlorine atom nor the fluorine atom is a metal. Neither is willing to release its electrons to the other. The fluorine atom has a higher ionization energy; it holds on to its electron more tightly than does the chlorine. Even so, it is not capable of pulling an electron completely away from the chlorine atom. In other words, it is not practical to form a chlorine ion (Cl^+). However, it is possible to form a covalent bond in which both atoms hold on to the shared pair rather tightly. This bond holds the chlorine fluoride molecule (ClF) together.



Chlorine Fluoride

In forming covalent compounds, a nonmetal will make bonds as it needs to complete its octet. Hydrogen and the halogens need only one electron; so they form a single bond. Oxygen and sulfur need two electrons; so they form two bonds (as in H—O—H). Nitrogen needs three, and carbon needs four.

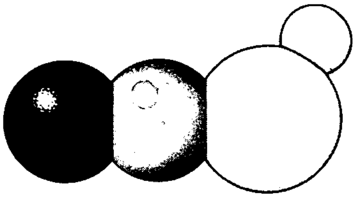
Working from the octet rule, it is easy to predict the formula of a compound if we know which elements are present. For example, ammonia is the pungent gas that burned your eyes and penetrated your respiratory tract if you ever incautiously smelled a bottle of "ammonium hydroxide" or a household cleaner with ammonia in it. (See section *I-26* for further discussion of these.) If you are told that ammonia is a compound of nitrogen and hydrogen, you can arrive at the reasonable formula for ammonia (NH_3). Later, in experiment *I-23 Structures of Molecules*, you will have an opportunity to try your hand at "making molecules."



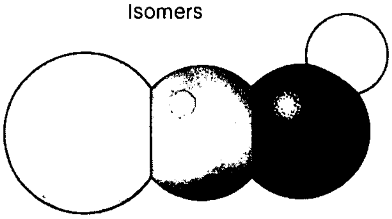
Water

There are two reasons why the simple rules described here do not result in an oversimplified, uninteresting chemistry. One is that even though it is possible to specify the valence of atoms, it is not always possible to predict which atoms will be attached to which other atoms. For example, consider a certain compound containing one nitrogen atom (valence three), one sulfur atom (valence two), one carbon atom (valence four), and one hydrogen atom (valence one). Note that both of the following molecules satisfy all the valence requirements:

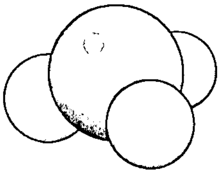
$$\mathrm{S{=}C{=}N{—}H} \quad \text{and} \quad \mathrm{N{\equiv}C{—}S{—}H}$$

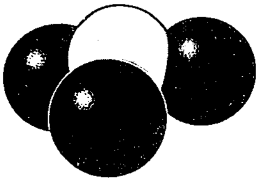


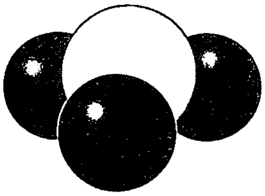
Isomers

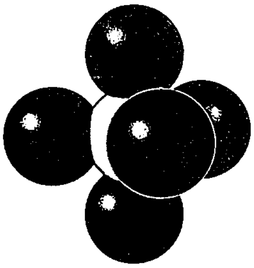


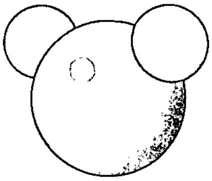
In both molecules, the nitrogen atom has formed three bonds, the carbon four bonds, the sulfur two bonds, and the hydrogen a single bond. Yet the two molecules are different. Such different compounds having the same formula are called *isomers*. Isomers are important in inorganic chemistry and even more so in organic chemistry (see *Form and Function: An Organic Chemistry Module*).

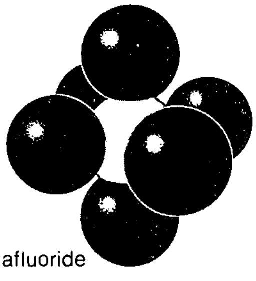

Ammonia


Nitrogen Trifluoride


Phosphorus Trifluoride

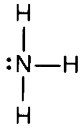

Phosphorus Pentafluoride


Hydrogen Sulfide


Sulfur Hexafluoride

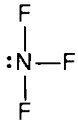
As we have noted, it is not always possible to predict with certainty what compound will form in a given situation. The second reason for this problem in prediction is that the octet rule is not always obeyed. A few nonmetals such as phosphorus and sulfur sometimes break the rule by having *more* than eight electrons in their valence shells.

Before looking at a couple of exceptions, let's review a molecule previously encountered, ammonia (NH_3). The octet of electrons in ammonia, as you may recall from *Reactions and Reason: An Introductory Chemistry Module*, consists of three bonding pairs that hold the hydrogen atoms and a fourth nonbonding pair.

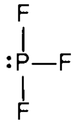


$$\begin{array}{c}\mathrm{H}\\ |\\ :\mathrm{N}-\mathrm{H}\\ |\\ \mathrm{H}\end{array}$$

A similar compound forms between nitrogen and fluorine and between phosphorus and fluorine:

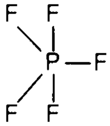


$$\begin{array}{c}\mathrm{F}\\ |\\ :\mathrm{N}-\mathrm{F}\\ |\\ \mathrm{F}\end{array}$$

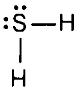


$$\begin{array}{c}\mathrm{F}\\ |\\ :\mathrm{P}-\mathrm{F}\\ |\\ \mathrm{F}\end{array}$$

The octet rule is obeyed in all of these compounds. However, phosphorus can also form a second compound with fluorine:

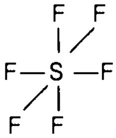


The valence shell now contains *ten* electrons. The octet rule has been broken, but the phosphorus has been able to form two more bonds. Chemists sometimes say that "phosphorus has expanded its octet." Sulfur can do the same thing:



octet rule obeyed

or

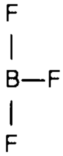


octet rule broken

There are also some elements that regularly violate the octet rule simply because they don't have enough electrons for an octet. Boron is the only element of this type that is common. It has three valence electrons. If it shares these three with three atoms of fluorine, it will still have only a total of six electrons:

a "missing" pair of electrons ⟶

or



$$\begin{array}{c}\mathrm{F}\\ |\\ \mathrm{B}-\mathrm{F}\\ |\\ \mathrm{F}\end{array}$$

In this instance, boron has no more valence electrons to share; so it cannot hope to complete an octet in such a way. Even though it violates the octet rule, it has formed three strong bonds. It is thus a stable compound, although exceedingly reactive. It is reactive because there is a special way it can achieve an octet—and it will do so if possible! (This is discussed later.)

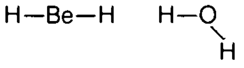
At this point you needn't worry too much about when the octet rule will be broken. These examples were included here to let you know that there are exceptions. The octet rule is useful and allows us to make a large number of correct predictions concerning the compounds that we encounter. Still, we must remember that it is a simple rule covering complex bonding situations. We should not be too upset if it is broken occasionally.

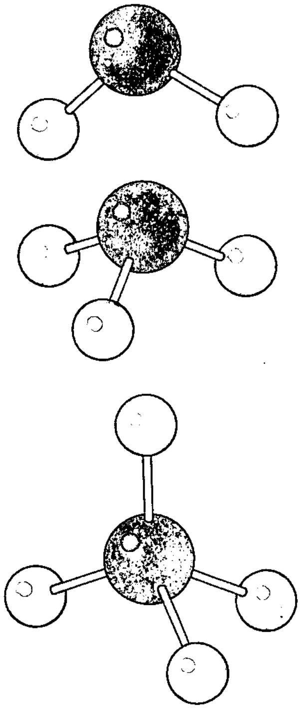
Finally, to restore some of your faith, there are some elements that *always* obey the octet rule. Among the most common of these elements are carbon, nitrogen, oxygen, and fluorine.

I-22 Molecular Shape

As soon as we start talking of molecules that have more than two atoms, it becomes possible to discuss their geometry, or shape. For example, if a molecule consists of three atoms, A and C (each valence one) and B (valence two), we might predict that the molecule formed would be A—B—C. Note, however, that the atoms need not lie in a straight line.

Because the typesetter likes to set type as neatly and simply as possible, it is common to write formulas of this kind as A—B—C or H—O—H (for water). However, molecules existed before typesetters (or textbook writers and readers, for that matter!), and so we find that while some molecules, H—Be—H, for example, are linear (that is, the atoms lie in a straight line), others are distinctly bent. H_2O is an example:





The shape of molecules is extremely important in determining the properties of compounds. For example, the shape of the water molecule determines the properties of this essential liquid. If the water molecule were linear, like BeH_2 (beryllium hydride), water would be a gas at room temperature, not a liquid. There could be no rivers, lakes, or oceans on earth; and life as we know it would be impossible!

You can clarify your understanding of molecular geometry by doing an experiment. The experiment that follows consists of some preliminary classwork and discussion followed by an attempt to determine molecular geometry from various models. The relation of the properties of molecules to their geometry and structure will be discussed in somewhat greater detail after you have done the experiment.

EXPERIMENT

I-23 Structures of Molecules

This experiment is divided into several parts. First, you will write graphic formulas. You then will construct ball-and-stick models of various molecules. Finally, you will investigate molecular geometry through the use of magnets and balloons.

Part 1: Graphic Formulas. This portion of the experiment consists of a class discussion to predict reasonable formulas for the following compounds:

NAME	DESCRIPTION
Molecular hydrogen	Molecule contains only H atoms
Hydrogen chloride	Molecule contains H and Cl atoms
Water	Molecule contains H and O atoms
Ammonia	Molecule contains H and N atoms
Methane	Molecule contains H and C atoms
Hydrogen peroxide	Molecule similar to water but contains *two* O atoms
Hydrazine	Molecule similar to ammonia but contains *two* N atoms
Nitrogen chloride	Molecule contains N and Cl atoms
Chloroform	Molecule contains one C, one H, and some Cl atoms
Methyl alcohol	Molecule contains one C, one O, and some H atoms
Methylamine	Molecule contains one C, one N, and some H atoms

As the discussion proceeds, write the correct (1) dot structure, (2) line structure, (3) formula for each compound.

Part 2: Molecular Models. Construct ball-and-stick molecular models, consistent with the formulas obtained in the previous section, for the following molecules:

Carbon Group	Nitrogen Group	Oxygen Group
H_2	H_2	H_2
CH_4	NH_3	H_2O
CH_3Cl	NCl_3	H_2O_2
CH_3NH_2	N_2H_4	$HOCl$

Your sketches of molecules in *Part 1* are necessarily two-dimensional because they are drawn on a sheet of paper. How

many of your molecular models are two-dimensional?
How many of your molecular models are three-dimensional?

Part 3: Using Magnets to Determine Molecular Geometry. Use a circular magnet of one polarity (that is, red up) to represent the positive nucleus and several other magnets of opposite polarity (that is, blue up) to represent the pairs of electrons that surround the nucleus (each magnet represents one electron pair). Determine the geometric arrangement for various numbers of electron pairs as outlined in the following. Sketch the geometric arrangement that the magnets assume. Label your sketches with + and − to indicate the nucleus and the electron pairs.

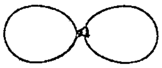
1. One nucleus surrounded by two electron pairs: What is the geometry of the arrangement of the magnets? In gaseous beryllium chloride ($BeCl_2$) only two electron pairs are found on the beryllium atom. Sketch your prediction of the arrangement of the atoms in beryllium chloride ($BeCl_2$).
2. One nucleus surrounded by three electron pairs: What is the geometry of the arrangement of the magnets in this case? Boron trifluoride (BF_3) has three electron pairs on the boron atom. Sketch your prediction of the arrangement of the atoms in boron trifluoride (BF_3).
3. One nucleus surrounded by four electron pairs. What is the arrangement of the magnets?

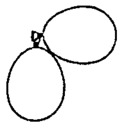
Part 4: Using Balloons to Determine Molecular Geometry. An electron pair occupies a region in space that is reasonably similar in shape to that of an inflated balloon. Use balloons to represent electron pairs. First, inflate each balloon to approximately the same size. Then tie the balloons together to form "molecules," as instructed in the following. When connecting two balloons, tie them close to the body of the balloon, not with long "necks." Construct the following units: *Six inflated balloons, tied into three pairs; one set of three inflated balloons attached in a single unit.*

In determining the following geometries, try to avoid distorting the structures as you hold the balloons. Let the balloons assume the geometry that seems most natural for them.

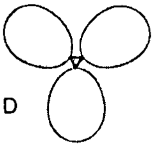
1. Two balloons attached together (two electron pairs about a single nucleus): Which of the following pictures most closely represents this situation?

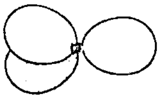

A

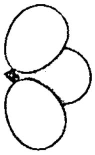

B


C

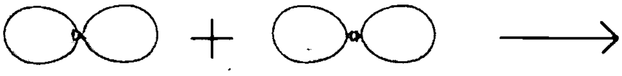
2. Three balloons attached together (three electron pairs about a single nucleus): Which of the following pictures most closely represents this situation?

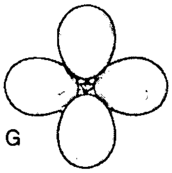

D

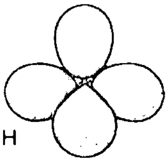

E


F

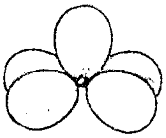
3. Four balloons attached together (four electron pairs about a single nucleus): Use two pairs of balloons. Which of the following pictures most closely represents this situation?

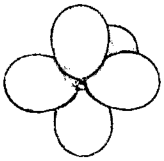


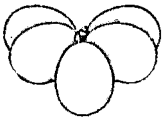

G


H

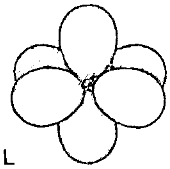
4. Five balloons attached together (five electron pairs about a single nucleus): Use the set of three plus another pair. Which of the following pictures most closely represents this situation?

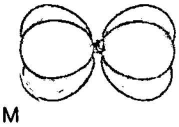

I

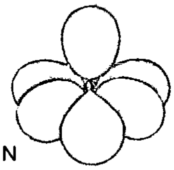

J


K

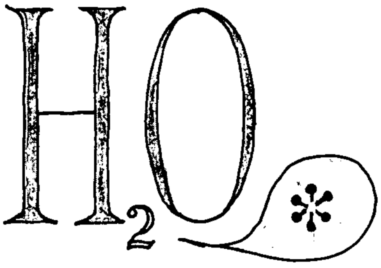
5. Six balloons attached together (six electron pairs about a single nucleus): Use three pairs of balloons. Which of the following pictures most closely represents this situation?


L


M


N

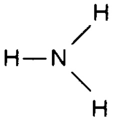
Nonbonding Pairs. All the molecules for which you built models (except H_2) had four electron pairs around the central atom. In methane (CH_4), all the electron pairs hold hydrogen atoms to the carbon atom. In ammonia (NH_3) and water (H_2O), one or more electron pairs are not used to hold other atoms. Instead, these electron pairs are *nonbonding pairs*. In determining the correct structure of these molecules, do you have to count all the electron pairs or can you discount the nonbonding pairs? Determine the answer by comparing the structure of your molecular models (which have been patterned after experimental results) with predictions based on the two ways of counting electrons:

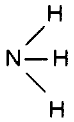


It's kind of damp down here!

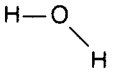
Molecules **Which are the correct structures?**

Ammonia (NH_3)
1 nonbonding pair
3 bonding pairs (to H)
Total pairs: 4





Water (H_2O)
2 nonbonding pairs
2 bonding pairs (to H)
Total pairs: 4

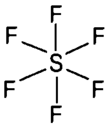


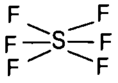
H—O—H

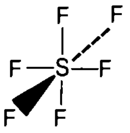
PROBLEMS

Predict the structures of the following molecules. Lines represent bonding electrons. Wedges (◀) are used to indicate bonds coming out of the page towards the viewer. A dashed line (---) represents bonds going back behind the central atom. The figure ◯ represents nonbonding electron pairs:

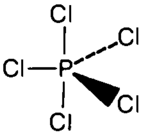
1. Sulfur hexafluoride (SF_6)

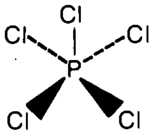


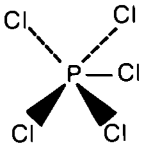




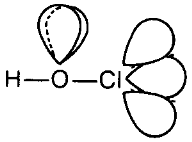
2. Phosphorus pentachloride (PCl_5)

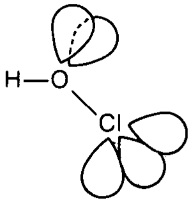


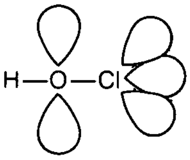




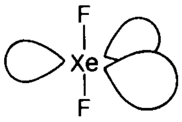
3. Hypochlorous acid (HOCl)

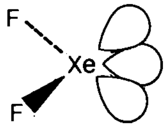






4. Xenon difluoride (XeF_2)





From the results of your experiment with molecular models, magnets, and balloons, you can see that the usual way that a chemist writes formulas inadequately describes the three-dimensional structure of molecules. Chemists develop the ability to look at a two-dimensional representation of a molecule and immediately imagine what it would look like if made into a three-dimensional model. Even if you don't intend to become a chemist, try to do this, too. It's fun, and it will help you to understand and enjoy many interesting aspects of chemistry.

I-24 A Matter of Life and Breath

We made an earlier reference to the importance of molecular structure in determining the properties of a compound. Let's think about two common molecules and see how their structures are important to us. The molecules are water and carbon dioxide. Water covers three-quarters of the earth's surface—the three-quarters found as lakes, streams, and oceans. Carbon dioxide and water are involved in photosynthesis, the process by which green plants capture the energy of the sun and convert it into foodstuffs:

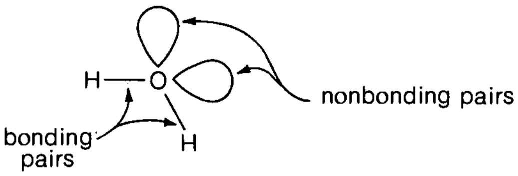
$$xCO_2 + xH_2O \xrightarrow{\text{sunlight}} (CH_2O)_x + xO_2$$

where $(CH_2O)_x$ is a generalized formula for carbohydrates (See *Molecules in Living Systems: A Biochemistry Module*); when $x = 6$, the sugar is dextrose, found in honey.

It is vitally important to all living organisms that carbon (valence four) and oxygen (valence two) readily form carbon dioxide, (CO_2):

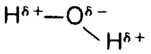
$$O{=}C{=}O$$

Because the electrons tend to repel each other, the best arrangement is with the oxygen atoms on opposite sides of the carbon atom (a linear molecule). On the other hand, we have seen that the water molecule, (H_2O), exists in a bent form because there are two nonbonding pairs on the oxygen atom in addition to the two bonding pairs (two covalent bonds) that hold the hydrogen atoms to the oxygen. Since all four pairs of electrons tend to repel each other, the best arrangement is a bent form:



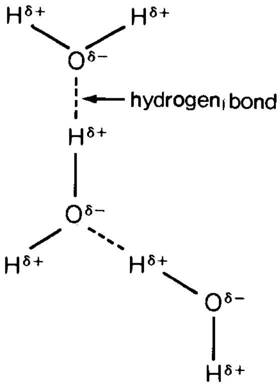
As we mentioned earlier with the chlorine fluoride (ClF) molecule, the fluorine atom is able to attract electrons more strongly than chlorine. In the same way, the oxygen atom is able to attract electrons more strongly than either hydrogen or carbon. It cannot take the electrons away completely to form an ionic compound, but it can partially pull the electrons toward it, forming a small charge on the atom.

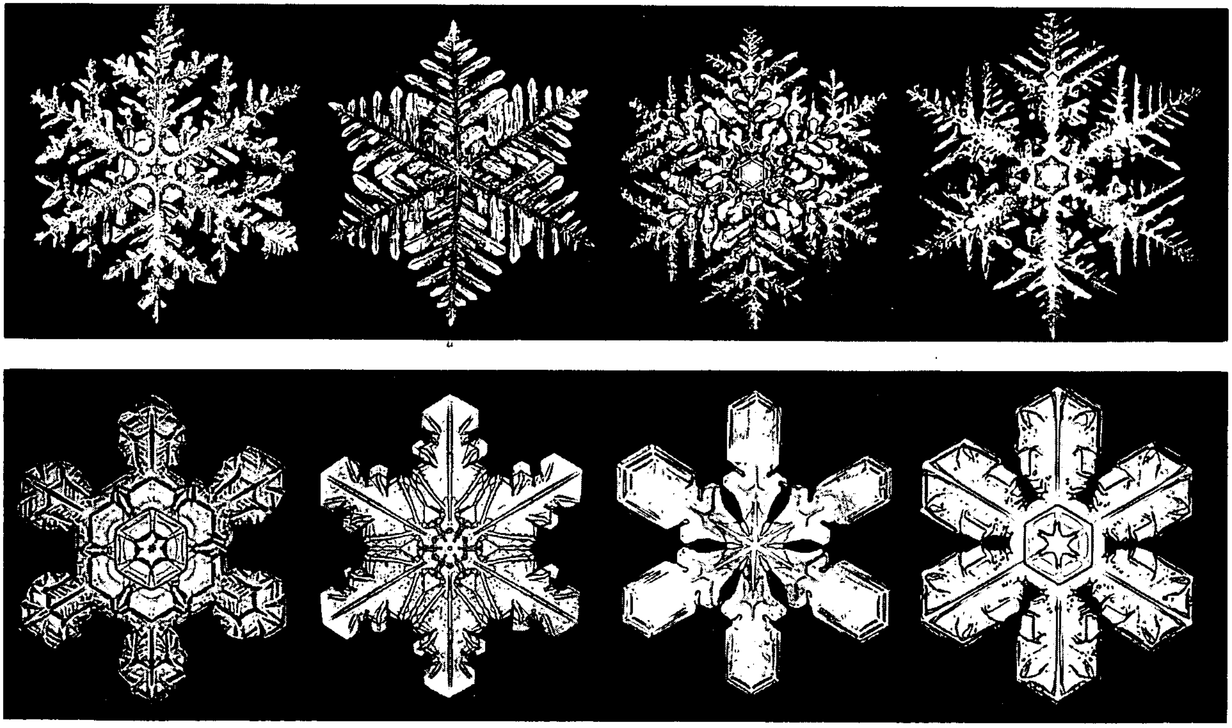
The small charges on the atoms are important. Chemists use the Greek letter delta (δ) to indicate these partial charges (much less than that corresponding to complete transfer of electrons). Thus, the water molecule might be depicted as



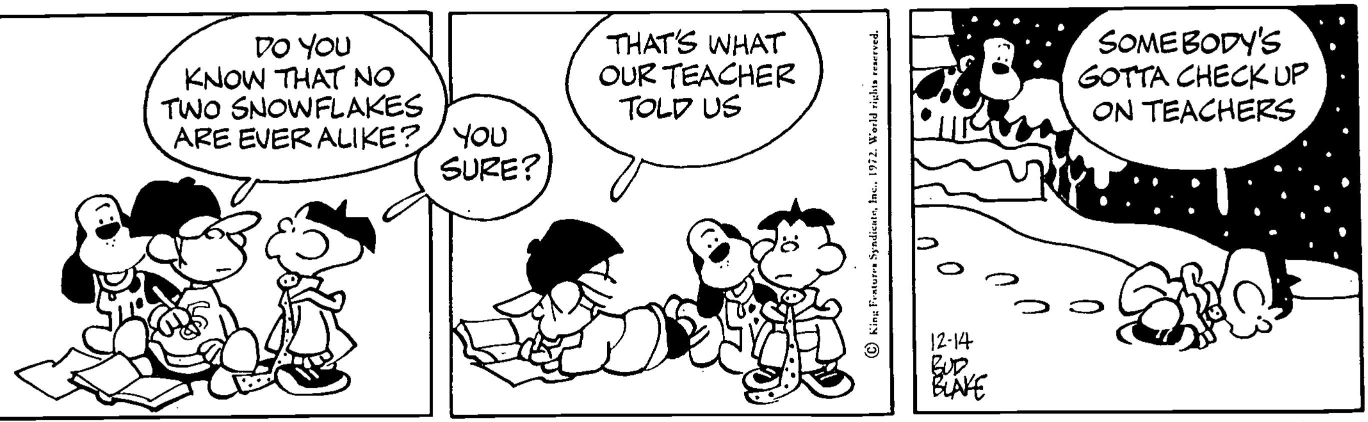
$$H^{\delta+}\text{—}O^{\delta-}\text{—}H^{\delta+}$$

where the hydrogen atoms have small positive charges (δ+) and the oxygen atom has a small negative charge (δ−). The oxygen





The beautiful symmetry of snowflakes is caused by hydrogen bonding. No two snowflakes are ever exactly alike. Impossible, you may say. Check for yourself.



is said to be more *electronegative* than either hydrogen or carbon. In both water (H_2O) and carbon dioxide (CO_2), the oxygen atoms carry a small negative charge.

When two carbon dioxide molecules come together and the negative oxygen atoms approach each other, they repel each other. The repulsion between the two negative oxygen atoms causes the carbon dioxide molecules to fly apart:

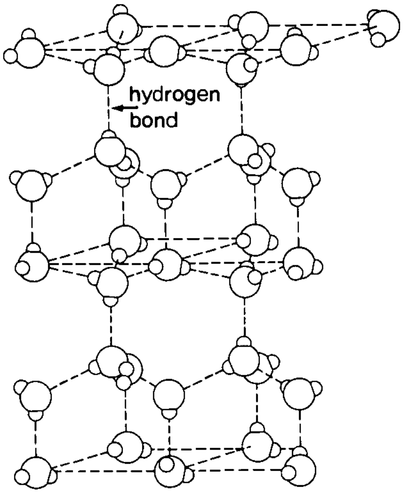
$$O^{\delta-}—C^{\delta+}—O^{\delta-} \quad \underset{\text{repulsive force}}{\longleftrightarrow} \quad O^{-}—C^{\delta+}—O^{\delta-}$$

On the other hand, when two water molecules come together, it is possible for them to align themselves in such a way that the positively charged hydrogen atom of one molecule can attract the negatively charged oxygen atom of another molecule. Many molecules can become involved in the attraction.

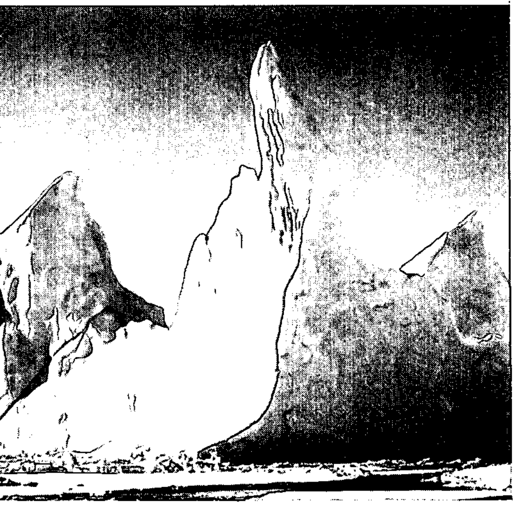
The net result of all of these attractions (called *hydrogen bonds*) in water is that it is a liquid at room temperature (the molecules tend to stick together). In contrast, when two carbon dioxide molecules come together there is little tendency for them to stick together. As a result, carbon dioxide (CO_2) is a gas at room temperature: It must be cooled to a low temperature to make the molecules come together to form a solid (Dry Ice). At room temperature, carbon dioxide is a gas, but water is a liquid.

What if the properties of water and carbon dioxide were reversed? We would find fish swimming around in seas of pure liquid carbon dioxide. (Actually, we would not find fish at all because they would suffocate in carbon dioxide!) There would be no liquid water because all of it would be a gas at room temperature. There would be no rivers running to the ocean, no sap in the trees, and no blood!

Hydrogen bonding accounts not only for the fact that water is a liquid but also for the structure of ice. The fact that snowflakes have six-fold symmetry is directly related to the shape of the

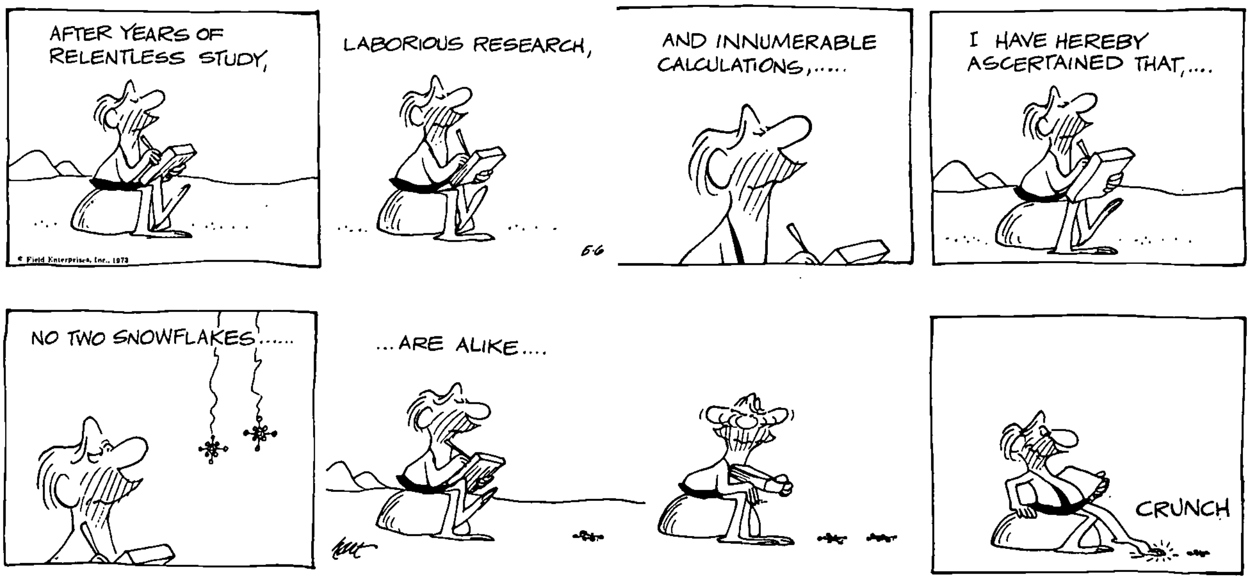


The structure of ice (*above*) is responsible for the iceberg (*below*)—one of the largest forms of floating ice. Also remember that 90% of an iceberg is under water. Why?



water molecule and hydrogen bonding. This geometry also requires that ice have a rather open structure and, unlike most solids, be lighter than the liquid from which it freezes.

The result of the structure of ice is that it is less dense than water; as we all know, ice floats on water. So what? Well, by floating, it provides a protective insulation to fresh water lakes. If the ice sank, not only would more form, but it would probably not all melt the next summer since it would be at the bottom. It is possible that all of our northern lakes would freeze solid, destroying all life. The geometry of molecules is worth thinking about!



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PROBLEM

The fact that ice floats is related to the fact that you have to put antifreeze in your car's radiator in winter. What is the connection? Think twice about this one!

The two snowflake cartoons, though meant to be humorous, *do* illustrate how a scientist can approach a subject such as snowflakes. Which do you think is the scientific way?

I-25 Some Important Molecules

We have seen that two compounds important to life (water and carbon dioxide) form from nonmetallic elements. Remember, too, that we have referred to ammonia (NH_3). Ammonia is an extremely important industrial chemical. It is used as the starting material

TIME MACHINE

1908	Henry Ford produces the first of the Model T automobiles.
1905–1909	**Fritz Haber finds a method for synthesizing ammonia from nitrogen and hydrogen.**
1910	Rayon is first commercially produced in the U.S.
1911	First Indianapolis 500 is run.
1912	Girl Scouts of America organized in Savannah, Georgia.
1913	**Carl Bosch develops Haber's method into a feasible commercial synthesis of ammonia. Later Haber directs the conversion of ammonia into wartime explosives for Germany.**
1914	World War I begins.
1915	Edgar Lee Masters publishes *A Spoon River Anthology.*
1918	World War I ends.
1919	**Fritz Haber receives the Nobel Prize for chemistry.**
1976	Annual U.S. production of ammonia by means of the Haber-Bosch process exceeds sixteen million tons, most of which is used to increase the world's food supply.

for a wide variety of nitrogen compounds. It is also important biologically as a part of the nitrogen cycle—a cycle that makes it possible for plants to obtain nitrogen from the air for their use.

Industrially, ammonia is synthesized by the Haber process. *Synthesis* is the preparation of a compound from simpler materials. After Fritz Haber, a German chemist, developed the process, it was used commercially to produce nitrogen compounds for fertilizer; but it soon became even more important in making explosives for Germany's army in World War I. The Haber process is a method of making ammonia directly from the elements nitrogen and hydrogen. Nitrogen is obtained from the air and hydrogen is obtained from water or other sources. The reaction is as follows:

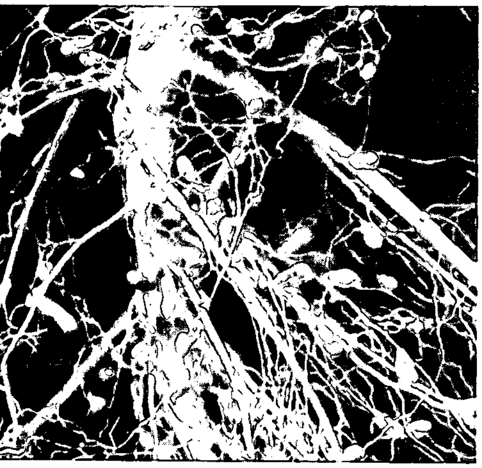
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

If we were to mix hydrogen and nitrogen gas in the laboratory, you would find that your mixture does not form ammonia (which is the main reason that the experiment is not included here!). In order to make this reaction take place, it is necessary to heat the gases to a rather high temperature and to compress them strongly. In his first successful laboratory synthesis, Haber carried out the reaction at red heat and at several hundred atmospheres of pressure. (Obviously, we can't include this experiment here either.)

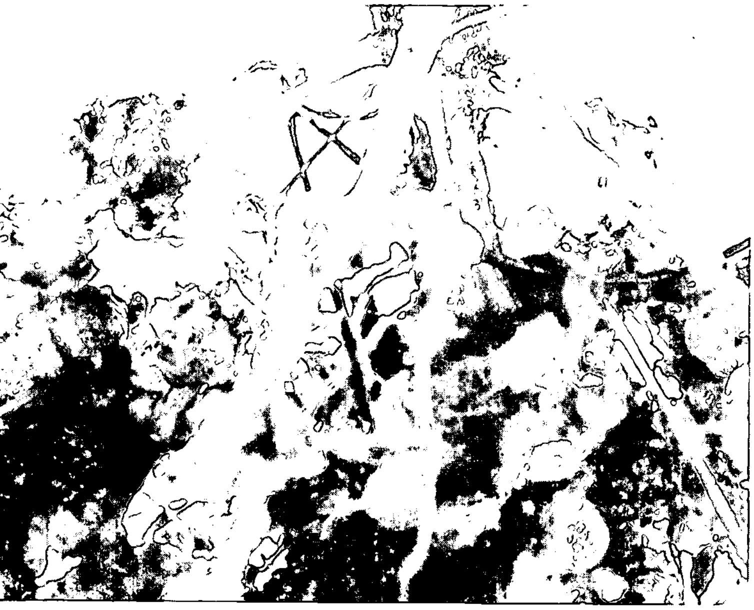
The reaction in Haber's experiment occurred slowly. Such a reaction occurs so slowly, in fact, that it would be impractical to make ammonia in this way. But Haber discovered a catalyst which allows the reaction to take place readily under conditions that can be achieved in a modern chemical laboratory. The discovery of the catalyst is the significant part of his experiment. A *catalyst* is a material that makes a reaction take place faster and/or at a lower temperature but otherwise doesn't change the reaction. Often a catalyst can be recovered from a reaction mixture unchanged.

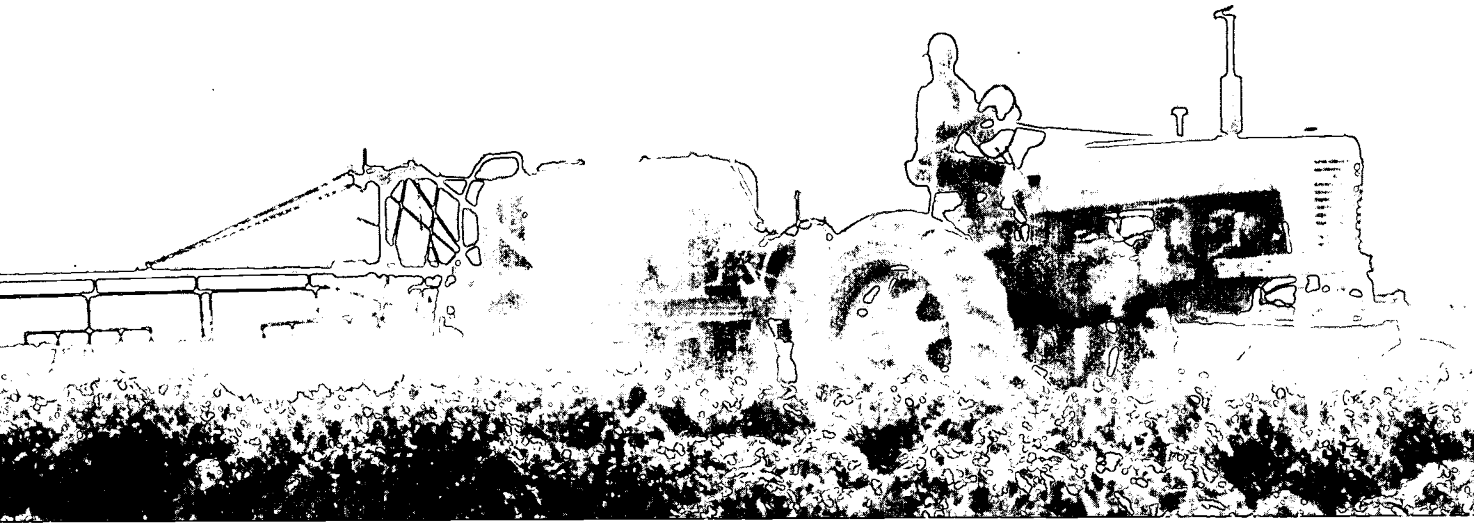
The best industrial catalyst for the Haber process is pure iron, with some potassium aluminate added. With the catalyst, it is still necessary to heat the hydrogen-nitrogen mixture to about 500°C and to apply about 200 atmospheres of pressure. Other catalysts are more efficient. Certain bacteria living in the nodules on the roots of legumes (peas, clover, alfalfa) can synthesize ammonia. The bacteria can do this at room temperature and at ordinary atmospheric pressure. (See *Form and Function: An Organic Chemistry Module.*)

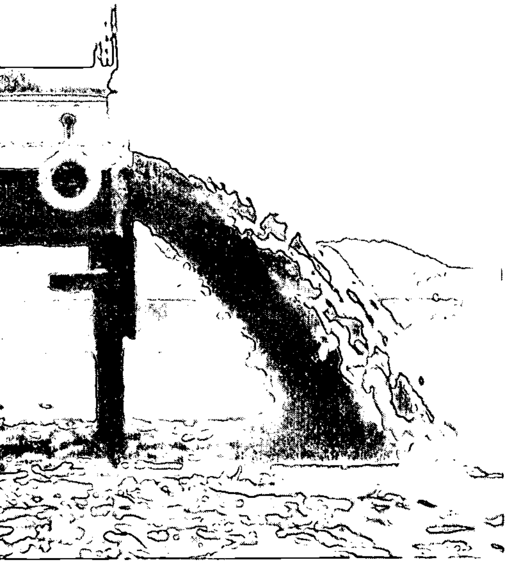
An *enzyme* is a catalyst operating in a biological system, enabling important life processes to take place at or near room temperature. (See *Molecules in Living Systems: A Biochemistry Module.*) We do not know much about the enzyme in bacteria that provides a catalyst for the synthesis of ammonia. We do know, however, that



Legumes, a system of biological catalysts, help provide necessary nitrogen to the soil. Clover (*above*) and peas (*top left*) are both nitrogen-producing plants. The nitrogen-fixating nodules can be seen on the root system of clover (*left*) and soybeans (*bottom left*). Cutting open one of the nodules exposes the nitrogen-fixing bacteria (*bottom right*).







the enzyme contains two metals: iron and molybdenum. Chemists are currently studying these systems, not only to understand the processes occurring in living organisms but also to develop, hopefully, better methods for synthesis in laboratory and factory.

A second nonmetallic compound of great importance is sulfuric acid (H_2SO_4). Because it is the cheapest and most versatile of acids, it is widely used in industry wherever an acid is needed (see the next section for the definition of acids and bases and some applications). It may be synthesized readily from sulfur:

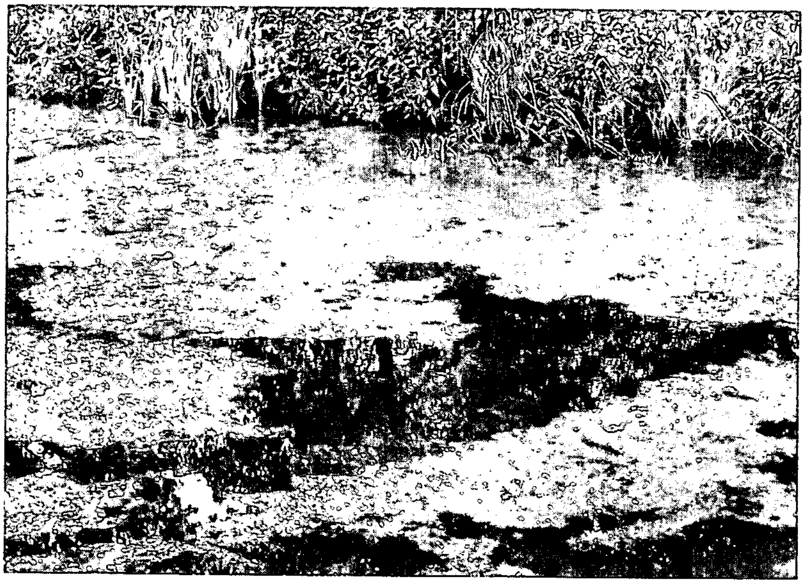
$$S + O_2 \longrightarrow SO_2$$
$$2SO_2 + O_2 \longrightarrow 2SO_3$$

The first reaction takes place readily if sulfur is burned in air. Once the sulfur dioxide is formed, it is not easily oxidized further to form sulfur trioxide. Again, the use of a catalyst makes the reaction take place under reasonable conditions and allows the synthesis of sulfur trioxide. The catalyst may be either vanadium pentoxide or platinum. Sulfur trioxide is then combined with water to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Another important nonmetallic compound is phosphoric acid (H_3PO_4). Industries use phosphoric acid to make fertilizers and detergent mixtures. Phosphates in detergent mixtures improve their cleaning action in areas where there is hard water (see *I-34*, *I-35*, and *I-36*).

From an ecological standpoint, detergents and fertilizers may be a problem. Detergents and fertilizers drain into lakes and streams. Algae can feed upon the phosphates in the detergents



and fertilizers. If algae grow and multiply, eventually massive colonies form on the surface of a lake or stream. The algae may die, rot, and consume oxygen which fish must have to live. Soon the algae become a pollutant, clogging waterways and threatening the lives of fish. Any large-scale addition of a nutrient such as phosphate to our waterways is a potential source of trouble.

Environmental problems such as those caused by detergents which contain phosphates are not easy to solve. Manufacturers now are producing detergents which contain no phosphates; but some critics contend that the phosphate-free detergents are likewise undesirable because the substitute chemicals that they contain are hazardous. The relationship of chemistry to the environment is discussed in greater detail in *The Delicate Balance: An Energy and the Environment Chemistry Module.*

PROBLEMS

1. Consider each of the elements H, Na, S, O, N, Cl, and Fe. Classify each as a metal or a nonmetal.
2. What will be the formulas of compounds between: (a) H and O; (b) H and N; (c) Na and Cl; (d) H, S, and O; (e) H and Cl?
3. Classify each of the compounds in problem 2 as ionic or covalent. If the compound is ionic, draw a portion of the lattice. If the compound is covalent, draw the structure of the molecule.
4. Choose two of the compounds in problem 2 and discuss their importance chemically.

Acids and Bases

There is a large group of compounds called *acids*, but not all acids are inorganic. Many are organic. Another large group of compounds consists of bases. A *base* (sometimes called an *alkali*) can be looked upon as the opposite of an acid. Acids and bases enter into many chemical reactions, and the chemist has long been interested in their behavior. We, too, will investigate acid-base reactions, but, first, what are acids and bases, and how are they different from other chemical compounds?

I-26 Getting Down to Basics (and Acidics)

The classical definition of an acid is that it is a substance that is sour. A lemon contains citric acid, and a lemon is sour. Milk can be sour. Sour milk contains lactic acid. Vinegar is sour, and it contains acetic acid. We could list many other examples of acid-containing substances that are sour.

But a chemist needs a better way to find out if a substance is an acid than by merely determining if it is sour. A chemist who goes around tasting unknown liquids may not have a long career! More commonly, the chemist uses dyes called *indicators* to identify a substance as an acid or a base. Litmus is a common indicator. An acid turns litmus paper red; a base turns litmus paper blue. Another indicator is phenolphthalein, which is colorless when exposed to an acid but which turns red when combined with a base.

INDICATOR COLORS

Indicator	Acid	Base
bromthymol blue	yellow	blue
litmus	red	blue
methyl violet	yellow	blue
methyl yellow	red	yellow
methyl orange	red	yellow
methyl red	red	yellow
phenol red	yellow	red
phenolphthalein	colorless	red
bromcresol green	yellow	blue

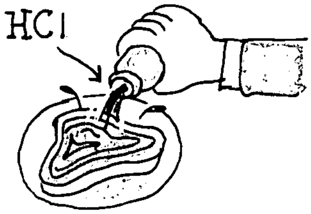
An indicator can be helpful to a chemist when he seeks to identify a substance as an acid or a base. But the indicator itself is not a definition. *What is an acid?* To define an acid, the chemist has observed the behavior of an acid when it dissolves in water. On the basis of his observation, the chemist defines an acid in this way: *An acid is a substance that donates hydrogen ions to water in solution to form the hydronium ion* (H_3O^+). Hydronium ions are formed when an acid dissolves in water. Thus, we have the following:

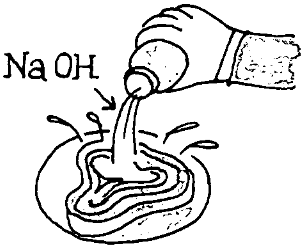
Hydrochloric acid: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$
Acetic acid: $CH_3COOH + H_2O \longrightarrow H_3O^+ + CH_3COO^-$
Sulfuric acid: $H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$

All acids form the same hydronium ion (H_3O^+) in water solutions. Every acid forms a characteristic anion (a negative ion, remember) that is simply the starting molecule from which a hydrogen ion has been removed. The term *hydrogen ion* and the symbol H^+ are often used in reference to acids. A hydronium ion is simply a hydrogen ion attached to a water molecule:

$$H^+ + H_2O \longrightarrow H_3O^+$$

As we have noted, the opposite of an acid is a *base*, or an *alkali*. A base may be characterized as having a bitter taste (with the same tasting difficulties we noted earlier for acids) or in terms of the color changes that it produces with indicators. But as he defined an acid, a chemist bases his practical definition of a base on the way it reacts in a water solution. The chemist's definition states the following: *A base is a substance that accepts hydrogen ions.* The hydroxide ion (OH^-), for example, can accept a hydrogen ion (H^+) to form water. The OH^- ion is a characteristic base used in water.





Bases may produce the hydroxide ion in solution in two ways. In one method, hydroxide ions are released when compounds known as *hydroxides* dissolve in water. An example of such a compound is sodium hydroxide (NaOH). Sodium hydroxide is an ionic compound similar to the ionic compounds discussed in section *I-17 Getting a Charge.* Sodium hydroxide consists of an equal number of sodium ions (Na^+) and hydroxide ions (OH^-). When dissolved in water, sodium hydroxide releases hydroxide ions and forms a basic solution:

$$Na^+OH^- \xrightarrow{\text{dissolve in water}} Na^+ + OH^-$$

A second method for forming basic solutions is the reverse of the process for forming acidic solutions. Acidic solutions form when the solute donates a hydrogen ion to a water molecule. Basic solutions form when *the solute removes a hydrogen ion from a water molecule.* If a hydrogen ion is removed from a water molecule, a hydroxide ion must be left:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

Ammonia (NH_3) is a base because it removes a hydrogen ion from a water molecule, leaving behind a hydroxide ion. This is why a solution of ammonia (NH_3) in water, household ammonia, is sometimes called ammonium hydroxide.

In some ways acids and bases are similar. For example, each forms a characteristic ion in solution (H_3O^+, acid; OH^-, base). In other ways they are different. For example, they have different effects on indicators. Further, it can easily be shown that acids and bases are antagonistic toward each other. For example, if you add some litmus to a test tube containing acetic acid, the solution will turn red. If you add sodium hydroxide to the same test tube, eventually the solution will turn blue. The color change can be reversed if more acetic acid is added, and so on.

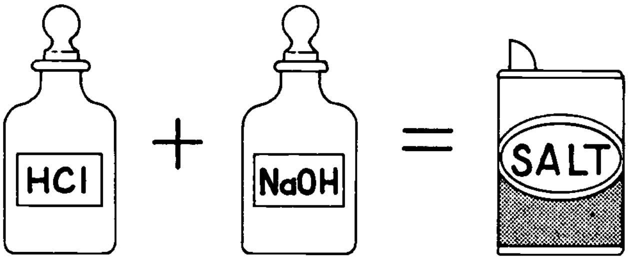
At any one time a solution can be either acidic or basic, depending on whether more acid or more base has been added. This is because the hydronium ions formed by the acid and the hydroxide ions formed by the base react with each other:

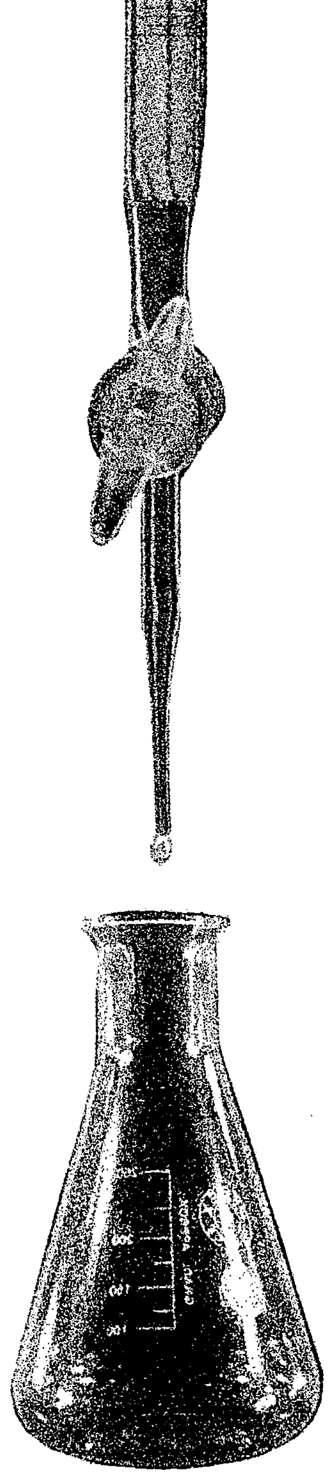
$$\begin{array}{l} H_3O^+ + OH^- \longrightarrow 2H_2O \\ \text{acid + base} \longrightarrow \text{water} \end{array}$$

This reaction, called a *neutralization reaction,* is another characteristic of acids and bases: *Acids and bases react with each other to neutralize the properties of both.* In addition to the water formed upon neutralization, the other ions present from the original acid and the original base are left to form a salt. For example, a solution of hydrochloric acid contains hydronium ions and chloride ions. A solution of sodium hydroxide contains sodium ions and hydroxide ions. When the two solutions neutralize each other, the hydronium ions and the hydroxide ions combine to form water leaving sodium ions and chloride ions behind to form NaCl.

$$(H_3O^+ + OH^- \longrightarrow 2H_2O)$$

If this is done carefully so that the number of moles of acid is exactly equal to the number of moles of base, the solution is exactly the same as one made by dissolving sodium chloride in water. (As you may recall, moles were first discussed in *Reactions and Reason: An Introductory Chemistry Module.*) Here we have an example of the amazing properties of neutralization reactions. You can take a corrosive, irritating solution of hydrochloric acid and add to it an equally corrosive, caustic, and poisonous solution of sodium hydroxide (household lye) to form the relatively harmless solution of sodium chloride, salt water!





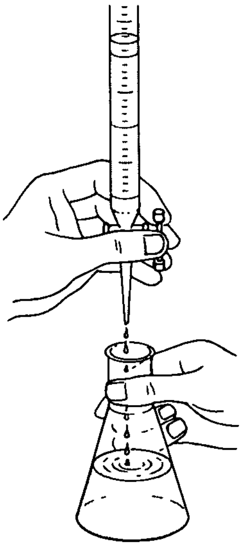
Neutralization reactions are quantitative because one hydroxide ion reacts with one hydronium ion to yield the products of the reaction. This makes it relatively simple to analyze a solution and determine how much acid or base is present. To find out how much acid there is in a sample, you need only to obtain an indicator and a base of known concentration (called a *standard solution*). Adding measured amounts of one solution to another solution until the indicator just changes color (a change called the *end point*) is known as *titration*. Titration is often used to determine the amount of acid or base in a sample.

Have you ever stopped to realize that many of the common materials in your home are acids and bases? Are you aware that reactions with such chemicals go on daily in the kitchen, in the bathroom, and in the laundry room? In the following experiment, you will use standard solutions of hydrochloric acid and sodium hydroxide to analyze some of these household substances.

I-27 Household Acids and Bases

EXPERIMENT

In this experiment the end point of the titration will be signaled by a change in color of an indicator, phenolphthalein. This indicator is red in basic solutions. It is colorless in acids.



If you are careful, you can identify the end point accurately by adding the titrant (the liquid from the buret) until the indicator just changes color by the addition of a single drop of the titrant from the buret. If you add too much titrant and overshoot the end point, throw out the sample and start over, proceeding more slowly as you approach the end point.

The figure shows how to use a buret properly. If you are right-handed, manipulate the stopcock with your left hand. Your right hand then is free to swirl the contents of the flask and to mix the contents. If you are left-handed, reverse the procedure.

Part 1: Acetic Acid in Vinegar. Household vinegar is a dilute solution of acetic acid made by the bacterial oxidation of ethanol in cider from apples or from synthetic acetic acid. Mark two Erlenmeyer flasks 1 and 2. Weigh each flask and record its mass. Next, measure 20 cm³ vinegar in your graduated cylinder. Pour this vinegar into flask 1. Repeat with flask 2. Weigh the flasks containing the vinegar and record the masses. Add 2 drops of phenolphthalein indicator to each flask. Titrate the contents of each flask with 1.00 M sodium hydroxide (NaOH) solution until the contents of the flasks barely turn pink. Record the volume of sodium hydroxide (NaOH) used for each titration.

Answer the questions on masses, volumes, moles, and percent composition on a worksheet similar to the sample provided in the margin. Compare your results with the information that appears on the vinegar-bottle label. Suggest sources of experimental error or reasons for differences in results.

Part 2: Acid Household Cleaners. Many household cleaners contain hydrochloric acid (HCl) or sodium hydrogen sulfate ($NaHSO_4$, "sodium bisulfate"). The acids dissolve rust and some hard-water deposits. Choose a household cleaner that contains acid. Determine the amount of acid that the cleaner contains.

Proceed as in *Part 1*. If your cleaner is a solid, put about 5 g of the solid in a weighed flask. Determine the amount of cleaner by a second weighing. Record. If your cleaner is a liquid, measure out about 10 cm³ in your graduated cylinder. (Why is the exact amount not important?) Pour the cleaner into a weighed flask. Weigh a second time. Record.

Add 25 cm³ distilled water. If your sample "fizzes," wait a few moments before proceeding. Titrate in the same manner as in *Part 1*, stopping the titration when the solution just turns pink. Calculate in cubic centimeters (cm³), liters, and moles (mol) the amount of sodium hydroxide (NaOH) needed to neutralize the cleaner. Both hydrochloric acid (HCl) and sodium

SAMPLE WORKSHEET

Acid household cleaner

Name of cleaner ____________

Acid contained ____________

Molecular mass ____________

	#1	#2
1. Mass of flask plus cleaner	___	___
2. Mass of empty flask	___	___
3. Mass of cleaner	___	___
4. cm³NaOH to titrate cleaner	___	___
5. Liters of NaOH	___	___
6. Moles of NaOH used	___	___
7. Moles of acid in cleaner	___	___
8. Mass of acid in cleaner	___	___
9. Percent acid in cleaner	___	___

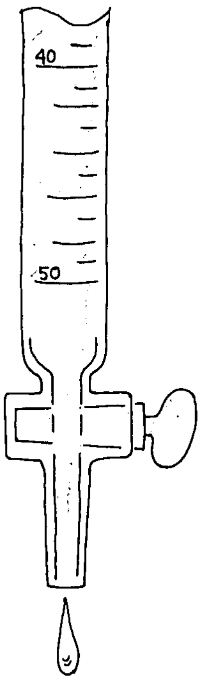
10. Manufacturer's claim ______

hydrogen sulfate ($NaHSO_4$) require one mole of sodium hydroxide to neutralize one mole of acid:

HCl + $NaOH$ ⟶ $NaCl$ + H_2O
hydrochloric acid + sodium hydroxide ⟶ sodium chloride + water

$NaHSO_4$ + $NaOH$ ⟶ Na_2SO_4 + H_2O
sodium hydrogen sulfate + sodium hydroxide ⟶ sodium sulfate + water

Check the label on the original container to determine which acid you have in your cleaner. Proceed with the calculation as in *Part 1* to determine the amount of the acid in the cleaner in moles, by mass, and in percent. After completing the experiment, check the percent acid as indicated by the manufacturer. Suggest sources of experimental error or reasons for differences in results.



A CHEMICAL DROP-OUT!

Part 3: Basic Household Cleaners. Many household cleaners contain compounds such as ammonia (NH_3) and sodium hydroxide ($NaOH$). Such compounds help to loosen grease and dirt. Ammonia and sodium hydroxide are bases. Choose a household cleaner known to contain a base. Determine the amount of base it contains.

Proceed as in *Part 1*. If your cleaner is a solid, measure out a portion into a weighed flask. Determine the amount of cleaner by a second weighing. If your cleaner is a liquid, measure out about 2 cm^3 in your graduated cylinder and pour into your weighed flask. (Why is the exact amount not important?) Weigh.

Add 25 cm^3 distilled water. If your cleaner was solid Drano, the aluminum present will react. Place the flasks in the hood until the reaction stops. Proceed with the titration as in *Part 1* except that the contents of the flask will be initially basic (red with phenolphthalein) and will turn colorless when the end point is reached by titration with hydrochloric acid. This end point is somewhat harder to obtain accurately than the other way around, so titrate carefully.

When one drop of hydrochloric acid from your buret removes the last pink color, record your volume of 1.00 M hydrochloric acid used. Complete your calculation of the cubic centimeters, liters, and moles of hydrochloric acid (HCl) used, as outlined in the worksheet. Both ammonia (NH_3) and sodium hydroxide ($NaOH$) require one mole of hydrochloric acid to neutralize one mole of base:

NH_3 + HCl ⟶ NH_4Cl
ammonia + hydrochloric acid ⟶ ammonium chloride

$NaOH$ + HCl ⟶ $NaCl$ + H_2O
sodium hydroxide + hydrochloric acid ⟶ sodium chloride + water

Now determine which base you have in your cleaner. Proceed with the calculation as in *Part 1*. Record the percent base as indicated by the manufacturer and compare your results. Suggest sources of experimental error or reasons for differences in results.

PROBLEMS

1. 5.14 g of a household cleaner containing hydrochloric acid requires 16.5 cm^3 of 1.0 M sodium hydroxide solution to neutralize. What is the percent of HCl in the cleaner? Be sure to write out the balanced equation for this reaction.

2. One of the reasons that acids are used in household cleaners is to dissolve "rust" stains from hard water containing iron. These stains may contain $Fe(OH)_3$. Write a balanced equation for the reaction of $Fe(OH)_3$ with HCl.

I-28 Acids and Bases Go to Work

Strong acids and bases are present in household products because of their powerful chemical action. Acids dissolve many substances, including metal oxides and deposits from hard water. Cleaners containing acids often are used to clean bathroom fixtures. The acids readily remove rust stains (iron oxide).

Bases act upon organic materials (including your hands, if you're sloppy!). Strong bases dissolve proteins such as hair. Bases combine with fatty substances such as cooking grease to produce soap (see *Form and Function: An Organic Chemistry Module*). Naturally, such strong materials should be handled in the home with at least as much caution as normally exercised in the chemistry laboratory, a point often not sufficiently emphasized on the label.

Acids and bases are widely used in industry. Acids are used in metallurgy, in the preparation of compounds of metals, and to dissolve metal oxides in cleaning. Acids sometimes act as catalysts in useful chemical reactions. More sulfuric acid is produced each year than any other chemical. It is used to manufacture superphosphate fertilizers and other organic and inorganic chemicals. Bases are used in large amounts in the manufacture of soaps and detergents. In addition, bases are used to neutralize acids and to form salts.

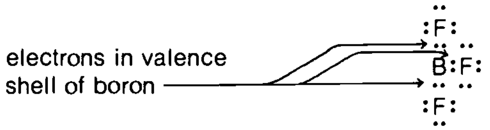
I-29 What's in a Name?

Our definitions for acids and bases (the production of H_3O^+ and OH^- in water) are simple and straightforward. These definitions, however, can be applied only to reactions taking place in water. Chemists do not always use water as a solvent because water is not always suitable. For example, many substances are not soluble in water. This problem is often encountered in organic chemistry. Instead of water, solvents such as benzene or carbon tetrachloride are used in many organic reactions.

Inorganic chemists also may occasionally have to use a solvent other than water. A substance that the inorganic chemist is investigating may not dissolve in water. Or in some instances, an inorganic compound may become troublesome in an experiment because it reacts so rapidly with water. If water is present, it may not be possible to get the substance to react with another compound in the mixture because the substance under investigation may react immediately with water and be ruined for further use.

There have been several attempts to formulate an adequate definition of acids and bases for use in systems where water, hydronium ions, and hydroxide ions are absent. Almost all of them have a certain usefulness, but we will consider only the most commonly used today. It is called the *Lewis definition*, after the great American chemist, G. N. Lewis. The Lewis definition can be easily summarized as follows: *An acid is any chemical species that lacks a complete octet and that may accept a pair of electrons from another molecule, the base, to complete its octet.*

Not all molecules, remember, obey the octet rule. For example, boron trifluoride (BF_3) forms from one boron atom (three valence electrons, a valence of three) and three fluorine atoms (seven valence electrons, a valence of one). The arrangement of electrons in the molecule is as follows:



Note that there are only six electrons around the boron atom. This molecule has not achieved its octet and therefore seeks more electrons. If a molecule such as ammonia is available, the boron atom will readily accept (share) the formerly nonbonding pair of electrons on the ammonia molecule to form a new bond:

$$H_3N: \quad + \quad BF_3 \longrightarrow H_3N:BF_3$$

nonbonding pair — need for electron pair — new bond

TIME MACHINE

1916	**Gilbert N. Lewis suggests octet rule.**
1917	The Trans-Siberian Railroad is completed.
1918	The "war to end all wars" comes to a close with the Armistice of November 1918.
1919	Famous pianist Ignace Paderewski becomes first premier of free Poland.
1919	Broadcasting is launched as an entertainment medium when British radio transmitter begins daily music programs.
1920	Sinclair Lewis publishes *Main Street.*
1921	Charlie Chaplin stars in his first feature film, *The Kid.*
1922	Pablo Picasso paints *The Three Musicians.*
1923	**Gilbert N. Lewis develops his definition of acids and bases.**

According to the Lewis system, bases are molecules or ions that have a pair of electrons that can be shared with a Lewis acid that has an incomplete octet.

The Lewis definition is most useful in accounting for a reaction such as that between ammonia and boron trifluoride and those reactions in which coordination compounds are formed (see next section). In the latter case, the compounds form between metal ions that need to accept electron pairs and Lewis bases that have electron pairs to donate.

PROBLEMS

1. Classify each of the following compounds as an acid or a base: $NaOH$, NH_3HCl, H_2SO_4, KOH, BCl_3.
2. Balance the following equations:

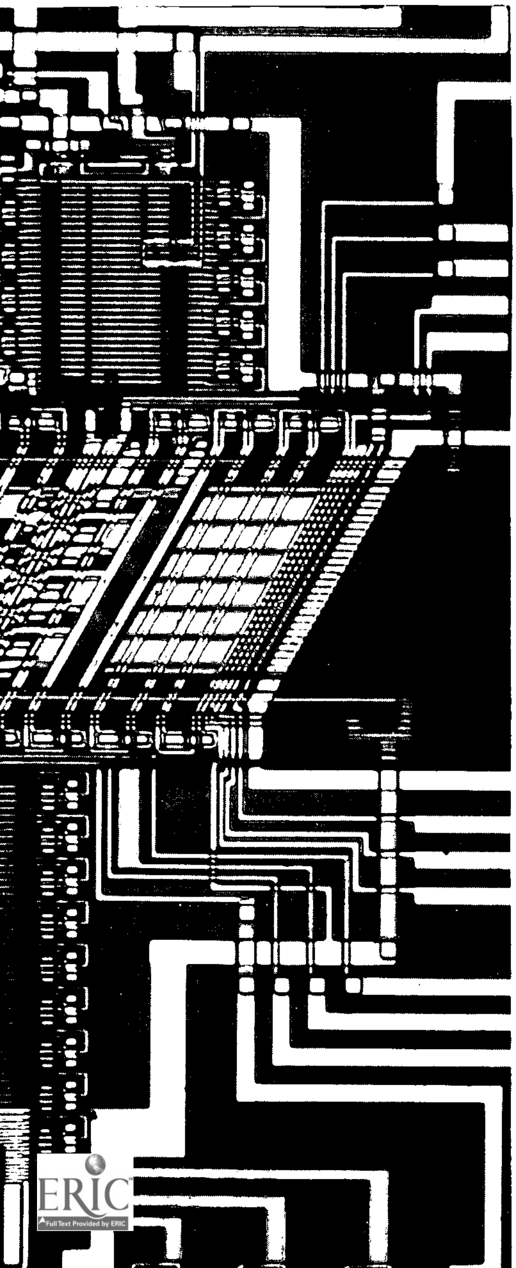
$$NaOH + H_2SO_4 \longrightarrow$$

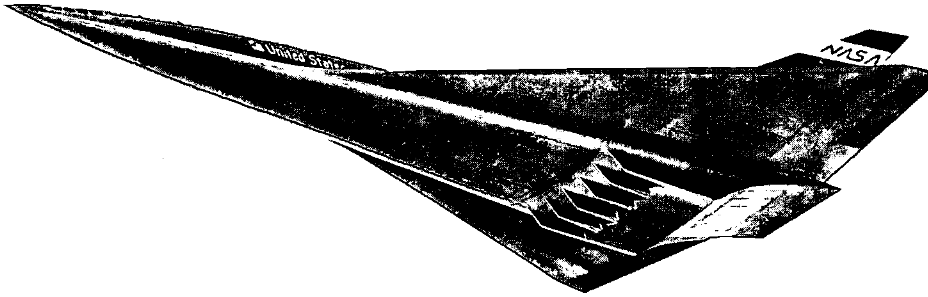
$$HCl + Al(OH)_3 \longrightarrow$$

$$H_3PO_4 + NH_3 \longrightarrow$$

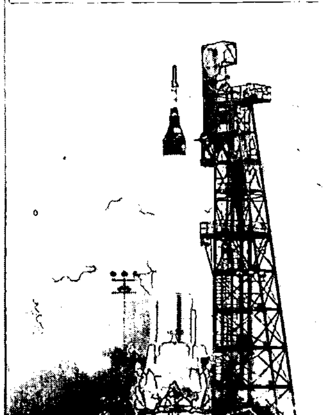
Chemistry of the Transition Elements

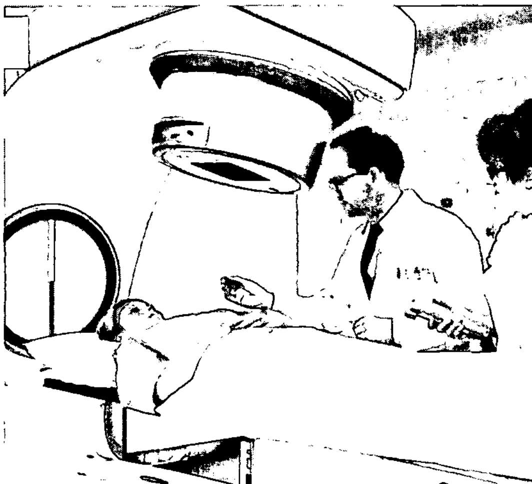
The elements with atomic numbers 21 through 30, 39 through 48, and 57 through 80 are called *transition metals*. In many ways these elements show properties intermediate between the metals and nonmetals. In some ways they are like nonmetals, but still, they are metals. The transition elements have the basic properties of metals, not those of nonmetals.





45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30
88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybd'm 42	(97) **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48
138.9 **La*** Lanthanum 57	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.8 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80





Iron crystal, highly oxidized—magnified over 2000 times by the electron microscope (*top*). Zinc oxide provides another interesting pattern under the electron microscope, magnified 1250 times (*below*).

I-30 You Can't Lose for Winning

The fundamental reactions of the transition elements are similar to those of the "typical" representative metals such as sodium and calcium. All the transition metals tend to lose electrons to nonmetals and form positive ions. In general, however, these metals are somewhat more reluctant to lose electrons and the loss is somewhat more complicated. For example, sodium *always* loses just one electron to form the +1 sodium ion. In contrast, copper can lose one or two electrons to form Cu^+ or Cu^{2+}. Sodium is a representative metal, and copper is a transition metal. Iron, a transition metal, can lose two electrons to form Fe^{2+}, but it can also lose a total of three electrons to form Fe^{3+}.

Chemists cannot easily predict how many electrons a transition metal will lose. As a rule of thumb, you can say that all transition metals will form a +2 ion. Usually they will also be capable of forming another stable ion (M^{n+}) where n might be 1, 3, or 4. It may be necessary to memorize this second ion because there are no simple rules for predicting it.

Before going further with a discussion of the possible ions formed by transition metals, let us first consider what is meant by *oxidation* and *reduction*. The term *reduction* comes from the days when almost all the chemistry known was related to the winning of metals from their ores. These ores were considered to be complex substances that, when treated with the proper materials, could be "reduced" to simple metals. Hence, the conversion of a metal salt to the pure metal was called *reduction*.

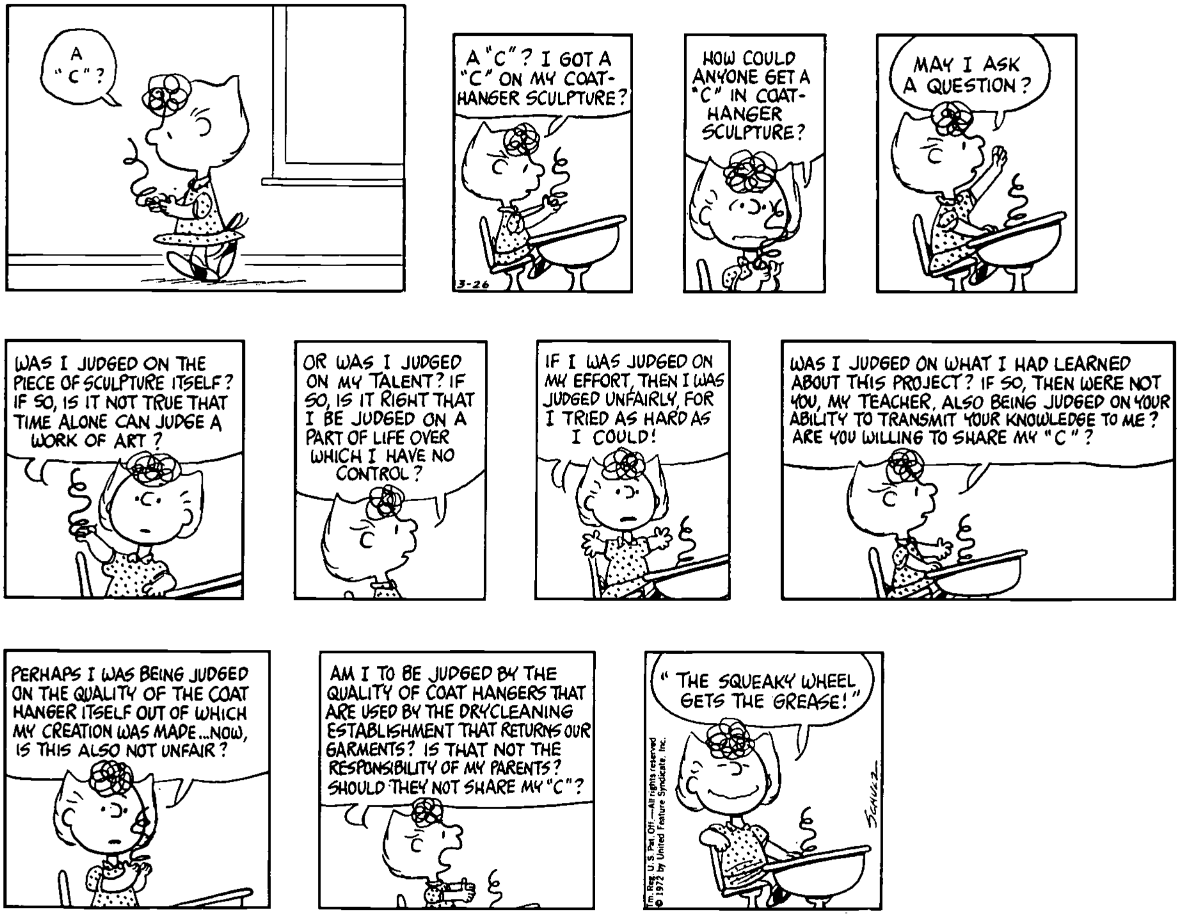
The term *oxidation* comes from the first reaction of metals that was understood, the oxidation of the metal by oxygen in the air: metal (Fe) + oxygen (O_2) = metal oxide (rust). The metal, iron, was "oxide-ized," or oxidized. Chemists soon recognized the similarity between the reactions in which a metal combines with oxygen to form an oxide, with sulfur to form a sulfide, or with a halogen to form a halide. So they decided to include all of these reactions under the term *oxidation*, just as the formation of the metal from a compound is reduction, no matter what compound is used as the starting material.

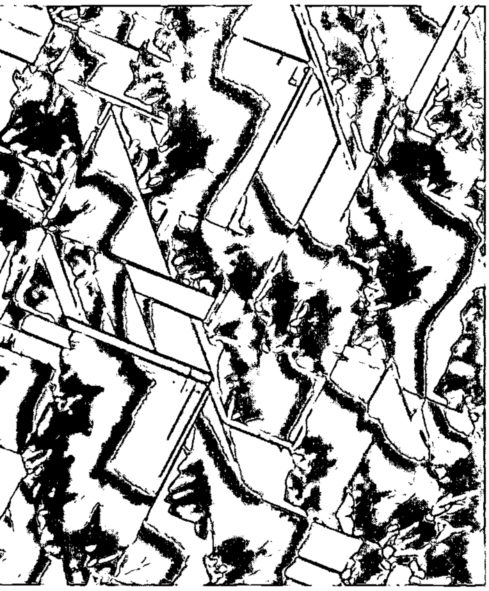
Before extending the concepts of oxidation and reduction to other metals, let's review the reaction of sodium with fluorine. The sodium atom loses an electron that the fluorine atom accepts. The sodium changes from a pure metal to an ion in a compound. It has therefore been oxidized, in the broad sense of the word. Now if the resultant sodium fluoride (NaF) is converted back to the original elements, the sodium is reduced. The electron must be taken away from the fluoride ion and given back to the sodium ion (which is difficult to do—the tendency is for the reaction to go the other way).

It is this transfer of electrons that can be looked upon as the basis for the modern definition of oxidation and reduction. The sodium atom was oxidized when it lost an electron; so *oxidation* is defined as the loss of electrons. The sodium ion (Na^+) was reduced when it accepted the electron back again; so *reduction* is defined as the gain of electrons. The entire process is called the *red*uction-*ox*idation behavior of sodium or *redox*, for short. Redox reactions always involve the gain or loss of electrons from one atom (or molecule) to another.

The redox behavior of the representative metals is fairly simple: a sodium atom can lose *one* electron; a sodium ion can gain *one* electron. A calcium atom can lose *two* electrons; a calcium ion can gain *two* electrons. Three electrons are always involved in reactions of aluminum. It can be said that these metals have only one positive *oxidation state* each: sodium (+1), calcium (+2), and aluminum (+3). The oxidation state of a metal is exactly what the name implies, the *state of oxidation of the element*, that is, the number of electrons it has lost.

Rusting is quite evident on this piece of ornamental iron (exact size).





A single crystal of oxidized tantalum as seen under the electron microscope produces another beautiful pattern by a transition element, magnified 700 times (*top*). The strange outer-space shape (*bottom*) is that of an oxide whisker grown on steel, magnified 3 times.

Transition metals have more than one oxidation state. Almost all have a +2 oxidation state; but in addition, they may also have a +1, +3, or higher oxidation state. The presence of more than one positive oxidation state allows transition metals to undergo extensive redox chemistry. For example, iron (Fe) can exist in either the +2 (Fe^{2+}) or +3 (Fe^{3+}) form.

In addition to reactions converting the free metal to one of these oxidation states, it is possible to convert from one state to the other:

$$\text{Oxidation: } 2FeO \text{ (contains } Fe^{2+}) + \tfrac{1}{2}O_2 \longrightarrow Fe_2O_3 \text{ (contains } Fe^{3+})$$
$$\text{Reduction: } Fe_2O_3 \text{ (contains } Fe^{3+}) - \tfrac{1}{2}O_2 \longrightarrow 2FeO \text{ (contains } Fe^{2+})$$

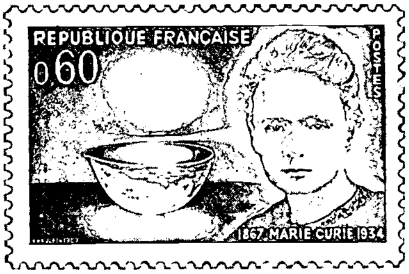
The oxidation state of the iron has changed from +2 to +3, corresponding to the loss of an electron in the first reaction. In the second reaction, the oxidation state has changed from +3 to +2, corresponding to the gain of an electron. The chemist symbolizes this loss or gain by the following:

$$\text{Oxidation: } Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$\text{Reduction: } Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

The electron (e^-) that is lost in the first reaction is picked up by the oxygen or other *oxidizing agent*, and the electron (e^-) that is accepted in the second reaction is furnished by some *reducing agent*. Thus, an oxidizing agent takes electrons away from other atoms; a reducing agent furnishes electrons.

The redox chemistry of the transition metals is extremely important. Many of the interesting reactions of the transition metals depend upon their ability to undergo this type of change. For example, we will see later that an important compound of iron in our bodies is constantly undergoing the type of electron exchange we have discussed. Other examples are the use of metal salts to oxidize or reduce other compounds.

Finally, the important field of electrochemistry is made possible by the redox chemistry of metals, especially transition metals. Electrochemistry includes the study of electroplating, dry cells, and storage batteries. You can further investigate electrochemistry in *Communities of Molecules: A Physical Chemistry Module.*



I-31 Coordination Chemistry! Hold On!

By far the largest area of current interest in inorganic chemistry involves a class of compounds known as *coordination compounds,* or *complexes.* They consist typically of a transition metal in a positive oxidation state and several attached groups known as *ligands.* Metal ion + ligands = coordination compound, or complex. *Ligand* means "something holding on." As we have noted, transition metals in some ways are intermediate between representative metals and the nonmetals. The transition metals resemble

TIME MACHINE

1893	**Alfred Werner begins his research on coordination compounds, developing both theory and synthetic techniques.**
1893	Henry Ford designs his first "gasoline buggy."
1893	Peter Ilyich Tchaikovsky composes his Symphony No. 6 ("Pathetique"), and Anton Dvorak writes his Symphony in E Minor ("From the New World").
1895	Paul Gauguin paints *Two Tahitian Women.*
1903	**Marie Curie discovers the radioactive elements radium and polonium and receives the Nobel Prize.**
1905	Albert Einstein formulates his theory of relativity.
1911	Roald Amundsen is the first explorer to reach the South Pole.
1913	**Alfred Werner becomes the first inorganic chemist ever to win the Nobel Prize.**

other metals by losing electrons, forming positive ions, and having positive oxidation states. On the other hand, they resemble nonmetals in their tendency to form covalent bonds. That is, they act like Lewis acids and accept electron pairs.

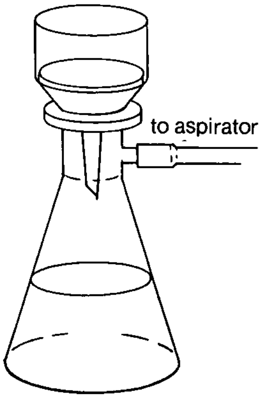
The Lewis bases that furnish the electron pairs are the ligands. Typical ligands are molecules, such as ammonia, that we have seen act as Lewis bases in other reactions. Any molecule that has a lone pair of electrons (most inorganic molecules do) can act as a ligand. Anions can also act as ligands. Typical ligands are water, ammonia, the halide ions, the nitrite ion (NO_2^-), and any molecule that, like ammonia and water, contains a nitrogen atom or an oxygen atom with a lone pair of electrons.

Further discussion of the properties of coordination compounds will be postponed until the following experiment has been completed. The experiment involves the synthesis and examination of a number of coordination compounds. In doing the experiment, the class will be working with several compounds. After everyone in the class has completed the experiment, compare notes on each different compound.

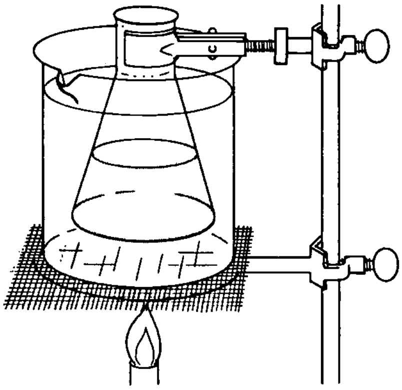
EXPERIMENT

I-32 Get Coordinated!

Study that portion of the experiment that you are assigned to do before you proceed with it. Think about the equipment you will need as well as the chemicals. Check your materials and apparatus. Do you have everything you will need in order to carry out the experiment?



For most inorganic syntheses, the separation of the product on a Büchner funnel is rapid and offers the most convenient method of washing the product. The application of a gentle vacuum by means of the aspirator draws the fluid through the filter. To wash the product on the filter, turn off the vacuum, pour the washing liquid over the crystals, and then turn the vacuum back on again. Often the product may be dried merely by drawing air over the crystals after the last wash.



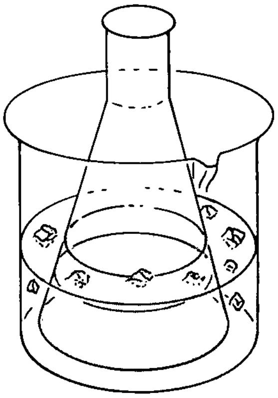
If you need a hot water bath in your experiment, you can make one by using a 600-cm³ beaker as shown here. Make the bath and then start the water heating gently before you proceed to weigh out your chemicals. Thus, you won't have to wait long for it to get hot when you are ready for it.

Part 1: Some Complexes of Copper(II)

A. Tetraamminecopper(II) sulfate:

$$CuSO_4 \cdot 5H_2O + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4 + 5H_2O$$

Weigh 12.5 g of powdered copper sulfate pentahydrate in an Erlenmeyer flask. Add 20 cm^3 concentrated ammonia solution and 12 cm^3 water. Swirl the contents of the flask until all the copper sulfate dissolves. Slowly add 20 cm^3 ethyl alcohol. Mix by swirling, and allow the flask to sit for 10–15 minutes in an ice bath. Then separate the crystals formed by filtering the solution through a Büchner funnel. Wash first with a mixture of 10 cm^3 ethyl alcohol and 10 cm^3 concentrated ammonia (**Caution:** *Add in the hood*), then with 10 cm^3 ethyl alcohol, and finally with 10 cm^3 acetone. **Caution:** *Acetone is flammable. Do not use it near a flame!* Transfer the crystals to a vial. Label the vial with your name and the name of your product. Unless the crystals are completely dry, do not cork. Instead, allow the crystals to stand open to dry until the next laboratory period.



Questions: How does the color of the ammonia complex compare with that of the starting material? Does anyone in class have a different product with a similar color? What do you suppose might happen if you heated this compound? If you added acid?

B. Bis(ethylenediamine)copper(II) sulfate:

$$CuSO_4 \cdot 5H_2O + 2H_2NCH_2CH_2NH_2 \longrightarrow [Cu(H_2NCH_2CH_2NH_2)_2]SO_4 + 5H_2O$$

Weigh 12.5 g powdered copper sulfate pentahydrate in an Erlenmeyer flask. Add 12 cm^3 ethylenediamine and 20 cm^3 water. Swirl the contents of the flask until all the copper sulfate dissolves. Slowly add 20 cm^3 ethyl alcohol. Mix by swirling, and allow the flask to sit for 10–15 minutes in an ice bath. Then separate the crystals formed by filtering the solution through a Büchner funnel. Wash with a mixture of 5 cm^3 ethylenediamine and 10 cm^3 ethyl alcohol, then with 10 cm^3 ethyl alcohol, and finally with 10 cm^3 acetone. **Caution:** *Acetone is flammable. Do not use it near a flame!* Transfer the crystals to a vial. Label the vial with your name and the name of your product. Unless the crystals are completely dry, do not cork. Instead, allow the crystals to stand open to dry until the next laboratory period.

Questions: How does the color of the ethylenediamine complex compare with that of the starting material? Does anyone in class have a different compound that looks like yours?

Part 2: Some Complexes of Cobalt(III)

A. Hexaamminecobalt(III) chloride:

$$2CoCl_2 \cdot 6H_2O + 10NH_3 + H_2O_2 + 2NH_4Cl \longrightarrow 2[Co(NH_3)_6]Cl_3 + 14H_2O$$

Weigh out 10 g ammonium chloride and add it to 20 cm^3 water in a 50-cm^3 beaker. Carefully heat this solution to the boiling point and add 15 g cobalt(II) chloride hexahydrate. Note the color. To a 250-cm^3 Erlenmeyer flask, add 1 g powdered charcoal, and then add the hot solution. Cool by running tap water over the flask. Add 32 cm^3 of concentrated ammonia solution (**Caution:** *Add in the hood*) to the 50-cm^3 beaker to wash out any remaining cobalt solution, and pour this into the Erlenmeyer flask. Chill the flask and its contents in an ice bath, and add 30 cm^3 of 20 percent hydrogen peroxide (H_2O_2) carefully (**Caution:** *H_2O_2 can cause skin burns!*), beginning with 1-cm^3 portions. Clamp your flask in a 60°C water bath. Allow the flask to remain in the bath until the end of the laboratory period. Then turn off the burner and let the preparation sit in the water bath until your next class period.

Continue the experiment by separating the crystals on a Büchner funnel. Transfer the crude product to a beaker containing a hot solution of 125 cm^3 water and 5 cm^3 of 12 M hydrochloric acid. **Caution:** *Handle the concentrated acid with respect!* Heat to the boiling point. When all the compound has dissolved, filter the hot liquid to remove the charcoal. Add 20 cm^3 of 12 M hydrochloric acid (HCl) to the filtrate. Cool the solution in an ice bath while stirring continuously. When the solution is thoroughly chilled, separate the crystals on a Büchner funnel. Wash the product in the funnel with 15 cm^3 of a 60 percent ethyl alcohol–40 percent water mixture, then with 15 cm^3 ethyl alcohol, and finally with 15 cm^3 acetone. **Caution:** *Acetone is flammable. Do not use it near a flame!* Transfer the crystals to a vial. Label the vial with your name and the name of your product. Unless the crystals are completely dry, do not cork. Instead, allow the crystals to stand open to dry until the next laboratory period.

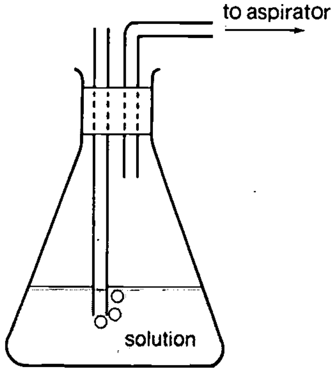
Questions: Compare the color of the finished product with that which you observed when you first dissolved the cobalt chloride and ammonium chloride in water. The latter color is that of the tetrachlorocobaltate ion that forms initially:

$$CoCl_2 + 2NH_4Cl \longrightarrow (NH_4)_2[CoCl_4]$$

This is yet another complex of cobalt, although one that is difficult to isolate in a pure form. How does the oxidation state of the cobalt differ in these two complexes? Look at the colors of some of the products that other members of the class have made. Find a compound that is different from yours but has a similar color.

B. Sodium Hexanitrocobaltate(III):

$Co(NO_3)_2 \cdot 6H_2O + 7NaNO_2 + 2HC_2H_3O_2 \longrightarrow Na_3[Co(NO_2)_6] + 2NaC_2H_3O_2 + 2NaNO_3 + NO + 7H_2O$



Dissolve 30 g of sodium nitrite and 10 g of cobalt(II) nitrate hexahydrate in 30 cm³ hot water. Let the solution cool to 40°C and slowly add, with constant stirring, 10 cm³ of 9 M acetic acid. Pass a current of air through the resulting solution for 15 minutes. Filter off and discard any precipitate. To the clear filtrate, slowly add 50 cm³ ethyl alcohol. Let it stand for 15 to 20 minutes.

Separate the product by filtering the solution through a Büchner funnel. Wash the precipitate with four 5-cm³ portions of ethyl alcohol and then with two 5-cm³ portions of acetone. **Caution:** *Acetone is flammable. Do not use it near a flame!* Transfer the crystals to a vial. Label the vial with your name and the name of your product. Do not cork. Instead, allow the crystals to stand open to dry until the next laboratory period.

Questions: Compare the color of the finished product with that of the cobalt(II) nitrate used as starting material. Look at the colors of some of the products that other members of the class have made. Find a compound that is different from yours but has a similar color.

Part 3: Some complexes of the ligand acetylacetone

A. Cobalt(III) acetylacetonate; [Tris(2,4-pentanedionato)-cobalt(III)]:

$2CoCO_3 + 6CH_3C(O)CH_2C(O)CH_3 + H_2O_2 \longrightarrow 2Co[CH_3C(O)CHC(O)CH_3]_3 + 2CO_2 + 3H_2O$

Add 2.5 g of cobalt(II) carbonate and 20 cm³ of acetylacetone ($CH_3C(O)CH_2C(O)CH_3$) to a 125-cm³ Erlenmeyer flask. Place the flask on a steam bath or immerse in a water bath, as shown in *Part 1*, and heat the water almost to boiling. Add 30 cm³ of 10 percent hydrogen peroxide (H_2O_2)—*a few drops at a time*. The reaction is vigorous at first, and the evolution of carbon dioxide can cause frothing if the reaction is allowed to proceed too rapidly. Toward the end of the reaction the rate can be increased somewhat, but it should take about 15–20 minutes to add all the hydrogen peroxide. Allow the solution to cool and chill in an ice bath.

Separate the crystals on a Büchner funnel. Transfer the crystals to a vial, and label with your name and that of your compound. If possible, dry your product overnight in an oven at 100°C before capping the vial.

Questions: What is the color of your product? Carbon dioxide (CO_2) is evolved by carbonates when they are treated with an acid. What is the acid in this experiment?

B. Chromium(III) acetylacetonate; [Tris(2,4-pentanedionato)-chromium(III)]:

$$CrCl_3 + 3CH_3C(O)CH_2C(O)CH_3 + 3NH_3 \longrightarrow Cr[CH_3C(O)CHC(O)CH_3]_3 + 3NH_4Cl$$

Dissolve 2.7 g of chromium(III) chloride hexahydrate in 100 cm^3 of water in a 250-cm^3 beaker. After all the chromium chloride has dissolved, add 20 g of urea and 6 cm^3 of acetylacetone [$CH_3C(O)CH_2C(O)CH_3$]. Cover the beaker with a watch glass and leave it on a steam bath overnight.

Resume the experiment by separating the platelike crystals on a Büchner funnel. Transfer them to a vial labeled with your name and that of your compound.

Questions: What is the color of your product? The function of the urea is to act as a source of ammonia: $OC(NH_2)_2 + H_2O \longrightarrow 2\ NH_3 + CO_2$. What do you suppose the ammonia does? (Compare the function of the ammonia here to that of carbonate in the previous preparation.)

C. Aluminum acetylacetonate; [Tris(2,4-pentanedionato)-aluminum]:

$$Al_2(SO_4)_3 \cdot 18H_2O + 6CH_3C(O)CH_2C(O)CH_3 + 6NH_3 \longrightarrow 2Al[CH_3C(O)CHC(O)CH_3]_3 + 3(NH_4)_2SO_4 + 18H_2O$$

Suspend 6 cm^3 of acetylacetone [$CH_3C(O)CH_2C(O)CH_3$] in 40 cm^3 of water in a 100-cm^3 beaker. Add 6 M ammonia solution dropwise with stirring until the oily acetylacetone just dissolves. Now add this solution to one made of 6 g of aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) in 60 cm^3 of water. Test the resulting solution with litmus paper. If it is not neutral, carefully add ammonia (or hydrochloric acid) dropwise until the solution is neutral. Separate the precipitate of aluminum acetylacetonate by filtering the mixture with a Büchner funnel. Wash the precipitate with a few cm^3 of water and allow it to dry overnight.

Questions: What is the color of the compound? Look at the colors of some of the products that other members of the class have made. Try to find a compound that is different from yours but similar in color.

D. Iron(III) acetylacetonate; [Tris(2,4-pentanedionato)iron(III)]:

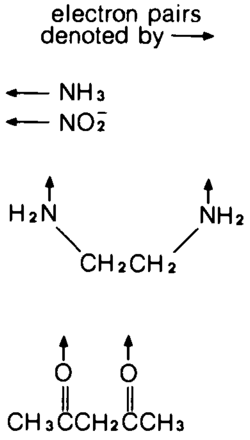
$$FeCl_3 \cdot 6H_2O + 3CH_3C(O)CH_2C(O)CH_3 + 3NH_3 \longrightarrow Fe[CH_3C(O)CHC(O)CH_3]_3 + 3NH_4Cl + 6H_2O$$

Proceed as in *Part 3 C*, using 3 g of iron(III) chloride hexahydrate in place of aluminum sulfate.

Questions: What is the color of your compound? Compare it with other compounds synthesized in this experiment.

I-33 Look to the Rainbow

Some of the common properties of coordination compounds will be obvious from your experimental work, and some will not. It is easy to see how the ligands satisfy the requirements discussed previously—they all have a lone pair of electrons and are Lewis bases; ammonia (NH_3), nitrite ion (NO_2^-), ethylenediamine ($NH_2CH_2CH_2NH_2$), acetylacetone [$CH_3C(O)CH_2C(O)CH_3$]. (*Form and Function: An Organic Chemistry Module* introduces compounds of this last type.)



Note that each nitrogen atom has a lone pair of electrons. Acetylacetone has pairs of electrons on the oxygen atom. Also note that all the metal ions involved in the experiment—copper (Cu^{2+}), cobalt (Co^{3+}), aluminum (Al^{3+}), chromium (Cr^{3+}), and iron (Fe^{3+})—are transition metal ions except one (aluminum). This is typical. Almost all coordination compounds form with transition metals, but there are a few with metal ions such as calcium (Ca^{2+}) and aluminum (Al^{3+}).

One property that cannot be observed readily in your laboratory but is simple enough to determine with appropriate analytical equipment is the formula for each complex. All the complexes discussed in the experiment as well as the vast majority of all known complexes are of the general formula ML_4 or ML_6, where M is the metal and L is the ligand coordinated to the metal. That is to say, the most abundant types of complexes are those in which the metal is surrounded by either four or six ligands. Other types are known, but they are not at all common.

A property that is easy to see is the color of complexes. This is a characteristic property of complexes of the transitional metals: *They are usually brightly colored.* In the following comparison of results from the previous experiment, we will try to see what conclusions we can draw about the colors of complexes.

PROBLEMS

1. Does the ligand determine the color of the complex? Several of the syntheses involved the same ligand but different metal ions. Poll the class and record the colors of these different compounds.
   a. Two complexes containing ammonia as a ligand:

      $Cu(NH_3)_4SO_4$ $Co(NH_3)_6Cl_3$

   b. Two complexes containing ethylenediamine (en) as a ligand:

      $Cu(en)_2SO_4$ $Co(en)_3Cl_3$

c. Four complexes containing acetylacetone (acac) as a ligand:

$Co(acac)_3$ $Al(acac)_3$
$Cr(acac)_3$ $Fe(acac)_3$

From the above results, do you think that the color of the complexes can be related simply to which ligand is present?

2. Does the metal ion determine the color of the complex? Several of the complexes contain the same metal ion. Poll the class and record the colors:

a. Two complexes containing Cu^{2+}:

$Cu(NH_3)_4SO_4$ $Cu(en)_2SO_4$

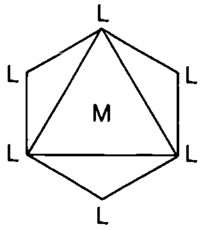
b. Four complexes containing Co^{3+}:

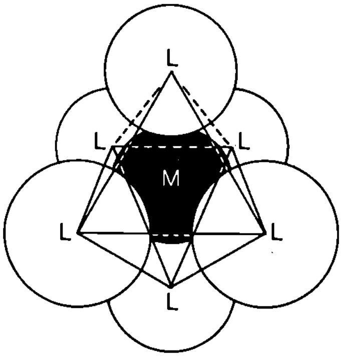
$Co(NH_3)_6Cl_3$ $Co(en)_3Cl_3$
$Na_3Co(NO_2)_6$ $Co(acac)_3$

From your results, do you think that the color of the complexes can be related simply to which metal ion is present?

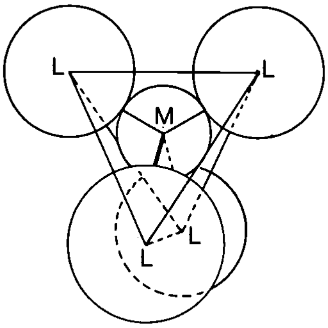
The colors of coordination compounds have received a lot of attention in the last few years. It is worth noting that something as simple as the color of coordination compounds was used by chemists to revolutionize bonding theory. If you continue your study of chemistry to more advanced levels, you'll become well acquainted with these theories.

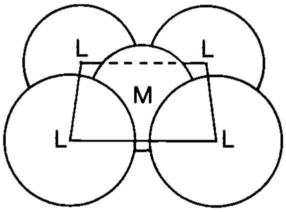
What are some further factors? Another property that is certainly important is the structure or geometry of these molecules. Determining molecular geometries requires a laboratory equipped with expensive and sophisticated equipment. In general, it can be said that almost all six-coordinate complexes (that is, those with six ligands) have an octahedral geometry with the six ligands spaced symmetrically about the metal. The drawings represent two views of an octahedral complex. The metal atom (M) is shaded black in the sketch on the right.



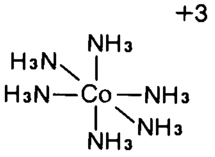


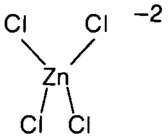
There are two types of structures found for complexes containing four ligands. They are the tetrahedral geometry and the square planar arrangement. An example of a tetrahedral complex is shown in the following illustration on the left. An example of a square planar complex is shown on the right.





Often a particular metal in a particular oxidation state will have a strong preference for one type of complex. For example, consider cobalt(III) (Co^{3+}), which forms only octahedral complexes with six ligands. On the other hand, zinc (Zn^{2+}) seems to prefer tetrahedral complexes with four ligands:





Some metal ions do not show a strong preference. For example, nickel (Ni^{2+}) forms octahedral, tetrahedral, and square planar complexes.

I-34 Using Coordination Compounds

There are so many uses of complex compounds that it is difficult to cover them adequately here. However, one good example that will give you some idea of the possible applications is the tying up of harmful ions.

Once a stable complex has been formed by a metal ion, it is no longer completely free to enter into some of the reactions that it might have otherwise participated in. For example, the presence of certain ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{3+}), in water make the water "hard" and much less suitable for cleaning than "soft" water. This is because these ions react with soaps to form precipitates (soap "scum" or bathtub "ring"). Synthetic detergents do not have this problem, but the presence of these ions still reduces their cleaning efficiencies.

In the following miniexperiment, you will investigate the effect of hard water on soap. (For an explanation of why soaps and detergents are good cleaners in the first place, see *Form and Function: An Organic Chemistry Module* and *Communities of Molecules: A Physical Chemistry Module.*)

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miniexperiment

I-35 Bathtub Rings and Things

Add 5 cm^3 of soap solution to each of six test tubes. Number the test tubes 1 through 6. Then add 1 cm^3 each of the following solutions to the test tubes:

1. 0.1 M aluminum nitrate [$Al(NO_3)_3$]
2. 0.1 M calcium nitrate [$Ca(NO_3)_2$]
3. 0.1 M cobalt(II) nitrate [$Co(NO_3)_2$]
4. 0.1 M iron(III) nitrate [$Fe(NO_3)_3$]
5. 0.1 M magnesium nitrate [$Mg(NO_3)_2$]
6. Distilled water

Record any changes that take place. Then cork or put your thumb over the end of each test tube and shake it vigorously for 10 seconds. Do soap bubbles appear? Record the presence or absence of soap bubbles.

Questions: What effect do the metal ions have on the soap solution? What would be the effect when trying to wash with each soap solution?

Most metal ions react with soap in the same way in which they reacted with the soap that you used in the miniexperiment. Usually, however, only three metal ions are common enough to cause water to become hard. These three metal ions are calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{3+}).

A water softener is a substance that can be used to make soft water out of hard water. Water softeners are commonly used in communities where the water is hard. A water softener removes the objectionable metal ions from the water and, thus, the water becomes "soft." You can do another miniexperiment to observe the action of water softeners on these ions.

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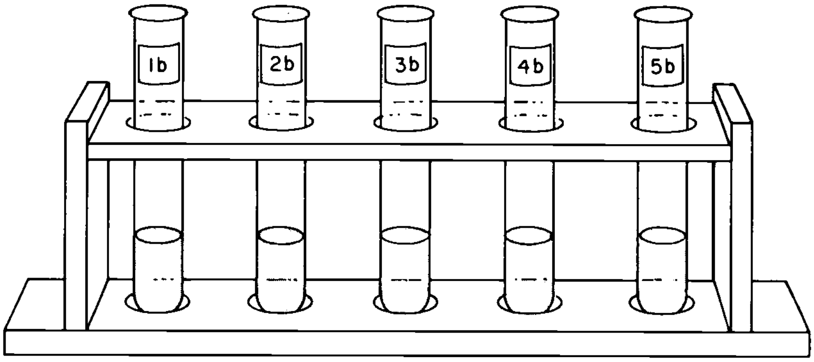
miniexperiment

I-36 Water Softening

Make up a solution of hard water, adding 10 cm^3 of 0.1 M calcium nitrate solution [$Ca(NO_3)_2$] to 10 cm^3 of magnesium nitrate solution, [$Mg(NO_3)_2$]. After mixing, measure out 2-cm^3

portions of this solution into five test tubes. Label the test tubes 1a, 2a, 3a, 4a, and 5a. To the remaining 10 cm³ of hard water add 1cm³ of 0.1 M iron(III) nitrate solution [$Fe(NO_3)_3$]. Mix and measure out 2-cm³ portions into five test tubes labeled 1b, 2b, 3b, 4b, and 5b.



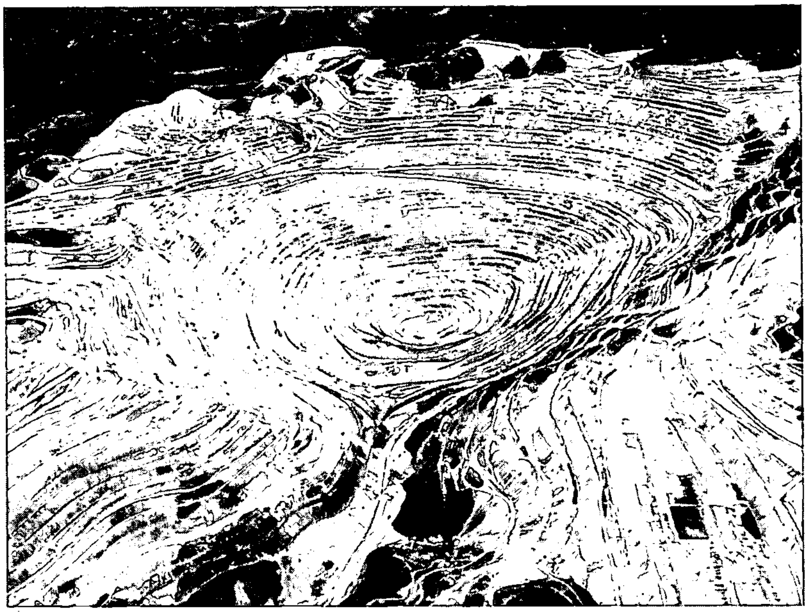
To each pair of test tubes add 10 cm³ of a 0.1 M solution of one of the water-softening agents: (1) sodium triphosphate ($Na_5P_3O_{10}$) to 1a and 1b; (2) sodium carbonate (Na_2CO_3) to 2a and 2b; (3) sodium tetraborate ($Na_2B_4O_7$) to 3a and 3b; (4) nitrilotriacetic acid [$N(CH_2COOH)_3$], better known as NTA, to 4a and 4b; (5) distilled water to 5a and 5b. Then add 1 cm³ of soap solution to each. Record any changes that take place. Shake the test tubes. Record the presence or absence of soap suds.

Questions: How effective are these chemicals as water softeners? If water softening were your only interest, which would you choose? Could cost be a factor? It is well known that ingredients such as sodium triphosphate ($Na_5P_3O_{10}$) add phosphate to waste waters and thus promote the growth of undesirable algae. (See *The Delicate Balance: An Energy and the Environment Chemistry Module.*) Do you suppose the use of sodium carbonate (washing soda) or sodium tetraborate (Borax) would be an improvement? Can you think of other problems that might arise?

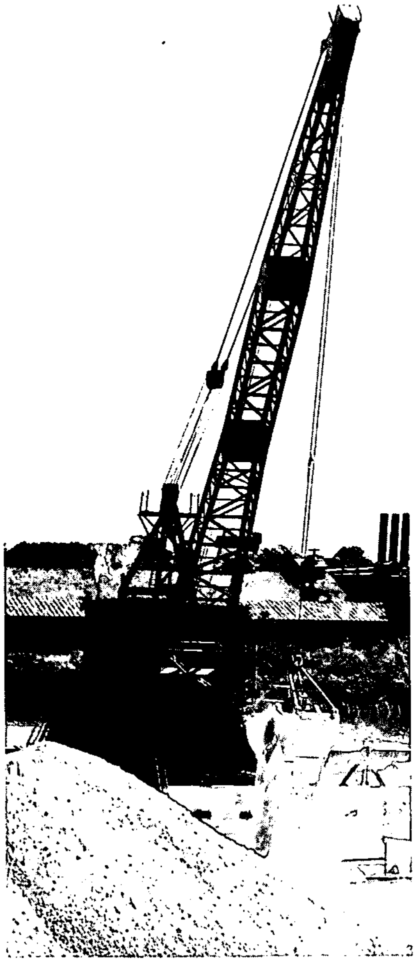
Water softeners can act against hard-water ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{3+}) by two methods. One type of reaction is simple precipitation:

$$Ca(NO_3)_2 + Na_2CO_3 \longrightarrow 2NaNO_3 + CaCO_3$$

This removes the undesirable ion. The ion then cannot interfere with the soap or detergent.



Changes that took place as the earth was formed tended to separate minerals by processes similar to extraction. In this way large deposits of sulfur (*below*) or copper ore (*right*) were formed. The open-pit copper mine is over four kilometers wide at the top and almost one kilometer deep.



A second method is the formation of a complex or coordination compound that effectively ties up the undesirable ion and prevents it from interfering with the soap or detergent even though it is still in solution. This method has the advantage of forming no precipitate, which is potentially as troublesome as "dirt." Triphosphate acts in this way. Industries and households use many tons of this chemical each year in water softeners.

NTA (an abbreviation for *n*itrilo*t*ri*a*cetic acid) would be equally as effective as triphosphate (or perhaps better). For a short period of time, some detergents contained NTA. But manufacturers discontinued its use when evidence indicated that it might cause problems in water supplies. NTA formed coordination compounds with other metal ions besides those responsible for hard water. Chemists suspected that these new coordination compounds might be harmful. NTA is still under study.

Preliminary tests by the Public Health Service indicated that birth defects in rats resulted from the presence of NTA and mercury (Hg^{2+}) or cadmium (Cd^{2+}). The search for an effective but thoroughly safe complexing agent for use in detergents continues.

I-37 Solvent Extraction: Chemical Tweezers

Often in the laboratory or in industry it is desirable to separate one metal from several others. There are various ways of doing this, but one method that often works well is *solvent extraction*. Solvent extraction can be used to separate metals when the desired metal forms a complex with a particular ligand. Suppose that the newly formed coordination compound is more soluble in a solvent such as benzene or ether than it is in water. If we dissolve the original mixture of metal compounds in water and add the ligand, a complex will form. Now the solution is shaken vigorously with benzene. Since the newly formed coordination compound is more soluble in benzene than in water, it leaves the water and enters the benzene. It is possible to separate the benzene solution because it floats on the water.

Finally, evaporation of the benzene leaves the desired metal compound. It is uncontaminated by the other metals that are left in the water. Solvent extraction is an important process. It provides an easy way to obtain pure materials. A similar process operates in nature to separate different elements in the earth's crust.

You can observe how solvent extraction works by doing a miniexperiment. You will attempt to extract two metal ions, iron (Fe^{3+}) and cobalt (Co^{2+}), into an organic solvent. The solvent that you will use is methyl isobutyl ketone [$CH_3C(O)CH_2CH(CH_3)_2$]. We can do as chemists do and abbreviate *m*ethyl *i*so*b*utyl *k*etone as MIBK. The properties of MIBK that are important for this experiment are its physical properties: (1) it is not soluble in water; (2) it is a good solvent for certain metal complexes.

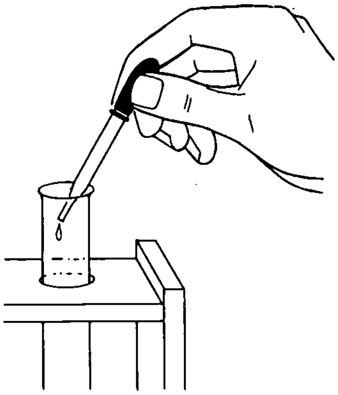
The first of these properties causes MIBK to separate after it is shaken with water. Since it has a lower density, MIBK floats on water. (It therefore will always be the upper layer in the solution used in the miniexperiment. You can verify this easily by mixing in a test tube 2 cm^3 of water and 1 cm^3 of MIBK.) If there is a metal complex present, the MIBK may extract it from the water. By that we mean that the metal complex will dissolve mostly in the MIBK layer.

In the following miniexperiment, note carefully the colors formed and the intensity of the colors in the two layers after shaking with MIBK.

I-38 Cation Lib

miniexperiment

Add 1 dropperful (about 0.5 cm^3) iron(III) nitrate [$Fe(NO_3)_3$] to each of three test tubes. Then add 1 dropperful of the following complexing agents, one to each test tube: (1) concentrated hydrochloric acid (HCl), (2) concentrated hydrobromic acid (HBr), (3) saturated sodium thiocyanate (NaSCN). Record any color changes you observe. Then add 2 dropperfuls (about 1 cm^3) MIBK to each test tube. Cork and shake each tube vigorously for 30 seconds. **Caution:** *Do not use your thumb to stopper the tube. Organic solvents such as MIBK can be absorbed into your body through the skin!* Allow the test tubes to stand until the two layers have separated. Record your results.



Repeat the procedure using a solution of cobalt(II) nitrate [$Co(NO_3)_2$] (0.1 M) in place of the iron (III) nitrate [$Fe(NO_3)_3$]. Add hydrochloric acid (HCl), hydrobromic acid (HBr), and sodium thiocyanate (NaSCN) as described earlier and extract with MIBK. Record your results.

The complexes formed in this miniexperiment are of the type MX_4, such as the following:

$$Fe^3 + 4Cl^- \longrightarrow [FeCl_4]^-$$
$$Co^{2+} + 4SCN^- \longrightarrow [Co(SCN)_4]^{2-}$$

Questions: Does the metal complex always extract preferentially into the MIBK? Suggest a method by which you could separate iron (Fe^{3+}) from cobalt (Co^{2+}).

I-39 Knock, Knock! What's There?

A final example of the usefulness of coordination compounds is found in their use to determine the presence or absence of certain metals in an unknown sample. Quite often coordination compounds have distinctive colors, and the formation of a particular color is strong evidence that a particular metal is present. For example, the addition of ammonia to a solution of copper (Cu^{2+}) results in a deep blue color.

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

A modification of this test (called the *biuret test*) uses copper (Cu^{2+}) to test for the presence of proteins (see *Molecules in Living Systems: A Biochemistry Module*). In the following miniexperiment you will use a distinctly colored complex to test for the presence of lead in the environment.

The element lead was extremely rare in the environment before people started mining and smelting. (See *The Delicate Balance: An Energy and the Environment Chemistry Module.*) However, modern technology brought about the production and use of lead in large quantities. It is now recognized that products containing lead can be dangerous.

For example, lead used in automobile gasoline as an antiknock agent causes pollution in the environment. Such pollution is dangerous because excessive amounts of lead can produce lead poisoning, resulting in damage to the brain and nervous system. Oil companies are now required to produce lead-free gasoline for two reasons: to cut down on lead pollution in the air and to assure the proper functioning of catalytic converters in cars. Lead can ruin catalytic converters—which change poisonous exhaust pollutants into harmless gases; this is why federal law prohibits the use of leaded gasoline in cars with catalytic converters. (See *Form and Function: An Organic Chemistry Module*.)

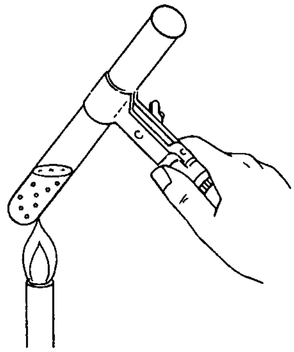
Paint also contains lead, which has been found effective in producing bright colors. Children who eat chips of lead-based paint may suffer mental retardation or even death. For this reason, another federal law restricts the use of lead in paints that are used in the home or in the manufacture of children's toys.

In the next miniexperiment you will collect samples at home and bring them to the laboratory to be tested for the presence of lead. Ask your teacher for suggestions and methods of obtaining these samples. You could bring some paint chipped off a wall— or off the pencil you might have been chewing on! (Why can't you get lead poisoning from chewing on the lead in a lead pencil?) Or perhaps you could test some homemade pottery. (Lead is sometimes used in glazes.) You could also use a piece of filter paper to wipe out some of the deposit inside the (cold!) tail pipe of a car.

I-40 Get the Lead Out!

miniexperiment

Put a sample of a material you have collected from home in a test tube with a few cubic centimeters of 0.1 M acetic acid. Slowly heat the mixture to boiling over your Bunsen burner. (If you are testing a piece of pottery, heat the acetic acid to boiling first. Then carefully rinse the acetic acid around the inside of the pottery and pour it back into your test tube.)



Cool the test tube and its contents in running water from the tap. Add 1 cm^3 of dithizone solution. Stopper the test tube with a cork and shake it vigorously for 10 seconds. Run a known positive by placing 1 cm^3 of lead nitrate solution [$Pb(NO_3)_2$] and 1 cm^3 of dithizone in a second tube. Shake this tube.

Run a control using distilled water and dithizone. Record your results and compare them with those of other members of the class. Was there lead in your sample—did you get it out?

PROBLEMS

1. Give an equation for the formation of a *coordination compound*. Identify the following: the ligand, the metal ion, the complex.
2. Give an example of the usefulness of complex formation in everyday life.
3. In what ways do transition metals differ from the "representative metals"?

Bioinorganic Chemistry

We have noted that the addition of phosphates and nitrates to rivers and lakes can cause undesirable amounts of algae to grow. It also doesn't take much imagination to realize that dumping large amounts of sulfuric acid, sodium hydroxide, or a poison such as potassium cyanide into our environment can be extremely harmful. When you hear about "inorganic chemicals in biological systems," you probably immediately think of this kind of pollution. This is important but only half of the story.

I-41 Bioinorganics: The "Bad News"

Knowing about the problems we are having with pollution, you may well be asking, "What have they dumped into the river or the air now?" Air pollution alone is a serious problem. If a manufacturer "roasts" copper ore to make it suitable for processing

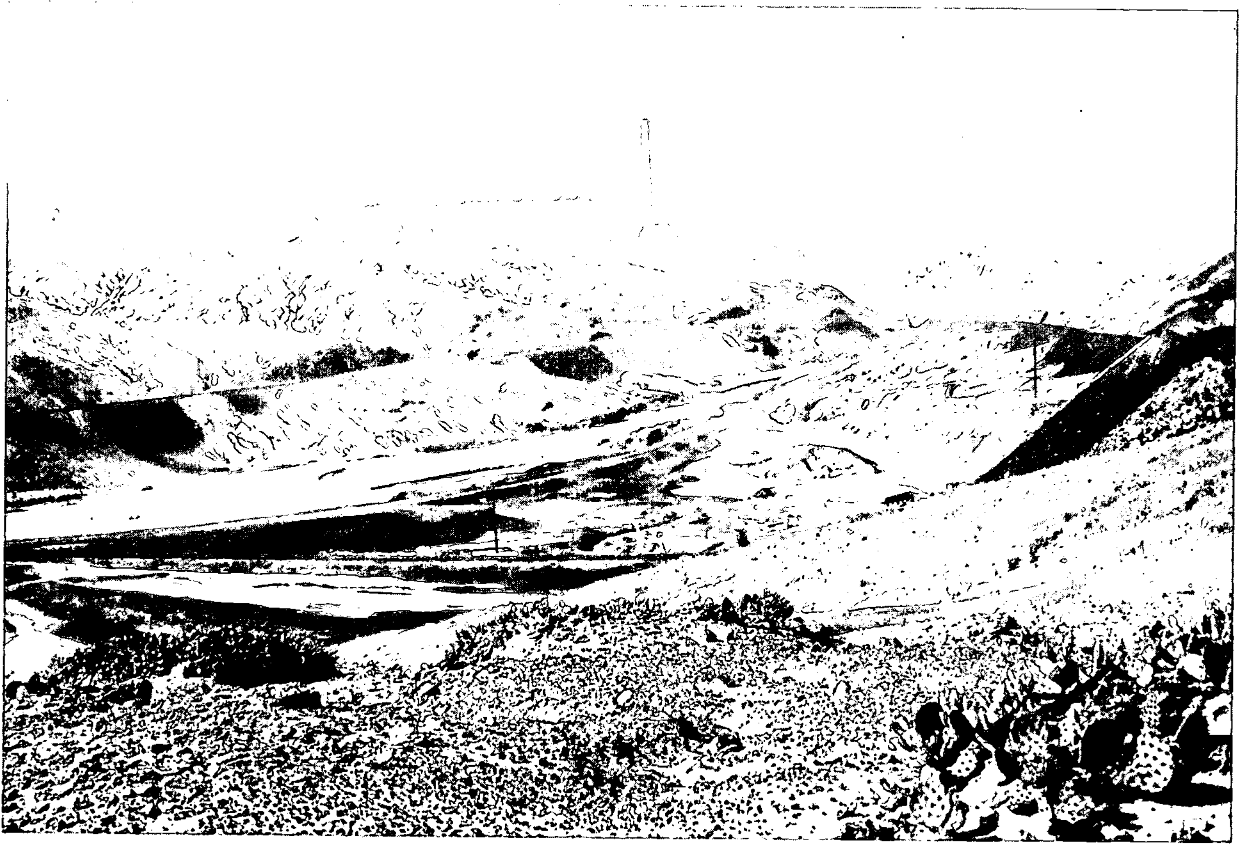
$$2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2$$

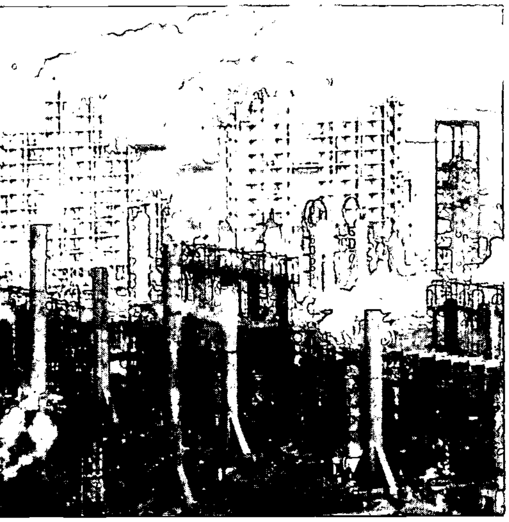
and doesn't bother to catch the sulfur dioxide that forms, it escapes into the atmosphere. Once in the atmosphere, the sulfur dioxide is slowly oxidized to sulfuric acid that corrodes our cities and kills our trees. In the meantime, the sulfur dioxide itself has become an irritant to everyone who breathes air!

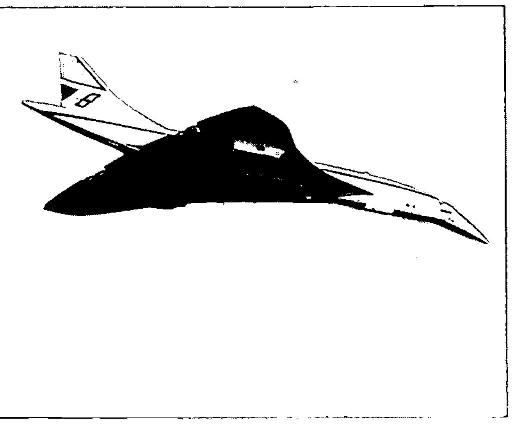
The conversion of sulfur dioxide (SO_2) to sulfuric acid (H_2SO_4) in the atmosphere is slow because there is no catalyst; but the sulfur dioxide keeps building up. It has nowhere to go. Eventually, the sulfur dioxide reacts with oxygen and water vapor in the atmosphere. With this reaction, sulfuric acid is synthesized:

$$\begin{aligned} 2SO_2 + O_2 &\longrightarrow 2SO_3 \\ SO_3 + H_2O &\longrightarrow H_2SO_4 \\ H_2SO_4 + \text{green plants} &\longrightarrow \text{brown plants} \end{aligned}$$

The copper smelter at Copperhill, Tennessee, released SO_2, which completely killed the vegetation on more than seven thousand acres. In 1917 emission was stopped, and the SO_2 turned into useful products. This photograph, taken in 1943, shows the lasting effects. Today, over a half century since the pollution was stopped, the scene is about the same.







Mining often produces similar problems. Drainage from coal mines often contains polluting amounts of acid as a result of the oxidation of sulfur compounds in the mines. Simply burning coal or oil that contains sulfur adds huge amounts of sulfur dioxide to the atmosphere.

At very high temperatures, such as those found in jet engines, nitrogen will combine with oxygen to form nitric oxide:

$$N_2 + O_2 \longrightarrow 2NO$$

Now you might suppose that since jet planes fly at fairly high altitudes, the resulting air pollution wouldn't matter much. It wouldn't except for the fact that if the planes are large enough and fly high enough, they inject nitric oxide into the ozone layer over the earth. The ozone layer acts a little bit like sunglasses. The latter absorb excess bright light to protect the eyes from glare. In the case of the ozone layer, the light that is absorbed is the invisible but high-energy ultraviolet (UV) light. UV light causes effects ranging from the irritation of sunburn to serious skin cancers. The NO problem is that it catalyzes the conversion of ozone to ordinary oxygen:

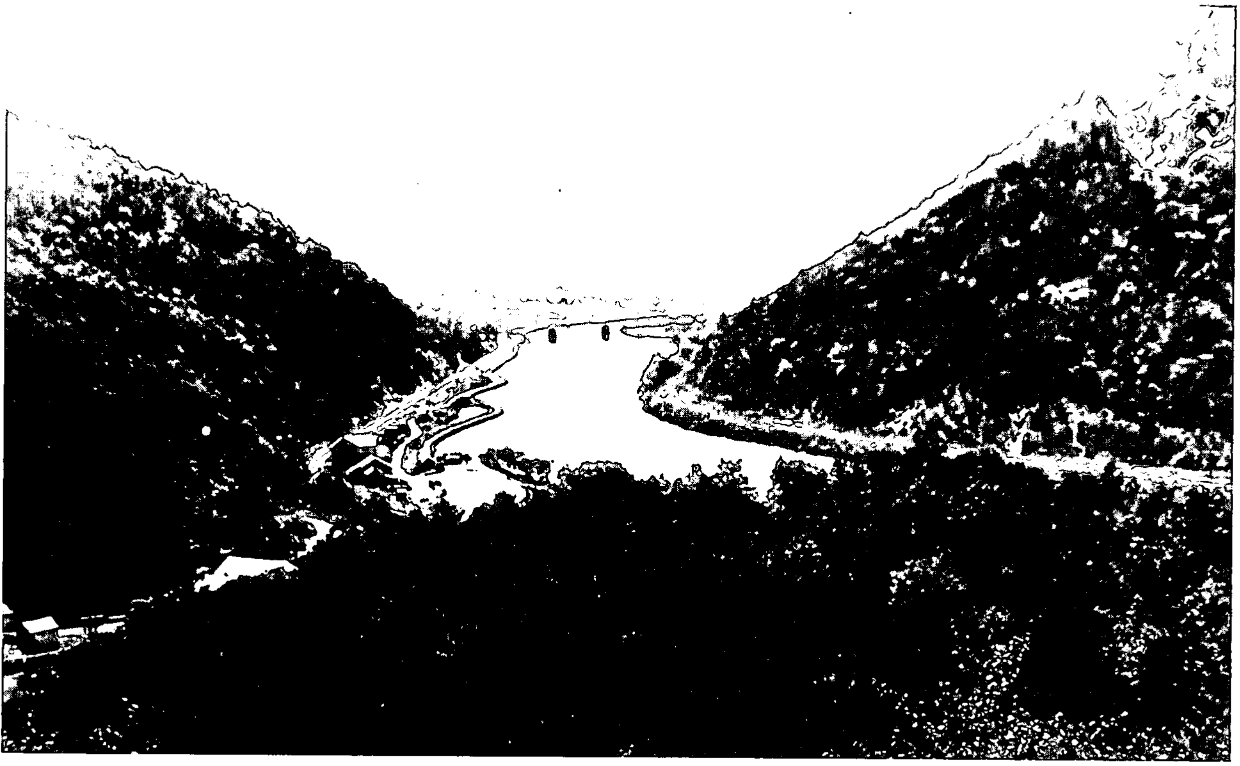
$$2O_3 \xrightarrow{NO} 3O_2$$

and thus reduces the shielding that the ozone layer provides us. Some scientists are worried that large numbers of SSTs flying in the ozone layer could cause the incidence of skin cancer and other related problems to increase (see *The Delicate Balance: An Energy and the Environment Chemistry Module*).

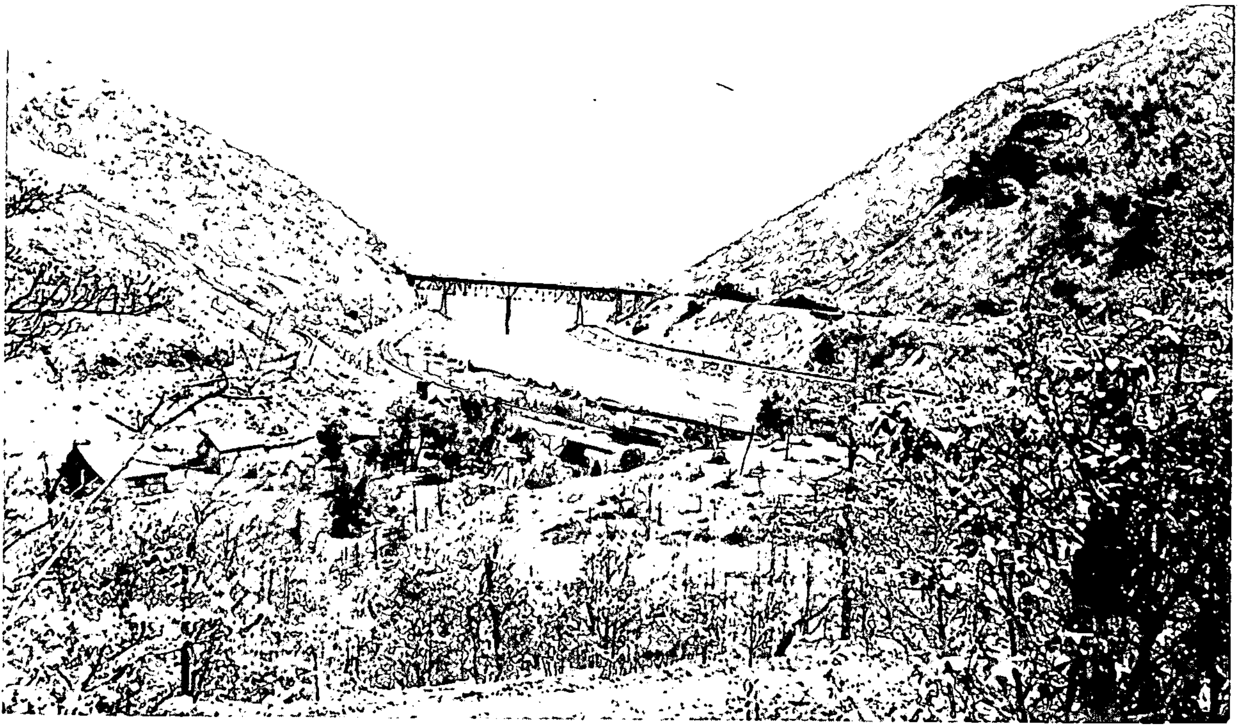
With the exception of some chemicals such as DDT, the vast majority of pollutants are inorganic in nature. Among these pollutants are mercury, lead, and carbon monoxide. The burning of polyvinyl chloride (plastic) releases hydrochloric acid into the environment. Arsenic is present in some insecticides. Then, too, there are those mountains of rusty "tin" cans (Fe/Fe_2O_3) and glass (silicate) bottles. Obviously, we could use the help of inorganic chemists to clean up the mess!

I-42 Bioinorganics: The "Good News"

It is perfectly proper to recall pollution problems when you hear the phrase "inorganic chemicals in biological systems." However, there are other inorganic chemicals that have been in biological systems even before man began his polluting efforts. These are the essential elements. They are a group of about twenty elements that are essential to living organisms. Both representative and transition metals and nonmetals are included.



The scene above was photographed during the 1880s before the construction of smelters for removing zinc from its ore. In the scene below, photographed about fifty years later, you can see the damage caused by the industrial pollutants from this smelting process.



A research chemist, interested in nutrition and trace elements such as copper and zinc, studies the diet requirements of laboratory animals. Deficiencies in the trace elements may be involved in heart disease.

In many cases we do not know the exact function of these trace elements even though we may have established that they are vitally necessary. In some cases we do know how they work. When we succeed in unlocking the mechanism of the action of a trace metal, we usually find that it is behaving exactly as we might expect, based on our knowledge of the usual inorganic chemistry of transition metals. As we have noted, the transition metal ions have two distinguishing properties: (1) a tendency to undergo redox reactions and (2) a tendency to form coordination compounds. Although both of these properties are important, the second is especially important because all the compounds of transition metals that occur naturally in biological systems are coordination compounds. Therefore, this aspect will be discussed first.

I-43 Enzymes: Chemical Meat Cleavers

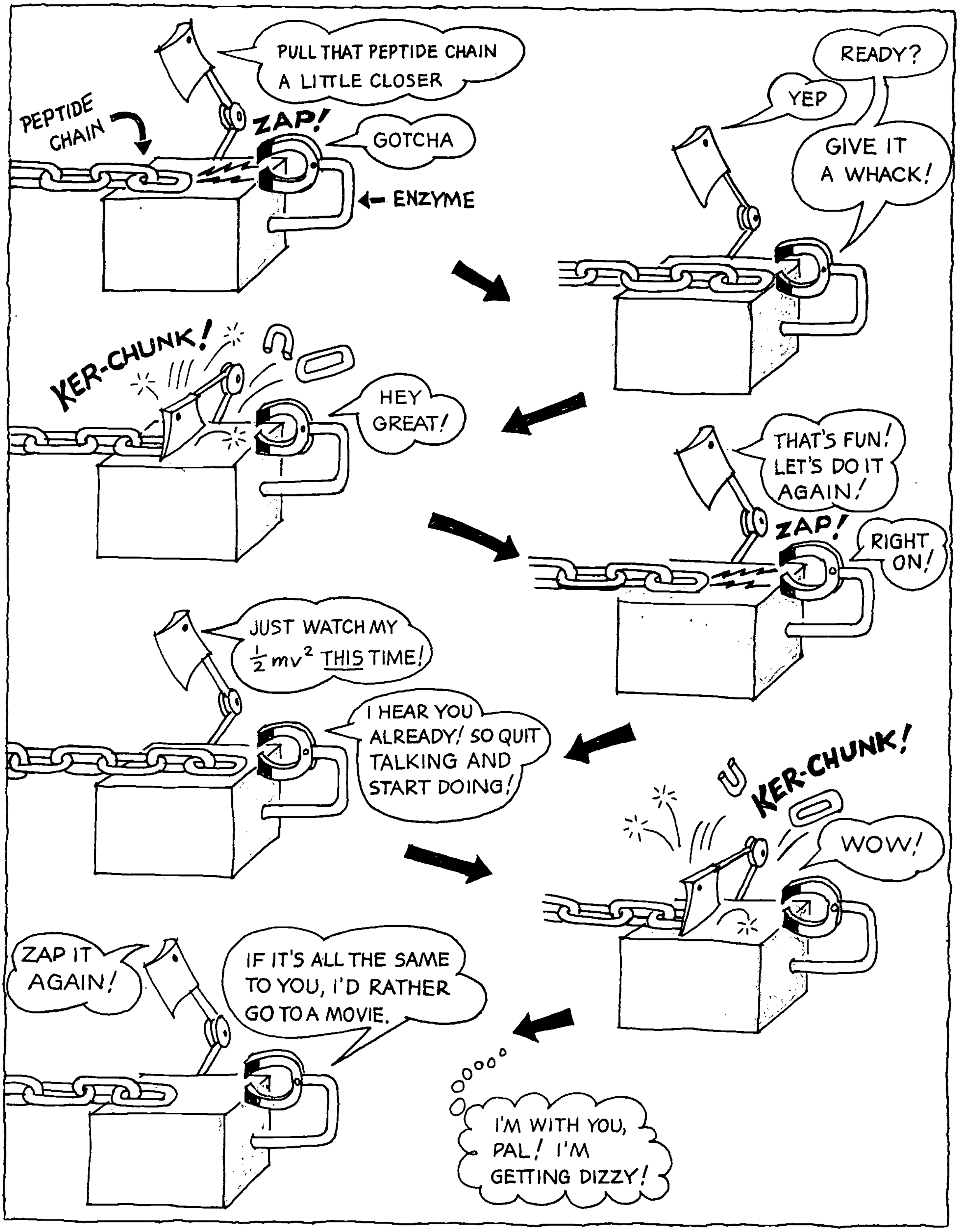
An enzyme, as we have noted, is simply a biological catalyst (for a complete discussion of enzymes, see *Molecules in Living Systems: A Biochemistry Module*). Many enzymes contain a metal ion. The ion is situated in such a way that it can coordinate to a molecule and make it undergo a reaction.

For example, consider the zinc-containing enzyme with the rather formidable name of *carboxypeptidase A*. This enzyme catalyzes the reaction that causes peptide chains to be chopped up into amino acids. We need not be concerned with the details of the reaction here (see *Molecules in Living Systems: A Biochemistry Module* for a discussion of amino acids and peptides); we need only to understand that a long chain molecule is chopped into small fragments.

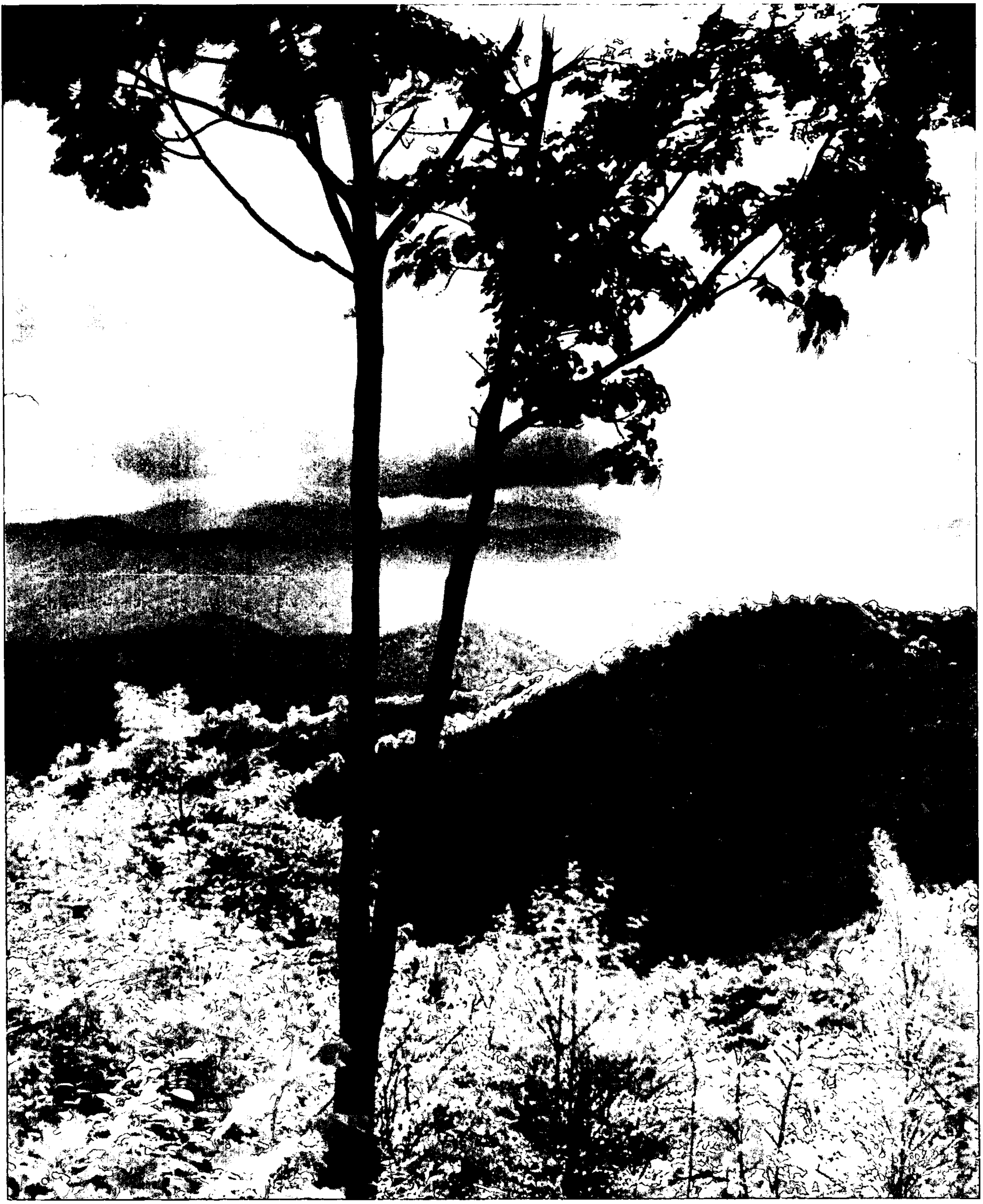
The zinc is coordinated to the enzyme at only three sites. Do you recall from the last section that zinc is almost always coordinated to four ligands that form a tetrahedron about it? If a peptide chain is nearby, the zinc coordinates to it through an oxygen atom in the peptide chain. This satisfies the zinc atom's desire to become four-coordinate. It also pulls the peptide chain into a position where it can be chemically attacked by the rest of the enzyme and broken.

Think of the peptide chain as an iron chain of several links and the zinc atom in the enzyme as a magnet. (All analogies can be carried too far. Don't be fooled into thinking that enzymes actually are magnets!) The remainder of the enzyme acts like a meat cleaver. In the first step, the zinc atom (magnet) coordinates to the chain and aligns it in position on the rest of the enzyme. Then the bonds holding one amino acid (link) to another amino acid are broken. The amino acid that has been chopped off can

Another research chemist analyzes materials for trace metals that may eventually pollute our environment.


PULL THAT PEPTIDE CHAIN A LITTLE CLOSER
PEPTIDE CHAIN
ZAP!
GOTCHA
ENZYME
READY?
YEP
GIVE IT A WHACK!
KER-CHUNK!
HEY GREAT!
THAT'S FUN! LET'S DO IT AGAIN!
ZAP!
RIGHT ON!
JUST WATCH MY $\frac{1}{2}mv^2$ THIS TIME!
I HEAR YOU ALREADY! SO QUIT TALKING AND START DOING!
KER-CHUNK!
WOW!
ZAP IT AGAIN!
IF IT'S ALL THE SAME TO YOU, I'D RATHER GO TO A MOVIE.
I'M WITH YOU, PAL! I'M GETTING DIZZY!

This scene was photographed at a site about eighty kilometers from the smelter at Copperhill, Tennessee (see page 87). It shows an ecosystem in which inorganic chemicals (mostly trace elements) are being used in a balanced way. Every plant and animal in this system is dependent upon inorganic chemicals.



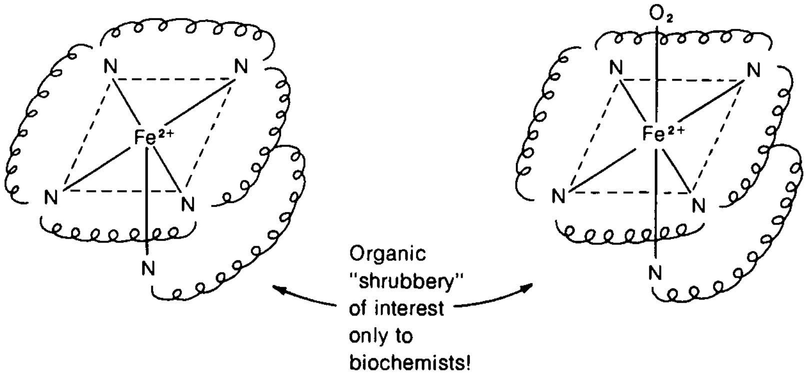
be removed. The chain is attracted to the zinc atom again, coordinated, and aligned. A second "chop" occurs, and a second amino acid is cleaved from the peptide chain. In this way, the amino acids are cleaved from the peptide chain one at a time.

Do not conclude that all metalloenzymes are used to chop up molecules. Other equally important enzymes are used in the synthesis of chemicals in the body. Their function is to pull molecules together and hold them in the right position while the chemical reaction takes place to fasten them together.

If metal ions such as mercury (Hg^{2+}), cadmium (Cd^{2+}), or lead (Pb^{2+}) are available, they may displace the original metal from its metalloenzyme. However, the enzyme was adapted to work with the original metal, not with mercury (Hg^{2+}), cadmium (Cd^{2+}), or lead (Pb^{2+}). When a different metal ion is present, the enzyme usually fails to work—it is "poisoned." This is why metals such as mercury, cadmium, and lead are such a problem in the environment. When they enter our bodies they poison our enzymes, the enzymes fail to work properly, and we suffer the consequences.

I-44 Take a Deep Breath

In the larger animals one of the big problems is getting oxygen to the tissues and storing it there for use in the cells. The molecule responsible for oxygen transport is called *hemoglobin*, and the one used for oxygen storage is known as *myoglobin*. These are very large molecules (see *Molecules in Living Systems: A Biochemistry Module* for a discussion of the long protein chains). As far as inorganic chemistry is concerned, the most interesting part of either molecule is an iron(II) ion (Fe^{2+}) surrounded by four nitrogen atoms in a square planar array. This group of atoms, together with some carbon and hydrogen atoms holding the group together, is called the *heme* group.



TIME MACHINE

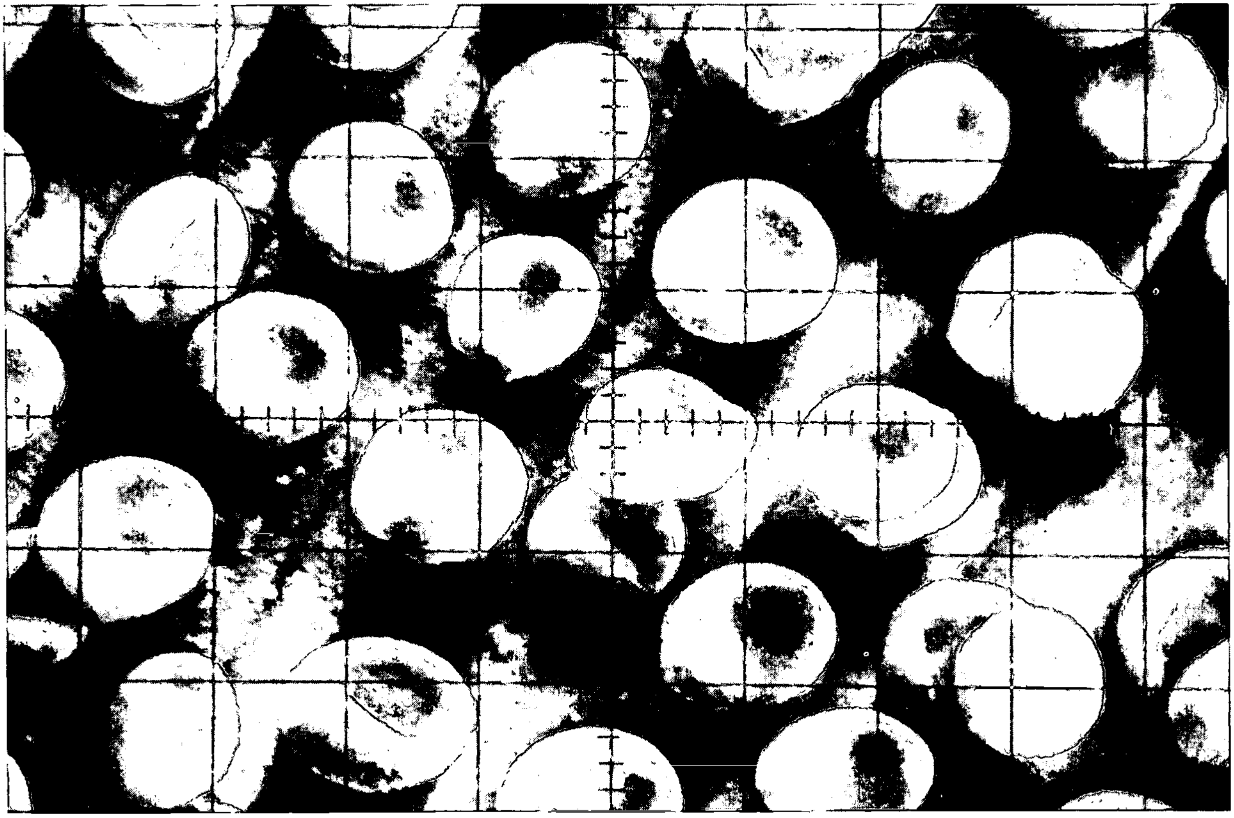
1961	First U.S. Peace Corps volunteers go abroad—to the Philippines.
1961	Yuri Gagarin (USSR) is first man in space.
1962	Alan Shepard is first American in space.
1962	**Max Perutz and John Kendrew win Nobel Prize in Chemistry for determining structures of myoglobin and hemoglobin, calling attention to the importance of bioinorganic chemistry.**
1963	Pop Art is recognized with a New York exhibit that includes works by Warhol, Rauschenberg, and Johns.
1964	Verrazano-Narrows Bridge, world's longest suspension bridge, is completed in New York.
1965	Op Art, based on optical illusion, becomes popular.
1965	Boeing 707 becomes first plane to fly around the world over both poles.
1960s	**Americans become aware of sickle-cell anemia, a genetic disease that occurs more frequently than the more commonly known diseases—leukemia, hemophilia, cystic fibrosis, and muscular dystrophy.**

Myoglobin has one heme group per molecule, and hemoglobin has four. Otherwise, the two molecules are similar from the inorganic chemist's point of view. In addition to the nitrogen atoms in the heme group, a fifth nitrogen atom on the protein chain is attached to the iron atom. Thus, the coordination number of the iron is only five, unless it can pick up another ligand. This it can do by binding a molecule of oxygen (O_2). The iron ion acts as a typical Lewis acid and is coordinated by an oxygen molecule acting as a Lewis base or sixth ligand.

Oxygen is an unusual ligand, and so the heme group is remarkable in being able to coordinate an oxygen molecule and later release it. The heme groups in hemoglobin (present in the red blood cells) take up oxygen from the lungs and carry it through the blood to the tissues. There the oxygen is transferred from the hemoglobin to the myoglobin, bonding it to the heme group in exactly the same way. The myoglobin stores the oxygen until it is used to burn food and release energy. The entire process, without which we would suffocate, is merely an elegantly balanced system of coordination compounds!

If the wrong chemicals are present, the delicate balance can be upset. For example, let's say that carbon monoxide (CO) is present in the atmosphere. It can bind to hemoglobin in the same way

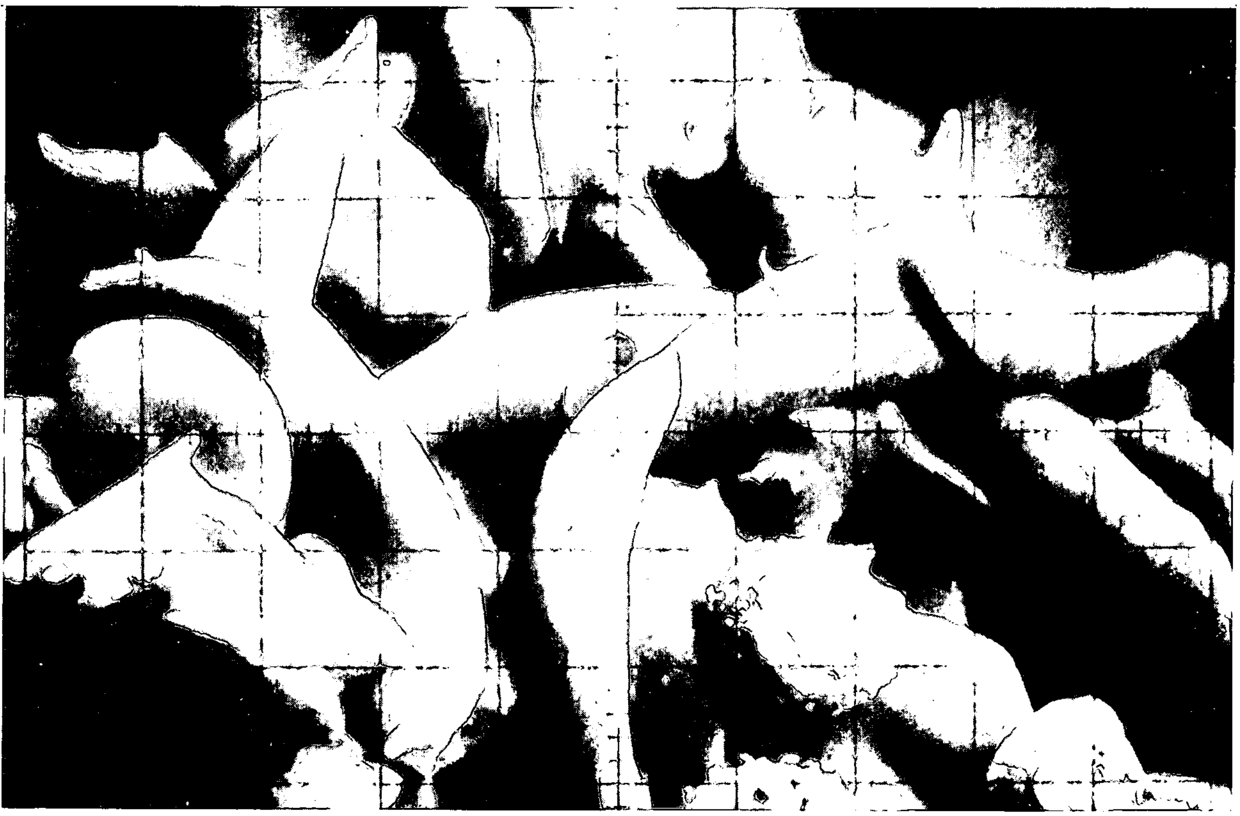
Normal human blood cells (magnified 3500 times) transport oxygen to the cells in the human body.



as the oxygen molecule. However, unlike oxygen, carbon monoxide does not come off again easily. If there is enough carbon monoxide present, all of the hemoglobin will be tied up and there will not be enough left to carry the required oxygen—you literally suffocate to death in an abundance of oxygen.

The mechanism by which hemoglobin carries oxygen and, more important, the way in which it transfers the oxygen to the myoglobin in the muscle are not completely understood; however, it is known that the iron atom and the protein chains move. The iron atom is probably the most important atom in the molecule, much to the inorganic chemist's delight!

The movement of the protein chains facilitates the transfer of the oxygen from the hemoglobin to the myoglobin. It sometimes has a second effect. If the hemoglobin is of a variant type called *Hemoglobin S,* the movement of the protein chains when the oxygen molecule is removed may cause it to polymerize to form rod-like structures that eventually grow long enough to distort the walls of the red blood cell (imagine the effect of opening a large umbrella in a very small tent). The cells often become sickle shaped and they tend to clog the capillaries and this causes various bad effects. People who have only Hemoglobin S thus suffer from *sickle-cell anemia*. The irony is that Hemoglobin S



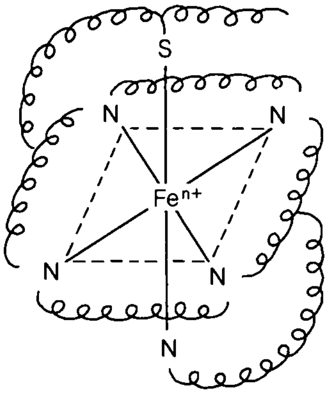
Human blood cells that have sickled, magnified 6500 times. This means that these cells can no longer transport the needed oxygen to the cells in the human body.

differs from the more common Hemoglobin A in only a *single* amino acid (see *Molecules in Living Systems: A Biochemical Module*) and that it is the *very system that allows most people to breathe and utilize oxygen from the air efficiently that also triggers sickle-cell crises!*

I-45 Redox Action

Redox reactions are important in biochemistry. The basic driving force of living things is the burning (oxidation) of carbohydrates. However, this "burning" is not so simple as setting fire to a sack of sugar. The oxidation involves many intricate steps.

This is where the transition metals come in. As we have seen, they are admirably suited for redox reactions. They are involved in many of the enzyme systems that transport the electrons that enter into the oxidation-reduction reactions involved in burning carbohydrates. Only one such enzyme will be included here, *cytochrome c*.



n = 2 or 3

Note that many of the same redox reactions may also be involved in the opposite process, photosynthesis, which is also basically an oxidation-reduction process.

In many ways, especially with respect to inorganic chemistry, cytochrome c is remarkably like myoglobin and hemoglobin. The functional part of the molecule is a heme group, identical to that found in the other molecules. There is one important difference, however. In cytochrome c, the heme group is completely surrounded by the protein portion of the molecule, and the *iron atom is coordinated to six different ligand atoms.* In addition to the five ligands present in hemoglobin and myoglobin, there is a sixth ligand bonding through a sulfur atom. There is no place for an oxygen molecule to coordinate. Iron has already achieved its maximum coordination of six ligands.

Faced with the impossibility of undergoing a reaction by further coordination, the molecule is left with only one other available reaction. This available reaction is a redox reaction. Cytochrome c reacts by accepting electrons (and being reduced to Fe^{2+}) and transferring them to other molecules (while being oxidized back to Fe^{3+}):

$$\text{cytochrome c } (Fe^{3+}) + e^- \longrightarrow \text{cytochrome c } (Fe^{2+})$$
$$\text{cytochrome c } (Fe^{2+}) \longrightarrow \text{cytochrome c } (Fe^{3+}) + e^-$$

The sole function of cytochrome c is to be endlessly reduced and oxidized. It acts as an intermediate in the redox reactions of metabolism.

PROBLEM

Give examples of the biological importance of the following elements or molecules: Fe, O_2, Hg, CO, Zn, Pb, NO, SO_2, N.

A Summing Up

The short series of experiments and discussions in this module only scratches the surface of inorganic chemistry. Out of the one hundred and six known elements, perhaps two dozen have been mentioned here. However, you should have developed some idea of what inorganic chemistry is all about and of what an inorganic chemist does.

TIME MACHINE

Neolithic period (?)	**Fermentation of honey to form mead is perhaps the first application of chemistry by man.**
3500 B.C.	**Applied chemistry develops with the extraction of metals from their ores and the manufacture of pottery.**
2600 B.C.	The Great Pyramid of Khufu is built in Egypt.
1370 B.C.	**The large-scale manufacture of glass begins in Egypt.**
1000 B.C.	The *Rig-Veda* is written in India.
500-300 B.C.	**The Greek philosophers Empedocles and Aristotle ponder atoms and elements.**
246-209 B.C.	The Great Wall of China is built.
A.D. 600	**Chemical arts begin to flourish in Arabian countries.**
A.D. 985–1011	Norsemen explore the coast of North America.
A.D. 1144	**Alchemy, from Arabic sources, is introduced in Europe.**
A.D. 1150	**The Chinese use gunpowder for fireworks.**
A.D. 1454	Johann Gutenberg uses movable type for printing.
A.D. 1803	**Dalton originates atomic theory; modern chemistry begins.**

Even the professional inorganic chemist will probably encounter barely half of the elements during a lifetime career in the laboratory. Thanks to the periodic chart, however, anyone who has studied chemistry will know quite a bit about the properties of any element. At this point, your knowledge of elements such as sodium, calcium, iron, cobalt, lead, sulfur, and bromine should give you a basic understanding of the elements available to a chemist for research in inorganic chemistry.

In this module you learned that inorganic chemistry includes the reactions of more than one hundred elements. Some of these elements are metals, some are nonmetals, and some have properties of both metals and nonmetals. There are elements, such as sodium, that have rather simple chemistries, while the chemistries of others are not so simple. Iron, for example, is used in such diverse activities as running a blast furnace, analyzing a sample of stainless steel, and even treating diseases of the blood. In this way, inorganic chemistry makes its own unique contribution while sharing the information and laboratory techniques of other areas, including analytical chemistry, physical chemistry, organic chemistry, and biochemistry.

Quite recently chemists have realized the direct connection between the chemistry of transition metals in coordination compounds and the chemistry of these same transition metals in living systems. With this realization a whole new area of interest and research—bioinorganic chemistry—was born. In the last fifteen years it has developed into a major effort to unlock the secrets of nature: How does hemoglobin work? Why is cobalt, a rather rare element, an essential one in living systems? We know that lead and mercury in the environment are bad, but how do they work? Why are they poisonous? Why does stannous fluoride help prevent cavities in teeth? Why is lithium helpful in certain kinds of mental problems? The questions are limitless, challenging the skill and ingenuity of the chemist as never before.

What can we expect of the future? It is obvious that the study of bioinorganic chemistry is still in its infancy—and we can expect that it will continue to expand, to answer questions, and to solve problems. Our understanding should increase in the areas of biological processes, the nature of certain diseases, and the prevention of pollution-related problems. Even from a nonbiological point of view, inorganic chemistry will always furnish important means of dealing with environmental issues.

The application of inorganic chemistry to the needs of our society has many benefits, including the production of leaded gasoline and paints, steel, sulfuric acid, and fertilizers, as well as many problems, including air pollution at Copperhill, Tennessee, mercury pollution in some rivers and bays, and lead poisoning.

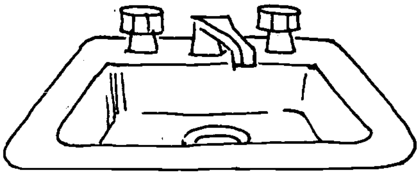
Chemists have provided some answers (unleaded gasoline and lead-free paints) and with further research will continue to provide the answers to many of today's problems. But it remains for the people of this earth to follow through.

A personal note from the author: By now you have undoubtedly come to the conclusion that I'm pretty enthusiastic about inorganic chemistry! I've been told that every time I write or talk about the subject, my enthusiasm shows. I can't expect all of you to share my enthusiasm for inorganic chemistry, just as few of you will share my enthusiasm for the Washington Redskins, real New Orleans jazz, the Cincinnati Reds, the Blue Ridge mountains, or Sherlock Holmes. However, I hope you've enjoyed inorganic chemistry, and if we ever meet, I'll be happy to share my other interests with you, just as I would hope you'd share yours, whether they be soccer or rock, modern dance or antique furniture, fast cars or slow trains, Shakespeare or San Francisco. After all, isn't that what it's all about?

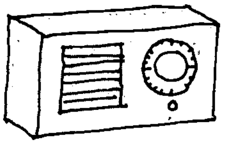
PROBLEMS

1. Give an example of each of the following:
   a) An acid or a base.
   b) An ionic compound.
   c) A covalent compound.
   d) A Lewis acid.
   e) A Lewis base.
   f) A coordination compound.
   g) A metal that is necessary for life.
   h) A metal that is poisonous to life.
2. Balance the following equations:
   a) $H_2SO_4 + KOH \longrightarrow K_2SO_4 + 2H_2O$
   b) $Na + Cl_2 \longrightarrow NaCl$
   c) $HCO_3^- + OH^- \longrightarrow ?$
   d) $HCO_3^- + H_3O^+ \longrightarrow ?$
   e) $P_4 + Cl_2 \longrightarrow PCl_5$
3. Give an example from everyday life where we make use of the following:
   a) An acid or a base.
   b) The formation of a coordination compound.
   c) The special physical properties of metals.
4. If element 107 (assume symbol X) is ever discovered, it might be isolated as the compound (XCl, KXO_4, KX_3; choose one). It will be a (metal, nonmetal) and most closely resemble (Cs, Re, B, I) in its properties.

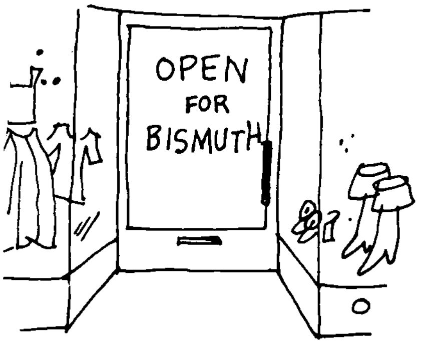
SOME MORE VERY UNCOMMON ELEMENTS!



ZINC



A RADIUM



Appendix

Safety

SAFETY IN THE LABORATORY

Proper conduct in a chemistry laboratory is really an extension of safety procedures normally followed each day around your home and in the outside world. Exercising care in a laboratory demands the same caution you apply to driving a car, riding a motorbike or bicycle, or participating in a sport. Athletes consider safety measures a part of playing the game. For example, football players willingly spend a great deal of time putting on equipment such as helmets, hip pads, and shoulder pads to protect themselves from potential injury.

Chemists must also be properly dressed. To protect themselves in the laboratory, they commonly wear a lab apron or a coat and protective glasses. Throughout this course you will use similar items. Hopefully their use will become second nature to you, much as it becomes second nature for a baseball catcher to put on a chest protector and mask before stepping behind home plate.

As you read through a written experimental procedure, you will notice that specific hazards and precautions are called to your attention. Be prepared to discuss these hazards with your teacher and with your fellow students. Always read the entire experimental procedure thoroughly before starting any laboratory work.

A list of general laboratory safety procedures follows. It is not intended that you memorize these safety procedures but rather that you *use* them regularly when performing experiments. You may notice that this list is by no means complete. Your teacher may wish to add safety guidelines that are relevant to your specific classroom situation. It would be impossible to anticipate every hazardous situation that might arise in the chemistry laboratory. However, if you are familiar with these general laboratory safety procedures and if you use common sense, you will be able to handle potentially hazardous situations intelligently and safely. Treat all chemicals with respect, not fear.

GENERAL SAFETY GUIDELINES

1. Work in the laboratory only when the teacher is present or when you have been given permission to do so. In case of accident, notify your teacher immediately.
2. Before starting any laboratory exercise, be sure that the laboratory bench is clean.
3. Put on a laboratory coat or apron and protective glasses or goggles before beginning an experiment.
4. Tie back loose hair to prevent the possibility of its contacting any Bunsen burner flames.
5. Open sandals or bare feet are not permitted in the laboratory. The dangers of broken glass and corrosive liquid spills are always present in a laboratory.
6. Fire is a special hazard in the laboratory because many chemicals are flammable. Learn how to use the fire blanket, fire extinguisher, and shower (if your laboratory has one).
7. For minor skin burns, immediately immerse the burned area in cold water for several minutes. Then consult your teacher for further instructions on possible additional treatment.
8. In case of a chemical splash on your skin, immediately rinse the area with cold water for at least one minute. Consult your teacher for further action.
9. If any liquid material splashes into your eye, wash the eye immediately with water from an eyewash bottle or eyewash fountain.
10. Never look directly down into a test tube—view the contents of the tube from the side. (Why?)
11. Never smell a material by placing your nose directly at the mouth of the tube or flask. Instead, with your hand, "fan" some of the vapor from the container toward your nose. Inhale cautiously.
12. Never taste any material in the laboratory.
13. Never add water to concentrated acid solutions. The heat generated may cause spattering. Instead, as you stir, add the acid slowly to the water or dilute solution.
14. Read the label on a chemical bottle at least *twice* before removing a sample. H_2O_2 is not the same as H_2O.
15. Follow your teacher's instructions or laboratory procedure when disposing of used chemicals.

This symbol represents three of the common hazards in a chemistry laboratory—flame, fumes, and explosion. It will appear with certain experiments in this module to alert you to special precautions in addition to those discussed in this Appendix.

Selected Readings

The area of gravest concern at present is the environment, and many recent articles about inorganic chemicals deal with this subject. Some of the articles worth reading include the following:

The Biosphere: Readings from *Scientific American*. San Francisco: W. H. Freeman & Co., Publishers, 1970.
This collection contains several articles on the cycling of elements through our environment.

Brill, Winston J. "Biological Nitrogen Fixation." *Scientific American*, March 1977, pp. 68–81.
The biology and chemistry of nitrogenase, the enzyme involved in the reduction of nitrogen to ammonia.

Gosnell, Mariana. "Ozone—The Trick Is Containing It Where We Need It." *Smithsonian*, June 1975, pp. 48–55.
Modern technology may be breaking down ozone in the stratosphere where it's essential and producing too much of it down here where it's poisonous.

Jenkins, Dale W. "The Toxic Metals in Your Future—and Your Past." *Smithsonian*, April 1972, pp. 62–69.
A realistic discussion of the changes in levels of toxic metals in the environment.

Putnam, J. J., and Madden, R. W. "Quicksilver and Slow Death." *National Geographic*, October 1972, pp. 507–27.
Discusses the particular problems of mercury as a poison.

Other worthwhile readings in the field of inorganic chemistry include the following:

Asimov, Isaac. *A Short History of Chemistry*. Garden City, N.Y.: Doubleday-Anchor, 1965. Paperback.

———. *Building Blocks of the Universe*. New York: Abelard-Schuman, 1974.

———. *Noble Gases*. New York: Basic Books, 1966.

———. *The Search for the Elements*. New York: Fawcett, 1962. Paperback.

Azbel', M. Ya.; Kaganov, M. I.; and Lifshitz, I. M. "Conduction Electrons in Metals." *Scientific American*, January 1973, pp. 88–98.
This discussion is related to the section presented in this module on properties of metals—it is rather difficult reading.

Bentley, W. A., and Humphreys, W. J. *Snow Crystals*. New York: Dover Publications, Inc., 1962. Paperback.
Discussion of snowflakes and thousands of photographs of snowflakes.

Davis, H. M. *Chemical Elements*. New York: Ballantine, 1959. Paperback.

Dickerson, R. E. "The Structure and History of an Ancient Protein." *Scientific American*, April 1972, pp. 58–72.
A discussion of cytochrome c, with some excellent illustrations of the molecule.

Hapgood, Fred. "When Ice Crystals Fall from the Sky Art Meets Science." *Smithsonian*, January 1976, pp. 66–73.
A nonchemical discussion of snowflakes and some meteorological problems.

Knight, Charles, and Knight, Nancy. "Snow Crystals." *Scientific American*, January 1973, pp. 100–107.
An interesting account. Note that the molecular bonding to which the authors refer is the hydrogen bonding discussed in section *I-24* of this module.

Lapp, Ralph E., and Editors of Time-Life Books. *Matter*. New York: Time Inc., 1969.
A general and easy to read discussion of the states of matter—extensively illustrated.

Weeks, Mary Elvira, and Leicester, Henry M. *The Discovery of the Elements*. 7th ed. Easton, Pa.: Chemical Education Publishing Co., 1968.
A very readable account of the discovery of the various elements studied by inorganic chemists.

Wohlrabe, Raymond. A. *Crystals*. Philadelphia: Lippincott, 1962.
An introduction to the science of crystallography, explaining how crystals are formed and how they function—illustrated.

In addition, interesting articles on inorganic chemistry as well as other phases of chemistry can be found in *Journal of Chemical Education, Chemistry, Science News*, and *Scientific American*.

Metric Units

PHYSICAL QUANTITY	SI BASE OR DERIVED UNIT		OTHER UNITS	
	NAME	SYMBOL AND DEFINITION	NAME	SYMBOL AND DEFINITION
length	meter*	m	kilometer centimeter nanometer	1 km = 10^3 m 1 cm = 10^{-2} m 1 nm = 10^{-9} m = 10^{-7} cm
area	square meter	m^2	square centimeter	1 cm^2 = 10^{-4} m^2
volume	cubic meter	m^3	cubic centimeter liter	1 cm^3 = 10^{-6} m^3 1 l = 10^3 cm^3
mass	kilogram*	kg	gram	1 g = 10^{-3} kg
amount of substance	mole*	mol		
concentration	moles per cubic meter	mol/m^3	moles per liter	1 mol/l = 10^3 mol/m^3
			molar concentration (molarity)	1 M = mol/l
Celsius temperature			degree Celsius	°C

*SI base unit, exactly defined in terms of certain physical measurements.

Acknowledgments

IAC Test Teachers

Linwood Adams, Bowie High School, Prince George's County, MD
Thomas Antonicci, Archbishop Curley High School, Baltimore, MD
Nicholas Baccala, Milford Mill High School, Baltimore County, MD
Rosemary Behrens, Bethesda-Chevy Chase High School, Montgomery County, MD
Virginia Blair, Holton-Arms School, Bethesda, MD
Ethyl duBois, Crossland and Oxon Hill High Schools, Prince George's County, MD
Sally Buckler, High Point High School, Prince George's County, MD
Therese Butler, Bowie High School, Prince George's County, MD
Kevin Castner, Bowie High School, Prince George's County, MD
Robert Cooke, Kenwood High School, Baltimore County, MD
Wilmer Cooksey, Woodrow Wilson High School, Washington, DC
Frank Cox, Parkville High School, Baltimore County, MD
Richard Dexter, John F. Kennedy High School, Montgomery County, MD
Elizabeth Donaldson, John F. Kennedy High School, Montgomery County, MD
Clair Douthitt, Chief Sealth High School, Seattle, WA
Lawrence Ferguson, Milford Mill High School, Baltimore County, MD
Harry Gemberling, DuVal and Eleanor Roosevelt High Schools, Prince George's County, MD
Alan Goldstein, Laurel High School, Prince George's County, MD
Marjorie Green, McLean High School, Fairfax County, VA
William Guthrie, Parkdale High School, Prince George's County, MD
Laura Hack, Annapolis High School, Annapolis, MD
Margaret Henderson, Fort Hunt High School, Fairfax County, VA
Martina Howe, Bethesda-Chevy Chase High School, Montgomery County, MD
Glendal Jenkins, Surrattsville High School, Prince George's County, MD
Martin Johnson, Bowie High School, Prince George's County, MD
Harold Koch, Southwest High School, Minneapolis, MN
Jane Koran, Arundel High School, Anne Arundel County, MD
Marilyn Lucas, Euclid High School, Euclid, OH
David McElroy, Albert Einstein High School, Montgomery County, MD
Marilu McGoldrick, Wilde Lake High School, Howard County, MD
John Malek, Meade High School, Ft. Meade, MD
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Doris Sandoval, Springbrook High School, Montgomery County, MD
Earl Shaw, Damascus High School, Montgomery County, MD
George Smeller, Robert Peary High School, Montgomery County, MD
Howard Smith, Parkville High School, Baltimore County, MD
Larry Sobotka, Parkville High School, Baltimore County, MD
Roger Tatum, Takoma Academy, Takoma Park, MD
Yvette Thivierge, Fairmont Heights High School, Prince George's County, MD
Barbara Tracey, Bishop McNamara High School, Forestville, MD
Ronald Trivane, Pikesville High School, Baltimore County, MD
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The editors would like to acknowledge the following persons for their invaluable assistance in providing sources and photographs: Marcia Bland, U.S. Department of Agriculture; Dr. Irving B. Sachs, Forest Products Laboratory, U.S. Department of Agriculture; and Lurie Shima, Goddard Space Center, NASA.

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TABLE OF INTERNATIONAL RELATIVE ATOMIC MASSES*

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227.0
Aluminum	Al	13	27.0
Americium	Am	95	(243)**
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.0
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(257)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	237.0
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.0
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.0
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.0
Radium	Ra	88	226.0
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	(97)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.8
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

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*Based on International Union of Pure and Applied Chemistry (IUPAC) values (1975).

**Numbers in parentheses give the mass numbers of the most stable isotopes.

PERIODIC TABLE OF THE ELEMENTS

1.008
H
Hydrogen
1

200.6 — atomic mass
Hg — symbol
Mercury — name
80 — atomic number

IA	IIA	IIIB	IVB	VB	VIB	VIIB		← VIIIB →		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
																	4.00 **He** Helium 2
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4											10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12											27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulfur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybd'm 42	(97) **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	138.9 **La*** Lanthanum 57	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.8 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84	(210) **At** Astatine 85	(222) **Rn** Radon 86
(223) **Fr**† Francium 87	226.0 **Ra** Radium 88	(227) **Ac**** Actinium 89	‡ 104	‡ 105	‡ 106												

*	140.1 **Ce** Cerium 58	140.9 **Pr** Praseody'm 59	144.2 **Nd** Neodymium 60	(145) **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
**	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	(242) **Pu** Plutonium 94	(243) **Am** Americium 95	(245) **Cm** Curium 96	(245) **Bk** Berkelium 97	(251) **Cf** Californium 98	(254) **Es** Einsteinium 99	(254) **Fm** Fermium 100	(256) **Md** Mendel'm 101	(254) **No** Nobelium 102	(257) **Lr** Lawrencium 103

†The most stable known isotopes are shown in parentheses.

‡The discovery of elements 104, 105, and 106 has been claimed by both American and Soviet scientists. The Americans have suggested the name *rutherfordium* and *hahnium* for 104 and 105; the Soviets have suggested the names *kurchatovium* and *nielsbohrium* for these same elements. No name has yet been proposed for element 106.

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