

7

The Periodic Table

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*It often matters vastly with what others,
In what arrangements the primordial germs
Are bound together, and what motions, too,
They exchange among themselves,
for these same atoms
Do put together sky, and sea, and lands,
Rivers and suns, grains, trees and
breathing things.
But yet they are commixed in different ways
With different things, with motions each its own.*

Lucretius (55 B.C.)

In this chapter we shall examine the correlations that exist between the physical and chemical properties of the elements and their compounds. These correlations lead directly to a fundamental classification scheme for matter, the periodic table. To Ernest Rutherford, who once remarked that there are two kinds of science—physics and stamp collecting—the periodic table would be the ultimate stamp album. If this were the final chapter of our book, his impression would be confirmed. But we organize the elements of the universe into the periodic table so chemistry can begin, not end. Once we have established the classification scheme, we must set out to explain it, in terms of electrons and the other subatomic particles from which atoms are constructed. This explanation is the task of later chapters. But before we begin to theorize about the world, let's see what it's really like.

7-1 EARLY CLASSIFICATION SCHEMES

Very early in the development of chemistry, chemists recognized that certain elements have similar properties. In the earliest classification scheme, there were only two divisions, metals and nonmetals. Metallic elements have a certain lustrous appearance, they are malleable (can be hammered into thin sheets) and ductile (can be drawn into wires), they conduct heat and electricity, and they form compounds with oxygen that are basic. Nonmetallic elements have no one characteristic appearance, they generally do not conduct heat and electricity, and they form acidic oxides.

Döbereiner's Triads

In 1829, the German chemist Johann Döbereiner observed several groups of three elements (*triads*) with similar chemical properties. In every case the atomic weight of one element in the triad was nearly the average of the other two. For example, each element in the triad *chlorine*, *bromine*, and *iodine* forms colored vapors containing diatomic molecules. Each element combines with metals and has a combining weight equal to its atomic weight. Each element forms ions with oxygen that have a single negative charge: ClO^- , ClO_3^- , BrO_3^- , and IO_3^- . The atomic weight of bromine (80) is approximately the average of those of chlorine (35.5) and iodine (127). Table 7-1 lists the similarities of elements in this and other triads.

In addition to recognizing the triads given in Table 7-1, Döbereiner observed a peculiar triad of the metals *iron*, *cobalt*, and *nickel*, all of which have similar properties and almost the same atomic weights. The metals are used in structural materials (steel) and may be ferromagnetic like iron; in their +2 and +3 states they form complex ions that are colored.

This discovery of families of elements (the number 3 per family proved to be insignificant) provided an incentive to those who were attempting to find a rational means of classifying the elements.

Newlands' Law of Octaves

Between 1850 and 1865 many new elements were discovered, and chemists made considerable progress in the determination of atomic weights. Thus, more accurate atomic weights were made available for old elements, and reasonably accurate values were presented for new elements. In 1865, the English chemist John Newlands (1839–1898) explored the problem of the periodic recurrence of similar behavior of elements. He arranged the lightest of the known elements in order of increasing atomic weight as follows:

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

Newlands noticed that the eighth element (fluorine, F) resembled the first (hydrogen, H), the ninth resembled the second, and so forth. His observation that every eighth element had similar properties led him to compare his chemical octaves with musical octaves, and he himself called it his *law of octaves*. Periodicity by octaves in chemistry suggested to him a fundamental harmony like the one in music. The comparison, although appealing, is invalid. Had Newlands known of the noble gases, his periodicity of properties would have been by nines rather than by eights. He never would have used his musical analogy, and he might have been spared some of the ridicule and indifference that he suffered. (See the Postscript for more on Newlands.)

Table 7-1

Döbereiner's Triads

Triad elements and atomic weights	Elemental form	Principal compounds	Special properties
(I) Cl, Br, I; 35.5, 80, 127	Colored diatomic molecules: Cl ₂ (yellow), Br ₂ (brown), I ₂ (violet)	Form simple salts containing — 1 ions Cl [–] , Br [–] , I [–] . Form oxyanions containing one to four oxygen atoms: ClO ₄ [–] , ClO ₃ [–] , BrO ₃ [–] , IO ₃ [–] , ClO [–] , IO ₄ [–] . Hydrogen compounds are molecular: HCl, HBr, HI.	Free elements react vigorously with electron donors to form negative ions Cl [–] , Br [–] , I [–] : $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{Na}^+ + 2\text{Cl}^-$ $\text{I}_2 + \text{S}^{2-} \rightarrow 2\text{I}^- + \text{S}$ Salts (like NaCl) are very soluble in water. Halide salts of Li, Na, and K give neutral solutions. Hydrogen compounds are strong acids and ionize completely in water: $\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-$
(II) S, Se, Te; 32, 79, 127.6	Colored crystalline nonmetals (Te somewhat metallic): S ₈ (yellow), Se ₈ (red)	Form simple salts with — 2 ions: S ^{2–} , Se ^{2–} , Te ^{2–} , and very smelly compounds with hydrogen: H ₂ S, H ₂ Se, H ₂ Te. Form oxyanions with up to four oxygen atoms: SO ₃ ^{2–} , ^a SO ₄ ^{2–} , SeO ₄ ^{2–} . Form dioxides and trioxides: SO ₂ , SO ₃ , ^a SeO ₂ , TeO ₂ , TeO ₃ .	Salts, except those with triads III and IV, are slightly soluble in water: CuS, ZnS, HgS. Soluble salts (Na ₂ S) give basic solutions: $\text{S}^{2-} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{OH}^-$ Hydrogen compounds are weak acids.
(III) Ca, Sr, Ba; 40, 88, 137	Reactive metals	Form salts containing + 2 ions: Ca ²⁺ , Sr ²⁺ , Ba ²⁺ in BaSO ₄ , CaCO ₃ , SrCl ₂ , and so on.	Salts give bright colors in flame: Ca (orange), Sr (red), Ba (green). Sulfates and carbonates are insoluble. Metals replace hydrogen slowly from water.
(IV) Li, Na, K; 7, 23, 39	Very reactive metals	Form salts containing + 1 ions: Li ⁺ , Na ⁺ , K ⁺ in Li ₂ CO ₃ , NaCl, K ₃ PO ₄ , and so on.	Almost all salts are soluble; metals and salts give brightly colored flames: Li (red), Na (yellow), K (purple). Metals react violently with water to produce hydrogen and soluble ionic hydroxides: $2\text{Na} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{Na}^+ + 2\text{OH}^-$

^aNote the importance of charge: SO₃^{2–} is very different from SO₃ (no charge).

Newlands' effort was admittedly a step in the right direction. However, three serious criticisms can be directed at his classification scheme:

1. There were no places in his table for new elements, which were being discovered rapidly. Moreover, in the later parts of the table, there were several places where two elements were forced into the same position. (See the Postscript.)

2. There was no scholarly evaluation of the work on atomic weights and no selection of probable best values.

3. Certain elements did not seem to belong where they were placed in the scheme. For example, chromium (Cr) is not sufficiently similar to aluminum (Al), nor is manganese (Mn), a metal, to phosphorus (P), a nonmetal. Iron (Fe), a metal, and sulfur (S), a nonmetal, do not resemble each other either.

7-2 THE BASIS FOR PERIODIC CLASSIFICATION

The development of the periodic table as we now know it is credited mainly to the Russian chemist Dmitri Mendeleev (1834–1907), although the German chemist Lothar Meyer worked out essentially the same system independently and almost simultaneously. So far as we know, neither man was aware of Newlands' work. Mendeleev's periodic table (Figure 7-1), presented in 1869, followed Newlands' plan of arranging the elements in order of increasing atomic weight, but with the following substantial improvements:

1. Long periods were instituted for the elements now known as transition metals. These long periods are shown folded in half in his original table, with each full period taking two lines. This innovation removed the necessity of placing metals such as vanadium (V), chromium, and manganese under nonmetals such as phosphorus, sulfur, and chlorine.

2. If the properties of an element suggested that it did not fit in the arrangement according to atomic weight, a space was left in the table. For example, no element existed that would fit in the space below silicon (Si). Thus, a space was left for a new element, which was named *ekasilicon*.

3. A scholarly evaluation of atomic weight data was made. For example, as a result of this work the combining capacity of chromium in its highest oxide was changed from 5 to the correct value of 6. The combining weight of chromium was known to be 8.66 g. Hence, instead of 43.3 (5×8.66), the revised atomic weight of chromium became 52.0 (6×8.66).

Indium (In), with a combining weight of 38.5, had been assigned a combining capacity of 2 and therefore an atomic weight of 77, and had been placed between arsenic (As) and selenium (Se). Since their properties were consistent with placement below phosphorus and sulfur, which were next to one another, arsenic and selenium also had to be side by side in

Row	Group I — R ₂ O	Group II — RO	Group III — R ₂ O ₃	Group IV RH ₄ RO ₂	Group V RH ₃ R ₂ O ₃	Group VI RH ₂ RO ₃	Group VII RH R ₂ O ₇	Group 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, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 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				Th = 231		U = 240		

Figure 7-1

The periodic table of Mendeleev as it appeared when published in English, in 1871. The elements appear in order of increasing atomic weight. Note the space left under Si for an unknown (at that time) element of atomic weight 72, and the incorrect atomic weights (for example, In). The letter R in the column headings is the general symbol for an element in the table. Elements in parentheses indicate the continuation of a period from the preceding row.

Mendeleev's scheme. A reevaluation showed that indium had an atomic weight of 114.8 and a combining capacity of 3, which is consistent with its position below aluminum and gallium (Ga) in the present table.

The atomic weight of platinum (Pt) had been thought to be greater than that of gold (Au). Mendeleev thought otherwise, because of the chemistry of the two metals and the places that they should occupy in his table. New determinations inspired by Mendeleev showed 198 for platinum and 199 for gold, thereby placing platinum ahead of gold and under palladium (Pd), which of all the other elements most resembles platinum.

4. On the basis of the known periodic behavior summarized in the table, predictions of the properties of the undiscovered elements were made. These predictions later proved to be amazingly accurate, as one can see by comparing the predicted properties of ekasilicon and the properties reported for the element called germanium (Ge), which now occupies the ekasilicon space. This comparison is given in Table 7-2.

From the table it is evident how Mendeleev was able to predict accu-

Table 7-2**Mendeleev's Predictions for the Element Eka-silicon (Germanium)**

Properties	Silicon (Si) and its compounds	Mendeleev's predictions for eka-silicon (Es)	Germanium (Ge) and its compounds	Tin (Sn) and its compounds
Atomic weight	28	72	72.6	119
Appearance	Gray, diamondlike	Gray metal	Gray metal	White metal or gray nonmetal
Melting point ($^{\circ}\text{C}$)	1410	High	958	232
Density (g cm^{-3})	2.32	5.5	5.36	7.28 or 5.75
Action of acid and alkali	Acid resistant; slow attack by alkali	Acid and alkali resistant	Not attacked by HCl or lye (NaOH); attacked by HNO_3	Slow attack by conc. HCl; attacked by HNO_3 ; inert to lye (NaOH)
Oxide formula and density (g cm^{-3})	SiO_2 , 2.65	EsO_2 , 4.7	GeO_2 , 4.70	SnO_2 , 7.0
Sulfide formula and properties	SiS_2 , decomposes in water	EsS_2 , insoluble in water, soluble in ammonium sulfide solution	GeS_2 , insoluble in water, soluble in ammonium sulfide solution	SnS_2 , insoluble in water, soluble in ammonium sulfide solution
Chloride formula	SiCl_4	EsCl_4	GeCl_4	SnCl_4
Boiling point of chloride ($^{\circ}\text{C}$)	57.6	100	83	114
Density of chloride (g cm^{-3})	1.50	1.9	1.88	2.23
Preparation of element	Reduction of K_2SiF_6 with sodium	Reduction of EsO_2 or K_2EsF_6 with sodium	Reduction of K_2GeF_6 with sodium	Reduction of SnO_2 with carbon

rately the physical and chemical properties of the missing element. Its position in the periodic table was below silicon and above tin (Sn). The physical properties of germanium are just about the average between those observed for silicon and for tin. To predict the chemical properties for eka-silicon Mendeleev also used information from the known relative properties of phosphorus, arsenic, and antimony (Sb) in the column to the right in the periodic table.

Correlations such as this guided the search for new elements and compounds and stimulated investigation when known data did not conform with other correlations. One consequence of this research was that we gained improved values for atomic weights and densities.

The Periodic Law

Mendeleev summarized his discoveries in the **periodic law**: The properties of chemical elements are not arbitrary, but vary with the atomic weight in a systematic way.

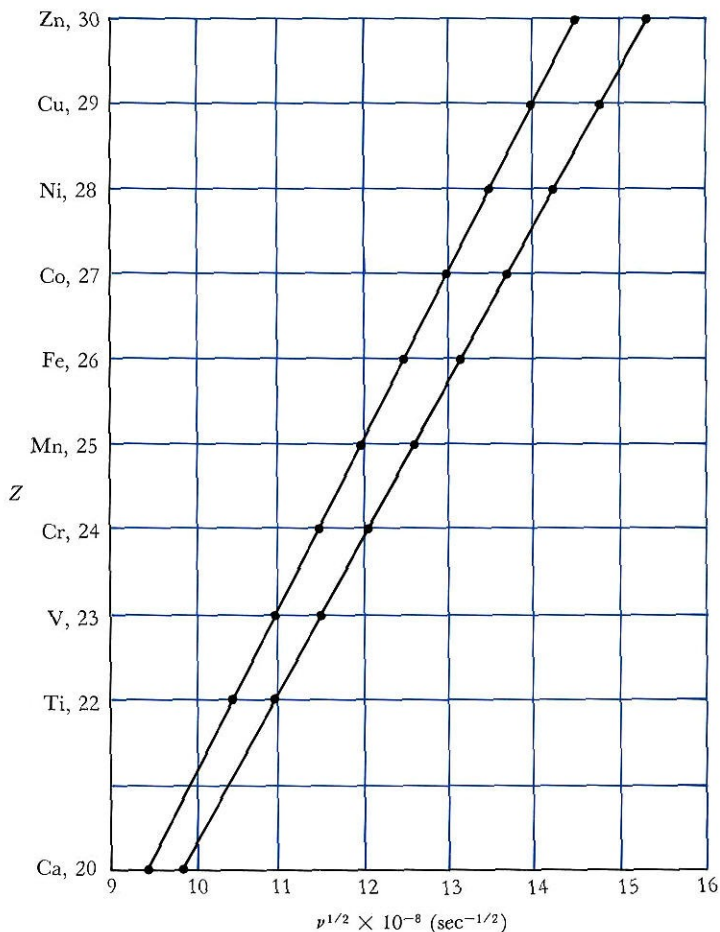
After most of the elements had been discovered and their atomic weights carefully determined, several discrepancies persisted. For example, the order of increasing atomic weight within Mendeleev's Group VIII (Figure 7-1) was found to be Fe, Co, Ni, Cu in the fourth period (row 4), Ru, Rh, Pd, Ag in the fifth (row 6), and Os, Ir, Pt, Au in the sixth (row 10). Yet Ni resembles Pd and Pt more than Co does. Again, Te has a higher atomic weight than I, but I clearly belongs with Br and Cl, and Te resembles Se and S in chemical properties. When the noble gases were discovered, it was revealed that Ar had a higher atomic weight than K, whereas all the other noble gases had lower atomic weights than the adjacent alkali metals. In these three instances, increasing atomic weight clearly is *not* acceptable as a means of placing elements in the periodic table. Therefore, the elements were assigned atomic numbers from 1 to 92 (now 105). (The atomic numbers of the elements *approximately* increase with their atomic weights.) When the elements are arranged according to increasing atomic number, chemically similar elements lie in vertical columns (families or groups) of the periodic table.

In 1912, Henry G. J. Moseley (1887–1915) observed that the frequencies of x rays emitted from elements could be correlated better with atomic numbers than with atomic weights. The relationship between an element's atomic number and the frequency (or energy) of x rays emitted from the element is a consequence of atomic structure. As we shall see in Chapter 8, the electrons in an atom are arranged in *energy levels*. When an element is bombarded by a powerful beam of electrons, electrons from the innermost levels or shells (closest to the nucleus) can be ejected from the atoms. When outer electrons drop into these shells to fill the vacancies, energy is emitted as x radiation. The x-ray spectrum of an element (the collection of frequencies of x rays emitted) contains information about the electronic energy levels of the atom. The important point for our present purpose is that the energy of a level varies with the charge on the nucleus of the atom. The greater the nuclear charge, the more tightly the innermost electrons are bound. More energy is required to knock off one of these electrons; consequently, there is more energy emitted when an electron falls back into a vacancy in the shells. Moseley discovered that the frequency of x rays emitted (designated by the Greek letter ν , nu) varies with atomic number, Z , according to

$$\nu = c(Z - b)^2$$

in which c and b are characteristic of a given x-ray line and are the same for all elements.

In April 1914, Moseley published the results of his work on 39 elements from $_{13}\text{Al}$ to $_{79}\text{Au}$. (Recall that the atomic number is indicated by a sub-

**Figure 7-2**

Moseley's plot of the square root of x ray frequency against atomic numbers for the elements calcium through zinc. The two lines come from two different, identifiable frequencies in each atom's spectrum.

script to the left of the symbol of an element.) A portion of his data is plotted in Figure 7-2. Moseley wrote the following:

"The spectra of the elements are arranged on horizontal lines spaced at equal distances. The order chosen for the elements is the order of the atomic weights, except in the cases of Ar, Co, and Te, where this clashes with the order of the chemical properties. Vacant lines have been left for an element between Mo and Ru, an element between Nd and Sm, and an element between W and Os, none of which are yet known. . . . This is equivalent to assigning to successive elements a series of successive characteristic integers. . . . Now if either the elements were not characterized by these integers, or any mistake had been made in the order chosen or in the number of places left for unknown elements, these regularities (the straight lines) would at once disappear. We can therefore conclude from the evidence of the x-ray spectra alone, without using any theory of atomic

structure, that these integers are really characteristic of the elements. . . . Now Rutherford has proved that the most important constituent of an atom is its central positively charged nucleus, and van den Broek has put forward the view that the charge carried by this nucleus is in all cases an integral multiple of the charge on the hydrogen nucleus. There is every reason to suppose that the integer which controls the x-ray spectrum is the same as the number of electrical units in the nucleus, and these experiments therefore give the strongest possible support to the hypothesis of van den Broek.”*

The three undiscovered elements mentioned by Moseley were later found to be elements 43 (technetium, Tc), 61 (promethium, Pm), and 75 (rhenium, Re). A confusing “double element” was cleared up in 1923, when D. Coster and G. Hevesy showed that one of the unoccupied horizontal lines of Moseley’s chart belonged to the new element hafnium (Hf, 72). Moseley’s work was perhaps the most fundamental single step in the development of the periodic table. It proved that atomic number (or the charge on the nucleus), and not atomic weight, was the essential property in explaining chemical behavior.

7-3 THE MODERN PERIODIC TABLE

The easiest way to understand the periodic table is to build it. Although this may seem to be a difficult task, surprisingly little knowledge of chemistry is required to understand that the form on the inside front cover of this book is inevitable. If we arrange elements by atomic number, as Moseley did, then certain chemical properties repeat at definite intervals (Figure 7-3, top). The chemically inert gases (at least thought to be inert until 1962, when chemists produced compounds containing xenon bound to fluorine and oxygen), He, Ne, Ar, Kr, Xe, and Rn, have atomic numbers 2, 10, 18, 36, 54, and 86, or numerical intervals of 2, 8, 8, 18, 18, and 32. Each of these gases precedes an extremely reactive, soft metal that tends to form a +1 ion: the **alkali metals** Li, Na, K, Rb, Cs, and Fr. And each gas is preceded by a reactive element that can gain an electron to form a -1 ion: hydrogen and the **halogens** F, Cl, Br, I, and At. These key elements are shown in color in the row at the top of Figure 7-3.

These chemical similarities are best represented by dividing the list of 105 elements into seven rows or **periods** (Figure 7-3). However, the first period has only 2 elements, the next two have 8, the next two, 18, and the sixth and probably the seventh periods have 32. How can we align 8 entries over 18, and 18 over 32?

The **alkaline earth metals**, Be, Mg, Ca, Sr, and Ba, are so similar in

*By the time these lines were published, Moseley was in the British army, and less than a year later he was dead, at the age of 27, on a hillside on Gallipoli.

Figure 7-3 illustrates the modern periodic table, showing the recurrence of similar chemical properties that suggests the folding of the periodic table into its characteristic 'super-long' form. The elements are listed in order of increasing atomic number, as shown in the strip at the top. The table is organized into periods (rows) and groups (columns). The elements are classified into three categories based on the extent to which chemical and physical properties change from one position in the table to the next:

- Metals of extremely similar chemical properties:** This category includes the **INNER TRANSITION METALS** (lanthanides and actinides) and the **TRANSITION METALS** (d-block elements).
- Metals of similar yet distinctive chemical properties:** This category includes the **TRANSITION METALS** (d-block elements).
- Metals and nonmetals with a great variety of chemical properties:** This category includes the **REPRESENTATIVE ELEMENTS** (s-block and p-block elements).

Figure 7-3

When elements are listed in order of increasing atomic number, as in the strip at the top, the recurrence of similar chemical properties suggests the folding into the "super-long" form of the periodic table shown below the strip. Elements can be classified into three categories, based on the extent to which chemical and physical properties change from one position in the table to the next.

chemical properties that we need little imagination to place them as shown. Nonmetals are at the right end of each period, and O, S, Se, and Te constitute a series of elements with a combining capacity of 2 and an increase in metallic behavior from O to Te: O is a nonmetal, and Te exists in the unspecific intermediate zone known as the **semimetals** or **metalloids**. Elements N, P, As, Sb, and Bi comprise a group whose characteristics are the ability to gain three electrons in certain compounds and a gradation from the nonmetallic N and P, to the semimetallic As, to the metallic Sb and Bi. The elements C, Si, Ge, Sn, and Pb all have a combining capacity of 4. For these elements, the border zone between metals and nonmetals is located at an earlier period; C is a nonmetal, Si and Ge are semimetals, and Sn and Pb are metals. Finally, the series B, Al, Ga, In, and Tl form +3 ions; B is semimetallic and the others are metallic. The properties of Al and Ga are more similar than those of Al and Sc. To bring Al above Ga, it is necessary to shift the 8-element periods to the extreme right above the 18-element period below.

The “superfluous” elements in Periods 4 and 5 ($_{21}\text{Sc}$ to $_{30}\text{Zn}$, and $_{39}\text{Y}$ to $_{48}\text{Cd}$) constitute a series of metals, all of which exhibit a great variety of ionic states, the +2 and +3 states seeming to be the most common. Their properties do not change from one element to another nearly as much as the properties in the series B, C, N, O, and F change. We call these “superfluous” elements **transition metals**. (We defer the question of *what* is in transition to Chapters 9 and 10.) When we look for chemical parallels between the fifth and sixth periods, we find that $_{40}\text{Zr}$ and $_{72}\text{Hf}$ are virtually identical in behavior. Again, our preferred arrangement is to place the elements in Period 5 beyond $_{38}\text{Sr}$ as far as possible to the right atop Periods 6 and 7. The extra elements in Period 6, $_{57}\text{La}$ to $_{70}\text{Yb}$, are practically identical in chemical behavior. These elements are called the **rare earths**, or **lanthanides**. Their partners in the seventh period ($_{89}\text{Ac}$ to $_{102}\text{No}$) are known as the **actinides**. Because the lanthanides are so similar in chemical properties, they are found together in nature and are extremely difficult to separate.

In summary, the elements can be classified into three groups (Figure 7-3): the **representative elements**, with diverse properties; the **transition metals**, more similar but yet clearly distinguishable; and the **inner transition metals** (lanthanides and actinides), with very similar properties. The representative elements are called representative because they show a broader range of properties than are found in the other elements, and because they are the elements with which we are most familiar.

(The radioactivity and nuclear instability of the actinides, especially uranium, have given them a historical significance that their chemical properties perhaps would not have justified. An old-time chemist is a person who still thinks of uranium as an obscure heavy element used in yellow pottery glazes and stained glass. It is ironic that a nuclear war would be fought with the raw material of stained-glass windows.)

There is a more compact form of the periodic table that indicates more clearly the relative variability of properties of neighboring elements (Figure 7-4). Trends in chemical behavior are often easier to understand if only the representative elements are examined, with the transition metals set to one side as a special case and the inner transition metals virtually ignored. In this table, the vertical columns are called **groups**, and those of the representative elements are numbered IA through VIIA and 0. The groups of the transition elements are numbered in a way to remind you that they should be inserted in the representative element table. The numbering includes Groups IIIB to VIIB, then three columns all labeled collectively Group VIIIB, then Groups IB and IIB. Group IIIB follows Group IIA in the representative elements, and Group IIB precedes Group IIIA. This kind of numbering is clearer in the standard, “long form” of the periodic table on the inside front cover. We can see that the standard form is a compromise between the compactness of Figure 7-4 and the completeness of Figure 7-3. The lanthanides and actinides have been of so little relative importance that they have not been given group numbers.

		Group											
		IA									0		
Period	1	1 H									2 He	1	Representative elements
	2	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne			2	
	3	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar			3	
	4	19 K	20 Ca	Transition metals	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		4	
	5	37 Rb	38 Sr		49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		5	
	6	55 Cs	56 Ba		81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn		6	
	7	87 Fr	88 Ra									7	

		Transition metals											
		IIIB	IVB	VB	VIB	VII B	VIII B			IB	IIB		
4	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn			
5	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd			
6	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg			
7	103 Lr	104	105										

		Inner transition metals															
6	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			
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			

Figure 7-4

This compact, folded form of the periodic table emphasizes the natural division of elements into three categories: the extremely variable representative elements, the more similar transition metals, and the quite similar inner transition metals. Nonmetals are in color, and semimetals in a lighter color. The standard long version of the periodic table on the inside front cover is a compromise between this table and the one in Figure 7-3.

7-4 PERIODICITY OF CHEMICAL PROPERTIES AS ILLUSTRATED BY BINARY HYDRIDES AND OXIDES

In this section we shall see how the periodic table enables us to predict the molecular formulas and the chemical properties of compounds of metals and nonmetals with hydrogen and oxygen.

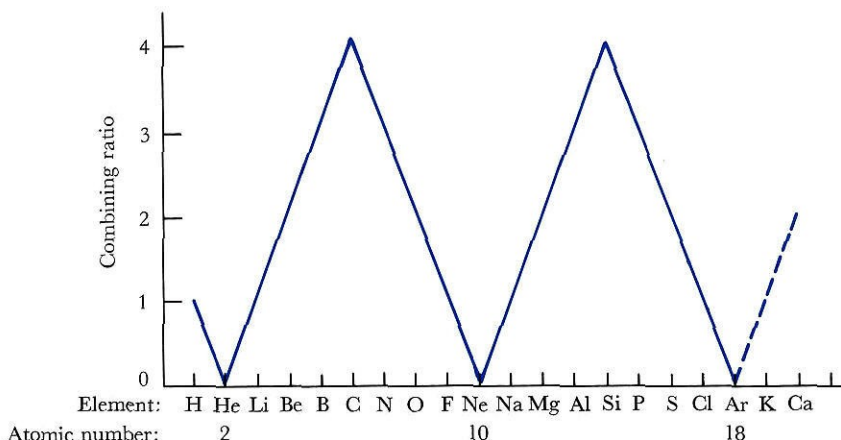
Binary Hydrides

The number of hydrogen atoms that combine with one atom of a given representative element in the first three periods of the periodic table varies (as shown in Figure 7-5) from 1 to 4 and back to 1 again across each period. This number is equal to either the group number or 8 minus the group number, whichever is smaller. This fact alone offers a clue to the way in which H is bonded in each hydrogen compound.

Compounds of metals with hydrogen—called *hydrides*—are mostly ionic. In alkali hydrides such as KH or NaH, there is a transfer of negative charge to each hydrogen atom. Alkali hydrides have the NaCl crystal structure (Chapter 1), but BeH_2 , MgH_2 , and AlH_3 manifest a new phenomenon, “bridging” hydrogen. In this arrangement each H atom in the crystal is equidistant between two metal atoms and appears to form a hydrogen bridge between them. Whenever H has a net negative charge, this extra charge can apparently be used to make a second bond to another atom, if there is enough potential bonding capacity in the other atom. The negatively charged H is present in NaH, but not the capacity for multiple bonds. However, Be, Mg, and Al satisfy both demands, and bridge structures are formed. The boron–hydrogen compound B_2H_6 (Figure 7-6) is an example of hydrogen bridging *within* a molecule, and the other known boron

Figure 7-5

Periodicity of combining ratios of the lightest elements in compounds with hydrogen. The number of hydrogen atoms combined with one atom of these elements is usually the group number or 8 minus the group number, whichever is smaller.



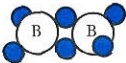
 Hydrogen $Z = 1$ $H/H = 1/1$ $mp = -259^{\circ}C$ $bp = -252^{\circ}C$						
$(LiH)_x$ Lithium $Z = 3$ $Li/H = 1/1$ $mp = 680^{\circ}C$ $bp = (decom.)$	$(BeH_2)_x$ Beryllium $Z = 4$ $Be/H = 1/2$ $mp = (decom.)$	 Boron $Z = 5$ $B/H = 1/3$ $mp = -165^{\circ}C$ $bp = -92^{\circ}C$	 Carbon $Z = 6$ $C/H = 1/4$ $mp = -182^{\circ}C$ $bp = -161^{\circ}C$	 Nitrogen $Z = 7$ $N/H = 1/3$ $mp = -78^{\circ}C$ $bp = -33^{\circ}C$	 Oxygen $Z = 8$ $O/H = 1/2$ $mp = 0^{\circ}C$ $bp = 100^{\circ}C$	 Fluorine $Z = 9$ $F/H = 1/1$ $mp = -83^{\circ}C$ $bp = 20^{\circ}C$
$(NaH)_x$ Sodium $Z = 11$ $Na/H = 1/1$ $mp = 700-800^{\circ}C$ $(decom.)$	$(MgH_2)_x$ Magnesium $Z = 12$ $Mg/H = 1/2$ $mp = (decom.)$	$(AlH_3)_x$ Aluminum $Z = 13$ $Al/H = 1/3$ $mp = (decom.)$	 Silicon $Z = 14$ $Si/H = 1/4$ $mp = -185^{\circ}C$ $bp = -111^{\circ}C$	 Phosphorus $Z = 15$ $P/H = 1/3$ $mp = -134^{\circ}C$ $bp = -88^{\circ}C$	 Sulfur $Z = 16$ $S/H = 1/2$ $mp = -86^{\circ}C$ $bp = -60^{\circ}C$	 Chlorine $Z = 17$ $Cl/H = 1/1$ $mp = -114^{\circ}C$ $bp = -85^{\circ}C$

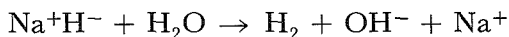
Figure 7-6

Hydrogen compounds of the elements in the first three rows of the periodic table. Combining ratios of the elements (with hydrogen) increase to four (in CH_4 and SiH_4) and then decrease. The hydrides of Li, Be, Na, Mg, and Al are solids at room temperature ($25^{\circ}C$) and have infinitely extended network structures. The simple molecules LiH , BeH_2 , NaH , and MgH_2 exist only at low pressures and high temperatures in the gas phase. AlH_3 is not an isolated molecule; it can exist only in the polymeric form $(AlH_3)_x$. The remaining hydrogen compounds are liquids or gases at room temperature. These compounds consist of discrete molecules having the composition and structure depicted schematically in the figure. The structure of the interesting B_2H_6 molecule is discussed in detail in Chapter 21. (Note: Z stands for atomic number; mp, melting point; bp, boiling point.)

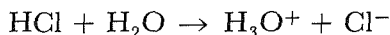
hydrides (such as B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , and $B_{10}H_{14}$) all make extensive use of such hydrogen bridges.

Compounds of hydrogen with elements in the right half of the periods are small molecular compounds in which the number of hydrogen atoms in a molecule is dictated by the number of covalent bonds that the other atom can form. Molecules of such compounds are held together in crystals only by weak forces between molecules; thus their melting and boiling points are very low (Figure 7-6).

Ionic hydrides react with water to produce basic solutions:



Conversely, the halogen compounds are acidic:

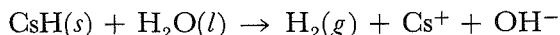


Example 1

What are the formulas of the hydrides of cesium (Cs) and selenium (Se)? Which hydride has the higher melting point? Write a balanced equation for the reaction of cesium hydride with water.

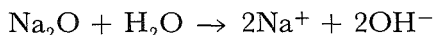
Solution

Cesium is in Group IA. Therefore the formula of its hydride is CsH. Selenium is in Group VIA, and its hydride is H₂Se. Cesium hydride is an ionic hydride with a much higher melting point than that of H₂Se, which is a molecular substance with a low melting point (and boiling point). The reaction of CsH with H₂O yields H₂, Cs⁺, and OH⁻:

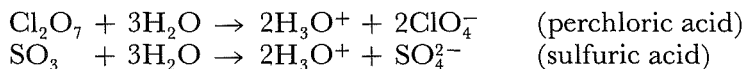


Binary Oxides

The representative elements form oxides with the formulas expected from the elements' positions in the periodic table; in the third period these oxides are Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, SO₃, and Cl₂O₇. Oxides of elements at the lower left of the table are strong bases. They have a large negative charge on the O atom, and are ionic. The melting points of these ionic oxides are typically around 2000°C, and many decompose before melting. They react with water to make basic solutions:



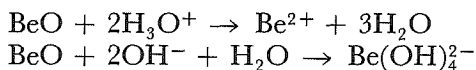
At the other extreme, oxides of elements at the upper right of the table are strong acids:



Cl₂O₇ is explosively unstable, and SO₃ reacts vigorously with water to produce acidic solutions. The acids have been represented here as completely ionized or dissociated, but this can be as misleading as writing them in their undissociated forms: HClO₄ and H₂SO₄. As we saw in Chapter 5, H₂SO₄ is only partially dissociated in water.

Between acidic and basic oxides lies a diagonal band of oxides that are amphoteric: BeO, Al₂O₃, and Ga₂O₃; GeO₂ through PbO₂; and Sb₂O₅ and

Bi_2O_3 . (Amphoteric oxides show both acidic and basic behavior.) They are virtually insoluble in water but can be dissolved by either acids or bases:



The notation in the first equation is conventional but inconsistent. The hydration of the proton is denoted by the symbol H_3O^+ . However, the Be^{2+} cation is also very strongly hydrated, especially so because of its small size. It should be written as $\text{Be}(\text{H}_2\text{O})_n^{2+}$, or at least $\text{Be}^{2+}(\text{aq})$. But so long as the hydration of cations is understood, it need not be spelled out every time.

The amphoteric and basic oxides are solids with high melting points. For instance, Al_2O_3 is the abrasive known as corundum, or emery; SiO_2 is quartz. Only the oxides of C, N, S, and the halogens are normally liquids or gases. The contrast between C and Si in carbon dioxide and quartz is analogous to the contrast between C and N in diamond and nitrogen gas. The difference between C and Si arises because C can make double bonds to O and therefore form a molecular compound of limited size. However, Si must make single bonds with four different O atoms; hence, it must assume a three-dimensional network structure in which tetrahedrally arranged Si atoms are connected by bridging O atoms.

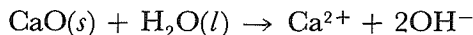
In all the oxides discussed so far, the chemical formula can be predicted from the group number. But there are other oxides whose formulas cannot be predicted from group numbers. For example, C can form CO as well as CO_2 . The compound N_2O_5 is not the only nitrogen oxide: NO_2 , N_2O_3 , and NO are others. Sulfur can form SO_2 , S_2O_3 , S_2O , and S_2O_7 , as well as SO_3 . But in these compounds the element does not make full use of its potential combining capacity. Thus, the general trends in properties are best illustrated by the oxides that we have been examining.

Example 2

Write a balanced equation for the reaction of calcium oxide with water.

Solution

Calcium (Ca) is in Group IIA. Its oxide is therefore CaO. The reaction is



The equation shows that CaO is a strong base, as its reaction with water yields OH^- ions.

Summary

Physical and chemical properties of elements are periodic functions, not of atomic weight, but of atomic number. Moseley suggested, and it later was

verified, that the atomic number is the total positive charge on the nucleus, equal to the total number of electrons around the nucleus in a neutral atom.

Particularly stable, inert elements occur at intervals of 2, 8, 8, 18, 18, and 32 in atomic number. These intervals, and only the most basic knowledge of similarities among elements, led to the formulation of a **periodic table**, in which similar elements are in vertical columns or **groups**, and in which chemical properties change in an orderly manner along horizontal rows or **periods**. The full, extended periodic table can be folded into a compact form that illustrates the division of the elements into three categories: the diversified **representative elements**, the more similar **transition metals**, and the virtually identical **inner transition metals**.

The correlation between combining capacity and group number in the periodic table may be illustrated by the hydrides and oxides of the representative elements. Elements at the lower left of the periodic table are metals. Their hydrides and oxides are ionic, and aqueous solutions of these compounds are basic. Elements at the upper right corner of the table are nonmetals. Their hydrogen compounds and oxides are small molecules with covalent bonds; they are gases or liquids, and are acidic. Between the two extremes at upper right and lower left in the table there is a gradation of properties. As the elements pass from nonmetals through semimetals to metals, their hydrogen compounds go from acidic, to neutral or inert, to basic (although there are many complications to this overall trend), and the oxides proceed in a more regular manner from acidic, to amphoteric, to basic.

Self-Study Questions

1. In what ways was Mendeleev's classification of the elements superior to Newlands'?
2. Why did Mendeleev's periodic classification lead to a reexamination of combining capacities?
3. How did Mendeleev predict the properties of *ekasilicon*?
4. What is incorrect about Mendeleev's periodic law?
5. How did Moseley deduce the existence of undiscovered elements?
6. What are the identifying characteristics of the following groups of elements: halogens, alkali metals, noble gases, alkaline earths?
7. What is a *group* in the periodic table? What is a *period*? How many elements are in each of the first six periods?
8. What are the differences among the elements in the three categories of representative elements, transition metals, and inner transition metals?
9. What does the letter *A* or *B* after a group number tell you about the category of the elements in that group?
10. How does metallic character vary within Groups IIIA, IVA, or VA? How does metallic character vary across a period?

11. How does the combining capacity of the representative elements vary with group number in the hydrogen compounds and the oxides?
12. What is the difference in bonding in the hydrogen compounds NaH , MgH_2 , and NH_3 ?
13. Why is there such a difference between the melting points or boiling points of CO_2 and SiO_2 ? Is there any similarity between this phenomenon and the difference in melting points of carbon and nitrogen?
14. How do the chemical properties of the oxides change from left to right across a period of the table?
15. Which elements are out of their proper sequence in Newlands' table in the Postscript? Why do you think that they are misplaced as they are? (Glucinium, G, was an early name for beryllium, Be.)

Problems

Elements

1. Efforts are presently being made to synthesize or discover new elements of very high atomic number [G. T. Seaborg, "From Mendeleev to Mendelevium and Beyond," *Chemistry*, 43, 6 (1970)]. Which existing element would be most like element 111? Like 112? Like 118?
2. Predict the empirical formulas of chlorides of elements 111, 112, and 118.
3. What are the group numbers of (a) N; (b) Al; (c) Cl; (d) Rb?
4. What are the group numbers of (a) Ga; (b) Sb; (c) Ba; (d) P?

Periodic properties

5. In the elements Si, Ge, Sn, and Pb, do the nonmetallic properties increase or decrease in the series?
6. Imagine that you are taking chemistry prior to the discovery of strontium ($Z = 38$). Considering strontium's position in

the periodic table, predict the following properties: (a) the chemical formula of its most common oxide; (b) the chemical formula of its most common chloride; (c) the chemical formula of its most common hydride; (d) the solubility of its hydride in water, and the acidity or basicity of the resulting solution; (e) the principal ion formed in aqueous solution.

Hydrogen compounds

7. Write a balanced equation for the reaction of hydrogen iodide with water.
8. Write a balanced equation for the reaction of calcium hydride, CaH_2 , with water.
9. What would you predict as the formulas of the hydrogen compounds of the following elements: Ca, Te, Ge, W? Which compounds will be ionic? In which will the hydrogens behave as cations? In which will they be anions? Which aqueous solution will be most basic?

Postscript to the Classification of the Elements

The story of John A. R. Newlands is a melancholy illustration of the fact that in science a good idea alone is not enough. The idea must be substantiated with enough evidence to gain acceptance. Newlands' story is also an example of the dangers of poor nomenclature.

Newlands, the son of a Scottish minister, was a graduate of Glasgow University. From his mother, who was of Italian descent, he inherited a love of music and the fervor that led him to join Garibaldi in the struggle for Italian independence in 1860. On his return to England he completed his chemical studies and established himself as a private analytical chemist for industry. His reputation in chemistry was based on his expertise in sugar chemistry, but his lifelong hobby was chemical periodicity.

The high point of his work on periodicity was to occur on March 1, 1866, when he presented his "law of octaves" before the Chemical Society in London. He expected acclaim, but received only indifference and heavy-handed humor. The paper on which his talk was based was rejected by the *Journal of the Chemical Society*. The account of the meeting was reported in *Chemical News* [13, 113 (1866)] as follows:

“Mr. John A. R. Newlands read a paper entitled ‘The Law of Octaves and the Causes of Numerical Relations among the Atomic Weights.’ The author claims the discovery of a law according to which the elements analogous in their properties exhibit peculiar relationships, similar to those subsisting in music between a note and its octave. Starting from the atomic weights on Cannizzaro’s system, the author arranges the known elements in order of succession, beginning with the lowest atomic weight (hydrogen) and ending with thorium (= 231.5); placing, however, nickel and cobalt, platinum and iridium, cerium and lanthanum, etc., in positions of absolute equality or in the same line. The fifty-six elements so arranged are said to form the compass of eight octaves, and the author finds that chlorine, bromine, iodine, and fluorine are thus brought into the same line, or occupy corresponding places in his scale. Nitrogen and phosphorus, oxygen and sulfur, etc., are also considered as forming true octaves. The author’s supposition will be exemplified in Table II, shown to the meeting, and here subjoined:

Table II—Elements Arranged in Octaves

H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 43	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Os 51
G 3	Mg 10	Ca 17	Zn 24	Sr 31	Cd 38	Ba & V 45	Hg 52
B 4	Al 11	Cr 18	Y 25	Ce & La 32	U 39	Ta 46	Tl 53
C 5	Si 12	Ti 19	In 26	Zr 33	Sn 40	W 47	Pb 54
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 42	Au 49	Th 56

Dr. Gladstone made objection on the score of its having been assumed that no elements remain to be discovered. The last few years had brought forth thallium, indium, cesium, and rubidium, and now the finding of one more would throw out the whole system. The speaker believed there was as close an analogy subsisting between the metals named in the last vertical column as in any of the elements standing on the same horizontal line.

Professor G. F. Foster humorously inquired of Mr. Newlands whether he had ever examined the elements according to the order of their initial letters? For he believed that any arrangement would present occasional coincidences, but he condemned one which placed so far apart manganese and chromium, or iron from nickel and cobalt.

Mr. Newlands said that he had tried several other schemes before arriving at that now proposed. One founded upon the specific gravity of the elements had altogether failed, and no relation could be worked out of the atomic weights under any other system than that of Cannizzaro. ”

And so dies a good story. The questioner did not ask about “chords and arpeggios,” as is sometimes said, but only about alphabetical order. The disbelief was apparent, however, and the unfortunate musical analogy made Newlands’ ideas look more like numerology than science. The lack of space for new elements and the crowding of two elements into one space were serious flaws. Perhaps the main feature that made Mendeleev’s scheme superior was the introduction of the long periods after the first two eight-element ones. Mendeleev buttressed his table with a host of chemical evidence, including his famous predictions for new elements and their chemistry. He clearly deserves his reputation as the creator of the periodic table.

Yet we should not forget Newlands, struggling to have his contribution recognized. He published note after note in *Chemical News*, first elaborating on his table, and then welcoming Mendeleev’s table in 1869 as the vindication of his own. Seven years after the *Journal of the Chemical Society* rejected his 1866 paper, he was given a reason, of sorts, by the Society president, Dr. Odling. The paper had not been published, he said, because they “had made it a rule not to publish papers of a purely theoretical nature, since it was likely to lead to correspondence of a controversial character.”

Newlands collected all his papers and published them as a book in 1884, and documented his claims to priority in the pages of *Chemical News* and in an account to the German Chemical Society. Perhaps in an outburst of conscience, the Royal Society of Great Britain awarded him the Davy medal in 1887, five years after it had presented the same award to Mendeleev.

Suggested Reading

- J. L. Hall and D. A. Keyworth, *Brief Chemistry of the Elements*, W. A. Benjamin, Menlo Park, Calif., 1971.
- J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Macmillan, New York, 1922. See especially Chapter VI.
- R. L. Rich, *Periodic Correlations*, W. A. Benjamin, Menlo Park, Calif., 1965.
- R. T. Sanderson, *Chemical Periodicity*, Van Nostrand Reinhold, New York, 1960.
- M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Chemical Education Publishing Co., Easton, Pa., 1968, 7th ed.