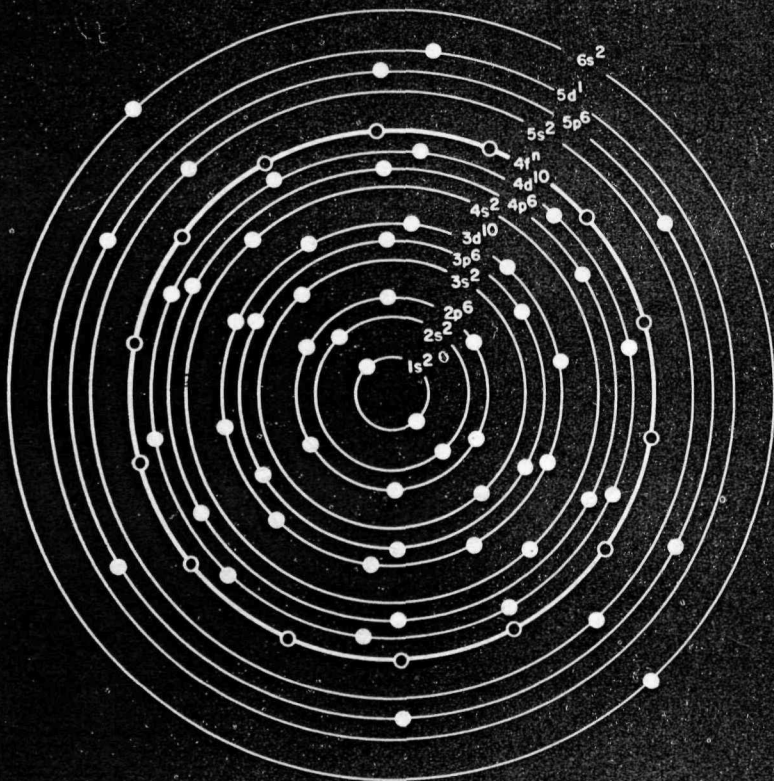
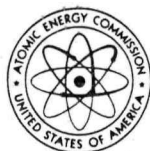


Rare Earths

The Fraternal Fifteen



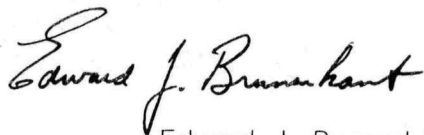
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The Understanding the Atom Series

Nuclear energy is playing a vital role in the life of every man, woman, and child in the United States today. In the years ahead it will affect increasingly all the peoples of the earth. It is essential that all Americans gain an understanding of this vital force if they are to discharge thoughtfully their responsibilities as citizens and if they are to realize fully the myriad benefits that nuclear energy offers them.

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Rare Earths

The Fraternal Fifteen

by Karl A. Gschneidner, Jr.

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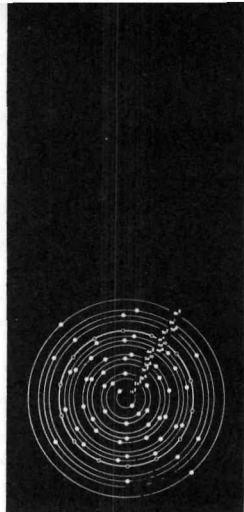
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been granted several patents for uses of rare earth and plutonium alloys.



Rare Earths

The Fraternal Fifteen

By KARL A. GSCHNEIDNER, JR.

INTRODUCTION

An Analogy

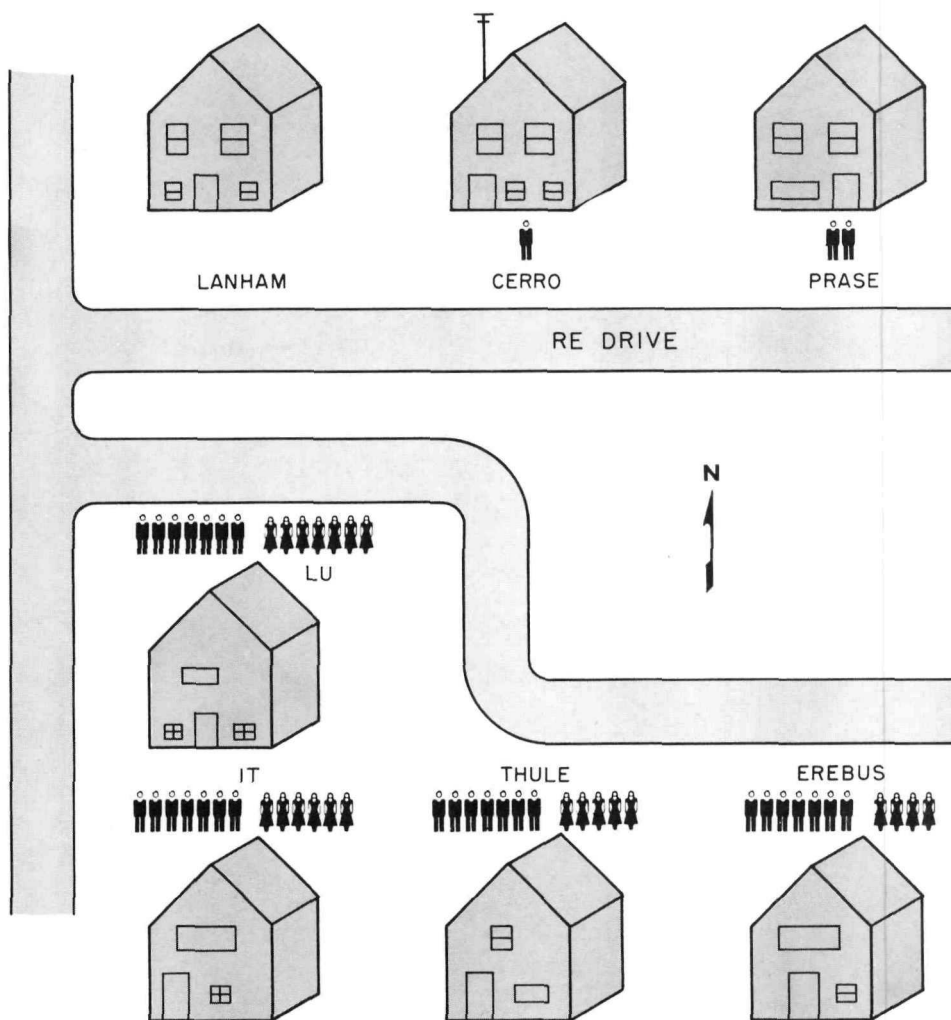
The rare earths make up a fascinating family of elements which for many years were something of a scientific mystery because:

They have such nearly identical chemical properties they are difficult to tell apart.

They make up about one-sixth of all naturally occurring elements, but the entire group occupies only one position in the Periodic Table.

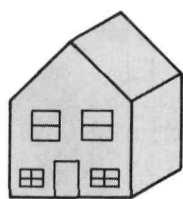
They are not naturally radioactive, but often are found in the same minerals with radioactive thorium or uranium, may be formed as nuclear fission products, and have other important relationships with nuclear science and technology.

Perhaps by using a simple analogy, we can learn something about the rare earths.

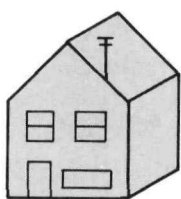


Let us pay a visit to RE Drive (Figure 1), a street with 15 houses that at first seem identical. A close look, however, shows minor variations from house to house and reveals that not one house really is the same as any other.

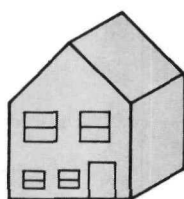
In a real street it is the people who live there who give the houses their individuality. And, as we get to know the people living on RE Drive, we will find some amazing differences here, too.



NEODIM



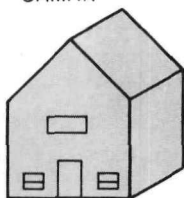
PROME



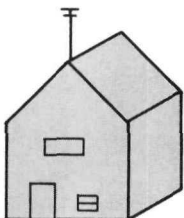
SAMAR

Figure 1 A map of RE Drive showing the residences of the 15 families living on this street and the children of these families.

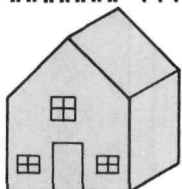
EURUS



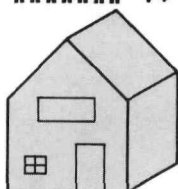
GAD



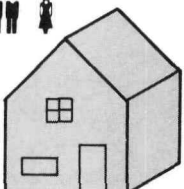
HOLM



DISPRO



TERBEE



The rare earths are like the houses on RE Drive. To most people they are metals that look much alike. But to scientists studying them closely each has its own personality making it different from its neighbors.

In Figure 1 we see something quite interesting about the children. The Lanham family has no children, while Mr. and Mrs. Cerro have one boy, Mr. and Mrs. Prase have two boys, and so forth, until we reach the Gad family, which has

seven boys. Amazing—of these first 8 families, each has all boys or no children whatsoever!

If we continue along RE Drive, we see that Mr. and Mrs. Terbee, who live next to the Gads, have seven boys and one girl. Each remaining family has seven boys, and the number of girls increases by one in each house until at the end of the block there are seven boys and seven girls at the home of Mr. and Mrs. Lu.

Highly unlikely in a real neighborhood! True—but for the rare earths this is a fairly accurate analogy. What do we mean? Just this: The children represent what scientists call the “ $4f$ electrons”. (The term $4f$ gives the location, or address, of the electron in the atom. We shall discuss this a little later.) The electron has an interesting property called “spin”. We can visualize the spin of an electron as that of a top spinning on its axis. There are two possible directions in which a top can rotate, clockwise or counterclockwise. An electron, like a top, can spin clockwise, in which case it is represented by a boy in Figure 1, or counterclockwise, represented by a girl.

If an atom has one $4f$ electron with a clockwise spin (a boy) and another $4f$ electron with a counterclockwise spin (a girl), these electrons are “paired up”. Conversely if an atom has several $4f$ electrons, all of which have the same spin, these electrons are called “unpaired” electrons. Thus the first rare earth, lanthanum, has no $4f$ electrons; cerium has one electron, which obviously is unpaired; praseodymium has two unpaired $4f$ electrons, and so forth until we reach gadolinium, which has seven unpaired electrons. (See tabulation on facing page.)

The next rare earth, terbium, has seven $4f$ electrons with clockwise spin and one with counterclockwise spin, giving six unpaired $4f$ electrons; dysprosium, the next rare earth, has five unpaired $4f$ electrons, and so forth until we reach lutetium, the last rare earth, which has no unpaired $4f$ electrons.

It is these $4f$ electrons which give each element its particular personality and thus distinguish one rare earth from another. For example, two of the outstanding differences among these very similar metals is the occurrence of ferromagnetism in gadolinium and of superconductivity in lantha-

NUMBER OF 4f ELECTRONS IN RARE EARTH ELEMENTS

Rare Earth Element	Clockwise Spin Electrons (No. of Boys)	Counterclockwise Spin Electrons (No. of Girls)	Unpaired Electrons (No. of Extra Boys)	Total Electrons (Boys + Girls)
Lanthanum	0	0	0	0
Cerium	1	0	1	1
Praseodymium	2	0	2	2
Neodymium	3	0	3	3
Promethium	4	0	4	4
Samarium	5	0	5	5
Europium	6	0	6	6
Gadolinium	7	0	7	7
Terbium	7	1	6	8
Dysprosium	7	2	5	9
Holmium	7	3	4	10
Erbium	7	4	3	11
Thulium	7	5	2	12
Ytterbium	7	6	1	13
Lutetium	7	7	0	14

num. At room temperature gadolinium metal is attracted to a magnet because it is ferromagnetic (see Figure 2), but the other rare earth metals are not. At low temperatures lanthanum is the only rare earth metal that loses all its resistance to electrical flow. At about 6°K^* it becomes a perfect conductor of electricity, that is, a "superconductor". Shortly we shall discuss why these two show these interesting properties and the others do not. As you may have guessed, it is probably due to the number of 4f electrons.

Definition

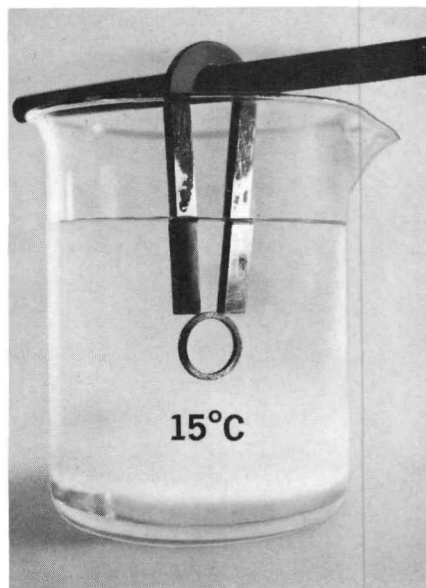
The term rare earths has its origin with the early discovery of these elements. The word *rare* arises from the fact that these elements were discovered in scarce minerals. The word *earth* comes from the facts that they were first isolated from their ores in the chemical form of oxides and that the old chemical terminology for oxide is earth. The words lanthanides and lanthanons, which are de-

*Temperature measured on the Kelvin scale; 6°K is equal to -267° centigrade, or -449° Fahrenheit.

rived from lanthanum, the first member of this series of elements, are also commonly used to describe the rare earths.

The name rare earths is actually a misnomer for these elements are neither rare nor earths. They are metals, and they are quite abundant. Cerium, which is the most abundant, ranks 28th in the abundances of the naturally occurring elements and is more plentiful than beryllium, cobalt, germanium, lead, tin, or uranium. The least abundant naturally occurring rare earth, thulium, is more plentiful than cadmium, gold, iodine, mercury, platinum, or silver. Indeed, 25% of the elements are scarcer than thulium.

Figure 2 *A ring of gadolinium metal is attracted to the magnet. This illustrates the ferromagnetic behavior of gadolinium when it is cooled below room temperature. If gadolinium were warmed to above room temperature, it would not be attracted to the magnet and would sink to the bottom of the beaker.*



Location

The Periodic Table in Figure 3 shows the location of the rare earth elements (the shaded row) with respect to the other elements. The rare earths, which pop out of the sixth period (row) of elements, are members of the Group IIIA elements, along with scandium (Sc) and yttrium (Y). Scandium and yttrium are quite similar to the rare earths and because of this similarity occasionally are included in discussions of them. As you undoubtedly remember from your

PERIOD	GROUP																VIII B															
	IA	II A															III B	IV B	V B	VI B	VII B	VIII B										
1	1 H																2 He															
2	3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne										
3	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar																								
4	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														
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	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 At	86 Rn
7	87 Fr	88 Ra	89 Ac																													

Figure 3 The shaded elements rising out of the sixth row (period) are the rare earths.

Figure 3 The shaded elements rising out of the sixth row (period) are the rare earths.

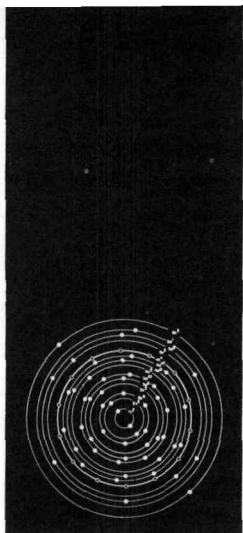
study of chemistry, elements in the IIIA Group behave chemically as trivalent* substances. Thus the rare earths are quite similar to one another in chemical properties, but differ from one another by the number of 4f electrons each has. As we shall see, these 4f electrons are responsible for the variety of differences among these Fraternal Fifteen.

Why the Interest?

There are several reasons why people are interested in the rare earths. Today, we know what we know about the Fraternal Fifteen essentially because of scientific curiosity, and this is still one of the most important reasons for studying the rare earths. Because we do not fully understand them, they present a great challenge to fundamental scientists. It was scientific curiosity which led to the discovery of these

*Valence is a measure of an element's chemical combining power. A trivalent atom can hold three atoms of hydrogen in combination.

elements, and applied research has developed a number of commercial uses for them. This is the second important reason for knowing more about the rare earths—to develop commercial products which are beneficial to mankind. Scientific curiosity also led to the discovery of atomic fission, and it was found subsequently that some of the rare earths are important fission products. In the 1940s the Atomic Energy Commission (AEC) began a program, which is being continued today, to obtain more information about the rare earths and their role in atomic energy—the third important reason.



HISTORY

The Age of Discovery

Although the existence of the rare earths dates back to the formation of the earth, man's first acquaintance with them occurred in 1787. Little did Lt. C. A. Arrhenius of the Swedish Army realize that his attraction to a unique black mineral, which he stumbled on while examining a number of ores in a quarry in Ytterby (a small town near Stockholm, Sweden), would set off the most complex element hunt in the history of science. This finally was culminated in 1947 with the discovery of promethium.

The history of the individual rare earth elements is both complex and confused, mainly because of the great similarity of these Fraternal Fifteen. Many so-called "newly discovered elements" which were hailed over the years were, in fact, not one element but mixtures of as many as six different rare earth elements. Furthermore, there were claims of discovery of a large number of other "elements", which were supposed to be members of the rare earth series, but were not.

Confusion Gives Way to Understanding

By the time the last naturally occurring rare earth was discovered (lutetium in 1907), the chemistry of the rare

earths was hopelessly snarled, since no one knew how many rare earth elements there could actually be. Fortunately, in 1913-1914 the physicists Niels Bohr and H. G. J. Moseley laid the groundwork that eventually resolved this situation. Bohr's theory of the hydrogen atom enabled theoretical physicists to show that only 15 rare earths could exist. Moseley's experimental studies verified the existence of 14 of these elements and showed that the 15th rare earth should be element 61 and lie between neodymium and samarium.

In the 1920s the search for element 61 was intensified, and a number of scientists claimed to have isolated and identified it. The furor of these claims and counterclaims slowly died down by 1930; but it was not until 1947, after the fission of uranium, that element 61 definitely was isolated and named promethium by J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, at the AEC Oak Ridge National Laboratory. Further research showed that promethium is radioactive and that the longest half-life* of any promethium isotope† is 18 years and therefore promethium could not occur in nature.

A New Era

During the 160 years of discovery (1787 to 1947) the separation and purification of the rare earth elements was a difficult and time-consuming process. Indeed, some men spent their whole lives attempting to obtain a rare earth 99% pure. Then, in a brief additional period as atomic research continued, it was found that the rare earths often result from the fission of a uranium nucleus and are, in fact, important fission products.

Because of the AEC's interest, an intensive effort was made to find a fast, efficient method for separating the rare earths. In 1947 G. E. Boyd and his co-workers at the Oak Ridge National Laboratory and F. H. Spedding and his co-

*The time required for a radioactive substance to lose half its radioactivity.

†Isotopes of a given element are atoms that have the same number of protons and electrons but different numbers of neutrons. The fact that they have the same number of electrons causes them to be identical in chemical behavior. The fact that they have different numbers of neutrons causes them to differ in weight. For more about atomic structure, see *Our Atomic World*, a companion booklet in this series.

workers at the Ames Laboratory simultaneously published data which showed that the ion-exchange process (to be explained later) offered a means for separation, at least on a small scale. Shortly thereafter, Spedding, J. E. Powell, and their co-workers began to prepare large quantities of individual rare earths that were 99.99% pure.

Today there are about a half-dozen companies that commercially produce high purity rare earths in pound quantities. Cerium and lanthanum metals cost about \$30 per pound. The most expensive rare earth metals (europium, terbium, thulium, and lutetium) cost about \$1000 to \$1500 per pound. This compares to about \$5 per pound for high-purity lead, mercury, and zinc; \$50 to \$150 per pound for silver, titanium, and chromium; and \$500 to \$1200 per pound for gold, platinum, and palladium.

Derivation of the Names and a Recapitulation

LANTHANUM, atomic number 57, was discovered by C. G. Mosander in 1839. The name was derived from the Greek word *lanthanein*, which means to be hidden or concealed, because it was found in a mixture of oxides which for 36 years had been thought to be pure cerium.

CERIUM, atomic number 58, was named after the newly sighted asteroid Ceres in 1803. Cerium was discovered by M. H. Klaproth, and by J. J. Berzelius and Wilhelm Hisinger, independently.

PRASEODYMIUM, atomic number 59, was discovered in 1885 by C. A. von Welsbach to be one of the two major components of didymium.* The name is derived from the Greek words *prasios* and *didymos*, meaning green twin.

NEODYMIUM, atomic number 60, was discovered in 1885 by C. A. von Welsbach to be the other major component of didymium. The name is derived from the Greek words *neos* and *didymos*, which mean new twin.

PROMETHIUM, atomic number 61, was discovered in 1947 by J. A. Marinsky, L. E. Glendenin, and C. D. Coryell in the

*Didymium was thought to be a pure element by C. G. Mosander, who derived the name didymium from the Greek word *didymos*, which means twin, because it was codiscovered along with lanthanum. The word didymium today commonly refers to alloys consisting primarily of praseodymium and neodymium.

fission products of uranium. The name, from Greek mythology, was derived from Prometheus, who stole fire from heaven and gave it to man.

SAMARIUM, atomic number 62, was discovered by Lecoq de Boisbaudran in 1879 and was named after a Russian mine official, Colonel M. Samarski.

EUROPIUM, atomic number 63, was discovered in 1889 by Sir William Crookes and named after the continent Europe.

GADOLINIUM, atomic number 64, was named after the Finnish chemist Johan Gadolin by J. C. G. Marignac, who discovered it in 1880.

TERBIUM, atomic number 65, was discovered by C. G. Mosander in 1843, who originally called it erbium. Later workers confused erbium and terbium, and today, because of common usage, element 65 is known as terbium. The name terbium is derived from the town of Ytterby, Sweden.

DYSPROSIUM, atomic number 66, was discovered by Lecoq de Boisbaudran in 1886; he coined this name from the Greek word *dysprositos*, which means hard to get at, because it was one of the last rare earth elements discovered.

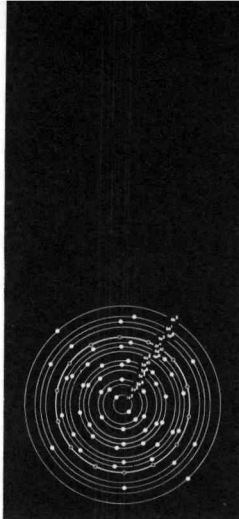
HOLMIUM, atomic number 67, was discovered independently by P. T. Cleve and J. L. Soret in 1879. The name holmium is derived from the Latinized word for the city of Stockholm, *Holmia*.

ERBIUM, atomic number 68, was discovered by C. G. Mosander in 1843, who originally called it terbium. Because later workers by accident called "Mosander's terbium" erbium, element 68 is now known as erbium. The name erbium is also derived from the village of Ytterby.

THULIUM, atomic number 69, was discovered in 1879 by P. T. Cleve and was named for Thule, the ancient name of Scandinavia.

YTTERBIUM, atomic number 70, was discovered by J. C. G. Marignac in 1878 and obviously is named for the town of Ytterby.

LUTETIUM, atomic number 71, was independently discovered by G. Urban in 1907 and C. A. von Welsbach in 1908. Urban named element 71 for the ancient name of Paris, Lutetia.



ATOMIC STRUCTURE

From Simple to Complex

Let us look at the atomic structures of these rare earth elements to understand both their similarities and their differences. But first we shall briefly review the atomic structures of some of the simpler elements.

As we remember from our studies of chemistry or physics matter is made up of atoms, which, according to one model used to visualize them, consist of a nucleus (containing protons and neutrons) and planetary electrons which revolve about the nucleus like a tiny solar system (see Figure 4). Since an atom is electrically neutral, the negative charges of the planetary electrons are balanced by an equal number of positive charges (the protons) in the nucleus. The number of electrons (and also protons) a particular element has is the atomic number of the element. For example, in Figure 4 the carbon atom, whose atomic number is 6, has 6 electrons, which travel about the nucleus, N. (The nucleus of course contains 6 protons, but these are not shown in Figure 4.)

The electrons are restricted to particular orbits, or "shells". Hydrogen has 1 shell with 1 electron in it. Helium also has 1 shell but with 2 electrons in it. Lithium has 2 shells, the inner one with 2 electrons and the outer with 1. The elements that follow lithium in the Periodic



Figure 4 *The carbon atom has 6 planetary electrons (solid circles) revolving about the nucleus, N.*

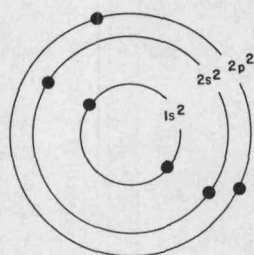
Table (see Figure 3) up to neon all have 2 shells, but the number of electrons in the outer shell of each varies, from 2 for beryllium to a maximum of 8 for neon. The next element, sodium, has 3 shells; the inner 2 have 2 and 8 electrons, respectively, and the third (or outer shell) has 1 electron.

The electronic structures of the other elements are built up in a similar regular manner, with a maximum of 2 electrons in the first shell, 8 in the second, 18 in the third, 18 in the fourth, and so on; the outermost shell, however, is always limited to a maximum of 8.

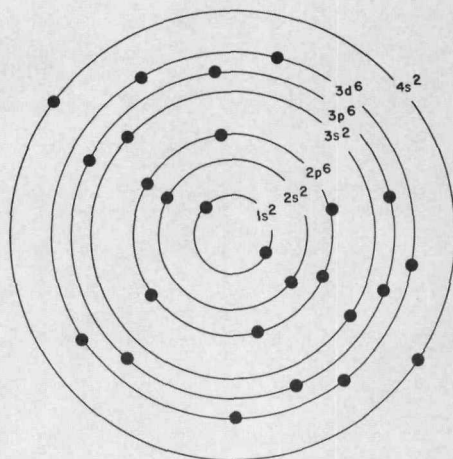
For example, argon's configuration is 2:8:8, krypton's is 2:8:18:8, and xenon's is 2:8:18:18:8. (See Table on pages 22 and 23.)

Actually, to understand the atomic structure of the rare earths, we must go beyond this simple picture of the atom and examine sublevels (or suborbitals) of the shells. The sublevels are designated by the letters *s*, *p*, *d*, and *f*. To distinguish which main level (or shell) we are referring to, the letters for sublevels are prefixed by a number from 1 to 7, where 1 refers to the innermost level, 2 to the next level, 3 to the next, etc. For example, carbon, which is shown in Figure 5a, has 2 electrons designated as $1s^2$ (the superscript after a letter always tells us the number of electrons in the sublevel). The second level is divided into two sublevels, $2s$ and $2p$, each of which has 2 electrons.

Any *s* sublevel can have only 1 or 2 electrons in it, any *p* can contain up to a maximum of 6, any *d* a maximum of 10, and any *f* a maximum of 14. Thus, for elements beginning with carbon, it is possible to put 4 more electrons in the $2p$ sublevel before it becomes filled, which occurs at neon; each additional electron results in a new element. A more complex example is that of iron, shown in Figure 5b. Iron has a $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^6$, and $4s^2$ configuration; its sublevels all have the maximum permissible number of elec-



(a) *Electronic structure of carbon.*



(b) *Electronic structure of iron.*

trons except the $3d$, which could contain 4 more. We should note that the $4s$ sublevel is completed before the $3d$ level is filled. This schedule of filling is the general rule, not an exception, for the elements that have an atomic number of 21 or greater.

Let us proceed from iron to elements with higher atomic numbers. If we continue to add electrons to the $3d$ sublevel, remembering only 4 more are needed to fill it, we will reach zinc. The next electrons are added to the $4p$ sublevel, which when filled constitutes the rare gas krypton.

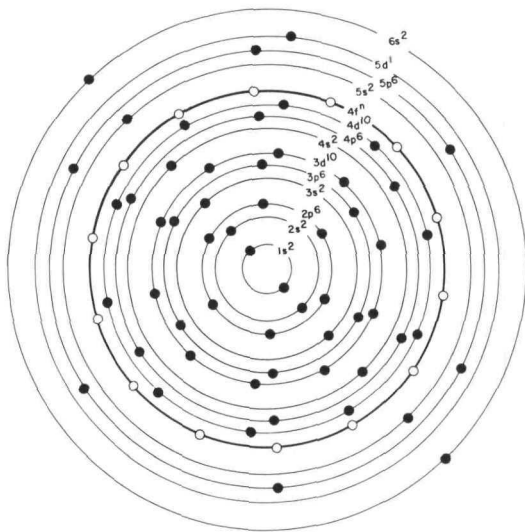
The next row of elements is built up in the same manner: The first two electrons go into the $5s$ sublevel, before the $4d$ and $5p$ sublevels are filled, at which point we have reached the end of the fifth period, with xenon. The next 2 electrons go into the $6s$ sublevel (barium), and it looks as if the same process is about to repeat itself for a third time. This is, indeed, true for the next electron added—but thereafter the Periodic Table is never the same again!

The Rare Earths

After barium, the next added electron goes into the $5d$ sublevel, giving us lanthanum—the first of the Fraternal Fifteen. That is, lanthanum has a $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 5d^1, 6s^2$ configuration with no

4*f* electrons (see Figure 6). The next electron that is added does not go into the 5*d* sublevel, as might be expected from the pattern of the fourth and fifth periods, but goes in the 4*f* sublevel; in Figure 6 one of the open circles would be shaded to represent the electronic configuration of cerium. The

Figure 6 *The open circles represent the possible 4*f* electrons a rare earth may have. That is, no 4*f* electrons for lanthanum, 1 for cerium, 2 for praseodymium, etc., up to 14 for lutetium.*



next 13 electrons also go one by one into the 4*f* sublevel, which then is completely filled at lutetium. (One more open circle in Figure 6 would be shaded for each new electron.)

We notice several interesting features in Figure 6. For all of the 15 rare earths, the outermost electrons are always the same: $6s^2$ and $5d^1$. Also, between these outer electrons ($6s^2$ and $5d^1$) and the 4*f* electrons, there are six 5*p* and two 5*s* electrons, which shield the 4*f* levels from external influences. Since the chemical and most of the physical properties of any element depend most strongly on these outer electrons ($6s^2$ and $5d^1$), we see why the rare earths are trivalent (the outermost 6*s* and 5*d* subshells give up 3 electrons), why they are so similar to one another, and why 4*f* electrons do not enter into chemical bonding. Moreover, we can appreciate the difficulties the discoverers had in separating, isolating, and identifying the individual rare earths.

Similar but Different

If the rare earths are so similar to one another, why are they not identical? Why do they show some minor variation from one rare earth to the next? Why do they show some major differences? We will try to answer these questions, but to do so we must examine the structure of the atom in more detail.

As we proceed from one rare earth to the next, an electron is added to the $4f$ level, and a proton, which has a positive charge, is added to the nucleus. Naturally the electronic charges are balanced in this process, as they must be; but something else occurs at the same time. The sublevels that lie outside the $4f$ level, specifically the $5s$, $5p$, $5d$, and $6s$ levels, do not "see" or "feel" the same nuclear charge in any one rare earth as in the next. That is, the effective nuclear charge influencing these outer electrons increases as we proceed from lanthanum to cerium to praseodymium, and so forth, all the way to lutetium. What do we mean by "ef-

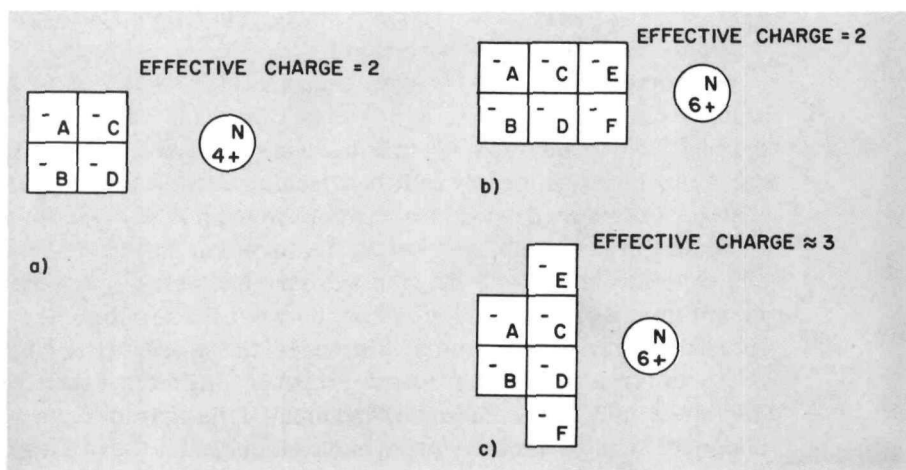


Figure 7 Illustration of the effective charge "seen" by electrons A and B from the nucleus, N. Initial condition, a, where A and B "see" an effective charge of 2. In b and c, 2 additional electrons, E and F, have been added. In b, the effective charge remains at 2 because of complete shielding by the additional electrons. In c, the effective charge increases to about 3 because the additional electrons do not completely shield electrons A and B from the nucleus.

fective nuclear charge"? Perhaps an illustration may help us here. In Figure 7a we see 4 electrons, represented by the 4 boxes labeled A, B, C, and D, near a nucleus, represented by a circle N, which has a positive charge of 4. Electrons C and D see the full positive charge of 4; but electrons A and B only see an effective positive charge of 2, since the negative charges of C and D cancel 2 of 4 positive charges.

If we now add 2 more electrons and 2 more positive charges and if we restrict the addition of these 2 electrons to one of the positions shown in Figures 7b or 7c, then we note in Figure 7b that electrons A and B still only see an effective positive charge of 2 since the 2 new electrons (E and F) cancel the additional positive charge. If, however, electrons are added as in Figure 7c then we note that electrons E and F, since they do not lie directly between electrons A and B and the nucleus, cancel only a part of the additional positive charge in the nucleus; therefore, electrons A and B see a larger effective positive charge. When electrons are added to the $4f$ level, they behave as in the last case; that is, they only partially cancel the nuclear charge.

What effect has this increasing effective nuclear charge on the outer electrons? As we know, charges of opposite sign attract one another, and thus the negative electrons in the $5s$, $5p$, $5d$, and $6s$ sublevels are drawn closer to the nucleus as one proceeds from lanthanum through this series to lutetium. Specifically, the actual size of the lanthanum atom is larger than the cerium atom, which is larger than praseodymium, and so on; this continues to lutetium, which is the smallest. This effect is known as the *lanthanide contraction* and is illustrated in Figure 8 for the trivalent rare earth ions. It is this lanthanide contraction which accounts for the slight differences and systematic variation in many chemical and physical properties of the Fraternal Fifteen. We have now answered the first two questions: why the rare earths are not identical and why they show minor variations.

In order to answer the third question—why do they show some major differences—we must continue to explore the structure of the atom. Our answer can be found in F. Hund's brilliant discovery in the 1920s that the states of atoms which have a completely filled or half-filled sublevel are

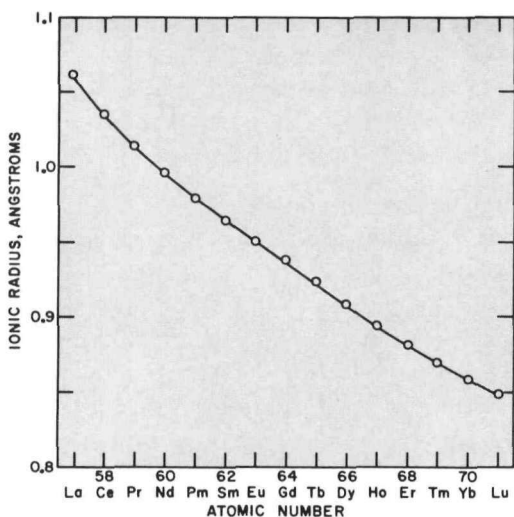


Figure 8 A plot of the trivalent ionic radii in Angstroms, against the atomic numbers of the rare earths. The decrease in size of the radius with increasing atomic number illustrates the lanthanide contraction.

stable states. This means that, if we have a half-filled p state, that is, p^3 , this is more stable than the p^2 or p^4 states. Or, if we have a completely filled p state (p^6), it is more stable than p^5 . Similarly d^5 , d^{10} , f^7 , and f^{14} are more stable than states which are less than half filled or more than half filled but less than completely filled.

In the rare earths, gadolinium has a half-filled state ($4f^7$) and lutetium has a completely filled state ($4f^{14}$). Europium, which has a $4f^6$ state, and ytterbium, which has a $4f^{13}$ state, under some conditions give up their $5d$ electron to the $4f$ level, forming a $4f^7$ state for europium or a $4f^{14}$ state for ytterbium. In so doing, the europium and ytterbium become divalent, that is, the outermost electrons are only the two $6s$ electrons. Terbium, which has a $4f^8$ state, can assume the $4f^7$ level under very limited conditions by transferring an electron from the $4f$ level to the $5d$ level. In this case terbium has a valence of 4 since the outermost sublevels ($6s$ and $5d$) each have 2 electrons in them. In some instances a state with no $4f$ electrons is more stable than a state with one $4f$ electron. This is the situation with cerium, in which its one $4f$ electron under some conditions transfers to the $5d$ level to give tetravalent cerium.

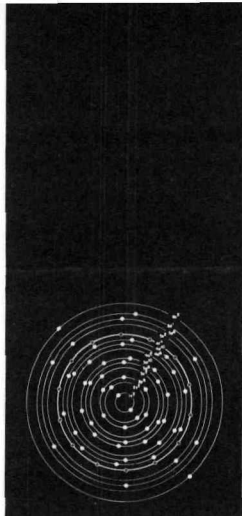
Now we have seen that europium and ytterbium can exhibit both di- and trivalency and cerium and terbium both

tri- and tetravalency. The ability of these four to change valence states will be pointed out again as we discuss chemical and physical properties of these 15 rare earths.

Unpaired Electrons

One more point must be examined before we can proceed. This was brought up in the Introduction but now needs to be emphasized. As is shown in Figure 1 and in the tabulation on page 5, as electrons are added to the $4f$ sublevels from cerium to gadolinium, they have only a clockwise spin, but from terbium to lutetium the additional electrons now have a counterclockwise spin. Every time an electron with counterclockwise spin is added, an electron with clockwise spin is paired up. That is, the number of unpaired electrons increases from 0 for lanthanum to 7 for gadolinium, and then again decreases to 0 for lutetium as we proceed along this series. The number of unpaired $4f$ electrons is quite important to several properties of the rare earths.

With this background of the atomic structure of the Fraternal Fifteen, we are in a position to discuss some of their interesting properties and behaviors.



CHEMISTRY AND SEPARATION

The chemistry of the Fraternal Fifteen played an important role in their early history. Indeed, it took the early rare earth chemists many years—yes, years—to separate some of these elements from one another and to purify them. For a few elements, however it is a simple matter, requiring only several hours work, to separate them from the other 14 elements. Why is this? To find the answer, we must turn again to their atomic structure.

Oxidation–Reduction Reactions

As we have noted, normally the rare earth elements easily give up 3 electrons to form trivalent ions; but for a few of them there is a tendency to form either divalent ions, such as Eu^{+2} and Yb^{+2} , or tetravalent ions, such as Ce^{+4} and Tb^{+4} . It is possible by oxidation or reduction reactions to separate some of these four rare earths, especially cerium and europium, from a mixture containing all of the rare earths.

If we have in solution a mixture of rare earths in the form of nitrates, $\text{R}(\text{NO}_3)_3$ (where R represents the rare earths), we

Electronic Configuration of the Elements†

Atomic No.	Element	K	L	M	N	O	P	Q								
		1	2	3	4	5	6	7								
		s	s	p	s	p	d	f	s	p	d	f	s	p	d	f
1 2	H He	1 2														
3 4 5 6 7 8 9	Li Be B C N O F	2 2 2 2 2 2 2	1 2 2 2 2 2 2													
10	Ne	2	2	6												
11 12 13 14 15 16 17	Na Mg Al Si P S Cl	2 2 2 2 2 2 2	2 2 2 2 2 2 2	6 6 6 6 6 6 6	1 2 2 2 2 2 2											
18	Ar	2	2	6	2	6										
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35	K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	1 2 2 2 2 3 5* 5 6 7 8 10* 10 10 10 10 10 10											
36	Kr	2	2	6	2	6	10	2	6							
37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53	Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10											

* Note irregularity.

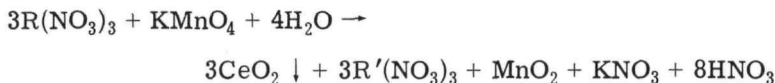
† This applies to a free gaseous atom. The rare earth values for 4f electrons may differ from those given in the table on page 5 or in Figure 15, page 35, in that the latter values refer to solid or liquid states, or to chemical compounds.

Atomic No.	Element	K		L		M		N		O		P		Q	
		1	2	3	4	5	6	7	8	9	10	11	12		
		s	s	p	s	p	d	f	s	p	d	f	s	p	d
54	Xe	2	2	6	2	6	10	2	6	10	2	6			
55	Cs	2	2	6	2	6	10	2	6	10	2	6	1		
56	Ba	2	2	6	2	6	10	2	6	10	2	6	2		
57	La	2	2	6	2	6	10	2	6	10	2	6	1	2	
58	Ce	2	2	6	2	6	10	2	6	10	2*	2	6	2	
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6	2	
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6	2	
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6	2	
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6	2	
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6	2	
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	
65	Tb	2	2	6	2	6	10	2	6	10	9*	2	6	2	
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6	2	
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6	2	
68	Er	2	2	6	2	6	10	2	6	10	12	2	6	2	
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6	2	
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6	2	
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4	2
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9*	0
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10	2
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	2

* Note irregularity.

Source: *Handbook of Chemistry and Physics*, 45th Edition, Chemical Rubber Publishing Company, 1965.

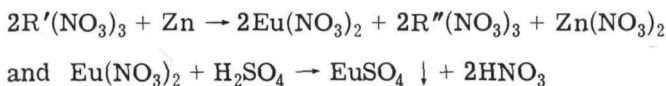
can separate cerium by oxidation, using potassium permanganate (KMnO_4) according to the equation:



where R' represents the rare earths with the cerium removed.

In this reaction the manganese in the Mn^{+7} state oxidizes Ce^{+3} to Ce^{+4} (in the form CeO_2). The CeO_2 which is formed is insoluble if the nitric acid (HNO_3) is neutralized by sodium carbonate.

If we wish to separate the europium from this mixture of rare earths, we pass this solution of rare earth nitrate over zinc metal, and the europium is reduced. The addition of sulfuric acid causes the divalent europium sulfate to precipitate out of solution. This process is summarized as:



where R'' represents the rare earths with both the cerium and europium removed.

These chemical reactions can usually be carried out in a few minutes, and therefore commercial producers regularly use them to separate cerium and europium from a mixture of rare earths. Separation of the remaining rare earths is not so easily accomplished, as we shall see.

Fractional Crystallization

Before World War II the most common procedure for separating a mixture of rare earths from which cerium and europium already had been removed was fractional crystallization. In discussing atomic structure, we noted that the properties of neighboring rare earths are not exactly alike. Specifically, the solubility of the double rare earth ammonium nitrates, $\text{R}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, increases as we proceed along the series from lanthanum to lutetium. Therefore, if we slowly reduce the solubility by lowering the tem-

perature, lanthanum ammonium nitrate (still containing a small amount of praseodymium and neodymium) crystallizes out of the solution, which still contains some lanthanum. If we then remove the liquid from the crystallized salt, we find that the salt contains more lanthanum and the liquid less lanthanum than the original mixture of rare earths. By dissolving the salt in water and repeating the process, we get further purification.

This purification process is illustrated schematically in Figure 9, where the less soluble compound is represented by the dark half of A and the more soluble compound by the light half of A. At the start of the process at A, all of the rare earth salts are soluble in the liquid. Then the less soluble salt (lanthanum ammonium nitrate) is allowed to crystallize out of solution by evaporating some of the liquid or by lowering the temperature of the solution. If the liquid is poured (decanted) off the crystallized salt, we have now proceeded from A to B (the crystallized salt) and B' (the liquid). We see that at B the salt contains more lanthanum, and at B' the liquid contains less lanthanum, than it did at A. If we repeat this process, the salt that crystallizes out contains more lanthanum as we proceed from step B to C to D, and so on.

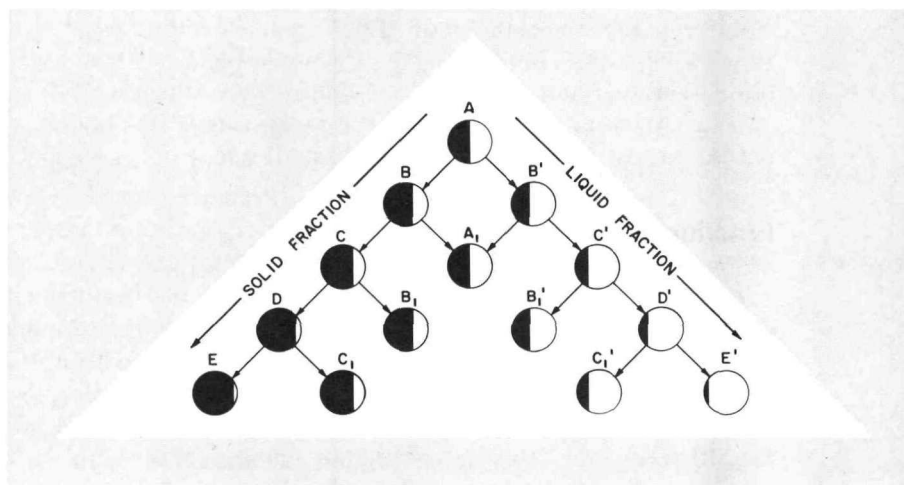


Figure 9 Schematic drawing showing how rare earths are separated from one another by fractional crystallization.

Meanwhile at the liquid fraction B' , the solubility is lowered forcing additional lanthanum to crystallize out of B' , and the liquid at C' contains less lanthanum. Continuing this process, we see that the liquid continues to become poorer in lanthanum as we proceed from step C' to D' to E' , and so on. The materials left over at steps A_1 , B_1 , B'_1 , C_1 , and C'_1 are saved until the next run of a similar mixture of rare earths and are combined at the appropriate step— A , B , B' , C , or C' —of this second run.

Ion Exchange

Today, ion exchange is the best and most popular way of separating a mixture of rare earths. This process, which also is used in some home water softeners, is explained in Figure 10. In Figure 10a we have portrayed a column containing fine beads or granules of a solid chemical compound (called a resin), which has an easily ionized hydrogen atom, H . When a chloride solution containing a mixture of rare earths is added to the top of the column, it percolates down through the granules of the resin and the rare earth ions, R^{+3} , are exchanged for the hydrogen ions on the resin. That is, a mixture of rare earths, A and B , is absorbed by the resin in the column (Figure 10b). In Figure 10c the entire column has been loaded with the rare earth mixture; at this stage a solution containing a "complexing agent" is added to the column.

The complexing agent, which is an organic compound, forms stable compounds with the rare earths by exchanging ammonium ions, NH_4^+ , for the R^{+3} on the resin. The stability of this rare earth complex depends very heavily on the size of the rare earth ion. Lutetium, the smallest rare earth ion, forms the most stable complex, and lanthanum, the largest ion, the least stable complex. As the complexing agent passes down the column, it preferentially forms a complex with B , the smaller rare earth ion, leaving the larger rare earth ion, A , on the resin (Figure 10d). The ammonium ion which is absorbed on the resin, in exchange for B , is indicated in Figure 10d by N . The complexed B , which is free of A , is collected as it leaves the column. After all of the B has been complexed, the A is complexed, in turn, and col-

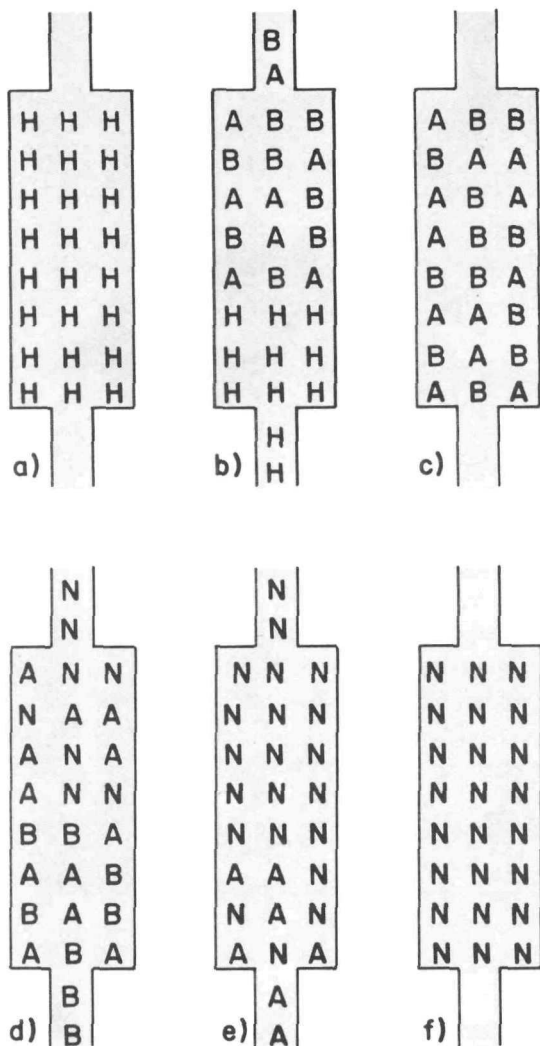


Figure 10 Schematic representation of events that occur during ion-exchange separation of the rare earths.

lected as it leaves the column (Figure 10e). The resin containing ammonium ions (Figure 10f) then is treated with an acid to convert the resin to its original condition (Figure 10a).

The advantage of ion exchange is that this process proceeds on an atomic scale, whereas the fractional crystalliza-

tion method involves perhaps as much as 100 grams of rare earth in solution. Not only is the ion-exchange method much faster, but it achieves higher purities than were possible by the older methods (such as fractional crystallization).

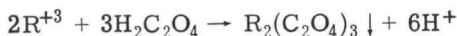
In Figure 11 we see some ion-exchange columns that are used to separate mixtures of rare earths at the Ames



Figure 11 *Ion-exchange columns used to separate the rare earths from one another. Individual rare earths are collected in the large carboys as they are removed from the columns. The jars in front of the chemist contain the oxides of the individual rare earth elements.*

Laboratory on the Iowa State University campus. The last column on the right shows a number of distinct bands of the separated rare earths as they pass through. An artificial mixture of rare earths, containing only ytterbium, erbium, yttrium, samarium, neodymium, and praseodymium had been added to this column. Since the smallest size rare earth passes down the column first and the largest rare earth last, we see that ytterbium complex, Yb, is the lowest band

in this column, followed by erbium complex, Er; yttrium complex, Y; samarium complex, Sm; neodymium complex, Nd; and praseodymium complex, Pr, in that order. Above the praseodymium band is the final band containing ammonium ion, NH_4^+ . As the rare earths leave the column, the solutions flow into the large glass jugs (carboys). Each rare earth is removed from the solution by precipitation with oxalic acid, according to this equation:



The rare earth oxalate is converted to the oxide form by heating in a furnace at about 800°C .



The rare earth oxides are shown in the small jars in front of the three large carboys and the chemist. The oxides are shown from left to right in the order they are removed from the ion-exchange column, beginning with lutetium oxide, Lu_2O_3 , and ending with lanthanum oxide, La_2O_3 . The two dark jars contain terbium oxide, Tb_4O_7 (near the center, between Y_2O_3 and Gd_2O_3), and praseodymium oxide, Pr_6O_{11} (near the right side, between Nd_2O_3 and CeO_2).

Preparation of the Metal

Purified rare earth oxide is the starting material for the preparation of rare earth metal. If we mix the oxide with ammonium bifluoride and heat this mixture to about 300°C , we form the rare earth fluoride, according to the following equation:



The rare earth fluoride is mixed with calcium metal; this mixture is placed in a tantalum crucible and heated to between 1000 and 1500°C . At this elevated temperature the calcium metal reduces the rare earth fluoride to pure metal, according to the equation:



At this temperature, both the rare earth metal and the calcium fluoride, CaF_2 , are liquid and insoluble in each other. Since the calcium fluoride is less dense than the rare



Figure 12 Some rare earth metals as prepared from their fluorides. The four samples in the back row are 10 cm in diameter, and the five in the front row are 5 cm in diameter. The chemist is weighing out a rare earth fluoride, which he will mix with the calcium chips to prepare some more rare earth metal.

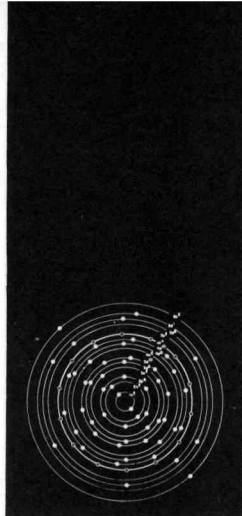
earth metal, it floats to the top, and the rare earth sinks to the bottom, just as a mixture of water and oil separates. After cooling the mixture to room temperature, we have pure rare earth metal by simply lifting off the disk of calcium fluoride sitting on top of it. A group of these rare earth

metals is shown in Figure 12. The chemist shown is preparing to reduce a rare earth fluoride with calcium.

The rare earth trifluorides of samarium, europium, and ytterbium cannot be reduced by calcium to give the pure metal because the difluoride is all that is obtained. It is possible, however, to reduce oxides of these three elements by mixing lanthanum metal with one of them and then heating the mixture to about 1000°C. At this temperature the lanthanum reduces the oxide and the metal formed distills off much the same way steam escapes from a tea kettle. By making some sort of a provision for catching the metal vapor, we obtain the pure metal. The chemical reaction for this process is summarized as:



Thus, we are able to prepare all of the rare earth metals by one of the two processes just discussed.



PHYSICAL PROPERTIES

Most of the physical properties of the rare earths, such as the atomic volume, melting point, hardness, thermal expansion, specific heat, and compressibility, vary slightly and systematically from one element to the next. This variation is due to the filling of the $4f$ level, but in general this variation does not give us much information about the number of $4f$ electrons in an atom of a particular rare earth.

There are a few physical properties that are quite sensitive to the number of $4f$ electrons, however, and from these properties we are able to tell a good deal about the electronic structure of the rare earth. The magnetic properties and the atomic spectra belong in this class.

Melting Points

The melting points of the rare earths (Figure 13) are seen to vary in an almost smooth manner, from 920°C for lanthanum to 1650°C for lutetium. (For the time being we will ignore the low values for europium and ytterbium.) As noted when we discussed the atomic properties, (1) the outer electronic configuration remains the same, (2) the number of $4f$ electrons increases by one as we go from one rare earth element to the next, and (3) as a result of (1) and (2) the atomic size becomes smaller as we proceed from lanthanum

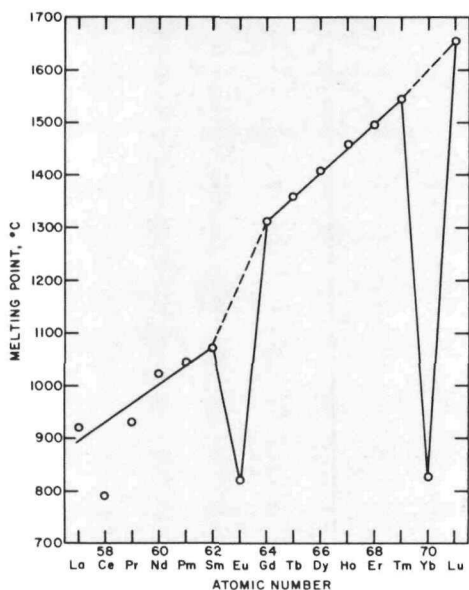


Figure 13 *The melting points of the rare earth metals.*

to lutetium (the lanthanide contraction). Because the atoms are closer together in lutetium than in lanthanum while the number of valence electrons remains constant, there is a stronger attraction between the lutetium atoms than between the lanthanum atoms. It is this effect which leads to an increase in the melting point as we proceed along the series.

One may wonder why the values for europium and ytterbium are low. As we remember from our discussion of atomic properties of the rare earths, europium and ytterbium had a tendency to become divalent. Examination of the melting points of the other elements in this portion of the Periodic Table shows that the melting points increase with increasing valence. Therefore, divalency in europium and ytterbium might explain their low melting points. As we shall see, this divalency is confirmed by magnetic measurements.

Magnetic Behavior

The relation between magnetic behavior and electronic structure is a very complex and difficult subject—well beyond the scope of this booklet to explain in detail. Perhaps we may be able to discuss this relation in a qualitative and elementary way by using our analogy between the boys and

the girls and the clockwise and counterclockwise spins of the 4f electrons.

Before we proceed, we should point out that because an electron spins it generates a magnetic field. Let us assume that if an electron has a clockwise spin the north pole of the magnetic field is pointed up (Figure 14) and if the electron has a counterclockwise spin the north pole is pointed down.

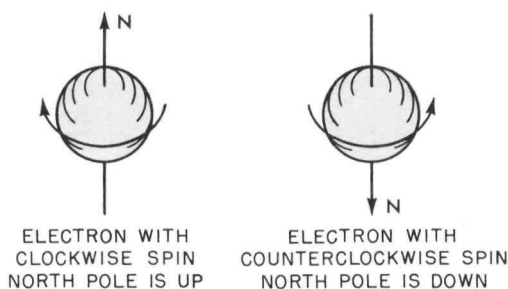


Figure 14 Relationship between the direction of the magnetic field (north pole) and the direction of spin of an electron.

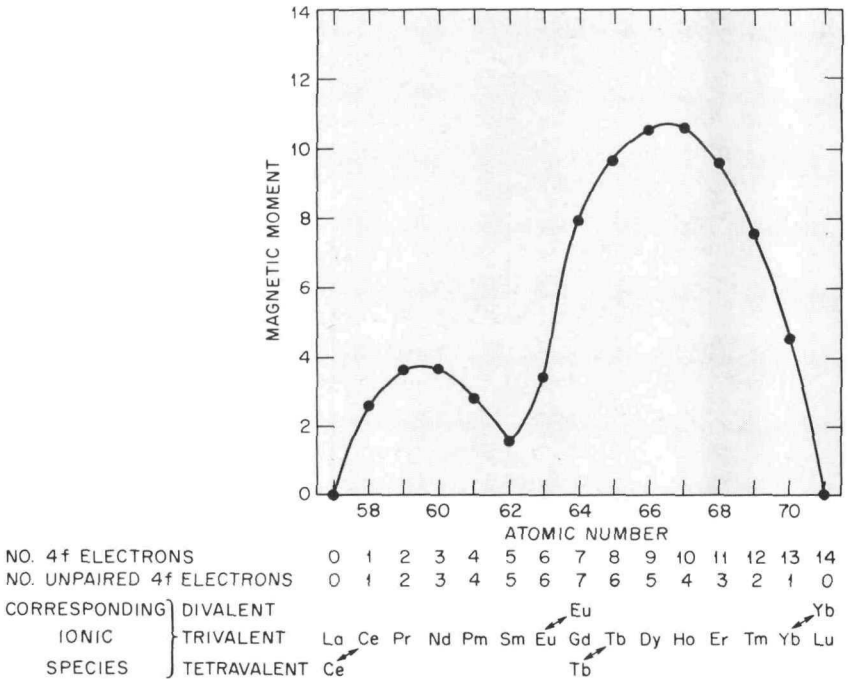
If two electrons are paired up, the magnetic fields cancel one another and no magnetic field can be found. If we have a material with one unpaired electron, this substance should exhibit some magnetic behavior; in general this behavior is measured in terms of a *magnetic moment*,* which is given in units called Bohr magnetons. We might conclude that, if a substance has two unpaired electrons, this material would have twice the magnetic moment of a substance that has only one unpaired electron, but this conclusion would be wrong. The true picture is quite complex. The reason is that the presence of a second unpaired electron has considerable influence on the first and vice versa. Let us now return to the analogy of the boys and girls.

In doing so, let us assume a fictional, perhaps rather naive, view of human nature and say that if one boy is given a task to perform he usually will do as expected, but if we

*A measure of the effectiveness of a force which tends to turn a magnet when it is at right angles to a uniform magnetic field of unit intensity.

present, or several girls are nearby, the boys will try to outdo themselves to gain the girls' attention and will exceed our greatest expectations to a remarkable degree.

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to the presence of other boys. Furthermore, the influence of girls on the boys' work is similar to the greatly enhanced magnetic moment of the rare earths terbium through thulium due to the presence of one or more down-spin electrons.

This simple analogy serves to illustrate the behavior in general. It is possible from quantum mechanics to calculate the magnetic moment exactly for each of the 14 different arrangements of $4f$ electrons. The agreement between the calculated values and the experimentally measured values is excellent and this is a very strong confirmation of modern quantum theory. Thus it is possible to use the experimental values to determine the number of $4f$ electrons in any given rare earth.

The magnetic moments of europium and ytterbium metals are found to be 7.9 (the same as gadolinium, which has seven unpaired $4f$ electrons) and zero (the same as lutetium, which has no unpaired $4f$ electrons), respectively. This indicates that europium metal has seven unpaired $4f$ electrons and ytterbium has none; that is, these metals have one more $4f$ electron than their respective trivalent ions. To gain a $4f$ electron, an electron from the valence (outer) shell must be transferred to the $4f$ shell, thereby reducing the number of valence electrons by one. From this, we conclude that europium and ytterbium are divalent in the metallic state, confirming our observation of variations in melting points of the rare earths. We now see that we have a powerful tool for studying the $4f$ electrons of the Fraternal Fifteen.

The magnetic moments of the rare earths as a group are the largest for any substances. The magnetic moments of all the other elements in the Periodic Table, except iron, cobalt, and nickel, are zero or very close to zero; therefore, we see that the magnetic properties of the rare earths make these elements unique. Since the magnetic moments of the rare earths are, in general, larger than those of iron, we might expect them to be better magnets than iron. The magnetic moment of a substance tells us very little concerning its usefulness as a magnet, however. The ability to serve as a magnet as iron does (that is, the property of attracting another nonmagnetic piece of iron) is called ferromagnetism. Of the trivalent rare earth metals, only terbium, dysprosium, holmium, erbium, and thulium become ferro-

magnetic below room temperature; gadolinium, however, becomes ferromagnetic at room temperature.

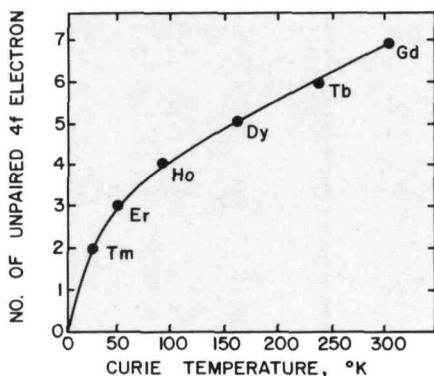


Figure 16 Relation between the number of unpaired 4f electrons and the Curie temperature.

The temperature at which a substance becomes ferromagnetic is called its Curie temperature. The Curie temperatures for these six rare earth metals are found to be proportional to the number of unpaired 4f electrons (Figure 16). This is the reason why gadolinium has the highest Curie temperature of all the rare earth metals. The Curie temperature of gadolinium, however, is much below that of iron, which is 776°C (1049°K). This difference is due to the fact that the magnetic properties of iron arise from unpaired 3d electrons.

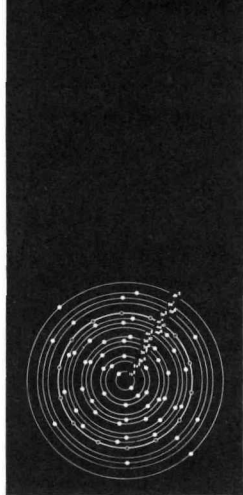
The Curie temperature of gadolinium is easily illustrated. If we cool gadolinium below room temperature by dunking it in cold water, it will be attracted to a permanent magnet, as shown in Figure 2; that is, it will be ferromagnetic. If we now warm gadolinium by placing it in hot water, we find it will no longer be ferromagnetic and will fall to the bottom of the beaker.

Miscellaneous Properties

The electrical resistivities of the rare earth metals are quite large (55 to 95 $\mu\text{ohm}\cdot\text{cm}$ compared to 1.6 to 25 $\mu\text{ohm}\cdot\text{cm}$ for the common metals). The electrical resistance of

*Microhms, or millionths of ohms.

most common metals vanishes at temperatures very close to absolute zero (-273°C); that is, they become perfect conductors, or superconductors. Of the rare earth metals only lanthanum becomes a superconductor at low temperatures. The other rare earths do not because they have unpaired $4f$ electrons which prevent this phenomenon. Again, it is the $4f$ electrons in the Fraternal Fifteen which account for difference in behavior.



APPLICATIONS AND USES

Atomic Energy

The rare earths have several properties of importance in the atomic energy field. Some of them are very capable of stopping or absorbing neutrons and are used in atomic reactors to control the rate of fission.* Long rods made of these materials are inserted into the core of a reactor before it is fueled; after fuel is added, if some of the rods are withdrawn fission begins. The more rods that are removed the greater the amount of fission. If all the control rods are inserted in the core, fission is stopped. Gadolinium has the largest known cross-section, or neutron-stopping capability, of all the elements; samarium is next, followed by europium and dysprosium. The remaining rare earths are not very useful as control rods. At present most reactor control rods are made either from cadmium or boron, but in the future the rare earths are expected to be used extensively.

A number of the rare earth isotopes have desirable properties for special applications. Rare earth isotopes have some potential uses in atomic batteries, as gamma-ray or X-ray sources, as radioactive materials for treatment of cancer and in tracer studies.

*For more information about reactors, see *Nuclear Reactors*, another booklet in this series.

The rare earths are also finding some use as moderators (materials which slow down neutrons in an atomic pile), as diluents of atomic fuels, materials to contain fuels and materials to separate undesirable fission products from atomic fuels.

Identification and definition of a second *f* type series of elements, the 5*f* series, have been greatly aided by our knowledge of the rare earths. Members of the 5*f* series include actinium (after which the actinide series is named); the well-known elements thorium, uranium, and plutonium; and lesser known, man-made transuranium elements.* During World War II American chemists used the rare earths as stand-ins, or substitutes, in developing techniques for preparing plutonium, which at that time was very scarce.

Commercial Uses

Most of us do not realize that the rare earths play important roles in everyday life. For example, the eye glasses you may be using to read this booklet probably were ground and polished by using cerium dioxide, CeO_2 . Most of the cigarette lighters in use today contain a flint composed of a cerium-iron alloy. Lanthanum oxide, La_2O_3 , is added to camera lenses to reduce the chromatic aberration (the spreading of colors as they pass through the lens). The steel, iron, copper, aluminum, and magnesium in our automobiles, cooking utensils, home appliances, metal furniture, and tools contain small amounts of rare earths to improve their properties. The light from carbon-arc searchlights and motion-picture projectors is stronger, steadier, and more uniform because of rare earths in the core of the electrodes. The color of beautiful stained glass windows and glass vases often is produced by one or more of the highly colored rare earth oxides dissolved in the glass.

One of the most exciting developments in rare earth technology came late in 1964 when europium was first used in color television tubes. The red color emitted by the europium-activated phosphor is about four times brighter than the phosphor previously used. This made it possible

*For more information about these elements, see *The Synthetic Transuranium Elements*, another booklet in this series.

to increase the brightness of color television images, because the intensity of the red was now more nearly equal to that of the other principal colors, blue and green.

Another recent advance has been made in using the laser properties of several of the rare earths. At least one commercial neodymium laser is available.

Besides these uses the rare earths are used as catalysts, paint driers, glass decolorizers, ceramic opacifiers, activators for fluorescent lighting, and reagent chemicals. They are valuable, also, in photosensitive glass, electronic equipment (such as vacuum tubes, capacitors, masers, and ferrites), nausea preventives, sunglasses, and glass blowers' and welders' goggles.

Research

The greatest demand for high purity individual rare earth elements is in research. Today an intensive effort is being made by chemists, physicists, and metallurgists to learn more about the rare earths and the influence they have on the properties of the other elements. Because of similar effort in the past, the many uses of the rare earths have been developed, and our understanding of atomic theory, magnetism, the actinide elements, superconductivity, and electronic transformations in solids has been greatly enhanced. It is expected that present and future research will contribute additionally to our understanding of the nature of matter, and to the development of new and better products.

Tomorrow

It is always difficult to say what tomorrow will bring. With hope and optimism we believe that the rare earths will play a much more important role in science and technology than in the past. The rare earths will be increasingly important as additives, not only to iron, steel, aluminum, copper, and magnesium, but also to the "new generation" metals—titanium, vanadium, zirconium, molybdenum, tungsten, and tantalum. The rare earths can be expected to find much greater use in atomic science and in materials studies as catalysts, refractory materials, semiconductors, magnetic materials, lasers, masers, and superconductors. As new

products and materials are born, the rare earths can be expected to be associated with a sizable number of them.

And finally, we expect that the Fraternal Fifteen will contribute much to our fundamental knowledge of nature because of their similarities and their $4f$ electrons.

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Group II. For Sophomore to Senior College Students

1. *The Rare Earth Elements and Their Compounds*, D. M. Yost, H. Russel, Jr., and C. S. Garner, John Wiley & Sons, Inc., New York, 1947, 92 pp., \$2.50. A brief review of the physical and chemical properties of the rare earth elements of the information available up to 1946. Particular emphasis is placed on the electronic and magnetic properties and the spectra of these elements. (Out of print but available through libraries.)
2. *Chemistry of the Lanthanons*, R. C. Vickery, Academic Press Inc., New York, 1953, 296 pp., \$6.00. A fairly detailed review of the chemical properties of the rare earth elements, but also includes some information on the physical properties. Author spends considerable detail in reviewing the older and out-of-date methods for obtaining pure rare earths. (Out of print but available through libraries.)
3. *Rare Earth Elements* (OTS-60-21172) (English translation of Russian book), D. I. Ryabchikov (Ed.), Clearinghouse for Federal Scientific and Technical Information, 5285 Port Royal Road, Springfield, Virginia 22151, 1960, 356 pp., \$3.75. This book consists of over 40 papers presented at a symposium in 1956 (published originally in Russian in 1959). Most of the papers deal with chemical problems, mainly on the separation and identification of the rare earths. Book gives a good insight into the state of the chemistry of the rare earths in Russia as of 1956.
4. *Rare Earth Alloys*, K. A. Gschneidner, Jr., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961, 449 pp., \$12.75. Detailed review of the physical and metallurgical properties of the rare earth metals alloys. About one-seventh of this book is a detailed review of the physical properties of the pure rare earth metals.
5. *Rare Earth Metals*, H. E. Kremers, Chapter 19, p. 393, *Rare Metals Handbook*, 2nd ed., C. A. Hampel (Ed.), Reinhold Publishing Corporation, New York, 1961, \$20.00. Brief review of the chemical, metallurgical, and physical properties of the rare earth metals.
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of the chemistry, history, and atomic theory of the rare earths and also a chapter which discusses the comparative chemistry of the rare earths and actinides.

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14. *The Industrial Chemistry of the Lanthanons, Yttrium, Thorium, and Uranium*, R. J. Callow, Pergamon Press, Inc., New York, 1967, 248 pp., \$9.50.

Group III. For College Seniors and Graduate Students

Some portions of items 3, 4, 6, 10, and 12 of the Group II reading list are sufficiently advanced and should properly be included here.

1. *Spectra of the Rare Earths* (AEC-tr-4403) (English translation of Russian book), Books 1 and 2, M. A. El'yashevich, 1961, Clearinghouse for Federal Scientific and Technical Information, 5285 Port Royal Road, Springfield, Virginia 22151, Book 1, 317 pp.; Book 2, 586 pp.; \$7.00 per set. A comprehensive study of the spectra of the rare earths. (Published originally in Russian in 1953.)
2. *Rare Earth Research*, E. V. Kleber (Ed.), The Macmillan Company, New York, 1961, 313 pp., \$10.95.

3. *Rare Earth Research*, J. F. Nachman and C. E. Lundin (Eds.), Gordon and Breach Science Publishers, Inc., New York, 1962, 354 pp., \$17.50.
4. *Rare Earth Research II*, K. S. Vorres (Ed.), Gordon and Breach Science Publishers, Inc., New York, 1964, 621 pp., \$29.50. (Books 2, 3 and 4 are conference proceedings that are concerned with current research problems covering the chemistry, physics, and metallurgy of the rare earths.)
5. *Rare Earth Research III*, L. Eyring (Ed.), Gordon and Breach Science Publishers, Inc., New York, 1965, 760 pp., \$44.50.
6. *Spectroscopic Properties of Rare Earths*, B. G. Wybourne, Interscience Publishers, New York, 1965, 236 pp., \$10.50. A recent comprehensive review of the rare earth spectra.
7. *Complexes of the Rare Earths*, S. P. Sinha, Pergamon Press, Inc., New York, 1966, 205 pp., \$7.50.

Motion Picture

Available for loan without charge from the AEC Headquarters Film Library, Division of Public Information, U. S. Atomic Energy Commission, Washington, D. C. 20545, and from other AEC film libraries.

Metals Frontier, 22 minutes, color, sound, 1961. Produced by Iowa State University for the Iowa State Institute of Atomic Research and the Ames Laboratory of the U. S. Atomic Energy Commission. This semitechnical film illustrates the investigation of the rare earths at the Ames Laboratory, showing how basic research, development, and production work together. The following steps in metal processing are shown: separation of yttrium from rare earths, conversion to fluoride, reduction and arc melting.

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