

A PERIODIC LAW OF ATOMIC RADII

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ABSTRACT

Packing radii of elements; periodic relationship is evident if the radii of the 44 elements for which the values have been determined from x-ray crystallographic data, are plotted as a function of the number of electrons in the outer shell. Beginning with each rare gas, the curves are similar, the ratios of the ordinates being constant for the following 9 or 10 elements, as far as the values are known. By making use of the new law, rough predictions are made of the radii of ten other elements whose crystal structures have not yet been experimentally determined.

MOST of the chemical properties and many of the physical properties of the chemical elements show periodic relationships when the elements are arranged in the order of their atomic numbers. The relationship between these properties and the architecture of the atoms is brought out in a modification of the Mendelejeff table proposed by Langmuir.¹ It is the purpose of this paper to point out one more such periodic law.

The effective radius (packing radius) of the atom of an element may be at once determined from the distance of closest approach of atoms in the crystal of the element. These distances have been tabulated by A. W. Hull² for the various elements whose crystal structures were known at that time. Additional measurements are available for the atoms of the inert gases (except He),³ beryllium,^{4,5} potassium,⁶ vanadium,⁷ germa-

¹ Langmuir, *Jour. Am. Chem. Soc.* **91**, 868 (1919). Such a table may be put in more convenient form by making the following changes in the ordinary Mendelejeff table. Put the elements in the horizontal rows starting with He and ending with Cl on the left hand side of their respective columns. Move Se, Br, Te, I, and element No. 85 over to the left hand side of their columns. The "rare earths" from Pr through Ha are retained in an unclassified group in the vertical columns of E_2O_3 , EO_2 . Then those elements on the left hand side of the vertical columns have atoms or ions of relatively simple structure. Those on the right hand side of the vertical columns are those which have a relatively complex structure.

² Hull, *Jour. Frank. Inst.* Feb. 1 22

³ Davey, *Phys. Rev.* **22**, 221 (1923)

⁴ McKeehan, *Proc. Nat. Acad. Sci.* **8**, 279 (1922)

⁵ Meier, Göttingen dissertation, (1921)

⁶ McKeehan, *Proc. Nat. Acad. Sci.* **8**, 254 (1922)

⁷ Hull, *Phys. Rev.* **20**, 113 (1922)

nium^{8,9} frozen mercury^{10,11} and white tin.¹² Altogether, dimensions are available from crystal measurements for the atoms of 44 elements ranging in atomic numbers from 3 to 90. Elements whose atoms pack in the crystal like spheres are considered to be spherical in their effective, or packing, shape. In such cases the radius of the atom is taken as half the distance of closest approach of atom-centers in the crystal. Atoms of the inert gases are assumed to be approximately spherical because the ions of the adjacent alkalis and halogens pack as spheres or as spheres with slight flat spots.³ Other atoms, because of the crystal structures into which they pack themselves, are considered to be spheroidal, and the major and minor radii are taken as half the "distance of closest approach" in directions corresponding to the major and minor axes of an ellipsoid of revolution.

Elements which tend to revert, upon chemical combination, to the Ni, Pd, Pt type of atoms are supposed to have a relatively complex outer structure. They are the elements which belong on the right hand side of the vertical columns of the older Mendelejeff table.¹ For brevity such atoms will be called "complex atoms." The other atoms, which tend to revert upon combination to the inert-gas type of atom, will be called "simple atoms."

Using the definitions given above the new law is as follows: *The ratio of the radii of any two simple atoms belonging to the same vertical column in the periodic table is the same as the ratio of the radii of any other two simple atoms on the same horizontal lines of the table provided that these atoms also belong to a common vertical column.*

TABLE I
RATIOS OF RADII OF ATOMS OF SIMPLE ELEMENTS

Ar/Ne = 1.57/1.26 = 1.25	Kr/Ar = 1.71/1.57 = 1.09	Ta/V = 1.42/1.32 = 1.08
K/Na = 2.25/1.86 = 1.21	(1) Zr/Ti = 1.62/1.48 = 1.09	W/Cr = 1.36/1.25 = 1.09
Ca/Mg = 1.96/1.61 = 1.22	(2) Zr/Ti = 1.59/1.45 = 1.10	(1) Os/Fe = 1.36/1.23 = 1.11
(1) Ti/Si = 1.48/1.17 = 1.26	Mo/Cr = 1.36/1.25 = 1.09	(2) Os/Fe = 1.33/1.23 = 1.08
(2) Ti/Si = 1.45/1.17 = 1.24	(1) Ru/Fe = 1.34/1.23 = 1.09	Ir/Co = 1.35/1.26 = 1.07
	(2) Ru/Fe = 1.32/1.23 = 1.07	Pt/Ni = 1.39/1.25 = 1.11
	Rh/Co = 1.35/1.26 = 1.07	

In case the elements concerned have two radii, the ratio may be taken either between the major radii or between the minor radii. For instance, Zr and Ti both have simple atoms and both fall in group IV of the periodic table. Mo and Cr both have simple atoms and fall in group VI of the table. The ratio of the major radii of Zr and Ti is 1.09; that of

⁸ Kolkmeijer, Proc. Acad. Sci. Amsterdam **25**, 125 (1922)

⁹ Hull, Phys. Rev. **20**, 113 (1922)

¹⁰ McKeehan and Cioffi, Phys. Rev. **19**, 444 (1922)

¹¹ Alsen and Aminoff, Goel. For. Stock. Forh., **44**, 124 (1922)

¹² Marx, Polangi and Schmid, Naturwis. **11**, 256 (1923)

their minor radii, 1.10. The ratio of the radii of Mo and Cr is 1.09. Similar data have been worked out covering the whole range of the periodic table. They are expressed in graphical form in Fig. 1. A few numerical illustrations of the law are given in Table I. It is quite evident from the graphs that the new law does not apply to atoms of "complex" structure. It is worthy of note that the type of crystal structure does not

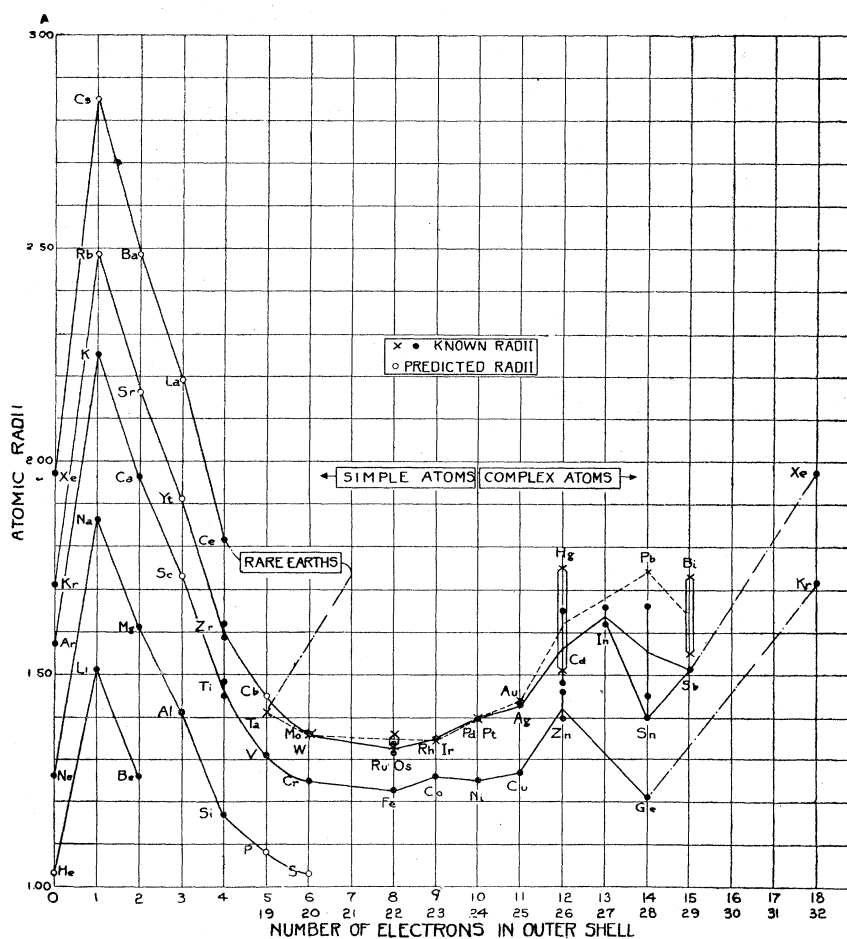


Fig. 1

enter into this law. Ratios may be taken indifferently between atoms which pack together in different crystallographic systems, provided only that the atoms are chosen in accordance with the law.

The new law does not hold for C, using the distance of closest approach in either diamond or graphite. This is not surprising, for there is every evidence that the C atom is tetrahedral in shape. Under such circum-

stances, the word "radius" is of course meaningless. Such an objection does not, however, apply to the same extent to Si, for it has (using Langmuir's terminology) a complete "IIa" shell beneath its valence electrons, thus giving it more nearly a real "radius."

Instead of the radius 1.43 Å for Al as given by Hull,² the value 1.41 Å has been used. This is the radius measured by the writer in some work not yet published on very pure Al. In the case of Ne, the value of the radius, based on the crystal lattice of NaF is 1.15 Å. The radii of Na⁺ and F⁻ are, however, quite variable,³ that of Na⁺ in NaI being 1.26 Å, so that no great precision can be claimed for the radius assigned to Ne. A radius of 1.26 Å for Ne is consistent with the new law in every case.

The new law is not what might have been expected from our ordinary ideas on atomic structure, for it might be imagined that increasing the atomic number would cause a definite increment or decrement in volume. Actual trial shows, however, that, although a few elements show constant differences in radii, this is the exception rather than the rule. The universal rule seems to be that the law for change of volume for any horizontal row of simple atoms is the same as that for any other horizontal row of simple atoms.

The new law makes it possible to predict the radii of certain atoms which have not yet been measured. Such predictions are given in Table II. The graph in Fig. 1 has been extended down to show a "radius"

TABLE II
PREDICTED ATOMIC RADII IN ANGSTROMS
(probably accurate to within 2 percent)

P	S	Sc	Rb	Sr	Yt	Cb	Cs	Ba	La
1.08	1.03	1.73	2.49	2.16	1.91	1.45	2.85	2.48	2.19

for He of 1.03 Å. This is to be compared with Rankine's value¹³ of 1.08 Å. The agreement is quite satisfactory, especially in view of the fact that He has a shell of only two electrons, so that it must on the average rotate with its axis in all possible directions in order to give any meaning to the word "radius."

Because of the large number of electrons in the Xe shell, it would be predicted *a priori* that Cs atoms should pack like spheres, thus giving either a hexagonal-close-packed lattice of axial ratio 1.633, or a face-centered-cubic lattice. The density of Cs as computed from the predicted radius is consistent with this idea.

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¹³ Rankine, Phys. Zeit. **11**, 497 (1910); Proc. Roy Soc. **84**, 182 (1910)