Estimation of the van der Waals radii of the d-block elements using the concept of bond valence†

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It is assumed that the valence *v* of the bond between a metal M and a non-metal X is negligibly small but not equal to zero when the distance between them is equal to the sum of their *R* values; the *R* value derived here for a d-block element with the Pauling R_X values does not seem to depend on the oxidation state of M.

The concept of van der Waals radius (R) was originally implicit in the volume correction appearing in the equation of state derived by van der Waals in 1873, but it was Pauling who first introduced the term "van der Waals radius" in 1939. The sum of the van der Waals radii of two atoms, as understood now, is the shortest possible distance between two neighbouring atoms (either in the same or a different molecule or ion) that are not bonded to each other nor otherwise constrained to be close in the solid state structure of a compound. Over the years, a number of approaches based on X-ray crystallographic data, molar volumes, physical properties and crystal-chemical considerations have been proposed to estimate R for the various elements. A recent comprehensive review is available.[1] Herein we use the concept of bond valence to estimate the R values of the d-block elements.

Bond valence v is defined as the oxidation number (or valence) V of an atom per bond. For an atom i the relation between V and v can be written as in eqn (1):

$$V_i = \sum_j^n v_{ij} \qquad (1)$$

where j symbolises a neighbouring atom and n is the number of neighbouring atoms around atom i. The concept of bond valence was originally introduced by Pauling.[2,3] Subsequently it has been developed by several workers.[4–9] It is understandable that v_{ij} bears an inverse relation with the distance (r) between two atoms i and j—a shorter bond implies higher v_{ij} and a longer bond indicates lower v_{ij}. However the exact relation between v_{ij} and r_{ij} is not yet known. Several empirical forms have been suggested over the years.[4–12] The currently accepted one is given in eqn (2):

$$v_{ij} = \exp[(r_0 - r_{ij})/b] \qquad (2)$$

where r_0 is a parameter characteristic of the bond between the i and j atoms under consideration[8,12–14] and b an empirical constant. In eqn (2) r_0 and r_{ij} are expressed in Å. The value of b is usually taken as 0.37 Å.[12] Thus

$$V_i = \sum_j^n \exp[(r_0 - r_{ij})/0.37] \qquad (3)$$

As pointed out elsewhere,[15,16] eqn (3) cannot be applied when $V_i \leq 0$. In terms of eqn (2), $v_{ij} = 0$ means that the valence of the bond between the atoms i and j is 0 or in other words, there is no bonding between the two atoms i and j. The corresponding internuclear distance r'_{ij} can be taken as the sum of the van der Waals radii of the two atoms i and j. Consequently, if the R of one of the atoms is known, the R of the other atom can be calculated from eqn (4).

$$r'_{ij} = R_i + R_j \qquad (4)$$

Eqn (2) shows that $v_{ij} \rightarrow 0$ as $r_{ij} \rightarrow$ infinity. In order to have a working solution of the situation we assume that at a distance of the sum of the van der Waals radii of atoms i and j, v_{ij} has a negligible but finite value δ. After experimenting with various values of δ, we have found that $\delta = 0.01$, which is quite small for all practical purposes, yields R values for the d-block elements comparable with their van der Waals radii derived by other workers (*vide infra*). Thus our working equation for the atom pair of M and X, where M is a d block element and X a non-metallic donor, is given in eqn (5):

$$r_{MX}|_{\delta=0.01} = R_M + R_X \qquad (5)$$

From eqn (2) with $b = 0.37$ Å, it follows that $r_{MX}|_{\delta=0.01} = r_0 + 1.704$. Consequently, eqn (5) becomes eqn (6):

$$R_M = r_0 + 1.704 - R_X \qquad (6)$$

To calculate R_M by eqn (6), knowledge of r_0 and R_X values are required. The r_0 values are either taken from the work of Brown and Altermatt[14] or calculated by the rules delineated by them. A number of sets of R values (derived by various workers using different approaches) are available for the non-metallic donor atoms. Unlike those of the metal atoms, these values are generally numerically very close to each other.[1] We have preferred to use the R values of Pauling[17] for some ten common X atoms (Table 1) because of their chemical significance. It is found that for a particular M, the R values obtained *via* eqn (6) for these ten X atoms have a standard deviation of 0.07 Å. Some examples are given in Table 2. The results of our calculations for all the d block elements can be found in the ESI (Table S1†). The R value of a

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† Electronic supplementary information (ESI) available: Table S1 containing the calculation of the R values of all the d-block elements in their possible oxidation states is given as supplementary material. See DOI: 10.1039/b701197k

Table 1 Donor atoms (X) used in this work and their R values (in Å)[a]

N	O	F
1.5	1.40	1.35
P	S	Cl
1.9	1.85	1.80
	Se	Br
	2.0	1.95
	Te	I
	2.20	2.15

[a] The R values are taken from ref. 17.

particular metal does not seem to depend on its oxidation state (see Tables 2 and S1 for examples). Thus an average of all the R values in different oxidation states can be taken as the van der Waals radius of a d-block element. These average values for the various d-block metal atoms are presented in Table 3. These are quite close to the values (Table 3) recommended by Batsanov in his comprehensive review.[1] In general, R increases as one goes down a column. For a particular row, the minimum value of R is encountered for the element which has s^2d^7 configuration, *i.e.* for Co in the first row, Rh in the second and Ir in the third.

Bond valence is a measure of the attractive force the valence electrons exert on the two atoms that form the bond. At equilibrium this force is equal to the repulsive force arising from the overlap of filled electron shells. Thus V in eqn (3) can be used to represent the repulsive force in the bond and can be set to a value that represents the repulsive force that is present in a van der Waals bond at equilibrium. This means that in principle a method for estimating R can indeed be developed from the concept of bond valence.[18–20]

Our method shows that the valence v of the bond between a metal M and a non-metal X is really negligible but not equal to 0 at a distance of the sum of their van der Waals radii. Since the electron density varies continuously at the periphery of an atom, a cut-off value is needed for the valence of the M–X bond. Here we have taken it as 0.01. Obviously a much smaller or some other value can be assumed. Our choice of $v_{ij} = 0.01$ has been prompted by the observation that the R_M values then obtained are comparable with those recommended by Batsanov after a thorough appraisal of all the available sets of van der Waals radii.[21] It should be noted that our approach yields the sum of the R values of an M–X pair and not the R values of the individual atoms of the pair. Hence, to calculate R_M, a prior knowledge of R_X is needed. Our R_M values do not depend on the oxidation state of a metal atom.

As mentioned above, r_0 values of many atom pairs M–X in different oxidations of the metal used here have been calculated by making use of the rules of Brown and Altermatt.[14] Though we have worked with the accessible oxidation states of a particular metal (*e.g.*, +1 to +3 for Cu, only +2 for Zn and +1 to +4 for Ni *etc.*), some of these bonds may not exist in reality. For example, by invoking Pearson's hard–soft acid–base principle,[22] it can be argued that a bond between

Table 2 Calculations of the R values of some d-block elements (M) *via* eqn (6)[a]

M		F	Cl	Br	I	O	S	Se	Te	N	P	$\langle R_M \rangle$
Cr^{+1}	r_0	1.69	2.18	2.34	2.60	1.80	2.29	2.40	2.60	1.89	2.10	
	R_M	2.04	2.08	2.09	2.15	2.10	2.14	2.10	2.10	2.09	1.90	2.08
Cr^{+2}	r_0	1.65	2.14	2.30	2.56	1.76	2.25	2.36	2.56	1.85	2.06	
	R_M	2.01	2.05	2.06	2.12	2.07	2.11	2.07	2.07	2.06	1.87	2.05
Cr^{+3}	r_0	1.66	2.11	2.27	2.53	1.72	2.22	2.33	2.53	1.82	2.03	
	R_M	2.01	2.02	2.03	2.09	2.03	2.08	2.04	2.04	2.03	1.84	2.02
Cr^{+4}	r_0	1.64	2.13	2.29	2.55	1.73	2.24	2.35	2.55	1.84	2.05	
	R_M	2.00	2.04	2.05	2.11	2.06	2.10	2.06	2.06	2.05	1.86	2.04
Cr^{+5}	r_0	1.66	2.15	2.31	2.57	1.77	2.26	2.37	2.57	1.86	2.07	
	R_M	2.02	2.06	2.07	2.13	2.08	2.12	2.08	2.08	2.07	1.88	2.06
Cr^{+6}	r_0	1.70	2.19	2.35	2.61	1.79	2.30	2.41	2.61	1.90	2.11	
	R_M	2.05	2.09	2.10	2.16	2.10	2.15	2.11	2.11	2.10	1.91	2.09
Mn^{+1}	r_0	1.65	2.14	2.30	2.56	1.74	2.25	2.36	2.56	1.85	2.06	
	R_M	2.00	2.04	2.05	2.11	2.06	2.10	2.06	2.06	2.05	1.86	2.04
Mn^{+2}	r_0	1.70	2.13	2.33	2.60	1.79	2.28	2.39	2.59	1.88	2.09	
	R_M	2.05	2.04	2.09	2.15	2.09	2.14	2.10	2.10	2.09	1.90	2.07
Mn^{+3}	r_0	1.65	2.14	2.30	2.56	1.76	2.25	2.36	2.56	1.85	2.06	
	R_M	2.00	2.04	2.05	2.11	2.06	2.10	2.06	2.06	2.05	1.86	2.04
Mn^{+4}	r_0	1.62	2.11	2.27	2.53	1.75	2.22	2.33	2.53	1.82	2.03	
	R_M	1.97	2.01	2.02	2.08	2.06	2.07	2.03	2.03	2.02	1.83	2.01
Mn^{+5}	r_0	1.64	2.13	2.29	2.55	1.75	2.24	2.35	2.55	1.84	2.05	
	R_M	1.99	2.03	2.04	2.10	2.05	2.09	2.05	2.05	2.04	1.85	2.03
Fe^{+1}	r_0	1.66	2.15	2.31	2.57	1.77	2.26	2.37	2.57	1.86	2.07	
	R_M	2.01	2.05	2.06	2.12	2.07	2.11	2.07	2.07	2.06	1.87	2.05
Fe^{+2}	r_0	1.62	2.11	2.27	2.53	1.73	2.22	2.33	2.53	1.82	2.03	
	R_M	1.97	2.01	2.02	2.08	2.04	2.07	2.03	2.03	2.02	1.83	2.01
Fe^{+3}	r_0	1.68	2.14	2.30	2.57	1.76	2.15	2.36	2.56	1.85	2.06	
	R_M	2.03	2.05	2.06	2.12	2.06	2.00	2.07	2.07	2.06	1.87	2.04
Fe^{+4}	r_0	1.62	2.11	2.27	2.53	1.73	2.22	2.33	2.53	1.82	2.03	
	R_M	1.97	2.01	2.02	2.08	2.03	2.07	2.03	2.03	2.02	1.83	2.01
Fe^{+5}	r_0	1.59	2.08	2.24	2.50	1.70	2.19	2.30	2.50	1.79	2.00	
	R_M	1.94	1.98	1.99	2.05	2.00	2.04	2.00	2.00	1.99	1.80	1.98

[a] The values of r_0 and R are given in Å.

Table 3 The van der Waals radii (in Å) for the d-block elements[a]

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
2.12	2.07	2.06	2.06	2.04	2.02	1.91	1.98	1.92	1.98
2.3	2.15	2.05	2.05	2.05	2.05	2.0	2.0	2.0	2.1
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
2.29	2.19	2.17	2.16	2.16	2.17	2.04	2.09	2.10	2.17
2.4	2.3	2.15	2.1	2.05	2.05	2.0	2.05	2.1	2.2
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
2.45	2.19	2.18	2.18	2.16	2.17	2.09	2.09	2.10	2.24
2.5	2.35	2.2	2.1	2.05	2.0	2.0	2.05	2.1	2.05

[a] The upper figures are derived *via* eqn (6) and the lower figures are the crystallographic van der Waals radii recommended by Batsanov.[1]

Fe^{5+} and P may never be realised. It is necessary to remember also that there are no crystalline compounds CuF, CuI_2, AuI_3, TlI_3, that $Pt(halide)_3$ actually is a combination of $Pt(halide)_2$ and $Pt(halide)_4$, *etc*. Thus the validity of our conclusions regarding the nature of the van der Waals radii of the d-block elements is to some extent dependent on the validity of the formulae laid down by Brown and Altermatt[14] to calculate r_0 of an atom pair.

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