The Atomic-Structure Chart of the Elements

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Difficulties in his periodic system were first recognized by Mendeleev himself. Although his original chart was essentially an 18-column one, within two years he rearranged it into an 8-column chart. Furthermore, he tried three versions of each type.

Since 1869 many other variations of Mendeleev's two charts have been proposed. However, the possibility of perfecting the periodic system by basing it upon electron configuration, and extending it to 32 columns, did not appear until nearly 60 years later.

The most widely used form of the 32-column atomic-structure chart of the elements has been derived from those proposed independently in 1930 by R. Gardner and A. Mazzucchelli (Fig. 1). Its advantages having been widely discussed, its popularity is increasing rapidly. It is now included or featured in textbooks and other books such as the Merck Index and the Reinhold "Encyclopedia of Chemistry." However, this chart has one flaw: the similar discontinuities at La and Ac. If these discontinuities can be eliminated, the long search for a satisfactory periodic system might be ended.

The La-Ac discontinuities

The differentiating electron *(D E)* of each element is the additional one that makes an atom of that element different from the preceding atom in order of increasing atomic number. For example, to specify the *D E* for Ca the electron configuration of Ca is compared with that of the preceding element, K:

$_{19}$K 2 8 8 1
$_{20}$Ca 2 8 8 2

Accordingly, the *D E* for Ca is the second electron in the fourth shell.

In the atomic-structure chart, the location of each element is determined by its differentiating electron. The number of the *D E* in a given main shell of an atom determines in which of the 32 columns of the chart that atom is located; the number of the main shell in which the *D E* is found determines in which of the *slanting* rows of the chart that atom is located. Thus, because the *D E* for Ca is the second in the fourth shell, Ca is located in the second column and the fourth slanting row of the

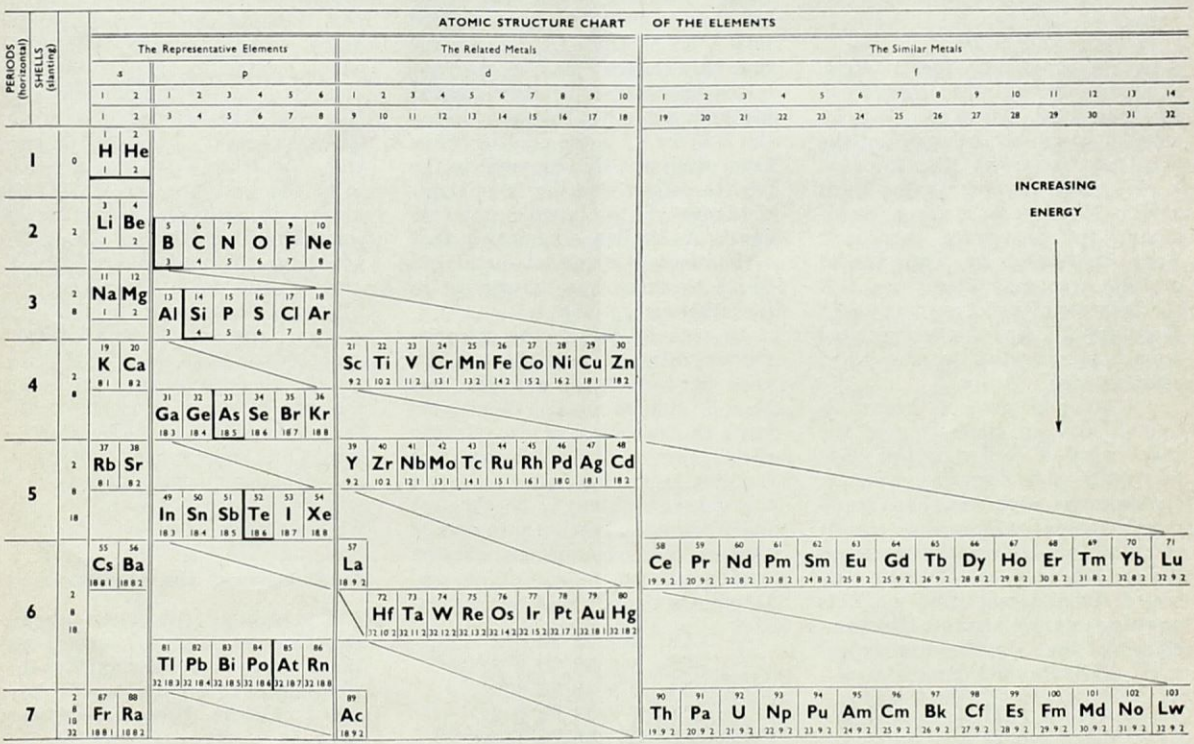

Figure 1

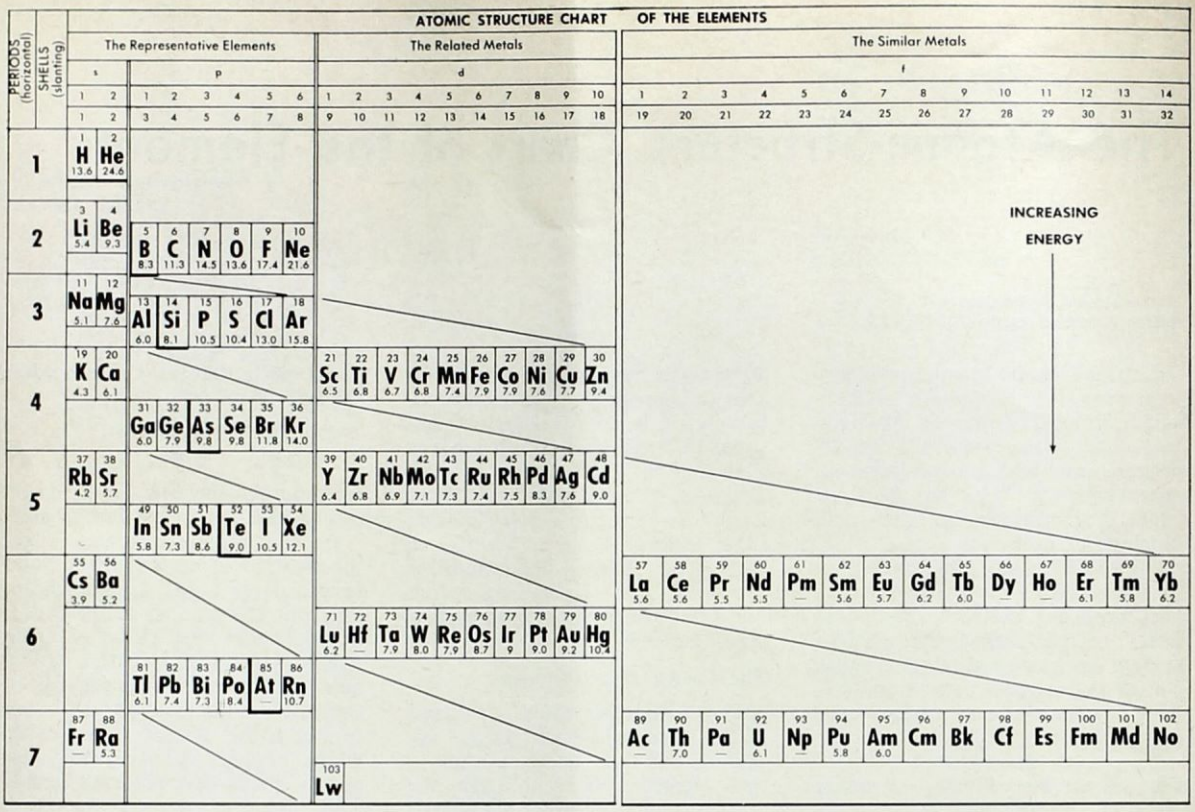

Figure 2

chart (Fig. 1). The *D E* in a Sc atom,

$_{21}$Sc 2 8 9 2

when compared with the Ca atom, is seen to be the ninth electron in the third shell. Therefore, Sc is located in the ninth column and the third slanting row (Fig. 1).

The ninth electron in the third shell is the first 3*d* electron, as indicated at the top of the chart. From Sc through Zn, while the 3*d* orbitals are being filled, the *D E* for each atom is in the third shell; therefore all ten of these related metals are located in the third slanting row.

According to present theory, although most of the atoms of the three rows of related metals have two 4*s*, 5*s*, or 6*s* electrons, some exceptions are observed. For example Cr is supposed to have one 4*s* electron. In these exceptions a question might arise as to which electron is the differentiating one. This question can be answered by considering the electron configurations of V, Cr, and Mn:

$_{23}$V 2 8 11 2
$_{24}$Cr 2 8 13 1
$_{25}$Mn 2 8 13 2

Noting that one 4*s* electron in the Cr atom appears to have shifted into a 3d orbital, one can assume that this electron may be returned to the 4*s* orbital until after a count has been made. On this assumption the *D E* for Cr is the twelfth in the third shell, and Cr is located in the twelfth column and the third slanting row of the atomic-structure chart. A similar assumption that each atom of a related metal has two *s* electrons may be applied to the other exceptions.

As seen in Fig. 1, the discontinuities after La and Ac are the gaps between them and the two rows of similar metals. These gaps arose in the following way. In the early years of the development of the atomic-structure chart, most of the elements from La-57 through Lu-71 were thought to have one 5*d* electron. For example, the electron configurations of La, Ce, Yb, and Lu were supposed to be as follows:

$_{57}$La 2 8 18 18 9 2
$_{58}$Ce 2 8 18 19 9 2
$_{70}$Yb 2 8 18 31 9 2
$_{71}$Lu 2 8 18 32 9 2

Compared with the Ba atom,

$_{56}$Ba 2 8 18 18 8 2

the La atom seems to have as its *D E* the first 5*d* electron, i.e., the ninth electron in the fifth shell, which located La in the ninth column and the fifth slanting row. However, because the Ce atom also was supposed to have one 5*d* electron, the *D E* in Ce was supposed to be the first 4*f* electron, i.e., the nineteenth electron in the fourth shell, which located Ce across the gap (Fig. 1) in the nineteenth column of the fourth slanting row. Likewise, because all the following elements through Yb and Lu were supposed to have one 5*d* electron, Lu was thought to have as its *D E* the last 4*f* electron, which located Lu in column 32 as the last lanthanon. This arrangement left La in an anomalous position, comparable only with Ac which was in a similar anomalous position.

Elimination of the discontinuities

The original 32-column atomic-structure chart of the elements was based upon the assumption that atoms of all the similar metals have one *d* electron. However, as more information has accumulated, this assumption is no longer accepted.

The number of lanthanons[1] supposed to have one 5*d* electron has gradually decreased to two: La and Gd. In view of this trend, the possibility might be considered that eventually these two could turn out not to have *d* electrons.

The electron configuration of Yb is now supposed to be

$_{70}$Yb 2 8 18 32 8 2

Referring all the way back to Ba,

$_{56}$Ba 2 8 18 18 8 2

one may see that the 4*f* subshell has been completed through the fourteen elements immediately following the addition of the 6*s* electrons of Ba. A comparable statement can be made about Ca and Zn:

$_{20}$Ca 2 8 8 2
$_{30}$Zn 2 8 18 2

At Zn, the 3*d* subshell has been completed through the ten elements following the addition of the 4*s* electrons of Ca. These observations suggest that Yb should end the first row of similar metals as Zn ends the first row of related metals. This suggestion is supported by reconsidering the location of the *D E* for Yb. Comparing the electron configuration of Tm,

$_{69}$Tm 2 8 18 31 8 2

with that of Yb shows that the *D E* for Yb is number 32 in the fifth shell. Therefore, Yb is placed in column 32 of the new chart (Fig. 2) as the last lanthanon. Having no *d* electrons, the elements from Yb-70 back to Gd-64 fall into place in the same way. If Gd is an exception in having one 5*d* electron, the location of its *D E* may be determined in a manner similar to the procedure used for Cr and other exceptions among the related metals, as discussed previously. Accordingly, the 5*d* electron is assumed to be in the 4*f* subshell and the *D E* is assumed to be number 26 in the fourth shell, which places Gd in column 26. The remaining elements back through Ce-58, having no *d* electrons, fall into their expected places. If La is the second exception, in having one 5*d* electron, its *D E* is located in the same manner as that for Gd, which places La in column 19 as the first lanthanon (Fig. 2)

The electron configuration of Lu is supposed to be

$_{71}$Lu 2 8 18 32 9 2

Comparison of this configuration with that of Yb establishes the *D E* for Lu as the ninth in the fifth shell. Therefore, Lu is located on the new chart in the ninth column and fifth slanting row, as the first related metal of the third row of related metals.

In the old chart, twelve of the fourteen lanthanons are now exceptions to the rule used to establish their locations. The new chart has only two such exceptions, La and Gd, with possibility that these eventually may turn out not to be exceptions. Furthermore, the new arrangement, in eliminating the former discontinuities, makes possible a clarification of the relationship between the periodic system and valence.

Valence electrons

From the beginning, one of the most important features of any periodic chart has been its interpretation of valence. However, this interpretation has been limited largely to the representative elements. For example, when the statement is made that the valence electrons of an atom are its outer *s* and *p* electrons, one is inclined to forget that this statement does not apply to the related metals nor to the similar metals. On the other hand, the interpretation of valence made possible by the new chart applies to all three classes of elements. Because this interpretation has been presented elsewhere [1], as a consequence of electron-repulsion theory, only an abbreviated summary without supporting evidence will be given here.

By analogy with the Ne atom, which has a completed valence shell of eight *s* and *p* electrons, the Zn atom may be regarded as the pattern model for the completed valence shell characteristic of the related metals [1]. After the third shell has been completed at Ar-18, a new valence shell is begun with the addition of the 4*s* electrons for K-19 and Ca-20 (Fig. 2). When the addition of the 3*d* electrons is continued through Sc-21 and the remaining elements of the first row of related metals, the new valence shell is complete with the twelve *s* and *d* electrons of the Zn atom. Some of the corresponding models resulting from electron-repulsion theory are pictured in Figs. 3 and 4.

In the model of the Zn atom (Fig. 3), the two spin-sets of *d* electrons are assumed to be at the corners of the bases of the two interpenetrating pentagonal pyramids; the *s* electrons are at the peaks of the pyramids. All twelve valence electrons are approximately on the surface of an imaginary sphere, at the center of which is the nucleus of the atom. Applying Hund's rule in reverse, and accordingly removing *d* electrons of the same spin one at a time from the Zn pattern model, gives the other models of Fig. 3. Similar models may be drawn for Ti and Sc [1]. However, to avoid a possible source of misunderstanding, Sc may also be drawn in another way, as in Fig. 4. Figure 4, which for comparison includes Ca as well as Sc, is drawn according to the suggestions of Linnett [3] and Gillespie [4] to indicate that the electrons are not to be thought of as motionless, fixed points. In the Ca model the "domain" of each electron is half the sphere shown in Fig. 4. In the Sc model the domain of each electron is approximately one-third of the sphere. Within these domains each electron can have the freedom of motion postulated by wave-mechanics. However, as implied in Fig. 3, one may assume that the larger the number of electrons in the valence shell of an atom the more restricted is their motion and the more they behave as particles.

By analogy with the Zn atom, the Yb atom can be regarded as the pattern model for the completed valence shell characteristic of the similar metals. Its valence shell is begun with the addition of the 6*s* electrons for Cs-55 and Ba-56 (Fig. 2). When the addition of the 4*f* electrons is continued through La-57 and the remaining elements of the first row of similar metals, the new valence shell is complete with the sixteen *s* and *f* electrons of the Yb atom. All sixteen valence electrons are on the surface of an imaginary sphere. Some of the electron-repulsion models[1] are pictured in Fig. 5. The valences of the similar metals, and of the related metals, are discussed elsewhere [1].

Atomic orbitals and valence electrons

When these new atom models, with corresponding models for the representative elements, were first proposed [2], they did not conform to the commonly accepted pictures of atomic orbitals. However, shortly afterward, apparently without knowledge of the models, Powell proposed new atomic orbitals that have the orientation in space required by the new models [3]. In his

(1) From here on, the lanthanons are considered to be the elements La through Yb.

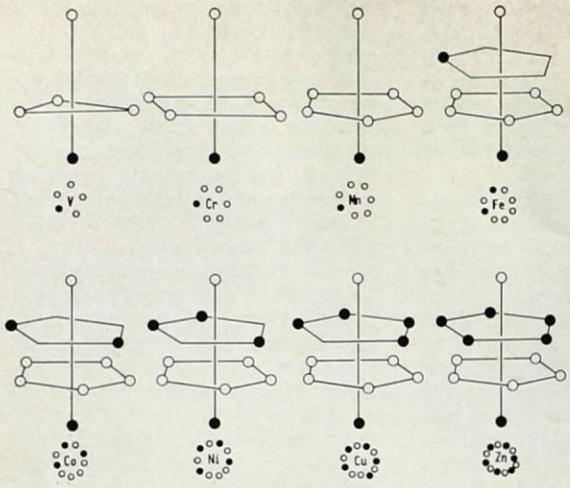

Figure 3 — Electronic structures of the valence shells (and electronic symbols) of some related metals.

Figure 4 — Domains of the valence electrons of the Ca and Sc atom models.

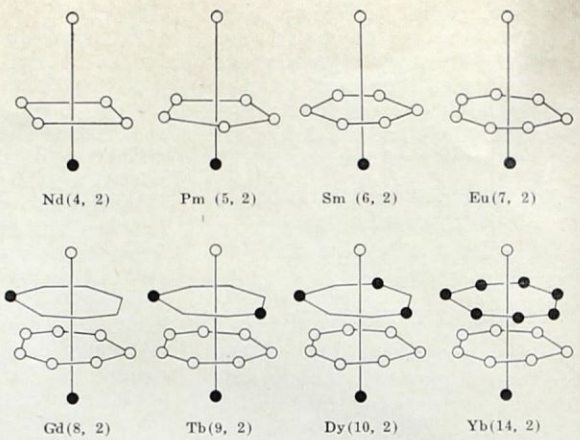

Figure 5 — Electronic structures of the valence shells (and electronic symbols) of some similar metals.

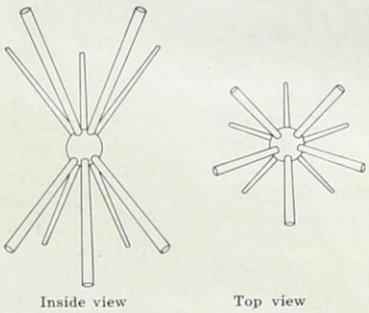

Figure 6 — Diagram of the five equivalent d *orbitals.*

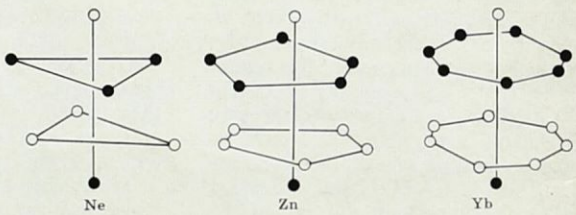

Figure 7 — Patterns for the valence shells of the three classes of elements. In each atom, all the valence electrons are approximately on the surface of an imaginary sphere.

paper, "The Five Equivalent *d* Orbitals," Powell, calling attention to an earlier paper by Kimball, has shown that five equivalent *d* orbitals can be directed along the slant edges of two staggered pentagonal pyramids [5].

Constrasting sharply to the earlier pictures of the *d* orbitals as five separate diagrams, Powell's representation of the *d* orbitals is one simple picture (Fig. 6). Although this picture shows only their direction, Powell's paper also gives the shape of the five equivalent orbitals as primarily two-lobed with very inconspicuous lobes of opposite sign. Therefore, the single picture is a reasonably good representation of the five equivalent *d* orbitals.

Powell also has proposed new *p* and *f* orbitals. Three equivalent *p* orbitals are directed along the slant edges of two staggered trigonal pyramids. Seven equivalent *f* orbitals are directed along the slant edges of two staggered heptagonal pyramids. Thus, all three kinds of the new atomic orbitals have the orientation in space required by the new models. Consequently, the models may be used to help one visualize the arrangement of valence electrons in the three classes of elements suggested by the atomic-structure chart.

In this chart, the valence shells of outer electrons are analogous for all three classes of elements (Fig. 7). For atoms of the representative elements the pattern of valence electrons is the arrangement of the eight *s* and *p* electrons in two spin-sets at the corners of two interpenetrating trigonal pyramids, as in the Ne atom. For atoms of the related metals the pattern of valence electrons is the arrangement of the twelve *s* and *d* electrons in two spin-sets at the corners of two interpenetrating pentagonal pyramids, as in the Zn atom. For atoms of the similar metals the pattern of valence electrons is the arrangement of the sixteen *s* and *f* electrons in two spin-sets at the corners of two interpenetrating heptagonal pyramids, as in the Yb atom.

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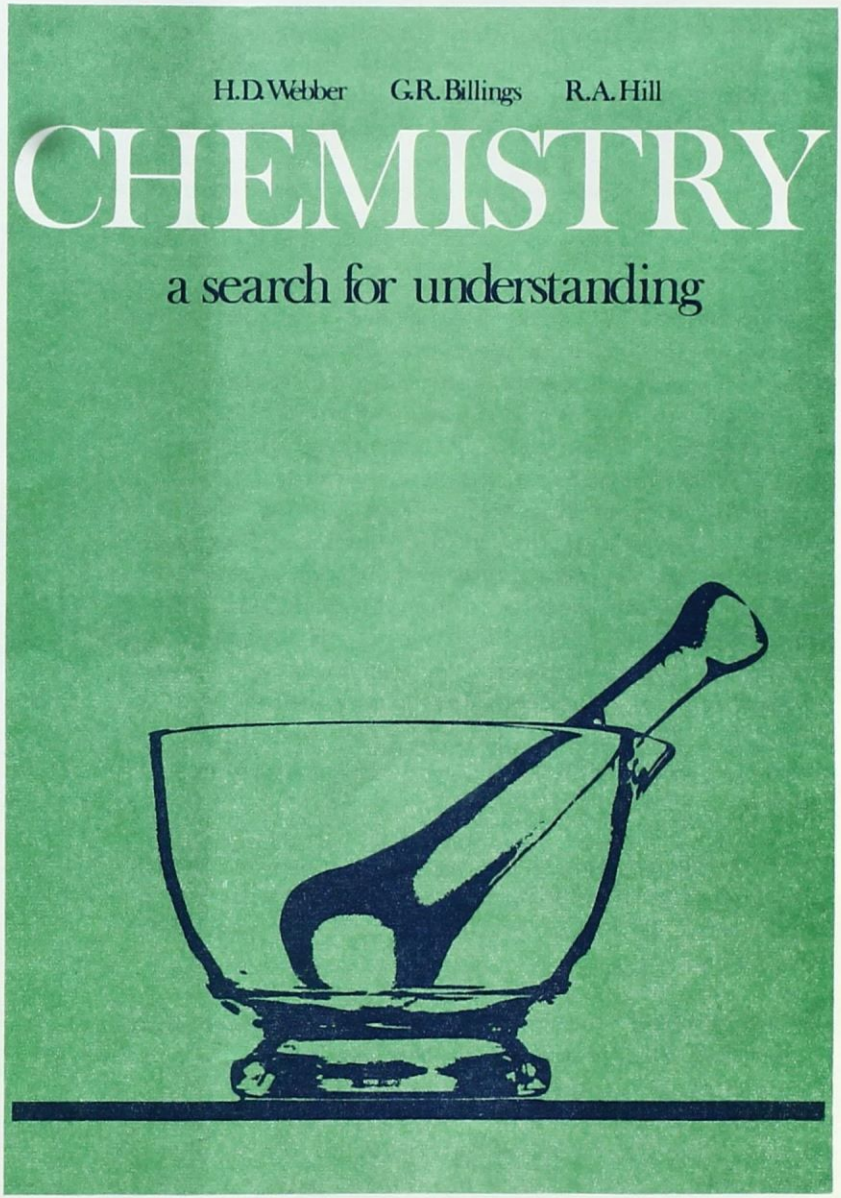

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