The values deduced from van der Waals equation are, respectively, 2.67 for the critical ratio, 3.38 for the reduced Boyle temperature and 6.75 for the reduced maximum inversion temperature. The average experimental value for the critical ratio is 3.7 and that for the reduced Boyle temperature is near 2.5. The maximum inversion temperature has been established for only a few substances. The reduced value for nitrogen[9] is 4.93, that for air[10] is 4.55. It is seen that the values predicted by equation (4) are considerably closer to the experimental ones than those deduced from van der Waals equation.

Summary

An equation of state for gases, equation (4) is proposed, in which all the constants can be calculated from the critical values of the temperature and pressure in a manner analogous to the evaluation of van der Waals constants. This equation is believed to reproduce the behavior of real gases with a higher degree of accuracy than the van der Waals equation. In the reduced form (5) it represents an analytical expression of the law of corresponding states.

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(9) J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **48**, 450 (1935).

(10) J. R. Roebuck and H. Osterberg, *ibid.*, **43**, 60 (1933).

Atomic Radii and Interatomic Distances in Metals[1]

BY LINUS PAULING

The problem of the nature of the interatomic forces in the elementary metals and in intermetallic compounds and other alloys continues to be puzzling, despite the clarification of some questions which has been provided by quantum mechanical considerations.[2] It has been my opinion,[1,3] contrary to that of other investigators,[4,5] that the metallic bond is very closely related to the covalent (shared-electron-pair) bond, and that each atom in a metal may be considered as forming covalent bonds with neighboring atoms, the covalent bonds resonating among the available interatomic positions. It was shown in the first paper of this series[1] that the number of covalent bonds resonating among the available positions about an atom (the metallic valence of the atom) increases from one to nearly six (5.78) in the sequence K, Ca, Sc, Ti, V, Cr in the first long period of the periodic table, remains nearly constant from Cr to Ni, and begins to decrease with Cu. This concept, which is substantiated by the magnetic properties of the metals and their alloys, provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as characteristic temperature (heat capacity at low temperatures), hardness, compressibility, coefficient of thermal expansion, and the general trend of interatomic distances. It will be shown in the following pages that it also permits the formulation of a system of atomic radii which can be used for the calculation of interatomic distances in metals and intermetallic compounds and for the interpretation of observed interatomic distances in terms of the electronic structure of the crystals. These atomic radii (which may be called metallic radii) are found, as expected, to show an intimate relation to the covalent radii of the atoms—a relation which, in its general nature, permitted Goldschmidt[6] over twenty years ago to use data taken from both metals and ordinary covalent crystals in formulating a table of atomic radii, and which has been recognized[3] as providing very strong support for the concept that metallic bonds are essentially resonating covalent bonds.

The Relation of Atomic Radius to Bond Type

In the discussion of metallic radii we may make a choice between two immediate alternative procedures. The first, which I shall adopt, is to consider the dependence of the radius on the type of the bond, defined as the number (which may be fractional) of shared electron pairs involved (corresponding to the single, double, and triple bonds in ordinary covalent molecules and crystals), and then to consider separately the effect of resonance in stabilizing the crystal and decreasing the interatomic distance. This procedure is similar to that which we have used in the discussion of interatomic distances in resonating molecules.[7a] The alternative procedure would be to assign to each bond a number, the bond order, to represent the strength of the bond with inclusion of the resonance effect as well as of the bond type.[8]

(1) "The Nature of the Interatomic Forces in Metals. II." For paper I of this series see L. Pauling, *Phys. Rev.*, **54**, 899 (1938).

(2) A. Sommerfeld and H. Bethe, "Handbuch der Physik," Vol. 24, second edition; N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford University Press, Oxford, 1936; F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940.

(3) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, 1940, chap. XI.

(4) J. D. Bernal, *Trans. Faraday Soc.*, **25**, 367 (1929).

(5) W. L. Bragg, *J. Roy. Soc. Arts*, **85**, 430 (1937).

(6) V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Vol. VII, Oslo, 1926.

(7) L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937); ref. 3, Chap. V.

(8) W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

Because the empirical information about the effect on interatomic distances of change in coördination number is not sufficiently extensive for our purpose, we make use of our knowledge of normal covalent radii. The available evidence indicates that the differences between single-bond, double-bond, and triple-bond radii are very nearly the same for all atoms,[9] and hence that an expression can be found for a term to be added to the single-bond covalent radius for any atom to give approximately the radius corresponding to another bond type. The carbon–carbon bond distances are 1.542, 1.330, and 1.204 Å. for a single bond, double bond, and triple bond, respectively, the double-bond and triple-bond radius corrections hence being -0.106 and -0.169 Å. The ratio of these numbers is just equal to log 2/log 3; accordingly the bond-type correction may be taken proportional to the logarithm of the bond number, n

$$-\Delta R(n) = 0.353 \log n \qquad (1)$$

Here ΔR is $R(n) - R(1)$, in Å., and n is the number of shared electron pairs involved in the bond. This logarithmic relation is, of course, to be expected in consequence of the exponential character of interatomic forces.

Atomic radii calculated with this expression need to be corrected for the stabilizing (bond-shortening) effect of resonance energy for use in resonating molecules or crystals. For example, the interatomic distance in benzene is not 1.418 Å., as given by equation 1 for $n = 3/2$, but is 0.028 Å. smaller, because of the effect of the resonance of the double bonds between two alternative positions. Of the several simple expressions which might be selected to represent empirically the effect of resonance on atomic radius, I have chosen the logarithm of the number of alternative bond arrangements among which resonance occurs, divided by the number of resonating bonds. The observed decrease in radius for benzene, corresponding to the resonance of a double bond between two positions, is 0.047 log 2; a similar expression, 0.017 = 0.036 log 3, is valid for graphite. In general we might expect the resonance correction for v single bonds resonating among N positions to be

$$-\Delta R \text{ (resonance)} = \frac{A}{v} \log \left\{ \frac{N!}{v! \, (N - v)!} \right\} \qquad (2)$$

in which A is approximately 0.04 or 0.05; the expression in brackets is the number of ways of distributing the v bonds among the N positions.

For the case $v = 1$ the expression in equation 2 reduces to $A \log N$, or, since $n = v/N$, to $-A \log n$; and it is found, moreover, that $-A \log n$ is a close approximation for $v > 1$ also, because of the rough approximation of $\{N!/v!(N-v)!\}^{1/v}$ to N/v. The resonance correction for the case of v single bonds resonating among N positions, with $N > v$, may accordingly be incorporated in equation 1

(9) Ref. 3, Chap. V.

simply by decreasing the value of the constant to about 0.31.

I have chosen to use the equation

$$R(1) - R(n) = 0.300 \log n \qquad (3)$$

in the following considerations. This equation, which is based upon the study of interatomic distances for non-resonating and resonating covalent bonds in simple non-metallic substances of known structure, is found to agree reasonably well with those data for metallic crystals which are suited to a check on its validity, and its use permits a penetrating analysis of the structure of metals and intermetallic compounds to be made. There is some evidence that the constant (taken as 0.300) varies with the kind of atom and with the type of bond; but the evidence is not sufficiently extensive to lead to the determination of the nature of this variation.

The Correction from the A2 Structure to Coördination Number 12

In the A2 structure[10] (with atoms at the points of a cubic body-centered lattice) each atom has eight neighbors at the distance $a_0 \sqrt{3}/2$ and six neighbors at the larger distance a_0. If the valence of the atom were used only for bonds to the eight nearest neighbors, the radius for the A2 structure would be that for coördination number 8 (CN8), which by equation 3 is 0.053 Å. less than the radius for CN12. But the bond number n of the eight stronger bonds is somewhat smaller than $v/8$, because part of the bond-forming power of each atom is used for the longer bonds, and accordingly the correction from A2 to CN12 is expected to be less than 0.053 Å.

The amount of this correction depends upon the value of the atomic radius. Zirconium, for example, has $a_0 = 3.61$ Å. for the A2 structure, the effective radii for the shorter and longer bonds being 1.563 and 1.805 Å., respectively. Application of equation 3 leads to $v/8.94$ for the bond number of the shorter bonds, and hence to 0.038 Å. for the correction to CN12. The value observed for this quantity (A3 structure, hexagonal close packing, six contacts with radius 1.583, six with 1.611, average 1.597 Å.) is 0.034 Å., which is slightly less than the calculated correction. A similar small discrepancy is shown by three of the four other metals for which direct experimental comparison of the A2 structure and CN12 can be made. (The fourth metal, chromium, which has a very much greater effective radius for CN12 than for the A2 structure, is discussed in detail in a later section.)

It is seen from Fig. 1 that the discrepancy, though small (≤ 0.01 Å.), is real, and that it depends upon the atomic radius. The discrepancy indicates that the six longer bonds in the A2 structure use more of the bond-forming power of

(10) The symbols A2, etc., are those used in the "Strukturbericht."

TABLE I

METALLIC RADII OF THE ELEMENTS

	Li	Be	B
v	1	2	3
R(CN12)	1.549	1.123	0.98
R(1)	1.225	0.889	.80

	Na	Mg	Al
v	1	2	3
R(CN12)	1.896	1.598	1.429
R(1)	1.572	1.364	1.248

	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
v	1	2	3	4	5	2.90 5.78	4.16 5.78	5.78	5.78
R(CN12)	2.349	1.970	1.620	1.467	1.338	1.357 1.267	1.306 1.261	1.260	1.252
R(1)	2 025	1 736	1.439	1.324	1.224	1.172	1.168	1.165	1.157

	Rb	Sr	Y	Zr	Cb	Mo	Tc	Ru	Rh
v	1	2	3	4	5	5.78	5.78	5.78	5.78
R(CN12)	2.48	2.148	1.797	1.597	1.456	1.386		1.336	1.342
R(1)	2.16	1.914	1.616	1.454	1.342	1.291		1.241	1.247

	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir
v	1	2	3	4	5	5.78	5.78	5.78	5.78
R(CN12)	2.67	2.215	1.871	1.585	1.457	1.394	1.373	1.350	1.355
R(1)	2.35	1.981	1.690	1.442	1.343	1.299	1.278	1.255	1.260

	Fa	Ra	Ac	Th	Pa	U	Np	Pu	Am
v	1	2	3	4	5	5.78			
R(CN12)				1.795		1.516			
R(1)				1.652		1.421			

	*Ce	Pr	Nd	Il	Sm	Eu
v	3.2	3.1	3.1		2.8	2
R(CN12)	1.818	1.824	1.818		1.85	2.084
R(1)	1.646	1.648	1.642		1.66	1.850

the atoms than is indicated by equation 3.[11] The curve may be made to pass through the experimental points by changing the factor of equation 3 from 0.300 to 0.70; this change, however, is not compatible with the great body of data on inter-

Fig. 1.—The correction $\Delta R = R$(CN12) $- R$(A2) from the A2 structure to coördination number 12. The dashed curve and its extension are calculated by equation 3; the full line passes through the experimental values.

(11) Dr. F. J. Ewing has suggested to me that the octahedral configuration of six atoms in A2, with three intersecting long-bond diagonals, may favor the long bonds through the stabilizing influence of the resonance of an electron pair among the three positions.

atomic distances which supports the equation with the smaller factor.

In these circumstances I have chosen to use the empirical curve[12] of Fig. 1 rather than the slightly different theoretical curve for calculating the value of R(CN12) from the observed radius for A2.
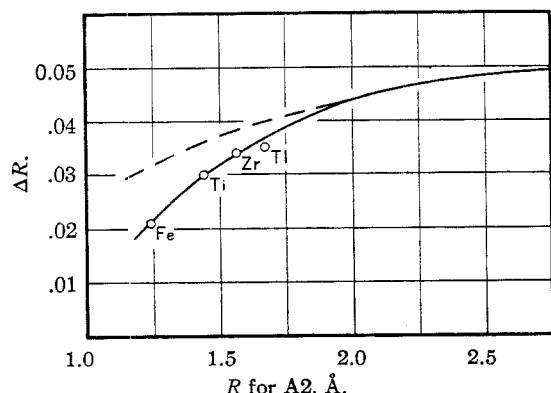
Values of Single-bond Radii and Metallic Radii for Coördination Number 12

In Table I there are given values of the metallic radii of the elements for CN12, and of the corresponding single-bond radii R(1), related to R-(CN12) by equation 3, with the bond number placed equal to $v/12$. The values of the valence v are those indicated by magnetic properties[1] or by the interatomic distances themselves, as described in the following discussion.

The derivation of the values of the metallic valence of the transition elements from the ob-

TABLE I
METALLIC RADII OF THE ELEMENTS

				C	N		O		F	
				4	3		2		1	
				0.914	0.88	0.92				
				.771	.70	.74	0.66	0.74	0.64	0.72

				Si	P	S	Cl
				4.	3	2	1
				1.316	1.28	1.27	
				1.173	1.10	1.04	0.994

Ni	Cu	Zn	Ga	Ge		As	Se	Br
5.78	5.44	4.44	3.44	4		3	2	1
1.244	1.276	1.379	1.408	1.366		1.39	1.40	
1.149	1.173	1.249	1.245	1.223		1.21	1.17	1.142

Pd	Ag	Cd	In	Sn		Sb	Te	I
5.78	5.44	4.44	3.44	2.44	4	3	2	1
1.373	1.442	1.543	1.660	1.620	1.542	1.59	1.60	
1.278	1.339	1.413	1.497	1.412	1.399	1.41	1.37	1.334

Pt	Au	Hg	Tl	Pb	Bi	Po	At
5.78	5.44	4.44	3.44	2.44	3	2	1
1.385	1.439	1.570	1.712	1.746	1.70	1.76	
1.290	1.336	1.440	1.549	1.538	1.52	1.53	

Cm

Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3	3	3	3	3	3	2	3
1.795	1.773	1.770	1.761	1.748	1.743	1.933	1.738
1.614	1.592	1.589	1.580	1.567	1.562	1.699	1.557

served saturation ferromagnetic moments may be summarized.[1] The saturation moment of iron is 2.22 Bohr magnetons, indicating that there are 2.22 unpaired (non-bonding) electrons. The presumption is that the remaining 5.78 electrons outside of the argon-like core are bonding electrons. The constancy of the number of bonding electrons at 5.78 is indicated by the equal change of saturation magnetic moment and average atomic number in alloys of iron with elements preceding or following it in the periodic table. When the average atomic number reaches about 18 + 8.22, however, the saturation magnetic moment ceases to increase, and begins to decrease at the same rate. This indicates that there are 2.44 non-bonding orbitals, which are being occupied by the pairing of electrons. At a point between nickel and copper these orbitals are filled with pairs, and further electrons decrease the metallic valence below 5.78.

These values of the number of bonding electrons are essentially empirical in nature, and their theoretical significance is not clear. The maximum valence of 5.78 is close to the value 6 found by Hultgren[13] for the maximum number of equivalent cylindrical orthogonal bond orbitals which can be formed by hybridization of one s,

(13) R. Hultgren, *Phys. Rev.*, **40**, 891 (1932).

three p, and five d orbitals. It is likely that a quantum mechanical treatment of metals can be developed which is compatible with the valence numbers assigned here. There now exists a contradiction with the approximate quantum mechanical calculations of electrons in metals which have been made, which, for example, indicate one bonding electron per atom in copper, instead of 5.44. This contradiction may well be resolved in the future by a more thorough theoretical study.

The valences of the rare-earth metals are calculated from their magnetic properties, as reported by Klemm and Bommer.[14] It is from the fine work of these investigators that the lattice constants of the rare-earth metals have in the main been taken. The metals lutecium and ytterbium have only a very small paramagnetism, indicating a completed $4f$ subshell and hence the valences 3 and 2, respectively (with not over 3% of trivalent ytterbium present in the metal). The observed paramagnetism of cerium at room temperature corresponds to about 20% Ce^{4+} and 80% Ce^{3+}, that of praseodymium and that of neodymium to about 10% of the quadripositive ion in each case, and that of samarium to about 20% of the bipositive ion in equilibrium with the tripositive ion.

(14) W. Klemm and H. Bommer, *Z. anorg. allgem. Chem.*, **231**, 138 (1937); **241**, 264 (1939); H. Bommer, *ibid.*, **242**, 277 (1939).

Bivalence is similarly shown for europium, and trivalence for the elements gadolinium to thulium.

The A2 structure is reported for europium, and A1 or A3 or both for the others, except samarium. For praseodymium and neodymium lattice constants have been reported for the A3 structure, with, however, the statement that some lines appear on the powder photographs indicating that c_0 should be doubled; possibly the structure is double-hexagonal close packing[3] instead of hexagonal close packing. Samarium is reported[15] to have a complex structure, probably tetragonal face-centered; the value of the radius given in the table is that calculated for a close-packed structure from the density, 6.93 g.cc^{-1}.

Except for chromium, tungsten, uranium, and manganese the metals in the first eleven groups of the table have the normal structures A1, A2, and A3.

Chromium is reported to be trimorphous, with the A2, A3, and A12 structures. The bond distance for the A2 structure, 2.493 Å., leads on correction to 1.267 Å. for $R(CN12)$, which is a reasonable value for the extrapolation of the sequence of the preceding five metals, and hence indicates that the valence is approximately 6; we use the value[1] 5.78 in calculating $R(1)$, which equals 1.172 Å. The value of $R(CN12)$ shown by the modification with the A3 structure (interatomic distances[16] 2.709 (6) and 2.717 (6)) is 1.357 Å., significantly larger than the above value. I think that this large radius is due to a smaller metallic valence of chromium in the A3 modification; that is, to its use of a smaller number of electrons as bonding electrons than in the A2 modification. Use of equation 3 leads to 2.90 for v, which has, with the corresponding value of R-(CN12), been entered in the table as an alternative for the chromium atom.

The meaning of the existence of this large chromium atom in the metal is not evident. The calculated valence near 3 suggests comparison with the common tripositive oxidation state of chromium, in the chromic compounds; but it would not be expected that the three unpaired $3d$ electrons of the chromic ion would fail to participate in metallic bond formation—presumably 2.58 of the five $3d$ orbitals are used in bond formation[1] (whereas the $4f$ orbitals of the rare-earth metals, because of their smaller size, are not so used). It might be thought that the recognized stability of a half-filled subshell (which, for example, causes metallic europium to be bivalent) would favor the introduction of 2.44 electrons in the 2.44 non-bonding $3d$ orbitals,[1] with parallel spins, causing the atom to have $v = 3.56$; this would lead to $R(1) = 1.199$ Å., only 0.027 Å. larger than $R(1)$ for the higher-valent type of

chromium atom, and this small difference might well result from the change in electronic structure. Another interpretation which is not easily ruled out is that the larger chromium atom contains a pair of $3d$ electrons, with opposed spins, and hence has $v = 4$ and $R(1) = 1.214$ Å.

Chromium is reported[17] also to have a modification with the A12 structure, for which, however, parameter values have not been determined.

Manganese crystallizes in three known modifications, no one of which, however, contains only atoms with the normal expected valence 5.78. For this valence we predict the value 1.168 Å. for $R(1)$, by interpolation between chromium and iron.

The simplest manganese structure is A6, which is cubic close packing with a small tetragonal distortion. The interatomic distances (2.582 (8), 2.669 (4)) lead to $R(CN12) = 1.306$ Å., and hence, with $R(1) = 1.168$ Å., to $v = 4.16$. This structure hence contains a lower-valent form of manganese, similar to that of chromium: in accordance with the foregoing discussion, the valence might really be 4 (three unpaired non-bonding electrons), 4.56 (2.44 unpaired non-bonding electrons), or 5 (a non-bonding electron pair), the last alternative being improbable.

The A13 modification of manganese[18] (β-manganese) contains 20 atoms in the unit cube, with $a_0 = 6.29$ Å. The atoms are of two kinds, with the following ligands[19]: MnI, 2.36 (3 MnI), 2.53 (3 MnII), 2.67 (6 MnII); MnII, 2.53 (2 MnI), 2.60 (2 MnII), 2.66 (4 MnII), 2.67 (4 MnI), 3.24 (2 MnII). The bond numbers of the bonds, calculated by equation 3 with $R(1) = 1.168$, and the corresponding valences are 0.92, 0.48, 0.28, and $v = 5.88$ for MnI and 0.48, 0.37, 0.28, 0.28, 0.03, and $v = 4.00$ for MnII. We hence conclude that β-manganese contains two kinds of manganese atoms in the chemical sense as well as in the crystallographic sense: in the unit cube there are eight atoms (MnI) with the normal large metallic valence and corresponding small size ($R(CN12) = 1.261$ Å.), and twelve atoms with the smaller valence and larger size ($R(CN12) = 1.306$ Å). found in the A6 modification.

This fact explains the occurrence of this unusual atomic arrangement, which has been reported for no other metallic element. Although coördination number 12 is the largest possible for spheres of equal size, the configurations of twelve spheres about another sphere shown in cubic close packing (A1) and hexagonal close packing (A3) and the combinations of these structures[3] do not represent the closest packing achievable

(15) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **241**, 268 (1939).

(16) The number in parentheses after each interatomic distance is the number of neighbors at this distance from the atom under consideration.

(17) SB II, 190.

(18) G. D. Preston, *Phil. Mag.*, **5**, 1198 (1928); SB I, 757; SB II, 3.

(19) The ligands of an atom may be defined as the neighboring atoms which are bonded to it. In a metal the nearer neighbors of an atom are considered to be its ligands; for convenience a neighboring atom is not called a ligand if its distance is much greater than that corresponding to bond number 0.05; that is, if the distance is more than about 0.80 Å. greater than the sum of the single-bond radii.

with CN12: this is instead obtained by grouping twelve equal spheres at the corners of a regular trigonal icosahedron about a smaller central sphere, with radius in ratio $\sqrt{2\sqrt{5}/\sqrt{5} - 1}$ — 1 = 0.901 to that of the surrounding spheres. The A13 structure is such that each of the smaller atoms (MnI) is surrounded by twelve atoms which approximate closely the regular trigonal icosahedron, whereas each of the larger atoms is surrounded by fourteen atoms (or by twelve, if the two distant atoms are ignored) in a configuration appropriate to a radius ratio slightly greater than unity.

The third modification (α-manganese) of the metal has the A12 structure, with 58 atoms, of four kinds, in a unit cube 8.90 Å. on edge.[20] According to the parameter values reported by Bradley and Thewlis, MnI has sixteen ligands, at 2.71 (12) and 2.82 (4), MnII has sixteen, at 2.49 (3), 2.69 (6), 2.82 (1), 2.89 (3), and 2.96 (3), MnIII has thirteen, at 2.45 (1), 2.49 (1), 2.51 (2), 2.66 (2), 2.67 (6), and 2.96 (1), and MnIV has twelve, at 2.24 (1), 2.38 (2), 2.45 (1), 2.51 (2), 2.66 (2), 2.69 (2), 2.82 (1) and 2.89 (1). The values of the valence of the four kinds of atoms calculated by equation 3 are 3.52, 4.70, 4.60, and 6.29, respectively, which indicate that of the 58 atoms in the unit cube thirty-four (2 MnI, 8 MnII, and 24 MnIII) are the low-valent kind found in the A6 structure, and twenty-four (MnIV) are the high-valent kind.[21]

The configuration of the twelve ligands about the small MnIV atom is that of an approximately regular icosahedron. The thirteen-cornered and sixteen-cornered coördination polyhedra about MnI, MnII, and MnIII are appropriate to axial ratios slightly greater than unity.

Tungsten, in addition to the A2 structure, which gives $R(1)$ = 1.299 Å. with v = 5.78, crystallizes also as the only representative of another cubic structure, A15, with 8 atoms (2 WI and 6 WII) in a unit cube 5.04 Å. on edge. WI has as ligands 12 WII at 2.816 Å., leading to v = 5.22, and WII has fourteen ligands, 2 WII at 2.519, 4 WI at 2.816, and 8 WII at 3.085, leading to $v = 2 \cdot 1.35 + 4 \cdot 0.43 + 8 \cdot 0.16 = 5.70$. We accordingly conclude that both kinds of atoms in the A15 structure are normal, with valence approximately 5.78. The somewhat low values of v suggest that $R(1)$ might be increased by about 0.010 Å.

It is interesting to note that there are strings of tungsten atoms WII in the A15 crystals with each atom between two very near neighbors: the interatomic distance 2.519 Å. leads to the bond number n = 1.35.

Uranium also has, in addition to the A2 structure, which gives $R(1)$ = 1.421 Å. with v = 5.78,

a unique structure,[22] A20 (α-uranium), in which each atom has the following ligands: 2.76 (2), 2.85 (2), 3.27 (4), and 3.36 (4). These distances correspond, respectively, to the bond numbers 1.36, 0.96, 0.19, and 0.14, which lead to v = 5.96, in excellent agreement with expectation. It is interesting to note that in this structure the four strong bonds use most of the bond-forming power of the atoms (4.64), leaving only 1.32 for the eight weak bonds; and also that the two strongest bonds, as in tungsten (A15), bind the atoms together into straight strings extending through the crystal. This structural feature may be significant with respect to the uranyl ion, UO_2^{++}.

The valence assumed for copper and its congeners, 5.44, is the number of unpaired electrons possible for eleven electrons occupying 8.22 orbitals[1] (the 2.44 stable non-bonding and 5.78 bonding orbitals). Similarly the valence 4.44 is assumed for zinc, cadmium, and mercury, and 3.44 for gallium and its congeners. The remaining 0.88 p-orbital seems to become stable at group IV of the periodic table: we use v = 4 for germanium and grey tin, but for white tin and lead the value v = 2.44 is indicated.

Zinc crystallizes in a deformed A3 structure with large axial ratio, causing the six equatorial neighbors (at 2.660 Å.) to be nearer than the six neighbors in adjacent planes (at 2.907 Å.). The bond numbers are 0.54 and 0.21, respectively, leading to $R(1)$ = 1.249 Å.

Cadmium has a similar structure, with distances 2.973 (6) and 3.287 (6), and bond numbers 0.57 and 0.17, leading to $R(1)$ = 1.43 Å.

Mercury has a structure obtained by compressing the cubic close packed structure along a three-fold axis, causing the six equatorial distances (3.463 Å.) to become greater than the six others (2.999 Å.). The values of n are 0.11 and 0.63, respectively, leading to $R(1)$ = 1.440 Å. The increasing weakness of the six longer bonds in the sequence zinc, cadmium, mercury is noteworthy.

Gallium has a unique structure,[23] in which each atom has one nearest neighbor, at 2.437 ± 0.010 Å., and six more distant ligands, at 2.706 (2), 2.736 (2), and 2.795 (2). With v = 3.44 the bond numbers are 1.21, 0.43, 0.38, and 0.31, and the single-bond radius is 1.245 Å. The strong bond is accordingly somewhat stronger than a single covalent bond, and it is proper to describe the structure, as has been done, as a metallic packing of Ga–Ga diatomic complexes.

Indium, with the tetragonal A6 structure, has coördination 3.242 (4), 3.370 (8), the bond numbers with v = 3.44 being 0.39 and 0.24, respectively, and the single-bond radius 1.497 Å.

The A1, A2, and A3 structures for **thallium** agree in giving 1.712 Å. for R(CN12), and, with v = 3.44, 1.549 Å. for $R(1)$.

(20) A. J. Bradley and J. Thewlis, *Proc. Roy. Soc.* (London), A115, 456 (1927); SB II, 756; SB III, 2.

(21) Hume-Rothery and Bradley have mentioned that the α-manganese structure can be explained only by assuming that the atoms are of different sizes (*J. Inst. Metals*, 11, 252, 257 (1944)).

(22) C. W. Jacob and B. E. Warren, THIS JOURNAL, 59, 2588 (1937); SB VI, 1.

(23) A. J. Bradley, *Z. Krist.*, 91, 302 (1935); SB III, 1.

Grey tin, with the diamond structure (A4), has effective atomic radius 1.399 Å., which may be taken as $R(1)$ because of the presumption from the structure that the valence is 4. This valence does not, however, apply to white tin: from the coördination 3.016 (4), 3.175 (2) for this metallic form the assumption $v = 4$ leads to $R(1) = 1.483$ Å., which is so much greater than the expected value 1.399 Å. as to eliminate the possibility of quadrivalence.[24] The alternative valence 2.44 leads to bond numbers 0.48 and 0.26 and single-bond radius 1.412 Å. This is not unreasonable, although from comparison with indium, thallium, and lead a value of about 1.46 Å. might be predicted for $R(1)$ for tin with $v = 2.44$. It is likely that in white tin the atoms have an average metallic valence between 2.44 and 4; the value $v = 3$, for example, would lead to the reasonable result $R(1) = 1.441$ Å. Because of uncertainty about the intermediate valence, the values for valence 2.44 are given in the table, together with those for $v = 4$ from grey tin.

The evidence for the existence of the reported third modification of tin is very weak. The hexagonal crystals which are formed by tin in the presence of mercury[25] have a simple structure, with atoms at the points of a hexagonal lattice,[26] with lattice constants[27] $a_0 = 3.198$ Å. and $c_0 = 2.980$ Å. for the alloy with 4.9% mercury. Neglecting the effect of the small number of atoms of mercury (which differ little in size from the atoms of tin), we calculate the value $R(1) = 1.401$ Å. from the coördination 2.980 (2), 3.198 (6) and the valence $v = 2.44$. Hence in this alloy tin has its lower valence.

It may be mentioned that the possibility of bivalence of tin in grey tin and the mercury alloy, suggested by the bipositive oxidation state of the element in many of its compounds, is ruled out because it leads to too small a value of $R(1)$—smaller than that for quadrivalent tin, whereas a larger value would be expected as the result of the appropriation of much of the s orbital by the unshared pair.

Lead, with the A1 structure, must have the low valence 2.44, which leads to $R(1) = 1.538$ Å.; the assumption $v = 4$ would give $R(1) = 1.603$ Å., which is much too large.

Bismuth is intermediate in the transition from a metallic to a normal covalent structure: each atom shows the effect of its normal tricovalence by having three nearest neighbors, at 3.10 Å.; and it has also three near neighbors at the larger distance 3.47 Å. The respective bond

numbers 0.80 and 0.20 lead to $R(1) = 1.52$ Å. For antimony the values are 2.87 (3), 3.37 (3); $n = 0.87, 0.13$; $R(1) = 1.417$ Å.; and for arsenic 2.51 (3), 3.15 (3); $n = 0.92, 0.08$; $R(1) = 1.244$ Å. It is not unlikely that the value for arsenic is too large.

The values of $R(1)$ given in the table for electronegative atoms are their normal covalent single-bond radii[28] (except for boron, discussed below). The possibility that the radius 0.74 Å. of Schomaker and Stevenson[29] should be used for nitrogen in the metallic nitrides should be borne in mind.

A reliable radius for boron can be calculated from the data for the hexaborides and carbon boride. In CaB_6 each boron atom has five boron neighbors, at 1.716 Å.[30] On the assumption that two electrons are transferred from the calcium atom to the boron framework, we calculate $n = 0.67$ and $R(1) = 0.806$ Å. A similar calculation for ErB_6, with B–B $= 1.699$ Å. and three electrons transferred,[31] gives $n = 0.70$ and $R(1) = 0.803$ Å. The larger B–B distances for other hexaborides[31] indicate that part of the bond-forming power is used in bonds to the metal atoms; the above values of $R(1)$ must be considered maximum values. In boron carbide,[32] B_4C, each boron atom forms six bonds, the average B–B distance being 1.77 Å. With $n = 1/2$, this leads to $R(1) = 0.795$ Å. We accept the value 0.80 Å. for $R(1)$ of boron.

In applying the metallic radii in the discussion of the structure of a metal or intermetallic compound either the observed distances may be used with the single-bond radii to calculate the bond numbers, the sums of which may then be compared with the expected valences, or the distances may be compared with the sums of radii for suitable coördination numbers, such as CN12. The correction to be added to $R(CN12)$ to give the radius for another coördination number, the va-

TABLE II

CORRECTION TO BE ADDED TO $R(CN12)$

Coördination number	Correction	Coördination number	Correction
1	−0.324	9	−0.038
2	− .234	10	− .024
3	− .181	11	− .011
4	− .143	12	0.000
5	− .114	13	+0.010
6	− .090	14	.020
7	− .070	15	.029
8	− .053	16	.037

(24) The indication from interatomic distances that less than 4 bonding electrons per atom are operating in white tin has been recognized by W. Hume-Rothery, "The Structure of Metals and Alloys," The Institute of Metals Monograph and Report Series No. 1, p. 26 (1936).

(25) N. A. Puschin, Z. anorg. allgem. Chem., **36**, 201 (1903).

(26) C. von Simson, Z. physik. Chem., **109**, 183 (1924); SB I, 570.

(27) S. Stenbeck, Z. anorg. allgem. Chem., **214**, 16 (1933). This structure has recently been verified by Mr. A. M. Soldate of these Laboratories (personal communication).

(28) Ref. 3, Chap. V.

(29) V. Schomaker and D. P. Stevenson, This Journal, **63**, 37 (1941).

(30) L. Pauling and S. Weinbaum, Z. Krist., **87**, 181 (1934).

(31) M. Stackelberg and F. Neumann, Z. physik. Chem., **B19**, 314 (1932).

(32) G. S. Zhdanov and N. G. Sevast'yanov, Compt. rend. acad. sci., U. R. S. S., **32**, 432 (1941); H. K. Clark and J. L. Hoard, This Journal, **65**, 2115 (1943).

lence remaining constant, is given in Table II, as calculated by equation 3.

An Example: Cementite.—As an example of the use of the radii we choose the very important substance cementite, Fe_3C, the orthorhombic crystals of which appear in white cast iron and as one phase of the eutectoid pearlite in steel. In cementite[33] the iron atoms are in reasonably close packing, each having twelve iron neighbors at the average distance 2.62 Å. (FeI) or eleven at the average distance 2.58 Å. (FeII), in each case ± 0.08 Å. Each carbon atom occupies a position at the center of a trigonal prism of six iron atoms, with the Fe–C distance 2.01 ± 0.01 Å.

The radius of .C for CN6, 0.82 Å., and that of Fe for CN13 and 14, 1.270 and 1.280 Å., indicate Fe–C distances 2.09 and 2.10 Å., somewhat larger than observed, and Fe–Fe distances 2.54 to 2.56 Å., somewhat smaller than observed. But the radii of iron for CN13 and 14 would be expected to apply to bonds with bond numbers $v/13$ and $v/14$, where $v = 5.78$; and it is expected that the bonds with carbon are stronger—namely, about $n = \frac{2}{3}$, since carbon is quadrivalent and has CN6 in this structure.

Indeed, if the bond numbers are calculated from the observed distances, the following results are obtained

C: 6 Fe at 2.01 Å., $n = 0.76$; $\Sigma n = 4.56$.

Fe I: 2 C at 2.01 Å., $n = 0.76$;
    12 Fe at 2.62 Å. (av.), n (av.) $= 0.33$; $\Sigma n = 5.48$.

Fe II: 2 C at 2.01 Å., $n = 0.76$;
    11 Fe at 2.58 Å. (av.), n (av.) $= 0.38$; $\Sigma n = 5.70$.

The bonds from iron atoms to carbon atoms are seen to be about twice as strong as those from iron to iron.

This calculation yields values of Σn in good agreement with the valence v of iron, 5.78, but somewhat larger than 4 for carbon. It seems not unlikely that the structure is under a slight strain, the Fe–C bonds being compressed a bit and the Fe–Fe bonds stretched a bit. If the Fe–C bonds are assigned the bond number 0.67, the FeI–FeI and FeI–FeII bonds the number 0.37, and the FeII–FeII bonds the number 0.43, the valences are exactly right and the following interatomic distances are predicted

$$Fe—C: 2.04 \text{ Å.}$$
$$FeI—FeI: 2.59$$
$$FeI—FeII: 2.59$$
$$FeII—FeII: 2.55$$

The calculated Fe–C distance is 0.03 Å. larger than that observed, and the average Fe–Fe distance, 2.57 Å., is 0.03 Å. smaller than the observed average. It is not unreasonable to expect the same deformation (with opposite sign) for each of six Fe–C bonds as for the opposing seventeen much weaker Fe–Fe bonds (the bond numbers

(33) S. B. Hendricks, *Z. Krist.*, **74**, 534 (1930); A. Westgren, *Jernkontorets Ann.*, 457 (1932); H. Lipson and N. J. Petch, *J. Iron Steel Inst.*, **142**, 95 (1940).

would equate six Fe–C to ten Fe–Fe bonds, and the additional factor would result from the well-known increase in stiffness of bonds with decrease in interatomic distance, as expressed, for example, in Badger's rule[34]); accordingly there is complete agreement between the calculation and experiment, and the conclusion can be reached that the carbon atoms in cementite are forced into holes slightly smaller (by 0.03 Å. in radius) than those into which they would fit exactly, and that the framework of iron atoms suffers a consequent small expansion.

Another Example: AuSn.—From among the many other intermetallic compounds which might be used as a second illustration, AuSn is chosen to show how the consideration of metallic valence and use of the radii contribute to the explanation of the choice of a suitable structure by a compound.

AuSn has the nickel arsenide structure, B8, with abnormally small axial ratio ($c/a = 1.278$, instead of the normal value 1.633). Each tin atom is surrounded by six gold atoms, at the corners of a trigonal prism, with Au–Sn $= 2.847$ Å.; and each gold atom is surrounded by six tin atoms, at the corners of a flattened octahedron, and two gold atoms, at 2.756 Å., in the opposed directions through the centers of the two large faces of the octahedron.

We expect gold to have valence 5.44, and tin 4 (or a smaller value). The Au–Sn bonds contribute equally to the two kinds of atoms; hence the extra valence of gold must find expression in Au–Au bonds. With the B8 structure (but not with the rather similar sodium chloride structure, B1) this can be achieved by compressing the structure along the c axis until the gold atoms are brought to the distance from one another suitable to the excess valence; that is, to the Au–Au distance corresponding to bond number $n = \frac{1}{2}(5.44 - 4) = 0.72$. With $R(1) = 1.336$, this distance is calculated by equation 3 to be 2.758 Å., in essentially exact agreement with observation.

The use of the values of $R(1)$ and equation 3 with the observed distances leads to the bond numbers 0.72 for Au–Au and 0.65 for Au–Sn, and hence to $v = 5.34$ for gold and 3.90 for tin, in satisfactory agreement with the normal valences of these metals.

It should not be thought that the structure of every intermetallic compound can be treated so simply; the discussion of such structural features as the transfer of electrons between atoms, the occurrence of strained bonds, the significance of relative atomic sizes, and the electron–atom ratio (Hume–Rothery ratio) must, however, be postponed to later papers.

The Dependence of the Radii on Atomic Number

In Figs. 2, 3 and 4 the single-bond metallic radii are plotted against atomic number, together

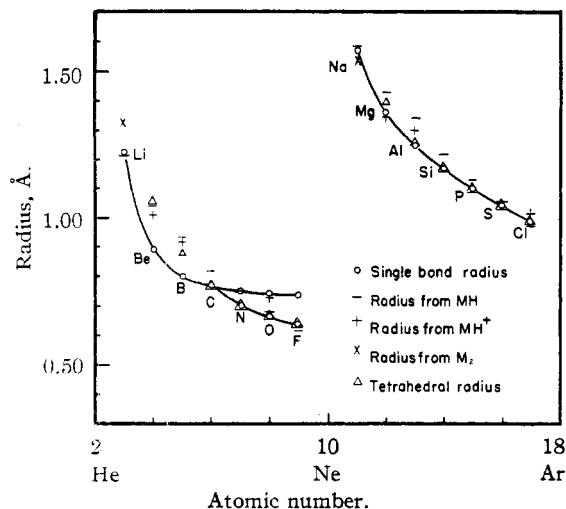(34) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

Fig. 2.—Covalent radii of the elements of the two short periods.

with values of covalent radii obtained from the observed interatomic distances in non-metallic substances. It is shown by the following discussion that these radii are very closely related; this investigation hence supports the thesis that the metallic bond is the resonating covalent bond.

radii lithium to carbon is continued smoothly by the Schomaker–Stevenson radii[29] for nitrogen, oxygen, and fluorine (the radii effective in normal covalent bonds, as in hydrazine, hydrogen peroxide, and the fluorine molecule, and to be used in other bonds with a correction for partial ionic character). The reasons for the deviation of the other set of normal covalent radii[35] of nitrogen, oxygen, and fluorine, the tetrahedral radii,[35] and the effective radii in diatomic hydrides (obtained by subtracting the normal hydrogen radius 0.30 Å. from the spectroscopic value of the interatomic distance) cannot be given with certainty; presumably the nature of the s–p hybridization is one of the important factors.

The curve of single-bond metallic radii for the elements of the first long period has a characteristic appearance (Fig. 3) which must be attributed in the main to variation in the type of bond orbital. The rapid decrease from potassium to chromium results from increase in bond strength due to increasing s–p and d–s–p hybridization. The linear section of the curve from chromium to nickel substantiates the assumption that the same bonding orbitals (hybrids of 2.56 $3d$ orbitals, one $4s$ orbital, and 2.22 $4p$ orbitals) are effective throughout this series. The increase in radius from nickel to copper is attributed not
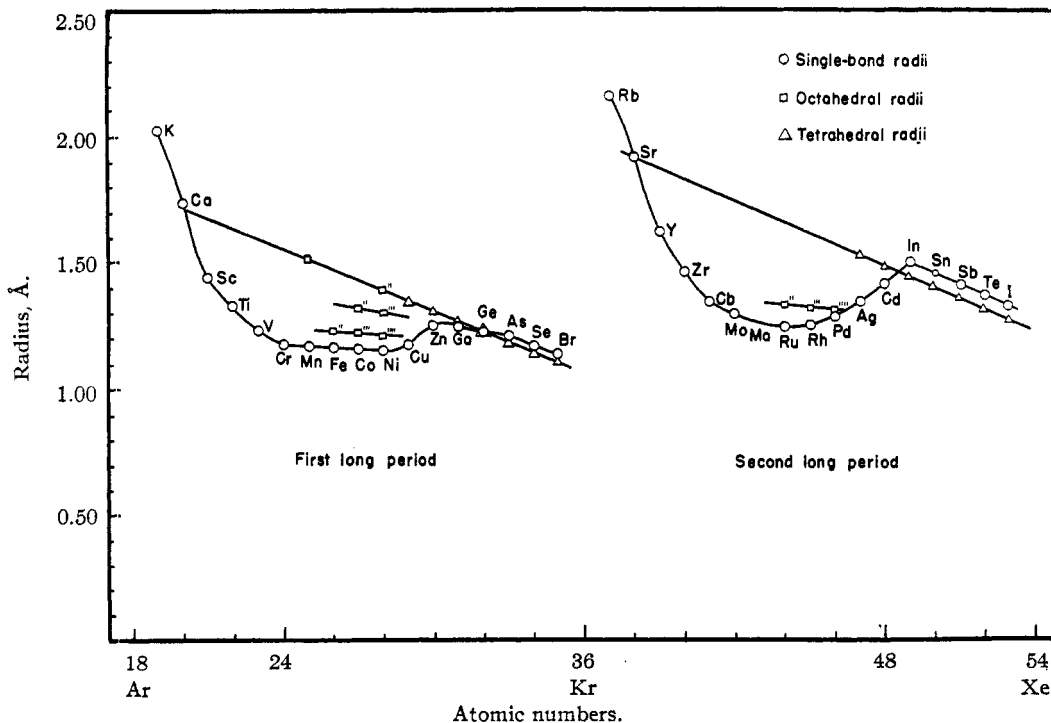

Fig. 3.—Covalent radii of the elements of the two long periods.

The radii for the elements of the two short periods are shown in Fig. 2. The metallic radii for the elements sodium to silicon lie on a common smooth curve with the normal covalent radii silicon to chlorine. Also the curve of the metallic

directly to decrease in valence (which has been corrected for by the calculation of the single-bond radii), but to the change in nature of the

(35) M. L. Huggins, Phys. Rev., 28, 1086 (1926); L. Pauling and M. L. Huggins, Z. Krist., 87, 205 (1934); Ref. 3.
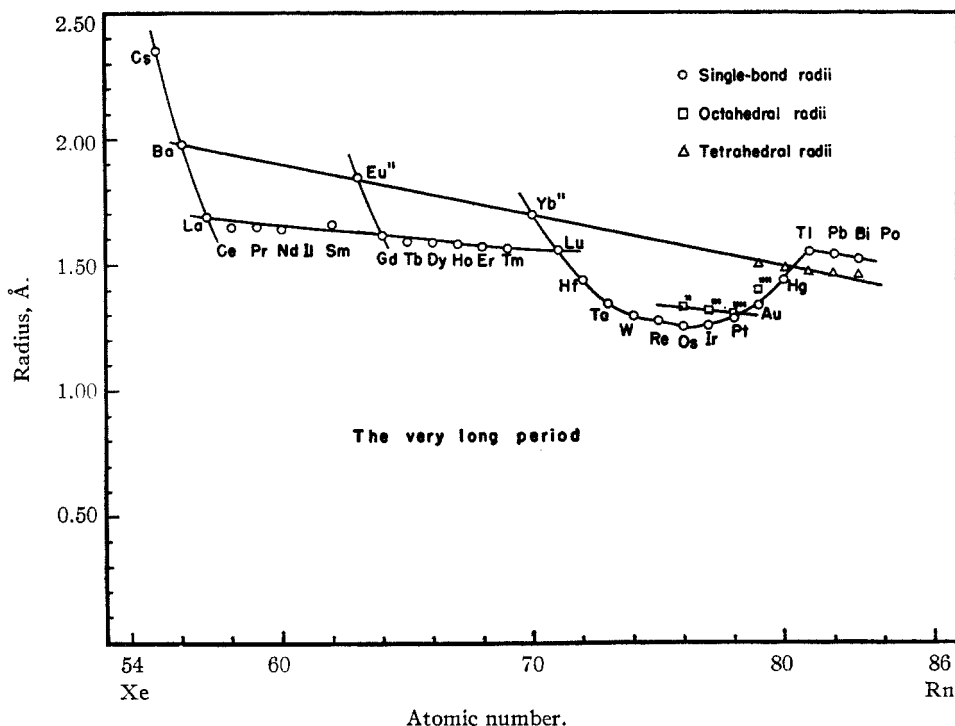
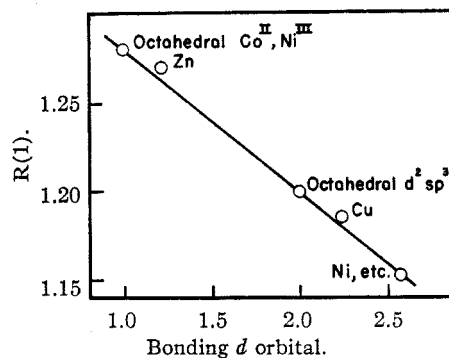Fig. 4.—Covalent radii of the elements of the very long period.

bond orbitals, which in copper are hybrids of 2.22 $3d$ orbitals, one $4s$ orbital, and 2.22 $4p$ orbitals: the decreased contribution of the d orbitals causes the bond strength of the hybrid orbitals[36] to decrease from 2.981 to 2.967, with a further decrease to 2.874 at zinc.

After rising at copper and zinc, the curve of metallic radii approaches those of the normal covalent radii and tetrahedral covalent radii (which themselves differ for arsenic, selenium, and bromine because of the difference in character of the bond orbitals, which approximate p orbitals for normal covalent bonds and sp^3 orbitals for tetrahedral bonds). The bond orbitals for gallium are expected to be composed of 0.22 d orbital, one s orbital, and 2.22 p orbitals, and hence to be only slightly stronger than tetrahedral bonds, as is indicated by the fact that $R(1)$ is smaller than the tetrahedral radius.

It is interesting that a straight line drawn through the tetrahedral radii passes through the metallic radius for calcium; this suggests that the metallic bonding orbitals for calcium are sp orbitals, and that those for scandium begin to involve d-orbital hybridization.

The octahedral d^2sp^3 covalent radii for Fe^{II}, Co^{III}, and Ni^{IV} are seen to lie on a straight line parallel to and just 0.06 Å. above the line of the metallic radii. This is reasonable in consideration of the decreased contribution of d orbitals to the bonding. A roughly linear relation is found to hold between the radius (corrected to atomic

(36) As calculated by use of the angular wave functions: L. Pauling, THIS JOURNAL, **53**, 1367 (1931); Ref. 3, Chap. III.

number 28) and number of d orbitals taking part in bond formation, as is shown in Fig. 5.

Fig. 5.—The dependence of single-bond radius on the number of bonding d orbitals.

The anomalously large radius[37] shown by manganese in hauerite, MnS_2, which has the pyrite structure, and in the similar substances $MnSe_2$ and $MnTe_2$ may now be accounted for in a satisfactory way. The magnetic properties of the crystals show that the five $3d$ orbitals of manganese are occupied by unshared electrons. The effective radius of manganese, 1.56 Å., corrected to 1.51 Å. for the resonance of four bonds among six positions, lies, as it should, very near the sp radius line.

The spectroscopic values[38] of interatomic dis-

(37) Pauling and Huggins, ref. 35; F. Offner, Z. Krist., **89**, 182 (1934); N. Elliott, THIS JOURNAL, **59**, 1958 (1937); ref. 3, Sec. 23d.

(38) From the summary given by G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, Inc., New York, N. Y. 1939.

<div align="center">

TABLE III

EFFECTIVE RADII OF TRANSITION METALS IN DIATOMIC HYDRIDES

</div>

	Fe	Co	Ni	Cu	Zn		
$r_s - 0.30$	1.176	1.243	1.175	1.163	1.295		
$R(1)$	1.165	1.157	1.149	1.173	1.249		

			Ag	Cd	In		
			1.318	1.462	1.552		
			1.339	1.413	1.497		

		Au	Hg	Tl	Pb	Bi
		1.224	1.441	1.570	1.539	1.509
		1.336	1.440	1.549	1.538	1.52

tances in diatomic hydrides of transition metals provide interesting evidence of the constancy in type of the bond orbitals of an atom except when the occupancy of orbitals by unshared electrons requires a change in hybridization. The effective radii (the observed distance minus 0.300 Å., for hydrogen) are for a number of metals within 0.02 Å. of the single-bond radii (Table III). The high value for cobalt and the low value for gold are hard to understand; the high values for zinc and cadmium, and perhaps also for indium, may be due to the occupancy of all d orbitals by unshared pairs.

There are few features of the curve for the second long period which differ enough from those of the first long period to require separate discussion. The curve does not have a linear segment in the neighborhood of ruthenium: this fact and the similar behavior of the hardness,[39] compressibility,[40] elasticity,[40] and related properties of the metals indicate clearly that the normal valence and bond type do not remain constant in the series molybdenum to palladium and tungsten to platinum, as they do in the series chromium to nickel; instead, the strength of the bond orbitals, and presumably also the valence, continue to increase somewhat until nearly the middle of each transition, at ruthenium and osmium, and then begin gradually to decrease. This effect is not a great one—the magnetic evidence and the evidence of hydride formation (to $PdH_{0.6}$) indicate that palladium and platinum, like nickel, contain 0.6 unpaired electron per atom; and the application of the relation shown in Fig. 5 leads to about 2.75 bonding d orbitals for ruthenium and osmium,[41] 2.6 for iridium and rhodium, and 2.3 for palladium and platinum. These numbers, and especially the numbers of bonding electrons, are, however, so uncertain that a change of valence values from those for the elements of the first long period is not yet justified.

The metallic radius for indium differs from that of gallium by being greater than the tetrahedral radius; it lies nicely on a straight line

(39) O. Winkler, Z. Elektrochem., 49, 221 (1943).

(40) W. Köster, ibid., 49, 233 (1943).

(41) The surprising stability of uni-negative rhenium, the complexes of which are undoubtedly covalent, may be related to the especial strength of the bonds formed by the neutral osmium atom.

passing through the normal covalent radii of antimony, tellurium, and iodine. This suggests that the metallic radius for tin might also lie on this curve, which would be achieved by assigning the intermediate valence 3.2 to white tin. The corresponding point is indicated by a small circle in Fig. 3.

The very long period is closely similar to the second long period, except for the interpolation of the rare-earth metals. It is interesting that a straight line can be passed through the points for barium, the two bivalent rare-earth metals, and the tetrahedral radii of the heavier elements.

The Dependence of Metallic Radius on Formal Charge.—A question of interest in the discussion of intermetallic compounds is that of the effect on its metallic radius of transferring an electron to or from an atom. A reasonable method of calculating the single-bond radius of an element of one of the long periods which has gained or lost an electron may be proposed: the radius is that determined by one of the straight lines shown in the figures, or by a similar line; namely, the line appropriate to the electronic structure of the atom. For example, if an atom of gold were to lose an electron it would achieve the configuration of a neutral platinum atom; its radius would then be 1.280 Å.; that is, the radius of platinum, 1.290 Å., corrected by the amount indicated by the octahedral radius line, -0.010 Å. If an atom of calcium were to gain an electron, its radius would be that of scandium, 1.439 Å., plus a correction of about 0.02 Å., giving 1.46 Å.

The proper treatment of elements of the short periods is uncertain. The equality of the tetrahedral radius and normal covalent radius for the electronegative elements indicates that for them no charge correction is needed. For the electropositive elements the same method as for the long periods may be satisfactory, with use of a line with slope about -0.05.

The Use of the Metallic Radii

The considerations presented in this paper have in some degree elucidated such complex elementary metallic structures as those of α- and β-manganese. They may also be applied with value to intermetallic compounds; the results which are yielded and the discussion of their

significance to the great problem of the nature of the metallic state will be communicated later.

Acknowledgment.—The work reported in this paper is part of a series of studies of metals and alloys being carried on with the aid of a grant from the Carbide and Carbon Chemicals Corporation.

Summary

An equation has been formulated to express the change in covalent radius (metallic radius) of an atom with change in bond number (or in coördination number, if the valence remains constant), the stabilizing (bond-shortening) effect of the resonance of shared-electron-pair bonds among alternative positions being also taken into consideration. This equation has been applied to the empirical interatomic-distance data for the elementary metals to obtain a nearly complete set of single-bond radii. These radii have been compared with the normal covalent radii, tetrahedral radii, and octahedral radii of the elements; their evident close relationship strongly supports the idea that the interatomic forces in metals are for the most part due to covalent bonds resonating among the available interatomic positions.

It is found that chromium atoms, manganese atoms, and tin atoms exist in metals in two forms, a small, high-valent form and a larger, low-valent form. The two kinds of manganese atoms coexist in α-manganese and in β-manganese.

In many metals each atom is attached to some of its neighbors by strong bonds and to others by much weaker bonds. An extreme case is β-tungsten, in which there are straight strings of strongly bonded atoms. Similar strings are also present in the α-uranium structure.

The use of the radii is illustrated by the discussion of two compounds, cementite and AuSn.

Some Spectroscopic Changes Connected with the Stereoisomerization of Diphenylbutadiene

BY A. SANDOVAL AND L. ZECHMEISTER

In the present study we wished to investigate how far some methods used and conclusions drawn in the field of cis–trans isomeric carotenoids[1] find their parallels in the structurally simpler case of diphenylbutadiene. As shown by Fig. 1, this stereoisomeric set includes only three members, the two cis forms of which represent sterically "hindered" isomers because two hydrogen atoms, one belonging to the nucleus and the other to the open chain, constitute a spatial conflict.[2] Since, however, as in the case of stilbene, these hindered cis forms are without competition by non-hindered ones, they may appear in substantial quantities under favorable conditions when all-trans-diphenylbutadiene undergoes a spatial change.

Although Kuhn and Winterstein[3] by their synthetic methods obtained exclusively the ordinary, all-trans form of diphenylbutadiene, Straus[4] had shown earlier in his remarkable contribution that by the reduction of diphenyldiacetylene the cis–cis form, m. p. 70–70.5°, can be prepared and by the hydrogenation of diphenylbutenine, the third, oily cis–trans isomer.

(1) General survey: L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

(2) L. Zechmeister and A. L. LeRosen, THIS JOURNAL, **64**, 2755 (1942).

(3) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

(4) F. Straus, *Ann.*, **342**, 190 (1905); confirmed and partly extended by C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912), as well as by E. Ott and R. Schröter, *Ber.*, **60**, 624 (1927). One of the present authors (ref. 1, p. 339) tentatively assigned a cis–cis configuration to the oily form; however, on the basis of recent experiments it seems now that Straus' original interpretation is more probable.
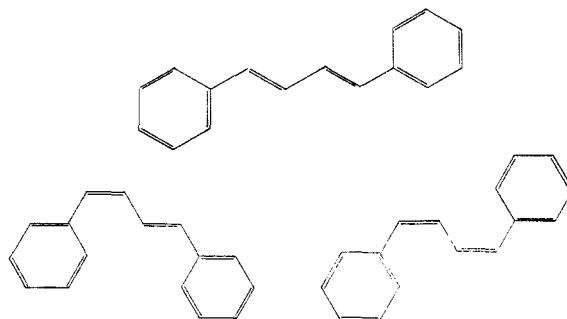

Fig. 1.—trans–trans-, cis–trans, and cis–cis-diphenylbutadienes (values used: C=C, 1.33 Å.; C—C, 1.46 Å.; and C=C—C angle, 124° 20′).

It has been reported that upon the addition of catalytic quantities of iodine, in light, for example, to a hexane solution of β-carotene, the height of the maximum extinction decreases very considerably, viz., by about 20%. We observed that the corresponding decrease in the case of diphenylbutadiene is less marked and amounts only to 3.5%, and that no noticeable change in the wave length occurs (Fig. 2).

While preparative quantities of diphenylbutadiene can be handled without apparent stereoisomerization, a conspicuous trans → cis shift takes place if a solution with a concentration as low as a few micrograms per milliliter is kept for half to one hour in diffuse daylight. As shown in Figs. 2 and 3 (dash–circle lines), the fine structure of the