Determination of McGowan Volumes for Ions and Correlation with van der Waals Volumes

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The McGowan volume has been widely used for the analysis of physicochemical and biochemical properties in chemistry and drug industry. Because McGowan volumes are not available for ions, its application is limited to only neutral compounds. Pauling radii of metallic ions have been collected and studied to obtain McGowan volumes for ions. Regression analysis was carried out between Pauling radii (R_p) and McGowan radii (R_x) for a wide range of compounds. It was found that Pauling radii and McGowan radii derived from McGowan volumes by using a volume-radius formula are linearly related ($R_x = 1.115R_p + 0.0623$, $r^2 = 0.995$). This equation is then used to calculate McGowan volumes for various ions and charged groups. McGowan volumes have been calculated for inorganic, organic, and organometallic compounds and correlated with van der Waals volumes. Results show that McGowan volumes (V_x) are entirely equivalent to computer-calculated van der Waals volumes.

INTRODUCTION

One of the most widely used methods for the analysis of physicochemical and biochemical properties is the solvation equation approach that Abraham has developed over the last 10 years. This approach utilizes a combination of chemical descriptors with correlation analysis and is accepted as a valuable method.[1−3] In a linear free energy relationship (LFER), solute properties are correlated with a dipolarity/polarizability term, a hydrogen-bonding term(s), and a volume term. The volume term is a resultant of the endoergic process of separating the solvent molecules to provide a suitably sized cavity for the solute and the exoergic solute−solvent general dispersion interaction. Originally, the volume used in LFERs was the bulk solute molar volume. This was calculated as the molar weight divided by the liquid density at 298 K. However, molar volumes are not true solute parameters since they are measured as a bulk property. A further disadvantage is that the use of these terms is restricted to solutes that are liquid at room temperature.[4]

A preferred alternative was the computer-calculated intrinsic volume of Leahy (V_1).[5,6] These intrinsic volumes could be calculated for both liquids and solids. Leahy showed that use of intrinsic volumes instead of molar volumes led to rather better constants in regressions of octanol−water partition coefficients. Abraham and McGowan[4] then showed that McGowan characteristic volumes are so well correlated with Leahy's intrinsic volume that they could be used as an alternative ($V_1 = 0.597 + 0.6823V_x$, $n = 209$, $r = 0.998$, SD = 1.24). The characteristic volume is now well-known and used in the volume term in the Abraham model[3,4] and other QSAR studies.[7] McGowan volumes (V_x) have an advantage in that they are more easily calculated than computer-calculated intrinsic volumes. V_x is calculated by simply adding up the atom contribution for the compound and then subtracting 6.56 mL/mol for each bond.[8]

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Tran and co-workers[9] have published a data set of van der Waals (intrinsic) volumes for a wide range of compounds, including inorganic, organic, and organometallic compounds. They found that there was a particularly simple relationship between the van der Waals volume of a molecule and its apparent molar volume in acetonitrile, methylene chloride, methanol, and aqueous solution.

The McGowan volume has been widely used in many areas to estimate the physicochemical and biochemical properties of molecules.[3−6] However, there is no doubt that the lack of McGowan volumes for ions limits application of the McGowan method. In this paper, Pauling radii of ionic metals are collected, and McGowan volumes for ions are derived from the radii. The results are then used to calculate McGowan volumes for ionic compounds and organometallics. The relationship between the McGowan volumes and computer-calculated van der Waals volumes is also studied for a wide range of compounds. The general aim of the paper is to provide a self-consistent set of McGowan volumes for ionic species.

METHODS

van der Waals Volumes. The van der Waals volumes were obtained from Tran's paper.[9] Tran et al. calculated volumes using the volume function of MacroModel (version 3.0). For comparison with molar volumes, the volume obtained, in $Å^3$/molecule, is converted to mL/mol by multiplying by 0.602.

Pauling and van der Waals Radii. Pauling and van der Waals radii (Å) were obtained from several reference papers. Ionic radii were obtained from Glasstone,[10] Pauling,[11] David and Vokhmin,[12] Lide,[13] and Marcus.[14] Radii of noble gas atoms were from Huheey.[15] Radii of some elements were obtained from a paper by Bondi.[16] Pauling radii of organic compounds derived from liquid molar volumes by using the Stearn-Eyring formula were obtained from Abraham and Liszi.[17]

Table 1. McGowan Volumes of Atoms

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I	H 8.71																	He 6.75
II	Li 22.23	Be 20.27											B 18.31	C 16.35	N 14.39	O 12.43	F 10.47	Ne 8.51
III	Na 32.71	Mg 30.75											Al 28.79	Si 26.83	P 24.87	S 22.91	Cl 20.95	Ar 18.99
IV	K 51.89	Ca 50.28	Sc 48.68	Ti 47.07	V 45.47	Cr 43.86	Mn 42.26	Fe 40.65	Co 39.05	Ni 37.44	Cu 35.84	Zn 34.23	Ga 32.63	Ge 31.02	As 29.42	Se 27.81	Br 26.21	Kr 24.60
V	Rb 60.22	Sr 58.61	Y 57.01	Zr 55.40	Nb 53.80	Mo 52.19	Tc 50.59	Ru 48.98	Rh 47.38	Pd 45.77	Ag 44.17	Cd 42.56	In 40.96	Sn 39.35	Sb 37.75	Te 36.14	I 34.54	Xe 32.93
VI	Cs 77.25	Ba 76.00	La 74.75	Hf 55.97	Ta 54.71	W 53.46	Re 52.21	Os 50.96	Ir 49.71	Pt 48.45	Au 47.20	Hg 45.95	Tl 44.70	Pb 43.45	Bi 42.19	Po 40.94	At 39.69	Rn 38.44
VII	Fr 75.59	Ra 74.34	Ac 73.09															

58 Ce 73.49	59 Pr 72.24	60 Nd 70.99	61 Pm 69.74	62 Sm 68.49	63 Eu 67.23	64 Gd 65.98	65 Tb 64.73	66 Dy 63.48	67 Ho 62.23	68 Er 60.97	69 Tm 59.72	70 Yb 58.47	71 Lu 57.22
90 Th 71.83	91 Pa 70.58	92 U 69.33	93 Np 68.08	94 Pu 66.83	95 Am 65.57	96 Cm 64.32	97 Bk 63.07	98 Cf 61.82	99 Es 60.57	100 Fm 59.31	101 Md 58.06	102 No 56.81	103 Lr 55.56

Figure 1. Plot of ionic volumes against charge number.

McGowan Volumes and Radii. The McGowan characteristic volume (V_x, mL/mol) is the actual volume of a mole when the molecules are not in motion. It is proportional to the parachor (V_p) which is the molecular volume at temperatures when surface tensions are equal ($V_p = M g^{1/4}/(d_l - d_g)$), where M is the molecular weight of a liquid, g is its surface tension, d_l is its density, and d_g is the density of the vapor in equilibrium with the liquid).[8] McGowan volumes were obtained from the parachors given in cgs[18] units which, when divided by 2.835, give V_x in mL/mol.[4,8] Table 1 lists the characteristic atomic volumes calculated by this method.

The McGowan volume of a molecule is calculated by addition of the atomic volumes for all the atoms in the molecule and subtraction, from the total, of 6.56 mL/mol for each bond regardless of whether it is a single, double, or triple bond, $V_x = \Sigma$all atom contribution $- \Sigma6.56B$. Calculating the number of bonds present is simplified by using an algorithm, $B = N - 1 + $Rg, where B is the number of bonds, N is the total number of atoms, and Rg is the total number of ring structures.[2] For example, the volume of ethanol is calculated as $V_x = 2 \times 16.35 + 6 \times 8.71 + 12.43 - 7 \times 6.56 = 51.47$ mL/mol.

Table 2. Pauling Crystal Radii (Å) and Their Volumes (Å³) of Ions and Noble Gas Atoms[a]

series	−2	−1	0	1	2	3	4	b (eqs 1 and 4)	(eqs 2 and 5)
I			He	Li⁺	Be²⁺				
radius			1.29	0.76	0.45			1.59	
vol			8.99	1.84	0.38				
II	O²⁻	F⁻	Ne	Na⁺	Mg²⁺	Al³⁺	Si⁴⁺		
radius	1.40	1.33	1.40	1.02	0.72	0.54	0.40	0.96	
vol	11.49	9.85	11.49	4.45	1.56	0.66	0.27		
III	S²⁻	Cl⁻	Ar	K⁺	Ca²⁺	Sc³⁺	Ti⁴⁺		
radius	1.84	1.81	1.71	1.38	1.00	0.75	0.67	0.72	6.00
vol	26.09	24.84	20.94	11.01	4.19	1.77	1.26		
IV	Se²⁻	Br⁻	Kr	Rb⁺	Sr²⁺	Y³⁺	Zr⁴⁺		
radius	1.98	1.96	1.80	1.52	1.18	0.90	0.72	0.64	9.59
vol	32.52	31.54	24.43	14.71	6.88	3.05	1.56		
V	Te²⁻	I⁻	Xe	Cs⁺	Ba²⁺	La³⁺	Ce⁴⁺		
radius	2.21	2.20	2.03	1.67	1.35	1.03	0.87	0.62	12.47
vol	45.21	44.60	35.04	19.51	10.31	4.58	2.76		

[a] The Pauling ionic radii for coordination number 6 were obtained from references listed in Table 3. The radii for noble gas atoms were obtained from ref 15.

The McGowan molecular radii (Å) are calculated from McGowan volumes by using a volume-radius formula. McGowan volume obtained, in mL/mol, is converted to Å/molecule by dividing by 0.602. Then the radius R_x, in Å, is calculated by the volume-radius formula, $V_x/0.602 = 4\pi R_x^3/3$.

Statistical Analysis. The linear regression analysis was carried out using Excel 97, and nonlinear regression was carried out using the JMP program (version 3.2.5, 1989−1999 SAS Institute Inc.). The coefficients of determination were obtained by least-squares regression analysis. For each regression, the following descriptive information is provided: number of observations used in the analysis (n), square of the regression coefficient (r^2), and standard error of the estimate (S).

Table 3. Pauling Radii (R_p) and McGowan Radii (R_x) of Ions, Elements, and Compounds

	R_p (Å)	$R_x{}^a$ (Å)	ref[b]		R_p (Å)	$R_x{}^a$ (Å)	ref[b]
Li$^+$	0.76	0.82	13	Ge	1.98	2.31	16
Na$^+$	1.02	1.09	13	Sn	2.16	2.50	16
K$^+$	1.38	1.54	13	C	1.70	1.86	16
Rb$^+$	1.52	1.73	13	Si	2.10	2.20	16
Cs$^+$	1.67	1.91	10,11,13,14	As	1.85	2.27	16
Be^{2+}	0.45	0.48	13	(C$_3$H$_7$)$_4$N$^+$	3.72	4.24	14
Mg^{2+}	0.72	0.79	13	(C$_4$H$_9$)$_4$N$^+$	4.13	4.62	14
Ca^{2+}	1.00	1.21	10,11,13,14	(C$_5$H$_{11}$)$_4$N$^+$	4.43	4.94	14
Sr^{2+}	1.18	1.39	13	(C$_6$H$_{13}$)$_4$N$^+$	4.69	5.23	14
Ba^{2+}	1.35	1.56	10,11,13,14	(C$_7$H$_{15}$)$_4$N$^+$	4.92	5.49	14
Al^{3+}	0.54	0.57	13	(C$_6$H$_5$)$_4$P$^+$	4.25	4.79	14
Sc^{3+}	0.75	0.95	13,14	(C$_6$H$_5$)$_4$As$^+$	4.26	4.81	14
Y^{3+}	0.90	1.12	10,11,13,14	B(C$_6$H$_5$)$_4{}^-$	4.21	4.75	14
La^{3+}	1.03	1.27	13	NH$_3$	1.80	2.02	17
Si^{4+}	0.40	0.41	10,14	(CH$_3$)$_4$C	3.06	3.18	17
Ti^{4+}	0.61	0.75	13	(CH$_3$)$_4$Sn	3.07	3.46	17
Zr^{4+}	0.72	0.91	10,11,13,14	(C$_2$H$_5$)$_4$C	3.29	3.79	17
Ce^{4+}	0.87	1.03	13	(C$_2$H$_5$)$_4$Sn	3.46	3.99	17
Th^{4+}	0.94	1.08	13	methane	1.90	2.15	17
F$^-$	1.33	1.61	10,11,13,14	ethane	2.21	2.49	17
Cl$^-$	1.81	2.08	10,11,13,14	propane	2.53	2.76	17
Br$^-$	1.96	2.30	10,11,13,14	butane	2.76	2.99	17
I$^-$	2.20	2.53	13	water	1.55	1.88	17
O^{2-}	1.40	1.70	10,11,13	methanol	2.04	2.30	17
S^{2-}	1.84	2.12	10,11,13,14	ethanol	2.30	2.61	17
Se^{2-}	1.98	2.35	10,11,13	1-propanol	2.50	2.93	17
Te^{2-}	2.21	2.59	10,11,13	diethyl ether	2.79	3.15	17
H	1.20	1.51	16	formamide	2.02	2.44	17
He	1.29	1.39	15,17	N-methylformamide	2.31	2.72	17
Ne	1.40	1.50	15,17	N,N-dimethylformide	2.52	2.95	17
Ar	1.71	1.96	15,17	dimethylsulfoxide	2.46	2.90	17
Kr	1.80	2.14	15,17	nitromethane	2.24	2.56	17
Xe	2.03	2.35	15,17	acetonitrile	2.22	2.52	17
F	1.47	1.61	16	nitrobenzene	2.77	3.36	17
Cl	1.75	2.03	16	acetone	2.49	2.79	17
Br	1.85	2.18	16	1,2-dichloroethane	2.55	2.93	17
I	1.98	2.39	16	1,1-dichloroethane	2.60	2.93	17
O	1.52	1.70	16	tetrahydrofuran	2.57	3.01	17
S	1.80	2.09	16	1,2-dimethoxyethane	2.79	3.15	17
Se	1.90	2.23	16	ethyl acetate	2.73	3.09	17
Te	2.06	2.43	16	ethyl benzoate	3.10	3.64	17
N	1.55	1.79	16	chlorobenzene	2.77	3.22	17
P	1.80	2.14	16	bromobenzene	3.05	3.28	17
Sb	2.12	2.46	16	benzene	2.65	3.14	17

^{a} McGowan radii are calculated from the formula of $V_x/0.602 = 4\pi R_x{}^3/3$. ^{b} The references for obtaining the Pauling radii.
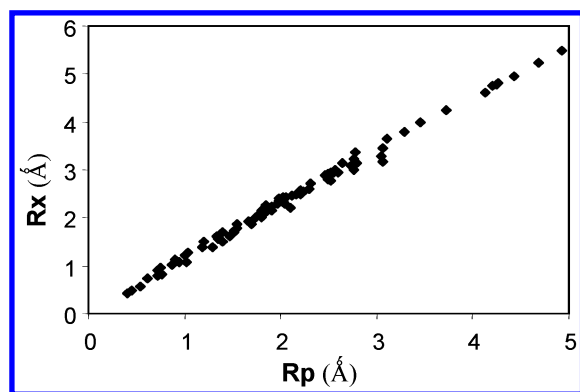
Figure 2. McGowan radii vs Pauling radii for 88 species in Table 3.

RESULTS AND DISCUSSION

Determination of McGowan Volumes for Ions from Pauling Crystal Radii. Atomic volumes are related to the number of electrons, nuclear charge, and quantum level.

Shielding by the electrons increases the atomic volume when the next electron is added to the quantum level.[15] When an electron is added to the next quantum level ($n+1$), not only is the most probable radius of the $n+1$ orbitals greater than that of the n orbitals but also shielding by the electrons in the nth level is much more effective (85%) when operating upon electrons in the $n+1$ level than when operating on the other n electrons (35%). This fact can be clearly seen if we compare the radii of neutral atoms and their ions. For example, the radius of the neutral atom potassium decreases by 54% on becoming an ion (K$^+$) because of the electron shielding effect of the next quantum level.[10,19,20] Chlorine, on the other hand, increases by only 3.4% on addition of an electron to give Cl$^-$.[10,16]

Attraction by the nuclear charge also decreases the atomic volume. Within a given series nuclear charge increases faster than does shielding, hence the effective nuclear charge increases, resulting in shrinkage with increasing atomic number.[15] Therefore, anions should be somewhat larger than neutral atoms from the added repulsion and shielding on the added valence electron. Cations should be much smaller than the corresponding neutral atoms from the attraction of extra valence charge on electrons.

Tables 2 and 3 lists the Pauling radii and volumes which were calculated by the volume-radius formula of $V = 4\pi R^3/3$ for different series. In each series, the elements and ions have the same number of electrons, and these electrons occupy the same quantum level. Their simple structures allow us to study the influence of charge on volume.

Figure 1 shows the correlation between volume and charge number, using the data in Table 2. Nonlinear regression analysis between the volumes and charges was carried out for different series. Results show that the simple nonlinear eq 1 can describe well the volumes of cations and noble gases; the simple nonlinear eq 2 can describe well the volumes of anions and noble gases; the sigmoidal eq 3 can describe well the whole data (cations, noble gases, and anions) for all the series in Figure 1.

$$\ln V = a - bN \tag{1}$$

$$V = a - be^N \tag{2}$$

$$V = a + b/(1 + e^{(-cN+d)}) \tag{3}$$

Here, V is the ionic and noble gas volume; N is charge number of ions; and a, b, c, and d are constants and are obtained from the regression analysis.

There is a significant relationship between intrinsic volumes and McGowan volumes for neutral compounds.[4] The relationship between noble gas volumes from the literature (Table 2) and McGowan noble gas volumes (Table 1) is also good and can be found by regression analysis. However, the absolute volume values of the two sets are different. To obtain McGowan ionic volumes that are comparable to Pauling ionic volumes, eqs 1 and 2 are converted to eqs 4 and 5, respectively. Then McGowan noble gas volumes in Table 1 are input into eqs 4 and 5. McGowan volumes of ions calculated by eqs 4 and 5 are

McGowan Volumes for Ions

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Table 4. McGowan Ionic Radii R_x (Å) Calculated from Eqs 4−6 and Volume (mL/mol) Calculated from $V_x = 0.602 \times 4\pi R_x^3/3$

ion	R_p (Å)	R_x (Å) (eq 6)	V_x (mL/mol)	ref[a]	ion	R_p (Å)	R_x (Å) (eq 6)	V_x (mL/mol)	ref[a]	ion	R_p (Å)	R_x (Å) (eq 6)	V_x (mL/mol)	ref[a]
						Anions								
F^-	1.33	1.61	10.47	10,11,13,14	I^-	2.20	2.53	40.81	13	Se^{2-}	1.98	2.35	32.90	10,11,13
Cl^-	1.81	2.08	22.78	10,11,13,14	O^{2-}	1.40	1.70	12.43	10,11,13	Te^{2-}	2.21	2.59	43.71	10,11,13
Br^-	1.96	2.30	30.66	10,11,13,14	S^{2-}	1.84	2.12	24.18	10,11,13,14					
						Cations								
Ac^{3+}	1.12	1.31	5.68	13	Ir^{3+}	0.68	0.82	1.39	13	Rh^{3+}	0.67	0.81	1.34	13
Ag^+	1.15	1.34	6.13	13	Ir^{4+}	0.63	0.76	1.13	13	Rh^{4+}	0.60	0.73	0.99	13
Ag^{2+}	0.94	1.11	3.45	13	Ir^{5+}	0.57	0.70	0.86	13	Rh^{5+}	0.55	0.68	0.78	13
Al^{3+}	0.54	0.57	0.47	13	K^+	1.38	1.54	9.21	13	Ru^{3+}	0.68	0.82	1.39	13
Am^{3+}	0.98	1.16	3.89	13	La^{3+}	1.03	1.27	5.11	13	Ru^{4+}	0.62	0.75	1.08	13
Am^{4+}	0.85	1.01	2.60	13	Li^+	0.76	0.82	1.38	13	Ru^{5+}	0.57	0.70	0.86	13
As^{3+}	0.58	0.71	0.90	13	Lu^{3+}	0.86	1.02	2.69	13,14	S^{4+}	0.37	0.47	0.27	13
As^{5+}	0.46	0.58	0.48	13	Mg^{2+}	0.72	0.79	1.24	13	S^{6+}	0.29	0.39	0.14	13
Au^+	1.37	1.59	10.13	11,13	Mn^{2+}	0.83	0.99	2.43	10,13,14	Sb^{3+}	0.76	0.91	1.90	13
Au^{3+}	0.85	1.01	2.60	13	Mn^{3+}	0.58	0.71	0.90	13	Sb^{5+}	0.60	0.73	0.99	13
Ba^{2+}	1.35	1.56	9.51	10,11,13,14	Mn^{4+}	0.53	0.65	0.70	13	Sc^{3+}	0.75	0.95	2.16	13,14
Be^{2+}	0.45	0.48	0.28	13	Mo^{3+}	0.69	0.83	1.45	13	Se^{4+}	0.50	0.62	0.60	13
Bi^{3+}	1.03	1.21	4.48	13,14	Mo^{4+}	0.65	0.79	1.23	13	Se^{6+}	0.42	0.53	0.38	13
Bi^{5+}	0.76	0.91	1.90	13	Mo^{5+}	0.61	0.74	1.03	13	Si^{4+}	0.40	0.41	0.18	10,14
Bk^{3+}	0.96	1.13	3.66	13	Mo^{6+}	0.59	0.72	0.94	13	Sm^{2+}	1.19	1.39	6.76	13
Bk^{4+}	0.83	0.99	2.43	13	Na^+	1.02	1.09	3.25	13	Sm^{3+}	0.96	1.13	3.66	13
C^{4+}	0.16	0.24	0.04	13	Nb^{3+}	0.72	0.87	1.63	13	Sn^{2+}	0.93	1.10	3.35	14
Ca^{2+}	1.00	1.21	4.46	10,11,13,14	Nb^{4+}	0.68	0.82	1.39	13	Sn^{4+}	0.69	0.83	1.45	13
Cd^{2+}	0.95	1.12	3.56	10,11,13,14	Nb^{5+}	0.64	0.78	1.18	13	Sr^{2+}	1.18	1.39	6.81	13
Ce^{3+}	1.01	1.19	4.23	13	Nd^{3+}	0.98	1.16	3.89	13	Ta^{3+}	0.72	0.87	1.63	13
Ce^{4+}	0.87	1.03	2.75	13	Ni^{2+}	0.69	0.83	1.45	10,13,14	Ta^{4+}	0.68	0.82	1.39	13
Cf^{3+}	0.95	1.12	3.56	13	Ni^{3+}	0.56	0.69	0.82	13	Ta^{5+}	0.64	0.78	1.18	13
Cf^{4+}	0.82	0.98	2.35	13	Np^{3+}	1.01	1.19	4.23	13	Tb^{3+}	0.92	1.09	3.25	13
Cm^{3+}	0.97	1.14	3.77	13	Np^{4+}	0.87	1.03	2.77	13	Tb^{4+}	0.76	0.91	1.90	13
Cm^{4+}	0.85	1.01	2.60	13	Np^{5+}	0.75	0.90	1.83	13	Tc^{4+}	0.65	0.79	1.23	13
Co^{2+}	0.65	0.79	1.23	13	Np^{6+}	0.72	0.87	1.63	13	Te^{4+}	0.97	1.14	3.77	13
Co^{3+}	0.55	0.68	0.78	13	Os^{4+}	0.63	0.76	1.13	13	Te^{6+}	0.56	0.69	0.82	13
Cr^{2+}	0.73	0.88	1.70	13	Os^{5+}	0.58	0.71	0.90	13	Th^{4+}	0.94	1.08	3.21	13
Cr^{3+}	0.62	0.75	1.08	13,14	Os^{6+}	0.55	0.68	0.78	13	Ti^{2+}	0.86	1.02	2.69	13
Cr^{4+}	0.55	0.68	0.78	13	P^{5+}	0.38	0.49	0.29	13	Ti^{3+}	0.67	0.81	1.34	13
Cr^{6+}	0.44	0.55	0.43	13	Pa^{3+}	1.04	1.22	4.60	13	Ti^{4+}	0.61	0.75	1.05	13
Cs^+	1.67	1.91	17.70	10,11,13,14	Pa^{4+}	0.90	1.07	3.05	13	Tl^+	1.50	1.73	13.17	13
Cu^+	0.77	0.92	1.97	14	Pa^{5+}	0.78	0.93	2.04	13	Tl^{3+}	0.89	1.05	2.96	13
Cu^{2+}	0.73	0.88	1.70	13,14	Pb^{2+}	1.19	1.39	6.76	13	Tm^{2+}	1.01	1.19	4.23	13
Dy^{2+}	1.07	1.26	4.99	14	Pb^{4+}	0.78	0.93	2.04	13	Tm^{3+}	0.88	1.04	2.87	13
Dy^{3+}	0.91	1.08	3.15	13	Pd^{2+}	0.86	1.02	2.69	13	U^{3+}	1.03	1.21	4.48	13
Er^{3+}	0.89	1.05	2.96	13	Pd^{3+}	0.76	0.91	1.90	13	U^{4+}	0.89	1.05	2.96	13
Eu^{2+}	1.17	1.37	6.44	13	Pm^{3+}	0.97	1.14	3.77	13	U^{5+}	0.76	0.91	1.90	13
Eu^{3+}	0.95	1.12	3.56	13	Po^{4+}	0.97	1.14	3.77	13	U^{6+}	0.73	0.88	1.70	13
Fe^{2+}	0.61	0.74	1.03	13	Pr^{3+}	0.99	1.17	4.00	13	V^{2+}	0.79	0.94	2.12	13
Fe^{3+}	0.55	0.68	0.78	13	Pr^{4+}	0.85	1.01	2.60	13	V^{3+}	0.64	0.78	1.18	13
Fr^+	1.80	2.07	22.34	13	Pt^{2+}	0.80	0.95	2.19	13	V^{4+}	0.58	0.71	0.90	13
Ga^{3+}	0.62	0.75	1.08	11,13,13	Pt^{4+}	0.63	0.76	1.13	13	V^{5+}	0.54	0.66	0.74	13
Gd^{3+}	0.94	1.11	3.45	13,14	Pu^{3+}	1.00	1.18	4.11	13,14	W^{4+}	0.66	0.80	1.28	13
Ge^{2+}	0.73	0.88	1.70	13	Pu^{4+}	0.86	1.02	2.69	13	W^{5+}	0.62	0.75	1.08	13
Ge^{4+}	0.53	0.65	0.70	13	Pu^{5+}	0.74	0.89	1.76	13	W^{6+}	0.60	0.73	0.99	13
Hf^{4+}	0.71	0.85	1.57	13	Pu^{6+}	0.71	0.85	1.57	13	Y^{3+}	0.90	1.12	3.58	11,13,14
Hg^+	1.19	1.39	6.76	13	Rb^+	1.52	1.73	12.95	13	Yb^{2+}	1.02	1.20	4.35	13
Hg^{2+}	1.02	1.20	4.35	13	Re^{4+}	0.63	0.76	1.13	13	Yb^{3+}	0.98	1.16	3.89	12
Ho^{3+}	1.02	1.20	4.35	12	Re^{5+}	0.58	0.71	0.90	13	Zn^{2+}	0.74	0.89	1.76	10,11,13
In^{3+}	0.80	0.95	2.19	11,13,14	Re^{6+}	0.55	0.68	0.78	13	Zr^{4+}	0.72	0.91	1.89	11,13,14

[a] The references for obtaining the Pauling radii R_p.

listed in Table 4. The b values used in the calculation are listed in Table 2.

$$V_{N+1} = V_N e^{-b} \qquad (4)$$

$$V_{N-1} = V_N + b(e^N - e^{N-1}) \qquad (5)$$

Table 4 shows that the volumes of all cations are much smaller than their parent atoms and decrease from left to right in a period. The volumes of anions increase with an increasing number of electrons from right to left in a period. However, the volume increase with an increasing electron added is not as significant as when compared with the volume decrease from a metal atom to its ion. This result is in agreement with the argument that increasing the atomic number results in shrinkage of volumes in a period because the net effect of nuclear charge is more important than electron shielding. Going down a group, however, the volumes of the anions become much bigger than their parent atoms, such as from O^{2-} to Te^{2-}. This is because the

Table 5. McGowan Radii Calculated from Eq 6 and Neutral Species for Some Fragments

	R_p (Å)	R_x (Å) (eq 6)	R_x (Å) (N)[a]	V_x[b] (mL/mol)	ref[d]		R_p (Å)	R_x (Å) (eq 6)	R_x (Å) (N)[a]	V_x[b] (mL/mol)	ref[d]
ClO_4^-	2.36	2.69	2.60	49.08	14	MnO_4^-	2.29	2.62	2.97	45.35	14
ClO_3^-	2.00	2.29	2.48	30.28[c]	14	OH^-	1.37	1.59	1.79	10.14	14
BrO_3^-	1.91	2.19	2.59	26.49[c]	14	SH^-	1.95	2.24	2.15	28.34	14
IO_3^-	1.82	2.09	2.74	23.02[c]	14	CN^-	1.82	2.09	2.12	23.02	14
CO_3^{2-}	1.85	2.13	2.38	24.37	14	N_3^-	1.95	2.24	2.28	28.34	14
NO_2^-	1.55	1.79	2.18	14.46	14	SCN^-	2.13	2.44	2.52	36.63	14
NO_3^-	1.89	2.17	2.33	25.77	14	BF_4^-	2.32	2.65	2.38	46.93	14
SO_4^{2-}	2.30	2.63	2.64	45.87	14	NH_4^+	1.48	1.71	2.09	12.61	10,14
SeO_4^{2-}	2.49	2.84	2.73	57.76	14	$(CH_3)_4N^+$	2.80	3.18	3.16	81.09	14
CrO_4^{2-}	2.56	2.92	2.99	62.78	14	$(C_2H_5)_4N^+$	3.37	3.82	3.78	140.56	14

[a] Radii of charged fragments are calculated by McGowan's method by treating them as neutral species. [b] $V_x = 0.602 \times 4\pi R_x^3/3$, this is the preferred volume, but see footnote c. [c] Our preferred volumes are 35.83, 40.56, and 47.71, see text. [d] References for Pauling radii R_p.

outermost electrons occupy shells that lie further from the nucleus, which leads to weak attraction of nuclear charge to the electrons.

F^- should be somewhat larger than Ne based on the above observation and analysis for different series. But the radii in Table 2 show that Ne is larger than F^-. This may simply be due to the different sources for the radii. Because there should not be a large difference between atomic volumes and corresponding anions in low quantum levels, atomic volume can be used in the calculation of McGowan volumes instead of the anionic volume F^- (Table 4).

Relationship between Pauling Radii and Radii Calculated from McGowan Volumes. The ionic radii (Å) calculated from McGowan volumes in unit of mL/mol should be well correlated with Pauling radii for the ions in Table 2 because the McGowan volumes were derived from the radii. However, the relationship between the volumes of ions, atoms, and compounds in the two sets is not known.

To study the relationship between Pauling radii (R_p) and radii calculated from McGowan volumes, three kinds of radii were selected and used for analysis: the radii of ions, the radii of noble gases and elements, and the radii of neutral compounds. The Pauling radii and radii calculated from McGowan volumes are listed in Table 3. Table 3 also contains some large ionic fragments. Because these fragments are quite large, charge should not have a big effect on their radii. Therefore, their radii can be taken as equal to that for the corresponding neutral species.

Equation 6 shows the correlation between the two sets in Table 3.

$$R_x = 1.115R_p + 0.0623$$

$$n = 88, S = 0.082, F = 15828, r^2 = 0.995 \qquad (6)$$

The correlation between the two sets is very good (Figure 2), which suggests that the radii analyzed are comparable between ions, elements, and neutral compounds in the two sets. If we take the intercept as zero, a simple regression equation is obtained, $R_x = 1.139R_p$ ($n = 88$, $S = 0.086$).

Equation 6 then can be used to calculate McGowan volumes if we know the Pauling or van der Waals radii of an ion or functional group. This is especially useful for complicated ionic functional groups whose volumes cannot be calculated by McGowan's method. Table 4 lists some McGowan radii of ions calculated by eq 6. The corresponding

McGowan volumes ($V_x = 0.602 \times 4\pi R_x^3/3$) are also listed in the table.

To see the difference between the volume calculated from eq 6 and volumes calculated from McGowan's method for neutral species, the radii of anion and cation fragments calculated from eq 6 and McGowan's method (the charges were treated as neutral species here) are listed in Table 5. The results show that the radius of NH_4^+ calculated by McGowan's method is much higher than that from eq 6. This case is similar to a metal and its ion where a positive charge has a significant effect on the radii or volumes. On the other hand, McGowan radii of anions are close to the radii calculated from eq 6. The results agree with the above observation that adding an electron does not significantly increase the radii/volumes for an element. The biggest difference between the radii calculated from eq 6 and McGowan radii is for IO_3^-. Based on McGowan's method, the radii increase from ClO_3^-, BrO_3^-, to IO_3^-. But the order of their ionic radii observed from the literature is the other way around (see Table 5). If we plot R_x from eq 6 against R_x for the neutral species, we calculate McGowan volumes as follows: ClO_3^-(35.83), BrO_3^- (40.56), and IO_3^-(47.71). These are our suggested volumes.

Correlation of McGowan Volumes and van der Waals Volumes. To test the relationship between McGowan volumes and van der Waals volumes for neutral compounds, salts, and organometallics, van der Waals volumes calculated by Tran et al.[9] for 92 compounds were chosen for analysis. One compound, $Co(dmg)_3(BF)_2$, was removed from the Tran's data set because we believed that the value of the van der Waals volume was wrongly calculated. This can be seen by comparing the differences of van der Waals volume between $Co(dmg)_3(BF)_2BF_4 - Co(dmg)_3(BF)_2$ (215.5−140.5 = 75) and $Co(nox)_3(BF)_2BF_4 - Co(nox)_3(BF)_2$ (253.1−230 = 23.1).

Table 6 lists the van der Waals volumes and McGowan volumes calculated by using the data in Table 1 for atoms and data in Tables 4 and 5 for ions and charged fragments. A good relationship is exhibited between van der Waals volumes and McGowan volumes (Figure 3 and eq 7).

$$V_x = 1.47V_{vdw} - 4.96$$

$$n = 92, S = 9.23, F = 52395, r^2 = 0.998 \qquad (7)$$

Tran and co-workers reported a data set of molar volumes

Table 6. van der Waals and McGowan Volumes[a,b]

compound	V_{vdw} (mL/mol)	V_x (mL/mol)	compound	V_{vdw} (mL/mol)	V_x (mL/mol)
AgNO$_3$	26.8	31.9	Fe(bpy)$_2$(CN)$_2$	205.1	297.8
CsCl	29.7	40.5	Fe(bpy)$_3$Cl$_2$	290.6	419.2
CsI	38.4	57.9	Fe(CH$_3$cp)$_2$	108.8	148.6
CuNO$_3$	23.3	27.8	Fe(cp)$_2$	86.2	120.4
I$_2$	42.9	62.5	Fe(cp)$_2$BF$_4$	110.4	167.0
KBr	29.0	39.9	Fe(phen)$_3$Cl$_2$	321.7	458.3
KCl	23.5	32.0	K$_2$Fe(CN)$_4$(C$_6$H$_6$N$_2$)	139.2	203.5
KI	32.3	50.0	KB(C$_6$H$_5$)$_4$	198.9	279.2
KPF$_6$	45.8	57.5	LiB(C$_4$H$_9$)$_4$	191.9	253.7
LiBr	22.0	32.0	NaB(C$_6$H$_5$)$_4$	194.0	273.3
LiCl	16.6	24.2	Na$_2$Co(EDTA)	151.4	200.5
LiI	25.3	42.2	Na$_2$Cu(EDTA)	142.9	200.9
NaBr	24.1	33.9	Na$_2$Ni(EDTA)	143.6	200.7
NaCl	18.7	26.0	Ni(en)$_3$Cl$_2$	154.8	224.0
NaI	27.4	44.1	Ni(phen)3Cl2	322.2	458.7
NaNO$_3$	24.7	29.0	Os(cp)$_2$	88.0	126.4
NH$_4$Br	28.8	43.3	Os((CH$_3$)$_5$cp)$_2$	186.7	267.3
NH$_4$Cl	23.4	35.4	Pd(Et$_4$dien)N$_3$N$_3$	195.5	290.8
NH$_4$NO$_3$	30.0	38.4	Pd(Et$_4$dien)NCSNCS	206.4	285.5
As(C$_6$H$_5$)$_4$Br	216.5	309.1	Ru(cp)$_2$	88.0	125.0
As(C$_6$H$_5$)$_4$Cl	211.1	301.2	Zr(acac)$_4$	228.6	330.9
As(C$_6$H$_5$)$_4$I	219.9	318.8	N((CH$_2$)$_2$CH$_3$)$_4$BF$_4$	162.8	239.0
As(C$_6$H$_5$)$_4$NO$_3$	217.7	304.2	N((CH$_2$)$_3$CH$_3$)$_4$BF$_4$	201.7	295.4
Co(acac)$_3$	171.4	247.7	N((CH$_2$)$_3$CH$_3$)$_4$BPh$_4$	366.8	518.5
Co(dmg)$_3$(BF)$_2$	140.5	264.4	N((CH$_2$)$_3$CH$_3$)$_4$I	200.6	288.7
Co(dmg)$_3$(BF)$_2$BF$_4$	215.5	310.9	N((CH$_2$)$_3$CH$_3$)$_4$ClO$_4$	204.0	303.4
Co(dmg)$_3$(BPh)$_2$BF$_4$	297.7	428.9	N(C$_2$H$_5$)$_4$Br	116.6	166.4
Co(dpg)$_3$(BPh)$_2$	447.6	662.6	N(C$_2$H$_5$)$_4$Cl	111.2	158.5
Co(dpg)$_3$(BPh)$_2$BF$_4$	472.7	709.0	N(C$_3$H$_7$)$_4$Br	157.7	222.7
Co(en)$_3$Cl$_3$	160.1	246.1	N(C$_4$H$_9$)$_4$Br	196.9	279.1
Co(NH$_3$)$_6$(ClO$_4$)$_3$	161.5	259.1	N(CH$_3$)$_4$BF$_4$	80.7	126.3
Co(NH$_3$)$_6$(NO$_3$)$_3$	143.5	203.2	N(CH$_3$)$_4$Br	75.9	110.0
Co(NH$_3$)$_6$Cl$_3$	123.6	194.2	N(CH$_3$)$_4$Cl	70.5	102.1
Co(nox)$_3$(BF)$_2$	230.0	316.4	C$_6$H$_5$CH$_2$OH	64.8	91.6
Co(nox)$_3$(BF)$_2$BF$_4$	253.1	362.8	CH$_3$CH$_2$OH	31.5	44.9
Co(nox)$_3$(BPh)$_2$	318.5	434.4	CH$_3$OH	22.2	30.8
Co(nox)$_3$(BPh)$_2$BF$_4$	343.4	480.9	I−CH$_3$(CH$_2$)$_2$OH	41.4	59.0
Co(phen)$_3$Cl$_2$	321.2	458.5	n-CH$_3$(CH$_2$)$_2$OH	42.7	59.0
Co(terpy)$_2$Cl$_2$	290.8	408.5	n-CH$_3$(CH$_2$)$_3$OH	51.4	73.1
Cr(acac)$_3$	171.4	248.3	2-CH$_3$(CH$_2$)$_3$OH	50.2	73.1
Cr(CNDiip)$_6$	733.2	1078.2	HC(C$_6$H$_5$)$_3$	146.5	207.3
Cr(CNDiip)$_6$(BF$_4$)$_2$	783.2	1171.9	bipyridine	88.0	124.2
Cr(CNDiip)$_6$BF$_4$	758.2	1125.1	dimethylglyoxime	63.9	90.3
Cr(en)$_3$Cl$_3$	170.0	246.4	nioxime	77.0	107.6
Cu(phen)$_3$Cl$_2$	326.7	458.9	phenanthroline	97.8	137.2
Fe((CH$_3$)$_5$cp)$_2$	186.6	261.3	terpyridine	128.6	180.9
Fe((CH$_3$)$_5$cp)$_2$BF$_4$	211.5	307.9			

[a] For a salt and organometallic compound, the volumes of cation and anion parts are calculated separately and added to obtain the compound volume. [b] Abbreviations: dgm, dimethylglyoxime; nox, cyclohexanedione dioxime; dpg, diphenylglyoxime; ph, phenyl; CNDiip, 2,6-diisopropyl-phenylioscyanide; cp, cyclopentadienide; acac, acetylacetonate; bpy, bipyridine; Et$_4$dien, tetraethyldiethylenetriamine; en, ethylenediamine; EDTA, ethylenediaminetraacetate; terpy, terpyridine; phen, phenanthroline.

for 92 inorganic, organic, and organometallic compounds. They demonstrated that, for the range of compounds they considered, there is a particular simple relationship between van der Waals volumes of a molecule and its apparent molar volume in four solvents. The molar volumes can be found in Table 1 of ref 9. The van der Waals volumes, McGowan volumes, and names of compounds are listed in Table 6. A summary of regression equations between molar volumes and volumes of van der Waals and McGowan in three solvents is given in Table 7. The same regression results further suggest that the use of McGowan volumes, which can be simply calculated for inorganic, organic, and organometallic compounds, is entirely equivalent to the use of computer-calculated van der Waals volumes.[4]

CONCLUSIONS

Our results show that the McGowan volume is equivalent to the computer-calculated van der Waals volume for inorganic, organic, and organometalic compounds. McGowan volume can simply be calculated by addition of the atomic volumes for all the atoms in the molecule and subtraction of 6.56 mL/mol for each bond (B) regardless of whether it is a single, double, or triple bond ($V_x = \Sigma$all atom contribution $- \Sigma 6.56*B$). For a salt or organometallic compound, the volumes of cationic and anionic parts are calculated separately and added to obtain the compound volume. For example, the volume of NaB(C$_6$H$_5$)$_4$ is calculated as $V(Na^+) + V[(C_6H_5)_4B^-]$. All the atomic volumes
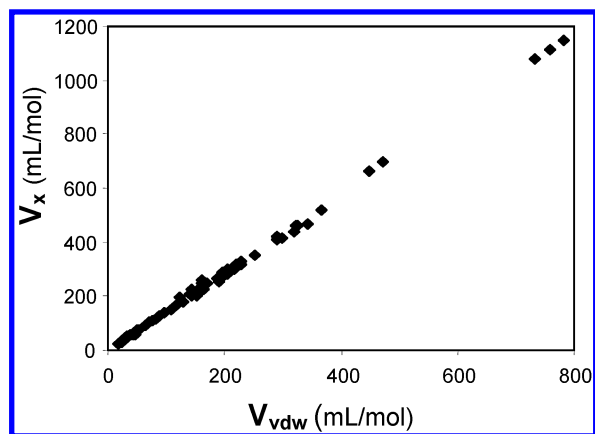
Figure 3. Plot of McGowan volumes against van der Waals volumes.

Table 7. Regression Equations between Molar Volumes and Volumes of McGowan and Tran

solvent	method	equation	r^2	n	S	F
CH_3CN	McGowan	$V_m = 1.07V_x - 17.71$	0.992	50	23	5623
	Tran	$V_m = 1.55V_{vdw} - 22.92$	0.991	50	23	5277
CH_3OH	McGowan	$V_m = 1.09V_x - 30.57$	0.991	31	11	3241
	Tran	$V_m = 1.53V_{vdw} - 28.64$	0.992	31	10	3419
H_2O	McGowan	$V_m = 0.976V_x - 9.25$	0.966	50	26	1391
	Tran	$V_m = 1.40V_{vdw} - 8.69$	0.973	50	23	1737

can be found in Table 1. Volumes of ions and functional groups are given in Tables 4 and 5.

Supporting Information Available: Tables 1, 3, 4, and 6 of McGowan volumes and van der Waals radii used in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. .

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